สกว
TRF

รายงานวิจัยฉบับสมบูรณ์

โครงการ
“การเกิดไมโครอิมัลชั่นของน้ำเสียที่มีน้ำมันปนเปื้อนโดยใช้สารลดแรงตึงผิวและความสัมพันธ์เกี่ยวกับกระบวนการแยกแบบทำให้ลอย”

โดย

รองศาสตราจารย์ ดร. สุเมธ ชวเดช และคณะ

วิทยาลัยปิโตรเลียมและปิโตรเคมี
จุฬาลงกรณ์มหาวิทยาลัย

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

Abstract

The main objectives of this research were to develop froth flotation technique to treat oily wastewaters and to understand the mechanisms of froth flotation how to remove oil from wastewaters. This work was hypothesized the use of microemulsion that the oil removal efficiency of froth flotation correlated to the ultralow interfacial tension (IFT) provided by the presence of a Winsor Type III microemulsion. In this study, several types of oils, orthodichlorobenzene (ODCB), ethylbenzene, diesel and cutting oil were investigated. The study consisted of three main parts, microemulsion formation, foam characteristic and froth flotation experiments in order to correlate the oil removal efficiency to the system IFT and foam properties. From the experimental results obtained from the ODCB system, the maximum oil removal of froth flotation corresponded to the maximum IFT under the presence of a Winsor Type III microemulsion. In addition, most of oil removed was found experimentally to come from the excess oil phase instead of the middle phase under the Winsor Type III microemulsion condition which was formed by the use of appropriate amount and type of surfactant(s). For the ethylbenzene system, the condition used for feed preparation was found to affect the process performance of froth flotation operation. Both feeds prepared under the conditions of equilibrium (1 month) and induced equilibrium (40 minutes of agitation) were found to provide much higher oil removal than that under a non-equilibrium condition. In addition, the ultralow interfacial tension (IFT) was found experimentally not only a sole factor, affecting the performance of froth flotation but also foam characteristics (foamability and foam stability) are important too. For diesel, Alfoterra ($C_{14-15}(PO)_5SO_4$), extended surfactant, was employed to form microemulsions which were further used to run froth flotation experiments. From the results of the batch froth flotation system, the maximum oil removal of 98% was achieved at 0.3%Alfoterra and 3%NaCl for 1:4 of oil-to-water ratio which corresponded to both of the maximum foamability and foam stability but not the minimum IFT of the system. For the continuous froth flotation experiments, the system could not be operated because of its poor foam stability. An addition of SDS was needed to improve the foam stability. The maximum diesel removal of 90.4% was achieved at 0.1%Alfoterra, 0.5% SDS, 4%NaCl and 49 minute of hydraulic retention time (HRT) for an oil-to-water ratio of 1:19. For cutting oil, a mixed surfactant system of Alfoterra and AOT (sodium bis(2-ethylhexyl)sulfosuccinate) was used to form microemulsions. The microemulsion condition having a minimum IFT was used to run froth flotation experiments with the continuous mode of operation. SDS was replaced in order to overcome the poor foam stability of the mixed surfactants during the froth flotation operation. Again, the foam stability was revealed experimentally to be the most important parameter affecting the performance of froth flotation. The system with 0.1% SDS, 5%NaCl, 0.15 L/min, 30 cm foam height and 60 min HRT was found to provide a maximum oil removal of 96%.

บทคัดย่อ

วัตถุประสงค์หลักของงานวิจัยนี้ คือ พัฒนาเทคนิคระบบฟองลอยเพื่อบำบัดน้ำเสียที่องค์ประกอบน้ำมันและทำความเข้าใจกลไกการทำงานของระบบฟองลอยในการแยกน้ำมันจากน้ำเสีย ในงานวิจัยนี้ได้ตั้งสมมุติฐานว่า ประสิทธิภาพการแยกน้ำมันโดยระบบฟองทำให้ลอยมีความเกี่ยวพันกับค่าต่ำมากของแรงตึงผิวระหว่างวัฏภาคซึ่งเกิดในสภาวะที่เป็นไมโครอิมัลชั่นแบบวินเซอร์ชนิดที่สาม ในงานนี้ น้ำมันหลายชนิด ได้แก่ ออโธไดคลอโรเบนซิน, เอทิวเบนซิน, ดีเซล และน้ำมันคัตติ้ง ได้ถูกศึกษา โดยงานทดลองประกอบด้วย 3 ส่วนหลัก ได้แก่ การเกิดไมโครอิมัลชั่น, ลักษณะสมบัติของฟอง และระบบฟองลอย ทั้งนี้เพื่อหาความสัมพันธ์และเกี่ยวข้องระหว่างประสิทธิภาพการแยกน้ำมันของระบบฟองลอยกับค่าแรงตึงผิวระหว่างวัฏภาคของระบบและคุณสมบัติของฟองที่ก่อตัวขึ้น จากผลการทดลองของระบบออโธไดคลอโรเบนซิน พบว่าประสิทธิภาพการแยกน้ำมันสูงสุดของระบบฟองทำให้ลอยมีความสัมพันธ์กับค่าต่ำสุดของแรงตึงผิวระหว่างวัฏภาคภายใต้สภาวะของไมโครอิมัลชั่นแบบวินเซอร์ชนิดที่สาม นอกจากนี้ ยังพบว่า น้ำมันที่แยกออกมาได้ส่วนใหญ่มาจากชั้นของน้ำมันไม่ใช่ชั้นของเฟสกลางภายใต้สภาวะไมโครอิมัลชั่นแบบวินเซอร์ชนิดที่สาม ซึ่งเกิดขึ้นได้เมื่อใช้สารลดแรงตึงผิวชนิดและปริมาณที่เหมาะสม สำหรับระบบเอทิลเบนซิน พบว่า สภาวะที่ใช้ในการเตรียมสารผสมระหว่างน้ำมันกับน้ำเพื่อสูบเข้าสู่ระบบฟองลอย มีความเกี่ยวข้องกับประสิทธิภาพการแยกน้ำมัน พบว่าการเตรียมสารผสมนี้โดยได้เข้าสมดุล (ใช้เวลา 1 เดือน) และโดยเหนี่ยวนำให้สมดุล (ใช้เวลา 40 นาทีในการกวน) ให้ประสิทธิภาพการแยกน้ำมันสูงกว่ามาก เมื่อเทียบกับการระบบไม่สมดุล นอกจากนี้ จากการทดลอง พบว่า ค่าแรงตึงผิวระหว่างวัฏภาคที่ต่ำมากๆนั้นไม่ใช่ปัจจัยหลักที่มีผลต่อประสิทธิภาพการแยกน้ำมัน แต่ลักษณะสมบัติของฟองมีผลอย่างมากด้วย สำหรับน้ำมันดีเซล สารลดแรงตึงผิวชนิดยืด อาโฟธอราถูกใช้ในการทำให้เกิดไมโครอิมัลชั่น ซึ่งนำไปใช้ในการทดลองระบบฟองลอย จากผลการทดลองของระบบฟองลอยแบบกะ พบว่าประสิทธิภาพการแยกน้ำมันสูงสุด 98% สามารถทำได้ที่สภาวะ 0.3% สารอาโฟธอราและ 3%เกลือแกง สำหรับอัตราส่วนน้ำมันต่อน้ำที่ 1 ต่อ 4 ซึ่งระบบมีความสัมพันธ์กับทั้งความสามารถการเกิดฟองและเสถียรภาพของฟองที่สูงสุด ไม่ใช่ขึ้นกับค่าต่ำสุดแรงตึงผิวระหว่างวัฏภาค สำหรับการทดลองระบบฟองลอยแบบต่อเนื่อง พบว่าระบบไม่สามารถทำงานได้ เนื่องจากเสถียรภาพของฟองต่ำมาก ดังนั้น จึงจำเป็นต้องเติมสาร เอสดีเอสเพื่อเพิ่มเสถียรภาพของฟองโดยระบบสามารถให้ประสิทธิภาพการแยกฟองสูงสุด 90.4% ที่ 0.1% อาโฟเธอรา, 0.5% เอสดีเอส, 4%เกลือแกง และที่เวลาเก็บกัก 49นาที สำหรับอัตราส่วนน้ำมันต่อน้ำที่ 1 ต่อ 19 สำหรับน้ำมันคัตติ้ง ได้ใช้สารลดแรงตึงผิวผสมระหว่างอาโฟเธอราและเอโอทีในการทำให้เกิดไมโครอิมัลชั่น โดยไมโครอิมัลชั่นที่เกิดขึ้นถูกนำไปทดลองระบบฟองลอย พบว่าจำเป็นต้องใช้สารลดแรงตึงผิวเอสดีเอสแทน ทั้งนี้เพื่อแก้ปัญหาเสถียรภาพของฟองที่ต่ำมากที่เกิดจากสารลดแรงตึงผิวผสมที่ใช้ โดยการทดลอง พบว่า เสถียรภาพของฟองมีความสำคัญที่สุดต่อประสิทธิภาพของระบบฟองลอย พบว่าระบบที่มี 0.1% เอสดีเอส, 5%เกลือแกง, 0.15 ล/นาที, ความสูงของฟอง 30 ซม และเวลาเก็บกัก 60 นาที ให้ประสิทธิภาพการแยกน้ำมันสูงสุดที่ 96%

โครงการวิจัย
“การเกิดไมโครอิมัลชั่นของน้ำเสียที่มีน้ำมันปนเปื้อนโดยใช้สารลดแรงตึงผิวและความสัมพันธ์เกี่ยวกับกระบวนการแยกแบบทำให้ลอย”

บทสรุปสำหรับผู้บริหาร (Executive Summary)

งานวิจัยนี้มีวัตถุประสงค์หลักเพื่อพัฒนาระบบฟองลอย (Froth Flotation) เพื่อใช้แยกน้ำมันจากน้ำเสียและสร้างความเข้าใจความรู้พื้นฐานกระบวนการทำงานระบบฟองลอย โดยมีสมมุติฐานว่าภายใต้สภาวะการเกิดไมโครอิมัลชั่นแบบที่ 3 (Winsor type III microemulsion) ซึ่งให้ค่าแรงตึงผิวระหว่างวัฏภาค (Interfacial Tension, IFT) ที่ต่ำมากๆ (Ultralow) ทำให้การเกิดฟองมากและพาน้ำมันออกไปกับฟองได้มาก ในการทดลองนี้ได้ใช้น้ำมันหลายชนิด ได้แก่ Orthodichlorobenzene (ODCB), Ethylbenzene, Diesel และ Cutting Oil โดยการทดลองอาจแบ่งได้เป็น 3 ส่วน ได้แก่ การศึกษาการเกิดไมโครอิมัลชั่น, การศึกษาลักษณะการเกิดฟอง และการศึกษาประสิทธิภาพการทำงานของระบบฟองลอย

ในส่วนของการศึกษา ODCB ซึ่งเป็นน้ำมันที่หนักกว่าน้ำ ได้ใช้สารลดแรงตึงผิวผสม ได้แก่ Sodium Dodecyl Sulfate (SDS) ซึ่งเป็นสารลดแรงตึงผิวชนิดประจุลบ และ Nonylphenol Ethoxylate ($NP(EO)_{10}$) ซึ่งเป็นสารลดแรงตึงผิวชนิดไม่มีประจุ พบว่าสารลดแรงตึงผิวผสมนี้สามารถทำให้เกิดไมโครอิมัลชั่นประเภท Winsor type III ซึ่งมี 3 ชั้น ซึ่งจะให้ค่า IFT ต่ำสุด โดยพบว่าที่ SDS : $NP(EO)_{10}$ = 0.4 : 0.6 และ NaCl = 1% จะให้ชั้นกลาง (Middle phase) กว้างสุด ซึ่งจะให้ค่า IFT ต่ำสุด น่าจะทำให้เกิดฟองสูงสุด จากนั้นได้ทำการทดลองที่สภาวะไมโครอิมัลชั่นดังกล่าวในระบบฟองลอย พบว่า ประสิทธิภาพการแยกน้ำมัน (ODCB) สูงสุดในระบบฟองลอยแบบกะ สอดคล้องกับสภาวะไมโครอิมัลชั่นที่ให้ค่า IFT ต่ำสุด นอกจากนี้ยังพบว่า ภายใต้สภาวะไมโครอิมัลชั่นแบบที่ 3 น้ำมันที่แยกได้ส่วนใหญ่มาจากชั้นน้ำมัน (Excess oil phase) ไม่ใช่มาจากชั้นกลาง (Middle phase)

ในส่วนของการศึกษา Ethylbenzene ซึ่งเป็นน้ำมันที่เบากว่าน้ำ และมักพบในผลิตภัณฑ์น้ำมันหลายชนิด ในส่วนของการศึกษาการเกิดไมโครอิมัลชั่นได้ใช้ Dihexyl sulfosuccinate (AMA) พบว่าสามารถทำให้เกิดไมโครอิมัลชั่นแบบที่ 3 (Winsor type III microemulsion) ได้ แต่ปริมาณชั้นกลางบางมาก ที่ 1%AMA และ 3%NaCl ให้ค่า IFT ต่ำสุด ประมาณ 0.02 mN/m ซึ่งนำไปใช้ในการทดลองในขั้นตอนที่ 2 ซึ่งเป็นการทดลองการแยกน้ำมันโดยใช้ระบบฟองลอย โดยพบว่าสภาวะสมดุลระหว่างน้ำและน้ำมันมีความสำคัญอย่างมากต่อประสิทธิภาพของการแยกน้ำมัน โดยการทดลองประกอบด้วย 3 ระบบ ระบบแรกให้สารผสมน้ำและน้ำมันเข้าสู่สภาวะสมดุล (Equilibrium) ซึ่งใช้เวลาประมาณ 1 เดือน ระบบที่สองนำน้ำและน้ำมันเทลงในคอลัมน์ ซึ่งเรียกว่าระบบไม่สมดุล (Non-equilibrium) ระบบที่สามเป็นการผสมน้ำและน้ำมันในเวลาสั้นเพียง 40 นาที ซึ่ง

3. Diesel การทดลองในส่วนของน้ำมันดีเซลแบ่งเป็น 2 ส่วน คือ การทดลองแบบกะ และแบบต่อเนื่อง ทั้งนี้เพื่อพยายามพัฒนาระบบฟองลอย (Froth flotation) ไปประยุกต์ใช้งานจริงต่อไป

3.1 Batch operation ในการทดลองนี้ได้เลือกสารลดแรงตึงผิวชนิดยืด (Extended surfactant) ที่เป็นแบบประจุลบและมีหางยาว ได้แก่ Branch alcohol propoxylate sulfate sodium salt (Alfoterra 145-5PO) ซึ่งจะช่วยทำให้เกิด Microemulsion ได้ง่ายขึ้น เนื่องจาก Alfoterra มีหางยาว และมีโครงสร้าง propylene oxide จึงทำให้ค่า HLB (Hydrophilic-Lypophilic Balance) มีค่าต่ำลง จึงมีความสามารถละลายน้ำมันได้สูงขึ้น โดยพบว่าที่ Alfoterra มีความเข้มข้น 0.1% และมีเกลือ 5% จะให้ค่า IFT ต่ำสุด (ประมาณ 10^{-2} mN/m) ซึ่งแสดงว่าระบบเป็น Winsor Type III Microemulsion เมื่อนำไปทดลองแยกน้ำมันโดยระบบฟองลอยที่ความเข้มข้น Alfoterra = 0.1% และเกลือ 3% พบว่ามีประสิทธิภาพการแยกน้ำมันสูงสุด ทั้งนี้ เนื่องจากระบบมี Foamability และ Foam stability สูงสุด ดังนั้น จึงสรุปได้ว่า ประสิทธิภาพการแยกน้ำมันโดยระบบฟองลอยขึ้นกับ 2 ปัจจัยหลัก ได้แก่ ค่า IFT ที่ยิ่งต่ำยิ่งดี กับคุณสมบัติของฟอง คือ การเกิดฟองได้ง่ายและเสถียรภาพของฟองต้องสูงด้วย

3.2 Continuous operation การทดลองระบบฟองลอยนี้ได้เปลี่ยนแปลงเป็นแบบต่อเนื่อง (continuous operation) กล่าวคือ มีการสูบน้ำที่มีน้ำมันเข้าคอลัมน์ตลอดเวลา ในส่วนของการศึกษาการเกิด Microemulsion พบว่าความเข้มข้น Alfoterra = 0.1% และ NaCl = 5% ระบบมีค่าแรงตึงผิวระหว่างชั้นน้ำและน้ำมันต่ำสุดประมาณ 0.02 mN/m ซึ่งอยู่ในช่วง Ultralow ระบบอยู่ใน Winsor Type III Microemulsion แต่ Middle phase มีปริมาณน้อยมากจึงไม่สามารถมองเห็นและวัดได้ เมื่อนำมาทดลองแยกน้ำมันดีเซลโดยระบบฟองลอย พบว่าไม่สามารถแยกน้ำมันได้เลย ทั้งนี้ เนื่องจาก ฟองมีความเสถียรต่ำมาก จึงไม่สามารถก่อตัวแล้วล้นออกจากคอลัมน์ได้เลย ดังนั้นจึงต้องเติมสารลดแรงตึงผิว Sodium dodecyl sulfate (SDS) ซึ่งเป็นสารลดแรงตึงผิวชนิดประจุลบ มีคุณสมบัติให้ฟองมาก พบว่าถ้าสัดส่วน SDS เพิ่มขึ้น จะทำให้อัตราการเกิดฟองสูงขึ้น แต่ประสิทธิภาพการแยกน้ำมันเพิ่มขึ้นในช่วงแรกและลดต่ำลงมามากในภายหลัง การเพิ่มเกลือในช่วง 2-4% สามารถเพิ่มประสิทธิภาพการแยกน้ำมันและ Enrichment ratio ให้สูงขึ้นได้ การเพิ่มหรือลดสัดส่วนน้ำมันต่อน้ำ ไม่มีผลต่อประสิทธิภาพการแยกน้ำมันและอัตราการผลิตฟอง ที่สำคัญ พบว่า ถ้าเพิ่มเวลาเก็บกัก (Hydraulic retention time) ทั้งประสิทธิภาพการแยกและ Enrichment ratio ของน้ำมันดีเซลเพิ่มสูงขึ้น โดยที่เวลาเก็บกัก 49 นาที สามารถแยกน้ำมันได้สูงถึง 90%

3.3 Colloidal gas aphon ในการทดลองนี้ ได้นำเทคนิคที่ทำให้น้ำมันผสมกับน้ำได้ดีขึ้น ซึ่งเรียกว่า Colloidal gas aphon (CGA) โดยการตีสารละลายน้ำกับน้ำมันดีเซลด้วยความเร็วสูง 4,000 – 8,000 รอบต่อนาที โดยใช้ Homogenizer สารลดแรงตึงผิว Alfoterra ยังคงใช้ในการทำให้เกิดไมโครอิมัลชั่น จากผลการทดลองระบบฟองลอย พบว่า ประสิทธิภาพการแยกน้ำมันสูงสุดที่ 97% เมื่อใช้ปริมาณ Alfoterra ($C_{14-15}(PO)_5SO_4$) ที่ 0.1% เติมเกลือ (NaCl) ที่ 3% โดยกวนผสมที่ความเร็ว 5,000 rpm เป็นเวลา 5 นาที และใช้ความเร็วเป่าอากาศ 15.27 cm/min

4. Cutting Oil น้ำมัน Cutting oil เป็นน้ำมันผสมหลายชนิดที่ใช้ในการหล่อชิ้นงานโลหะในขณะทำการตัดและเจาะเพื่อระบายความร้อนและลดแรงเสียดทาน ดังนั้น จึงเป็นปัญหาที่เกิดขึ้นในโรงงานหลายแห่ง โดยพบว่ามีปริมาณน้ำมัน Cutting oil สูงมากในน้ำทิ้งจากโรงงาน ดังนั้น จึงได้นำปัญหาที่เกิดขึ้นจริงในอุตสาหกรรมมาทดลองกับระบบฟองลอย ในการทดลองนี้ ได้ใช้สารลดแรงตึงผิวผสมได้แก่ Alfoterra ($C_{14-15}(PO)_5SO_4$) และ Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) เพื่อทำให้เกิดไมโครอิมัลชั่นกับน้ำมัน Cutting oil จากนั้นนำไมโครอิมัลชั่นที่เกิดขึ้นที่ปริมาณสารลดแรงตึงผิวต่างๆ ไปทำการทดลองแยกน้ำมันโดยระบบฟองลอยแบบต่อเนื่อง พบว่าระบบไม่สามารถแยกน้ำมันได้ เนื่องจากฟองที่เกิดมีเสถียรภาพต่ำมาก ดังนั้น จึงต้องเปลี่ยนสารลดแรงตึงผิวเป็น SDS แทน พบว่าประสิทธิภาพในการแยกน้ำมันสูงถึง 96% ที่สภาวะการทดลอง ดังนี้ 0.1%SDS; 5%NaCl, อัตราการเป่าอากาศ 0.15 L/min, ความสูงของฟอง 30 cm และเวลาเก็บกัก(HRT) 60 min

นอกจากนี้ ปัจจุบันยังกำลังทดลองกับน้ำมันเครื่อง (Motor oil) และศึกษาขนาดของฟองอากาศที่เกิดขึ้นในคอลัมน์และความเร็วของฟองอากาศที่ไหลขึ้น ทั้งนี้เพื่อสร้างความรู้ความเข้าใจของระบบฟองลอย อนึ่ง ในส่วนของผลงานวิจัยของ Cutting oil จะนำไปประยุกต์ใช้งานจริงเร็วๆนี้

Output ที่ได้รับจากโครงการ

ผลที่ได้รับจากโครงการวิจัยนี้ สามารถแยกได้ดังนี้

1. เผยแพร่ผลงานวิจัย การเผยแพร่ผลงานวิจัยแบ่งได้ ดังนี้

1.1 <u>ตีพิมพ์ในวารสารนานาชาติ (International Journals)</u> ได้ตีพิมพ์ไปแล้ว 4 เรื่อง และอยู่ระหว่างเขียนอีก 4 เรื่อง

1) Chavadej*,S., Ratanarojanatam, P., Phoochinda, W., Yanatatsaneejit, U. and Scamehorn, J.F. (2004), Clean-up of Oily Wastewater by Froth Flotation: Effect of Microemulsion Formation II: Use of Anionic/Nonionic Surfactant Mixtures, *Separation Science and Technology*, 39, 13, 3079-3096.

2) Chavadej*,S., Phoochinda, W., Yanatatsaneejit, U. and Scamehorn, J.F. (2004), Clean-up of Oily Wastewater by Froth Flotation: Effect of Microemulsion Formation III: Use of Anionic/Nonionic Surfactant Mixtures and Effect of Relative Volumes of Dissimilar phases, *Separation Science and Technology*, 39, 13, 3097-3112.

3) Yanatatsaneejit, U., Wittayapanyanon, A., Rangsunvijit, P., Acosta, E.J., Sabatini, D.A., Scamehorn, J.F. and Chavadej*, S. (2005), Ethylbenzene Removal by Froth Flotation under Conditions of Middle-Phases Microemulsion Formation I: Interfacial Tension, Foamability and Foam Stability, *Separation Science and Technology*, 40, 7, 1537-1553.

4) Yanatatsaneejit, U., Chavadej*, S., Rangsunvijit, P. and Scamehorn, J.F. (2005), Ethylbenzene Removal by Froth Flotation under Conditions of Middle-Phases Microemulsion Formation II: Effect of Air Flow Rate, Oil to Water Ratio and Equilibrium Time, *Separation Science and Technology*, 40, 7, 1609-1620.

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6) Watcharasing, S., Chavadej*, S., Scamehorn, J.F. and Yanatatsaneejit, U., (2005), Diesel Removal by Froth Flotation under Low Interfacial Tension Conditions II: Continuous Mode of Operation, *Separation Science and Technology* (In preparation)

7) Watcharasing, S., Angkathunyakub. P., Scamehorn, J.F. and Chavadej*, S., Diesel Removal from Water by Batch Froth Flotation under Colloidal Gas Aphon Formation, *Separation Science and Technology* (In preparation)

8) Watcharasing, S., Lapee-e, A., Scamehorn, J.F. and Chavadej*, S., Cutting Oil Removal by Continuous Froth Flotation under Low Interfacial Tension and Relation to Foam Characteristics, *Separation Science and Technology* (In preparation)

*corresponding author

1.2 ตีพิมพ์ในการประชุมวิชาการนานาชาติ (Proceeding) ได้เข้าร่วมประชุมวิชาการนานาชาติ และได้เสนอผลงานวิจัยในรูปวาจา (Oral presentation) และมีบทความวิชาการเต็มรูปแบบ (Full paper) รวมทั้งสิ้น 7 เรื่อง ดังนี้

1) Yanatatsaneejit, U., Watcharasing, S., Chavadej, S., Rangsunvijit, P. and Scamehorn, J.F. (2005), Removal of Diesel in Froth Flotation Operation: Comparison between Batch and Continuous Modes of Operation, *Proceedings of The* 7^{th} *World. Congress of Chemical Engineering*, Glasgow, Scotland, 10-14 July, 10 pages

2) Watcharasing, S., Yanatatsaneejit, U., Chavadej, S., Rangsunvijit, P. and Scamehorn, J.F. (2004), Diesel Removal by Continuous Froth Flotation: Effects of Ultralow Interfacial Tension and Foam Characteristics, *Proceedings of The* 10^{th} *APPCChE Congress*, Kitakyushu, Japan, 17-21 October, 10 pages

3) Chuyingsakultip, N., Chavadej, S., Malakul, P. and Scamehorn, J.F. (2004), Surfactant Recovery from Aqueous Phase Using Multi-Stage Foam Fractionation, *Proceedings of The* 10^{th} *APPCChE Congress, Kitakyushu, Japan, 17-21 October, 10 pages*

4) Chungchamroenkit, P., Yanatatsaneejit, U., Kittiyanan, B., Chavadej, S., Scamehorn, J.F. and Resasco, D.E. (2004), Separation of Carbon Black from Silica by Froth Flotation Technique as an Approach for Single-Walled Carbon Nanotubes Purification, *Proceedings of The 10th APPCChE Congress*, Kitakyushu, Japan, 17-21 October, 10 pages

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6) Yanatatsaneejit, U., Phoochinda, W., Ratanarojanatam, P., Chavadej, S., and Scamehorn, J.F. (2003), Effect of Microemulsion Formation on Oily Wastewater Treatment by Using Froth Flotation Technique, *Proceedings of First International Symposium on Process Intensification and Miniaturature in Biological, Chemical, Environmental and Energy Conversion Technologies*, The University of Newcastle upon Tyne, 18-21 August, 6 pages

7) Witthayapanyanon, A., Yanatatsaneejit, U., Scamehorn, J.F., and Chavadej, S. (2003), Light Oil Removal from Wastewater by Middle Phase Microemulsion and Froth Flotation, *Proceedings of First International Symposium on Process Intensification and Miniaturature in Biological, Chemical, Environmental and Energy Conversion Technologies*, The University of Newcastle upon Tyne, 18-21 August, 5 pages

1.3 ได้เสนอผลงานวิชาการในที่ประชุมนานาชาติ (Oral presentation) ได้เสนอผลงานวิจัยในที่ประชุมวิชาการนานาชาติในรูปวาจา (Oral presentation) ทั้งสิ้น 6 เรื่อง ดังนี้

1) Yanatatsaneejit, U., Witthayapanyanon, A., Chavadej, S., Acosta, E.J., Scamehorn, J.F. and Sabatini, D.A., effect of Middle-Phase Microemulsion Formation on Ethylbenzene Removal by Using the Froth Flotation Technique, *Presentation in 94th AOCS Annual Meeting and Expo*, Kansas City, Missouri, USA, May 4-7, 2003

2) Witthayapanyanon, A., Yanatatsaneejit, U., Scamehorn, J.F., Sabatini, D.A. and Chavadej, S., Light Oil Removal from Wastewater by Middle Phase Microemulsion and Froth Flotation, *Presentation in 95th AOCS Annual Meeting and Expo*, Cincinnati, Ohio, USA, May 9-12, 2004

3) Yanatatsaneejit, U., Chavadej, S., Rangsunvijit, P. and Scamehorn, J.F., Effect of Interfacial Tension and Foam Charateristics on Diesel Removal in Froth Flotation, *Presentation in 95th AOCS Annual Meeting and Expo*, Cincinnati, Ohio, USA, May 9-12, 2004

4) Angkathunyakul, P., Chavadej, S., Rangsunvijit, P. and Scamehorn, J.F., Diesel Removal from Wastewater by Froth Flotation with Colloidal Gas Aphon, *Presentation in The 58th*

Divisional Meeting on Colloild and Interface Chemistry, Utsunomiya University, Utsunomiya, Japan, September 8-10, 2005

5) Watcharasing, S., Chavadej, S., and Scamehorn, J.F., The Oily Wastewater Treatment by Continuous Froth Flotation: Foam Characteristics, *Presentation in 97th AOCS Annual Meeting and Expo*, Kansas City, Missouri, USA, April 30-May 3, 2006

6) Chavadej, S., Lapee-e.A., Watcharasing, S., Rangsunvijit, P. and Scamehorn, J.F., Continuous Froth Flotation to Remove Cutting Oil from Wastewater, *Presentation in the 59th Divisional Meeting on Colloid and Surface Chemistry*, Hokkaido University, Sapporo, Japan, September, 13-15, 2006

2. สร้างนิสิตบัณฑิต

ระดับปริญญาเอก 1 คน

- น.ส. อมราวดี ญาณทัศนีย์จิต (2548)

ระดับปริญญาโท 4 คน

- น.ส. อนุรดี วิทยาปัญญานนท์ (2546)
- น.ส. สุนิสา วัชรสิงห์ (2547)
- น.ส. คาริณี พิสูจน์จักรวาฬ (2548)
- น.ส. อัลวียา ลาปีอี (2549)

3. ประยุกต์ใช้กับภาคอุตสาหกรรม

บริษัท Single Point Parts (Thailand) จำกัด ตั้งอยู่ 41 หมู่ 9 สวนอุตสาหกรรมโรจนะ พระนครศรีอยุธยา ได้ติดต่อมายังโครงการ เพื่อช่วยแก้ไขปัญหาน้ำเสียของโรงงานที่มีปริมาณสารน้ำมัน (Cutting oil) สูงมาก ในขณะนี้ได้ทำการทดลองแยกน้ำมันโดยระบบฟองลอยแล้วเสร็จสมบูรณ์ คาดว่า ในปีหน้า (2550) จะนำผลงานวิจัยนี้ไปใช้แก้ปัญหาจริงของโรงงานต่อไป

4. ประโยชน์ต่อการเรียนการสอน

ได้นำผลงานวิจัยใช้ประกอบการเรียนการสอนวิชา “Surfactant Science and Technology” ที่วิทยาลัยปิโตรเลียมและปิโตรเคมี

5. เกิดแนวคิดงานวิจัยอื่นๆ

จากงานวิจัยนี้ ได้นำไปสู่แนวคิดใหม่ๆที่เกี่ยวข้อง เช่น การใช้ระบบฟองลอยในการทำให้นาโนคาร์บอนแบบผนังเดียว (Single-Walled Carbon Nanotube) มีความบริสุทธิ์สูงขึ้น และการนำสารลดแรงตึง

ผิวกลับมาใช้ใหม่โดยกระบวนการฟองแบบลำดับส่วน (Foam Fractionation) และ การสังเคราะห์วัสดุที่มีพื้นที่ผิวสูงโดยใช้สารลดแรงตึงผิวเป็นแม่แบบ ซึ่งปัจจุบันกำลังดำเนินการอยู่

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Clean-up of Oily Wastewater by Froth Flotation: Effect of Microemulsion Formation II: Use of Anionic/Nonionic Surfactant Mixtures

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ABSTRACT

Froth flotation can be an effective method to remove emulsified oil from wastewater. In this series of studies, the relationship between surfactant phase behavior (the type of microemulsion that is formed between the oil and water) and efficiency of the flotation of ortho-dichlorobenzene is being investigated. The phase behavior is related to surfactant composition and salinity in this work. Use of anionic/nonionic surfactant

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mixtures here permit examination of a wide range of conditions compared to the use of only anionic surfactants. Optimum oil flotation corresponds to a Winsor Type III microemulsion, which also corresponds to minimum interfacial tensions between oil and water and to maximum solubilization of water and of oil into a surfactant-rich microemulsion phase. In this work, high selectivity for oil compared to water in the overhead froth was demonstrated, a necessary criterion for an effective separation.

Key Words: Oily wastewater; Froth floatation; Microemulsion.

INTRODUCTION

Chlorobenzene and its derivatives, such as ortho-dichlorobenzene (ODCB), are classified as hazardous substances. However, they are widely used in several applications.[1] Ortho-dichlorobenzene is representative of pollutants found in wastewater and ranks high in the U.S. Environmental Protection Agency list of organic priority pollutants.[2] Removal of ODCB and similar compounds from wastewaters prior to discharge is a challenging chemical engineering operation. We focus here on removal of ODCB as emulsified droplets in water, rather than as molecularly dissolved pollutants, although froth flotation can be used to remove the latter,[3] which is sometimes called foam flotation or foam fractionation. For a sparingly soluble chemical like ODCB, oil loadings can be many orders of magnitude higher for emulsified oil compared to dissolved oil.

Flotation is a surfactant-based separation process[4-6] in which surfactant is added to an aqueous solution and air is sparged through the solution. Air bubbles from sparging air are used as a means of separation.[7] Dissolved molecules or ions, solid particles (e.g., ore colligend or ink), or droplets of an emulsified oil can attach to the air bubbles and be carried over to the top of a flotation cell with the foam (called a froth, in this case). As a result, the formation of stable bubble-particle aggregation is required in the flotation technique[8] to increase separation efficiency. Flotation operations are suitable for dilute waste treatment because it has several advantages including rapid operation, low space requirement, high efficiency of removal, flexibility of application to various pollutants at various scales, and low cost.[9] Consequently, flotation has been used in addressing many waste treatment problems.[3,7,9-16] For example, Feng and Aldrich[15] found that up to 99% of diesel oil could be removed from water by flotation with cationic surfactants.

The presence of surfactant located at the air-water interface in flotation operations promotes the formation of a froth. Moreover, surfactants dramatically increase the dispersion of air in the flotation column or tank, reduce the coalescence of individual bubbles within the liquid, and decrease the rate at which the bubbles rise to the surface. Zouboulis et al.[7] reported that without surfactant, air flotation alone had very little effect on separation. A pure liquid does not foam[17] and so addition of a surfactant is necessary to induce frothing. When a surfactant is added to water, the surface tension of the solution decreases as a result of preferential adsorption of surfactant molecules at the air/water interface. The surfactant molecules are arranged at the interface such that the hydrophilic or polar group (head group) is situated in the water phase and the hydrophobic or hydrocarbon chain (tail group) in the air phase.[6] Moreover, a suitable amount of surfactant[9] and a suitable amount of salt[1] are needed to optimize the flotation system.

Under normal conditions, surfactants can reduce the interfacial tension between an oil phase and a water phase from ca. 30 mN/m to ca. 1 mN/m due to the preferrable adsorption of surfactants at the oil/water interface. In the complex froth flotation process, this interfacial tension reduction is probably partially responsible for the surfactant being important. At an optimal mixing ratio of brine, oil, surfactant, and cosurfactant, a microemulsion is formed.[18] Microemulsions are transparent or translucent dispersions containing two immiscible liquids with droplets of 10 to 100 nm diameter,[17] which do not separate[19] because they are thermodynamically stable. It is well known that ultralow oil/water interfacial tension (e.g., 10^{-3} mN/m) corresponds to formation of a third phase, in equilibrium with the oil and water phases, called a middle phase;[20] the system under these conditions is known as a Winsor Type III microemulsion. It has been hypothesized by us that synergisms in froth flotation of oily wastewater could correspond to a Type III microemulsion. In the first paper in this series,[1] we showed that maximum ODCB removal did occur in an anionic surfactant system when the system was formulated so that a Winsor Type III microemulsion was present. However, limitations on formulation freedom do not permit flotation at the composition at which minimum interfacial tensions are expected in that system (called optimum conditions) because surfactant precipitation and liquid crystals form under these conditions for that system. When microemulsions are used in enhanced oil recovery, surfactant-enhanced subsurface remediation, and consumer products (to name just three applications), this problem is often avoided by adding a hydrotrope such as a low-molecular-weight alcohol (e.g., isopropanol), often at levels of a few percentage in solution. The hydrotrope reduces the tendency to form ordered surfactant structures like solid crystals or liquid crystals, avoiding phase-separation problems.[17]

The option of adding a hydrotrope at these fairly high concentrations is not feasible in the froth flotation process for two reasons. First, the hydrotrope can volatilize if its vapor pressure is too high, leading to air pollution. Second, the hydrotrope will probably remain in unacceptably high concentrations in the water, after the emulsified oil is removed, to permit discharge to the environment. It is interesting to note that in surfactant-enhanced subsurface remediation, if the surfactant is to be reused after flushing the solution through contaminated soil, and the contaminant is volatile (e.g., trichloroethylene), a stripping operation is commonly used to, for example, air strip to remove trichloroethylene from the surfactant solution. The presence of a high concentration of a volatile hydrotrope can dramatically increase the load on the stripper as well as requiring replacement of the hydrotrope upon recycle of the surfactant solution. Salvager's hydrophobic linker[21] and the use of cosurfactants (like long-chain alcohol) by Uchiyama et al.[22] were employed to replace the function of the hydrotrope by (hopefully, a much lower concentration of) a higher-molecular-weight material. In this study, mixtures of an anionic surfactant (sodium dodecyl sulfate) and a nonionic surfactant (nonylphenol polyethoxylate) were used to adjust phase boundaries without a volatile hydrotrope present.

In our previous study[1] of ODCB removal using an anionic surfactant, while enhancement of oil removal with the froth in the microemulsion region was established, water carryover with the foam was not measured. Measurement of both water and oil in froth carryover in this work indicates the selectivity of the separation for the oil.

EXPERIMENTAL SECTION

Materials

The oil used was ortho-dichlorobenzene (ODCB), obtained from Fisher Scientific Co., with 99.9% purity. The surfactants were sodium dodecyl sulfate (SDS) from Henkel company with at least 90% purity and nonylphenol ethoxylate ($NP(EO)_{10}$) obtained from ICI Australia Operations Pty Ltd. with a purity of greater than 99.9%. Sodium chloride (NaCl), analytical purity grade, was obtained from Aldrich Chemical Co. Deionized water was used in all of the experiments.

Methodology

In both the microemulsion phase behavior and the froth flotation experiments, the surfactant concentration and salinity were expressed as weight percent of the overall system; namely, water, oil, surfactant, and salt. All experiments were conducted at 30°C.

In investigation of phase behavior, 5 mL of a well-mixed aqueous solution, comprised water, surfactant, and salt, was mixed with 5 mL of ODCB in a vial and sealed with a screw cap and held in a constant temperature water bath at 30°C. The vials were shaken every 2 hr for 12 hr, and then left to stand in the water bath at 30°C for 1 month until equilibrium was achieved. The volume of each phase at equilibrium was determined by measurement of phase height.

A schematic diagram of the froth flotation apparatus used in this study is shown in Fig. 1. A cylindrical glass column with 5 cm internal diameter and 70 cm height was used as a froth flotation column. One liter of well-mixed solution was immediately transferred into the flotation column. The studied solutions were prepared according to the phase behavior results which will be described in detail later. Filtered air was introduced at the bottom of the froth flotation column at a constant flowrate of 250 mL/min through a sintered glass disk, having pore size diameter about 16–40 μm. Foam from the top of the column was collected at 20, 30, and 60 min and was then broken for analysis as a liquid. Concentrations of surfactants and ODCB in each phase of the solution were analyzed by a HPLC (Hewlett Packard, Series 1050) with a UV detector.

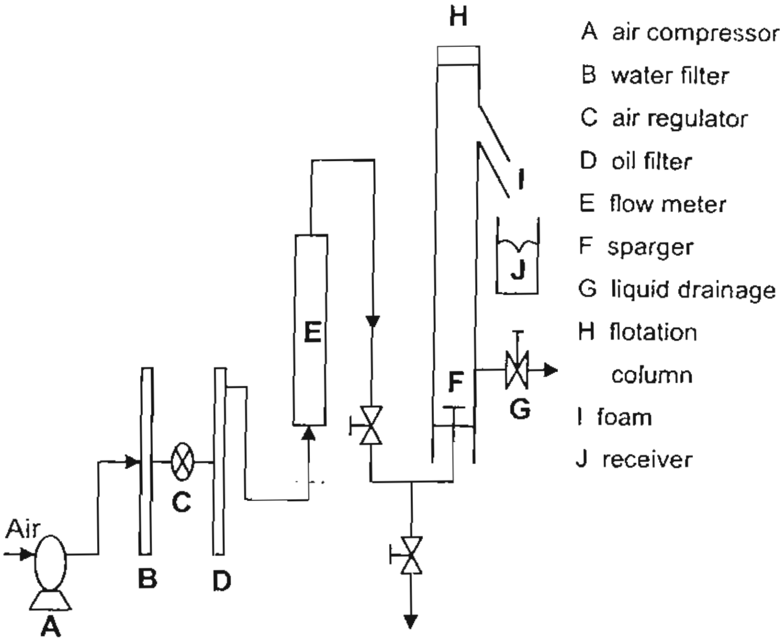

Figure 1. Schematic diagram of the froth flotation apparatus.

RESULTS AND DISCUSSION

In this study, X_{SDS} is defined as the weight fraction of SDS, which is the weight of SDS divided by a total weight of mixed surfactants (SDS and $NP(EO)_{10}$). Moreover, the total surfactant concentration is reported in units of weight percentage of total solution (water, oil, salt, and surfactants).

Phase Behavior Results

As reviewed in detail in part I of this series,[1] microemulsions can be classified as Winsor Type I, II, or III.[20,23,24] In a Type I system, the surfactant-containing water phase is in equilibrium with an excess oil phase which contains little surfactant while the surfactant-containing oil phase is in equilibrium with an excess water phase that contains little surfactant in a Type II system. For a Winsor Type III system, a third or middle phase is in equilibrium with an excess oil phase and an excess water phase. The middle phase forms between the excess phases since it has intermediate density between oil and water, and this middle phase contains almost all of the surfactants. In general, as the system is adjusted to make the surfactant more hydrophobic (e.g., increased salt concentration for an anionic surfactant; increased temperature for a nonionic surfactant), the order of transition is Type I to III to II. When the volume of water equals the volume of oil in the middle phase, interfacial tensions between phases are at a minimum, and this is known as the optimum condition. In part I of this series,[1] we showed that increasing salinity for a SDS system of ODCB and water caused a Winsor Type I to III transition. However, surfactant solubility problems did not permit the optimal salinity from being reached. The traditional solution to solve these solubility problems, adding low-molecular-weight alcohol to the system, is unacceptable in our wastewater application since this alcohol will be present at a substantial concentration in emitted water. So, in this work, a less hydrophilic cosurfactant ($NP(EO)_{10}$) was added to SDS to attain optimum conditions.

Effect of Single Surfactant Concentration on Microemulsion Formation

The effect of either SDS or $NP(EO)_{10}$ concentration on microemulsion formation in single surfactant system without added NaCl is illustrated in Figs. 2 and 3, respectively. When SDS concentration increases from 1% to 9% by weight, the volume of water phase slightly increases and that of oil phase slightly decreases because SDS solubilizes more oil into the water

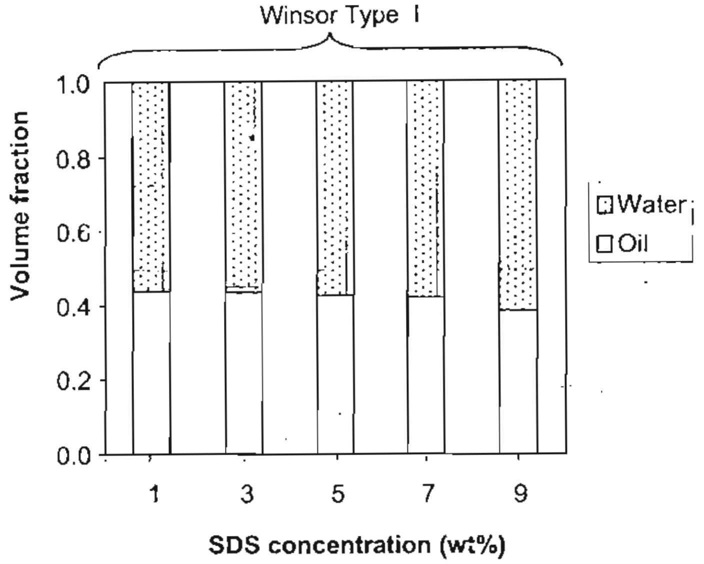

Figure 2. Volume fractions of water, middle, and oil phases at different SDS concentrations, with initial oil:water volume ratio of 1:1, and without NaCl.

phase. The system is a Winsor Type I microemulsion. In the case of $NP(EO)_{10}$, a Winsor Type III microemulsion is observed with a maximum relative volume of the middle phase microemulsion at 7% by weight of surfactant. At this composition, substantial amounts of both oil and water are solubilized (0.165 mL of oil and 0.335 mL of water). It is well known that the minimum interfacial tension (sum of water/microemulsion and oil/microemulsion interfacial tensions) corresponds to equal volumes of oil and water solubilized in the middle phase microemulsion; furthermore, the higher the volume of either oil or water solubilized at this "optimal condition," the lower the interfacial tension is observed.[25,26] In part I of this series,[1] it was found to be impossible to obtain conditions where a significant amount of water was solubilized in the middle phase microemulsion for the SDS-only system because liquid crystals were formed at high surfactant concentrations.

Effect of Mixed Surfactant Composition on Microemulsion Formation

The effect of mixed surfactant composition without added NaCl on phase behavior is illustrated in Figs. 4–8. The optimum volume fraction

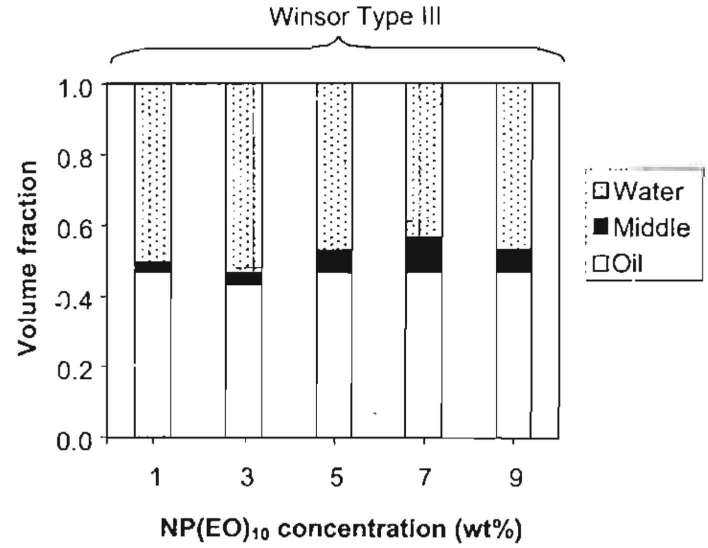

Figure 3. Volume fractions of water, middle, and oil phases at different $NP(EO)_{10}$ concentrations, with initial oil:water volume ratio of 1:1, and without NaCl.

of the middle phase microemulsion is at X_{SDS} of 0.2 to 0.4, indicating the synergism of surfactant mixtures compared to either anionic or nonionic surfactant alone. At total surfactant concentrations of 1 and 3% by weight, an insignificant amount of water is solubilized in the middle phase microemulsion, as was observed with SDS-only systems.[1] Therefore, optimal conditions (minimum interfacial tensions) are not achieved. However, at a surfactant concentration of 5% by weight and X_{SDS} at 0.5, approximately equal volume of oil and water are solubilized in the microemulsion phase, due to a proper balance between hydrophobicity and hydrophilicity of the surfactant mixture. When total surfactant concentration is equal to or greater than 7% by weight, liquid crystals appear. Consequently, 5% by weight of total surfactant concentration was chosen to study in froth flotation experiment because it has a high-volume fraction of the middle phase without liquid crystals, which corresponds to minimum interfacial tensions.

Phase scans like that in Figs. 4–8 have also been carried out for this system at added NaCl concentration up to 2.5% by weight. Since flotations were only performed without added NaCl, these phase volume plots are not reported here but available in a thesis.[27]

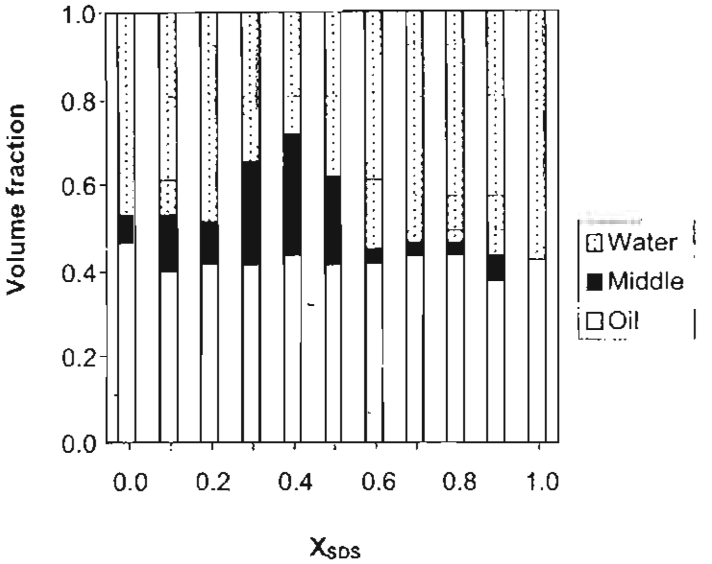

Figure 6. Volume fractions of water, middle, and oil phases at 5% by weight total surfactant concentration, with initial oil:water volume ratio of 1:1, and without NaCl.

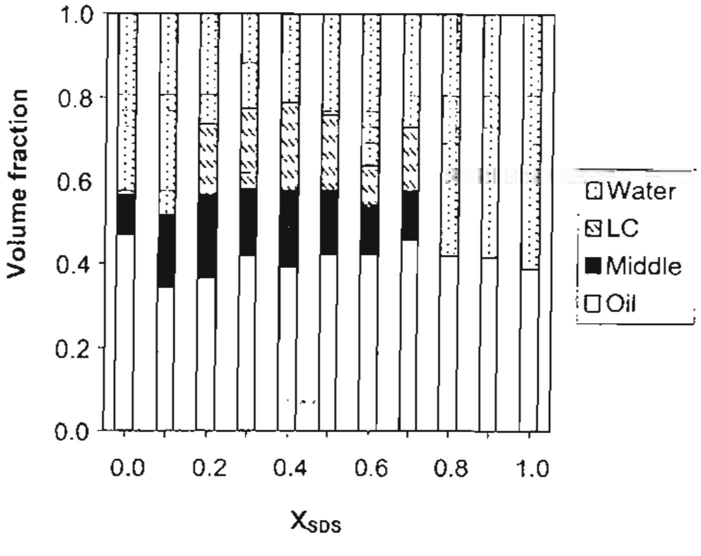

Figure 7. Volume fractions of water, middle, and oil phases at 7% by weight total surfactant concentration, with initial oil:water volume ratio of 1:1, and without NaCl.

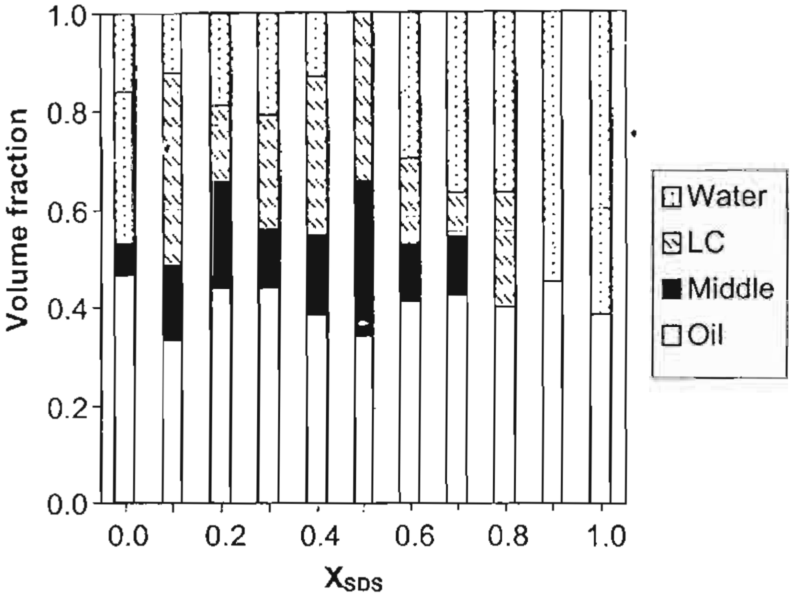

Figure 8. Volume fractions of water, middle, and oil phases at 9% by weight total surfactant concentration, with initial oil:water volume ratio of 1:1, and without NaCl.

Effect of NaCl on Microemulsion Formation of Mixed Surfactant System

For anionic or anionic/nonionic surfactant systems, added electrolyte can dramatically affect microemulsion phase behavior. From Fig. 9 at X_{SDS} of 0.4 and a surfactant concentration of 1% by weight, an increase in NaCl concentration leads to a Winsor Type III to Winsor Type II transition. This is because the surfactant solubility decreases for the mixed anionic/nonionic system (just like an anionic-only system), so the transition from the Type III to II occurs at lower values of X_{SDS} at higher NaCl concentrations. From the result, the optimum salinity is 1.5% by weight, which gives the highest volume fraction of the middle phase and equal volume of both oil and water solubilized. In wastewater clean-up, the added salt will largely end up in the excess water phase, which would be emitted to the environment and could make that water exceed total allowable dissolved solid content. All phase behaviors of the system with added NaCl between 0% and 2.5% by weight are available in a thesis.[27] The added salt gives the ability to adjust the phase behavior

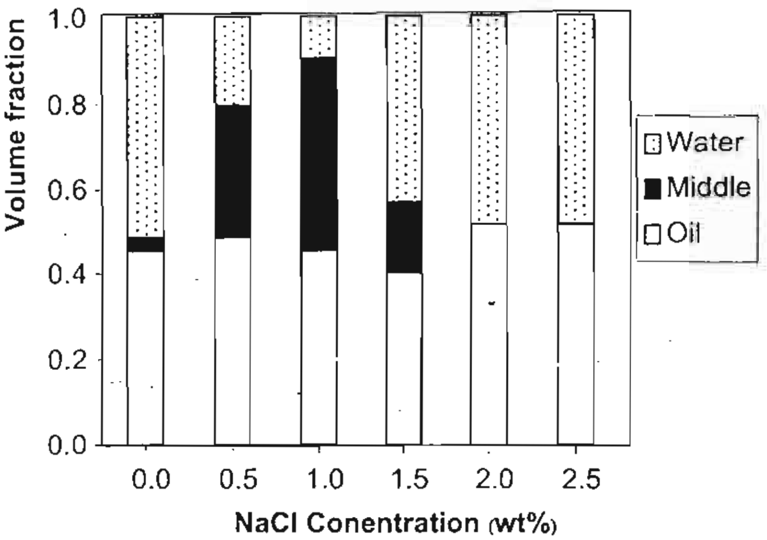

Figure 9. Volume fractions of water, middle, and oil phases at 1% by weight total surfactant concentration, X_{SDS} of 0.4, and initial oil:water volume ratio of 1:1.

of a system. Also, the effect of salinity is important to know because the natural salinity of a waste stream can vary widely.

Froth Flotation Results

Froth flotation studies were conducted at 5% by weight of total surfactant concentration since the system has the highest solubilization parameters of both oil and water in the absence of added salt. In this work, the effects of weight fraction of SDS (X_{SDS}) on oil removal, on surfactant removal, and on foam composition are shown in Figs. 10–14. As X_{SDS} increases, the tendency for foam production increases, perhaps because the repulsive force between the negatively charged head groups of SDS can electrostatically stabilize the film lamellae of the foam. Therefore, the efficiency of oil and of surfactant removal increases when X_{SDS} increases. At 5% by weight of total surfactant concentration, the optimum X_{SDS} from the phase behavior is 0.5. However, the highest oil and surfactant removal was achieved at $X_{SDS} = 0.8$, which is still in the Winsor Type III microemulsion region as shown in Figs. 10–12. Therefore, the efficiency of froth flotation depends on not only equilibrium microemulsion phase behavior with the maximum solubilization parameters but also other effects such as air dispersion, froth

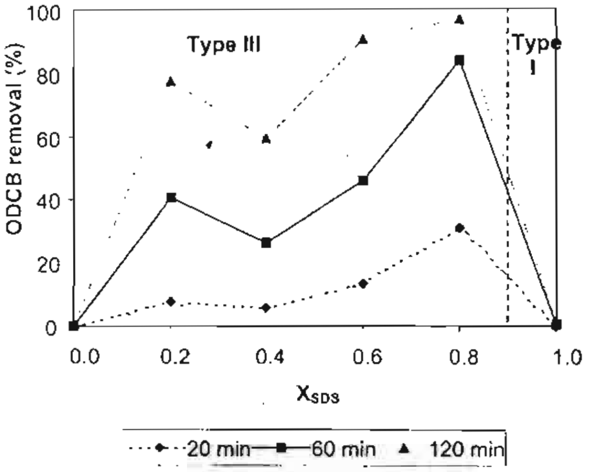

Figure 10. Dynamic removal efficiency of ODCB as a function of X_{SDS} at 5% by weight total surfactant concentration with initial oil:water volume ratio of 1:1, and without NaCl.

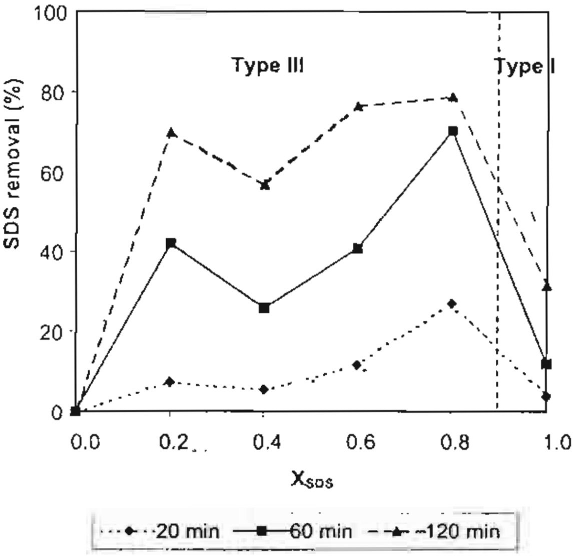

Figure 11. Dynamic removal efficiency of SDS as a function of X_{SDS} at 5% by weight total surfactant concentration with initial oil:water volume ratio of 1:1, and without NaCl.

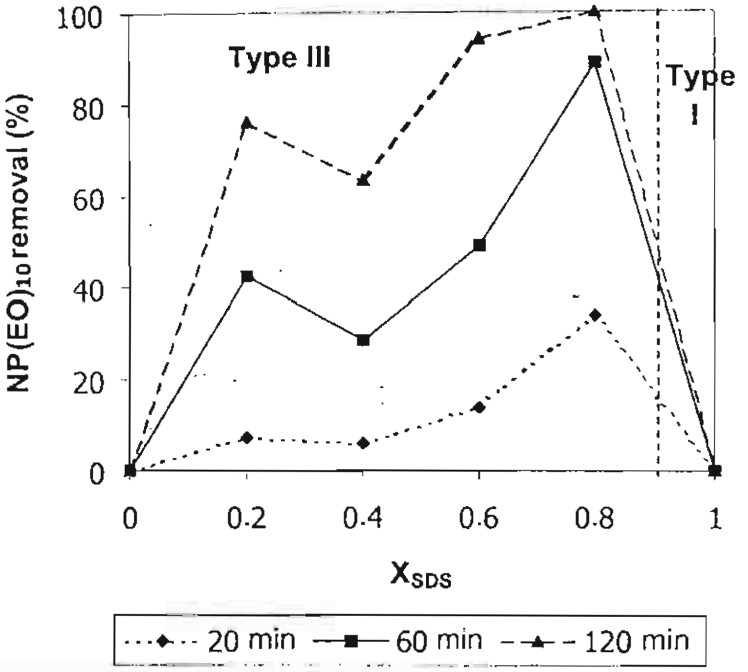

Figure 12. Dynamic removal efficiency of NP(EO)$_{10}$ as a function of X_{SDS} at 5% by weight total surfactant concentration with initial oil:water volume ratio of 1:1, and without NaCl.

stability, and nonequilibrium effects. An increase in aeration time directly enhances both surfactant and ODCB removal since more foam is produced with time. At an aeration time of 120 min, almost 100% removal of ODCB and NP(EO)$_{10}$ is observed while the removal of SDS is around 80% as shown in Fig. 13. This is probably because SDS is more hydrophilic than ODCB and NP(EO)$_{10}$, so SDS adsorbs less at the air bubble–water interface than the NP(EO)$_{10}$ does. It is particularly interesting that at higher concentrations of SDS, the additional SDS not only induces increased oil flotation but also induces increased NP(EO)$_{10}$ and SDS removal. This is probably because foam stability increases when SDS concentration increases, leading to an increase in the amount of surfactant associated with the froth. From Figs. 10–12, removal of ODCB, SDS, and NP(EO)$_{10}$ is higher in the Winsor Type III regime than in the Type I regime [as in previous results[11]], although not at the optimum conditions from equilibrium phase diagrams. So, ultralow oil/water interfacial tensions are important for good oil removal, although not the only factor. We will quantify foam stability and equilibration time effects in future work.

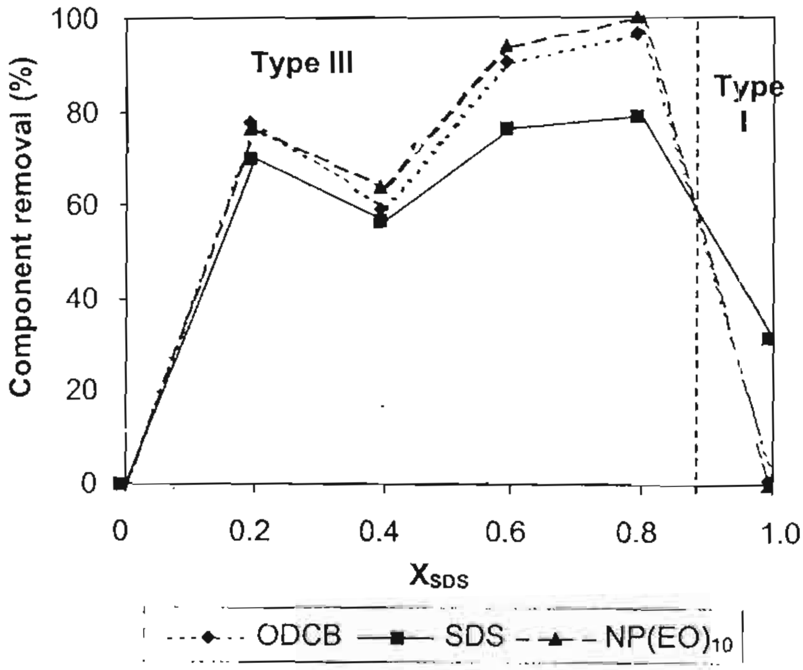

Figure 13. Comparison between removal efficiency of ODCB, SDS, and NP(EO)$_{10}$ at 5% by weight total surfactant concentration with initial oil:water volume ratio of 1:1, without NaCl, and 120 min aeration time.

High oil-removal efficiency is a necessity for an effective flotation operation, but it is not the sole factor to be considered. If oil and water are present in the froth in the same proportions as in the solution, no selectivity is present and no separation of oil and water is occurring. Figure 14 shows the relative fractions of oil and of water in the foam phase as a function of X_{SDS} at a total surfactant concentration of 5% by weight and at 120 min aeration time. When in the Winsor Type III microemulsion regime, more oil than water was indeed carried over with the foam. For example, at $X_{SDS} = 0.8$ (at which composition, fractional oil recovery is the highest observed), the weight ratio of ODCB:water is 2:1 in the collapsed foam. For all these experiments, the initial oil:water volume ratio was 1:1, corresponding to a very high oil loading in a wastewater. Selectivity may be improved further at lower oil loadings. It is very important to note that the separation efficiency of oil is worse when a Winsor Type I microemulsion is formed and which shows inverted results with more water than oil being carried overhead when a Type I

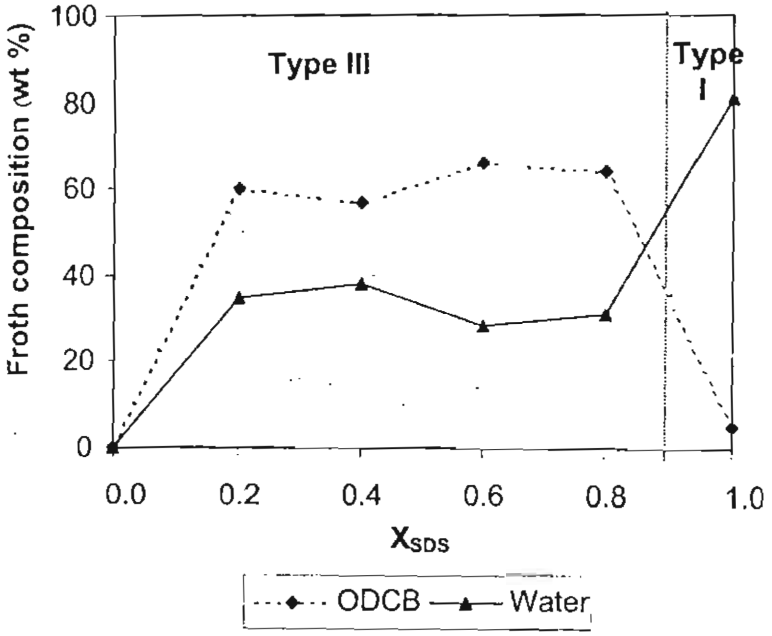

Figure 14. ODCB and water content in collapsed foam fraction as a function of X_{SDS} at 5% by weight total surfactant concentration with initial oil:water volume ratio of 1:1, without NaCl, and 120 min aeration time.

system is present. These results support further the advantages of formulating the system to be in Winsor Type III microemulsion regime.

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Chemical Company, Procter & Gamble Company, Reckitt Benckiser North America, Schlumberger Technology Corp., Shell Chemical Company, Sun Chemical Corporation, Unilever Inc., and Witco Corporation.

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Clean-up of Oily Wastewater by Froth Flotation: Effect of Microemulsion Formation III: Use of Anionic/Nonionic Surfactant Mixtures and Effect of Relative Volumes of Dissimilar Phases

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ABSTRACT

Froth flotation, a surfactant-based separation process, can be used to remove emulsified oil from water. In previous work, the maximum removal of ortho-dichlorobenzene from water using froth flotation was achieved when a Winsor Type III microemulsion was formed. However, the exact relationship between the equilibrium microemulsion characteristics and the froth flotation operation is still not clear. In the

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Winsor Type III microemulsion, three phases are present: an excess water phase containing little surfactant or oil, an excess oil phase containing little water or surfactant, and a middle phase containing almost all of the surfactant and large volume fractions of both oil and water (even equal volumes of oil and water). The Winsor Type III microemulsion also corresponds to a minimum in interfacial tension between liquid phases at equilibrium. In order to elucidate which aspect of the microemulsion is responsible for flotation of oil, flotation experiments were performed with three different combinations of phases: water and middle phases (w-m); water and oil phases (w-o); and water, middle, and oil phases (w-m-o). Since it was deduced that most oil being recovered when in the Winsor Type III microemulsion region is in the excess oil phase (not the middle phase), the reason why the Winsor Type III microemulsion results in excellent oil removal in flotation operation is probably the ultralow interfacial tensions present, and the formation of the middle phase is incidental.

Key Words: Oily wastewater; Froth floatation; Microemulsion.

INTRODUCTION

Flotation is widely used in several processes,[1-10] including selective separation of minerals,[4,6] removing ink from paper fibers in paper recycling, and removal of emulsified oil from water.[1,11] In part I of this series of papers,[1] it was demonstrated that the highest recovery of the model oil pollutant, ortho-dichlorobenzene (ODCB) occurred when a Winsor Type III microemulsion was present, compared to a Winsor Type I microemulsion when a single anionic surfactant, sodium dodecyl sulfate (SDS), was used. That was the first study to relate efficiency of froth flotation to microemulsion phase behavior. A limitation of that study was the formation of surfactant precipitate and liquid crystals to prevent investigation of a wide range of conditions; for example optimum salinity in the Winsor Type III system could not be studied. Not only the microemulsion type, but also the stability of froth have an effect on the efficiency of flotation operation. Matis and Zouboulis[12] reported that the stability of the froth is described by bubble coalescence and breakage parameters. The bubble coalescence is mainly due to the higher pressure inside the smaller bubbles, whereas the breakage is mainly caused by lowering the thickness of the film due to the force of gravity. The mechanism of froth flotation for the removal of insoluble organic contaminants from water is shown in Fig. 1.[1]

In part II of this series,[13] a mixture of SDS and nonionic surfactant, nonylphenol polyethoxylate ($NP(EO)_{10}$), was used to allow investigation of a

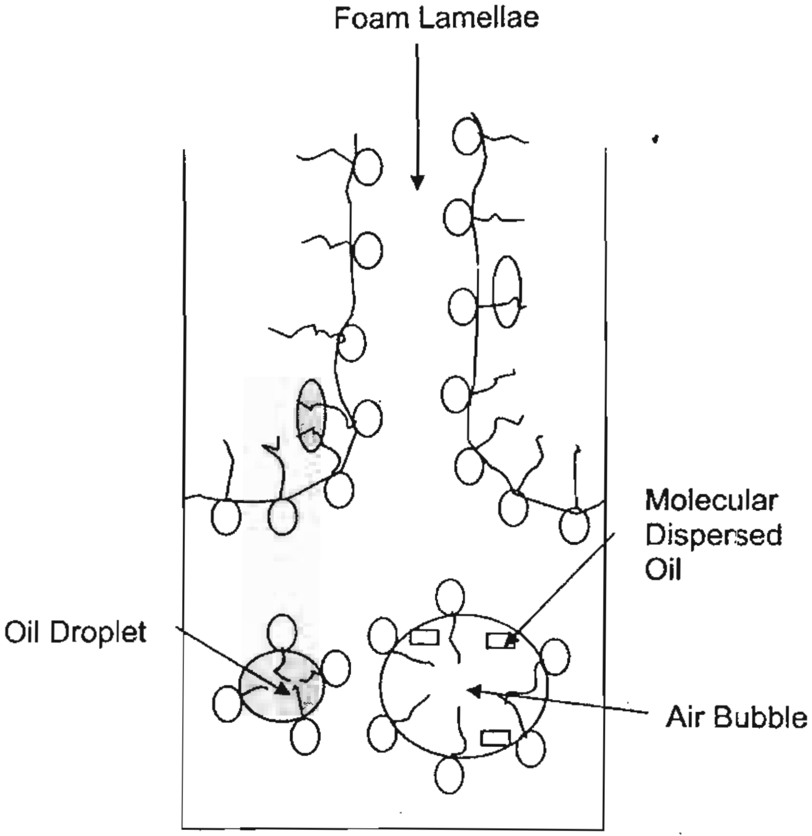

Figure 1. Schematic of the foam flotation process.

wide range of conditions. The composition of the foam was analyzed to address the issue of selectivity; i.e., high recovery of oil overhead in the froth is only of value if a small amount of water is being taken overhead. It was shown that the oil: water ratio in the foamate (broken foam from overheads) is substantially higher than that in the wastewater in a Winsor Type III microemulsion region where oil removal is maximized, so the separation has good selectivity. However, under some other conditions, more water than oil is carried over, making the separation inefficient and indicating the importance of relating operating conditions to phase space.

In this third part of the series, we address the following question: what is it about the Winsor Type III microemulsion that causes high flotation efficiency? Since the oil is present as both an excess oil phase and in the middle phase, from which phase is the oil coming overhead with the foam originating? Is the formation of the third or middle phase crucial or is it other characteristics (primarily ultralow interfacial tensions) of the Type III system that account for the high-separation efficiency during flotation? In order to address these questions, we have separated the three phases formed in the Winsor Type III microemulsion system after equilibration: excess oil (o), excess water (w), and middle phase (m). We then carried out the froth flotation experiments with different combinations of these phases (o-w; m-w, and w-m-o).

EXPERIMENTAL SECTION

Materials

Ortho-dichlorobenzene (product of Fisher Scientific Co.) with 99.9% purity was used as the model emulsified oil in this study. The surfactants were sodium dodecyl sulfate (SDS) from Henkel Co. with at least 90% purity and polydisperse nonylphenol ethoxylate ($NP(EO)_{10}$) from ICI Australia Operations Pty Ltd. with a purity greater than 99.9%. Sodium chloride (NaCl), analytical grade, from Aldrich Chemical Co., was used as added electrolyte. All the chemicals were used as received without purification. Deionized water was used in all experiments.

Methodology

In this study, the surfactant concentration and salinity were expressed as weight percent of the overall system composed of water, oil, surfactant, and salt. The experiments were conducted at 30°C.

Figure 2 shows a schematic diagram of the froth flotation apparatus used in this study. The froth flotation apparatus was composed of a cylindrical glass column with 5 cm internal diameter and 70 cm height and operated in batch mode. Filtered air was introduced into the bottom of the column at a constant flow rate of 250 mL/min through a sintered glass disk that has 16–40 μm pore diameter. At an initial oil:water ratio of 1:1 as just described, 1 L of different combinations of three phases (w-o, w-m, and w-m-o) was transferred into the column. These three phases were separated from the solution reaching equilibrium in a water bath at 30°C for 1 month under conditions corresponding to a Winsor Type III microemulsion. The foam overflown from the column was collected over different time intervals. After that, the foam was broken for analysis of the concentration of ODCB using an HPLC (Hewlett Packard, Series 1050) with a UV detector.

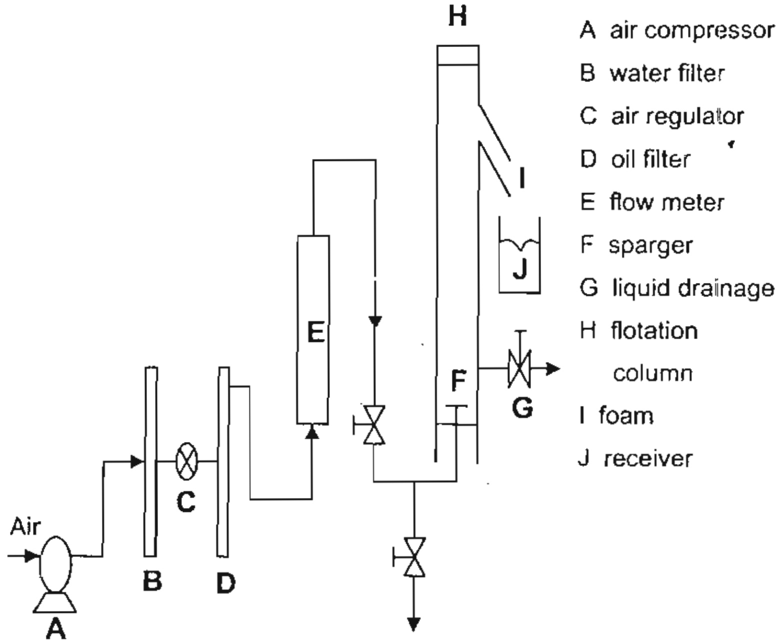

Figure 2. Schematic diagram of the froth flotation apparatus.

RESULTS AND DISCUSSION

In this study, X_{SDS} is defined as the weight fraction of SDS (the weight of SDS divided by the total weight of mixed surfactants). The total surfactant concentration in weight percent refers to the total mass of the system consisting of the total oil, water, salt, and surfactant. Phase behavior studies of all systems used in this work were shown in part II of this series.[13]

Effect of Initial Mixed Surfactant Concentration on ODCB Removal

As shown in Fig. 3, at low aeration time, the amount of oil removed increases when surfactant concentration increases. This is because increasing surfactant dosage can increase the number of air bubbles per unit volume and foam production.[3] Absolutely pure liquid does not foam.[14] Because one of the key mechanisms in the flotation is the attachment between air bubbles and oil droplets,[11] the amount of oil removal increases when the number of air bubbles increases. However, increasing surfactant concentration causes

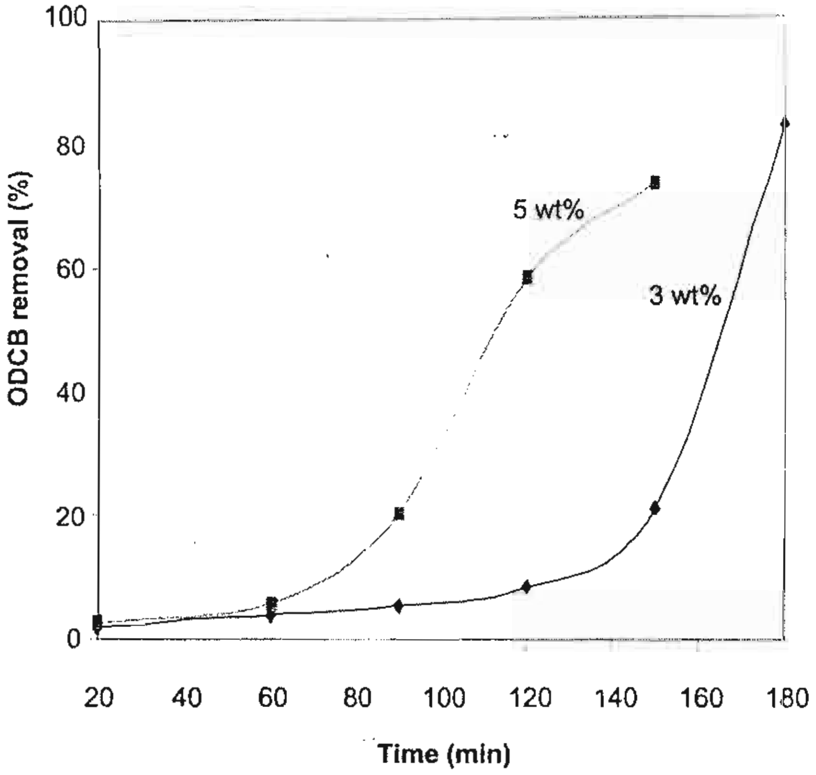

Figure 3. Comparison of ODCB removal between 3% and 5% by weight total surfactant concentrations at X_{SDS} of 0.2, without NaCl, and initial oil:water ratio of 1:1.

highly hydrated foam to be produced[2] due to an increase in the amount of water in the foam lamellae. As a result, the separation of oil and water in the overhead froth declines. Oil removal and selectivity for oil compared to water is a trade-off with respect to surfactant concentration.

Effect of NaCl Concentration on ODCB Removal

The system containing 3 wt% mixed surfactant concentration and X_{SDS} of 0.6 was used to study the effect of NaCl concentration on ODCB removal. As shown in Fig. 4, the amount of ODCB removal of the system containing 0.5 wt% is much higher than that of the system without NaCl. This might be because NaCl can reduce the repulsive force between anionic head

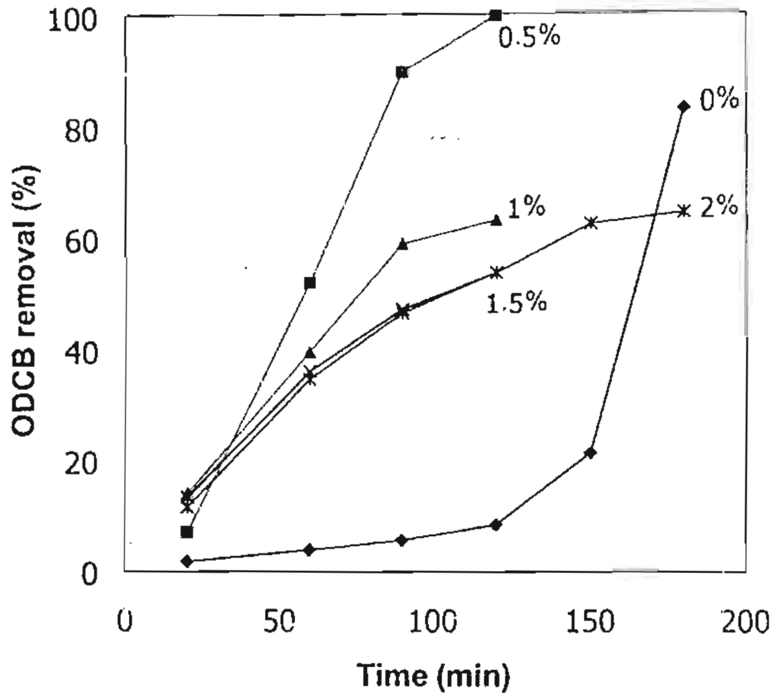

Figure 4. Comparison of ODCB removal at 3% by weight total surfactant concentration, X_{SDS} of 0.6, initial oil : water ratio of 1:1, and different NaCl concentrations.

groups of SDS leading to a higher density of surfactant molecule adsorbed at the surface of the foam lamellae. The resultant foam could be more stable and have a higher oil-carrying capacity. For ionic surfactant systems, at higher electrolyte concentrations, foam stability can decrease due to the reduction in repulsion between adsorbed surfactant monolayers on each side of the foam lamellae, providing a possible explanation for the observed maximum in oil removal with added NaCl concentration observed in Fig. 4.

Effect of the Presence of Different Phases on ODCB Removal

To investigate whether the formation of the third phase or middle phase in a Winsor Type III microemulsion influences the maximum oil removal, froth flotation of different combinations of three phases (w-o, w-m, and w-m-o) separated from Winsor Type III microemulsion solutions at equilibrium was performed. From Figs. 5–12 for both total surfactant concentrations of 3 and

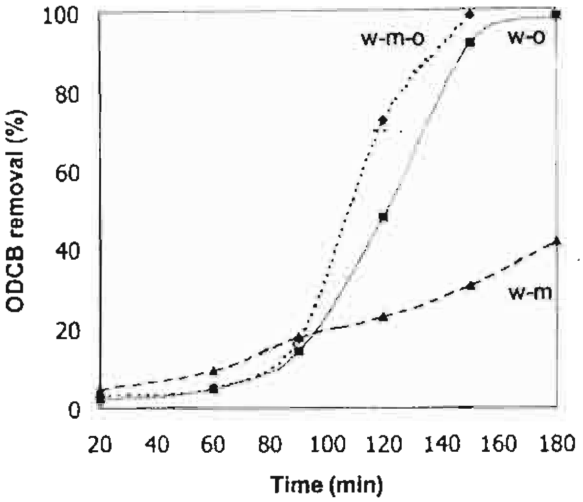

Figure 5. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, X_{SDS} of 0.2, without NaCl, and initial oil:water ratio of 1:1.

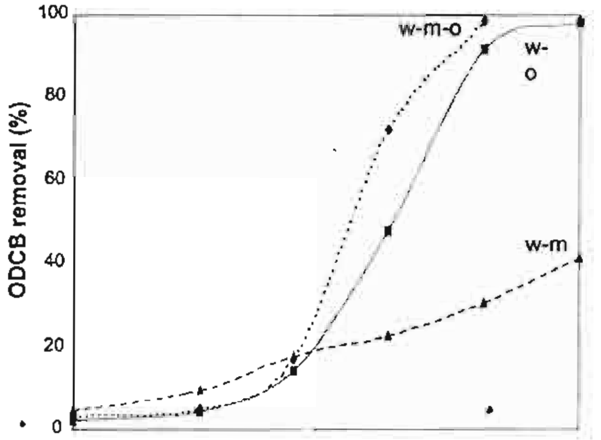

Figure 6. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, X_{SDS} of 0.4, without NaCl, and initial oil:water ratio of 1:1.

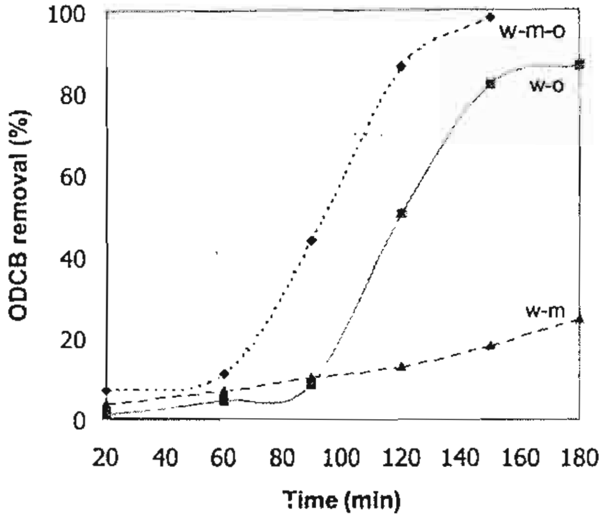

Figure 7. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, X_{SDS} of 0.6, without NaCl, and initial oil:water ratio of 1:1.

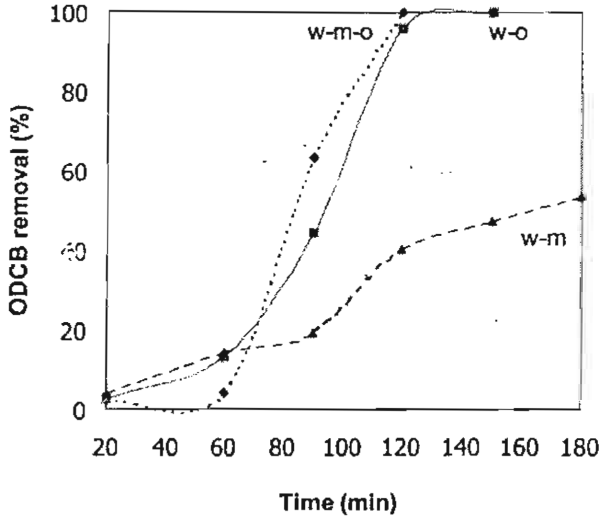

Figure 8. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, X_{SDS} of 0.8, without NaCl, and initial oil:water ratio of 1:1.

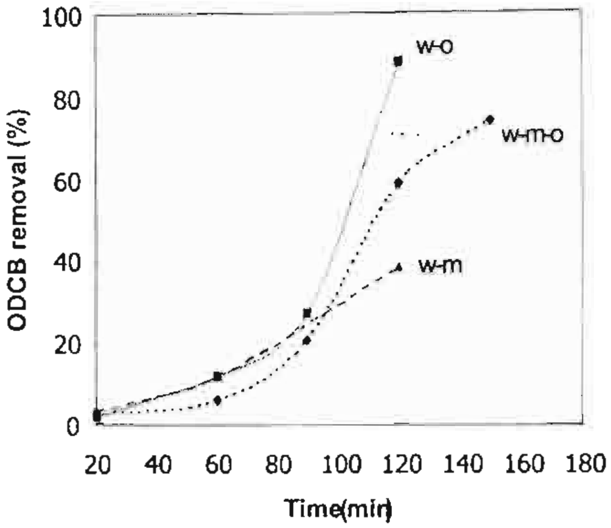

Figure 9. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 5% by weight total surfactant concentration, X_{SDS} of 0.2, without NaCl, and initial oil:water ratio of 1:1.

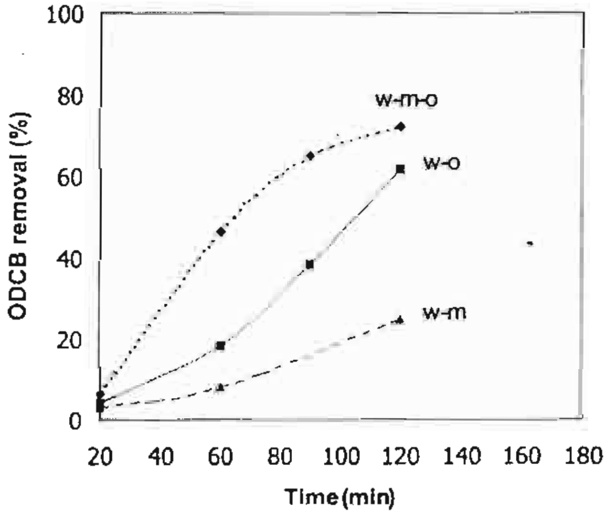

Figure 10. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 5% by weight total surfactant concentration, X_{SDS} of 0.4, without NaCl, and initial oil:water ratio of 1:1.

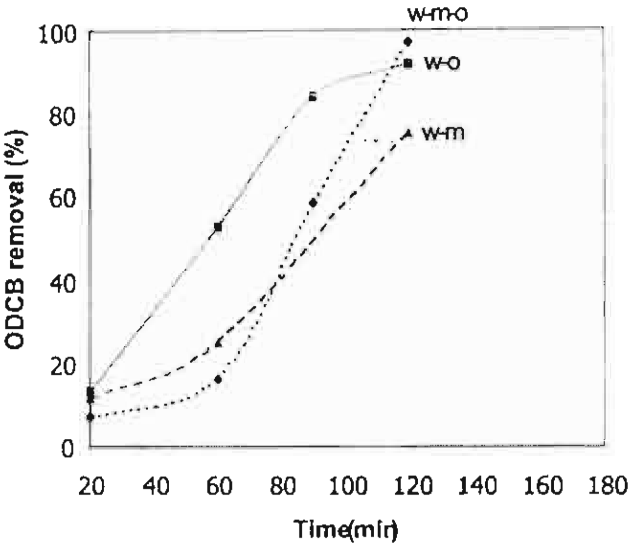

Figure 11. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 5% by weight total surfactant concentration, X_{SDS} of 0.6, without NaCl, and initial oil:water ratio of 1:1

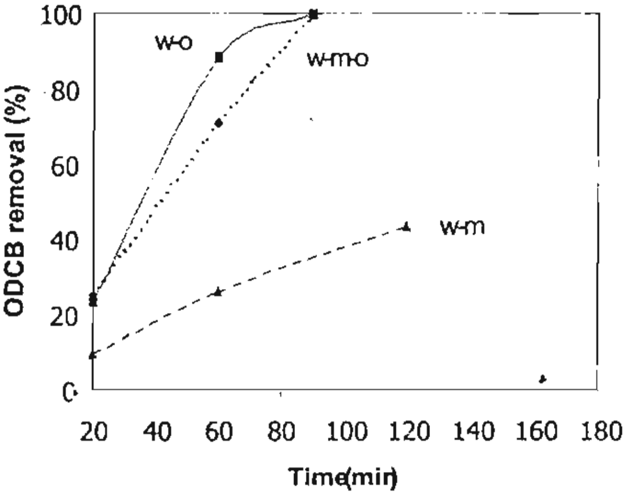

Figure 12. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 5% by weight total surfactant concentration, X_{SDS} of 0.8, without NaCl, and initial oil:water ratio of 1:1.

5% by weight, oil removal from w-o system is always higher than that from w-m system, and it is nearly as high as or higher as that from w-m-o system. It can be concluded that most of oil removed comes from the excess oil phase rather than from the middle phase in Winsor Type III microemulsion regime. This may be due to the oil surface in the middle phase being less hydrophobic than that in the excess oil phase. This is because oil droplets in the middle phase microemulsion are inside a bicontinuous structure.[15] This result implies that the third phase or middle phase the Winsor Type III microemulsion regime is not responsible for the high separation efficiency during flotation. Other characteristics in the Winsor Type III microemulsion such as ultalow interfacial tensions and foam stability are believed to also be important for high flotation efficiency. It is a coincidence that the middle phase is present when maximum oil removal is observed.

Effect of Weight Fraction of SDS on ODCB Removal

From Fig. 13 for the w-o system, foam volume increases with increasing weight fraction of SDS, but the weight fraction of SDS does not affect the

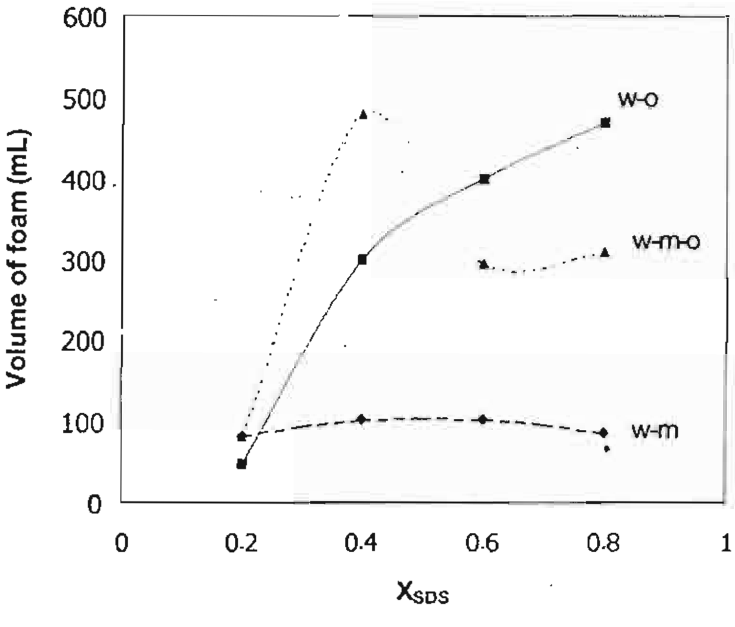

Figure 13. The foam volume of different systems having different X_{SDS}.

foam volume of the w-m system. The w-m-o system exhibits a maximum in foam volume with increasing weight fraction of SDS. The result also shows that anionic surfactant produces more foam than nonionic surfactant does. Ionic surfactants are commonly better foamers than nonionic surfactants,[16] so this is not unexpected. Consistent with this, high foam volume is achieved at high weight fraction of SDS. For all w-m-o, w-o, and w-m systems as shown in Fig. 14, increasing weight fraction of SDS increases the oil removal probably partly due to the effect of foam volume. The effect of the weight fraction of SDS on ODCB removal is important in both w-m-o and w-o systems as a result of high foam volume produced compared with that of the w-m system. However, the weight fraction of SDS utilized should be appropriate to keep a solution within Winsor Type III microemulsion regime in order to have high oil removal.

Effect of Weight Fraction of SDS and Initial Mixed Surfactant Concentration on Removal Time

In this study, only w-m-o and w-o systems can achieve 50% oil removal over the time intervals studied. Figures 15 and 16 show the effect of weight

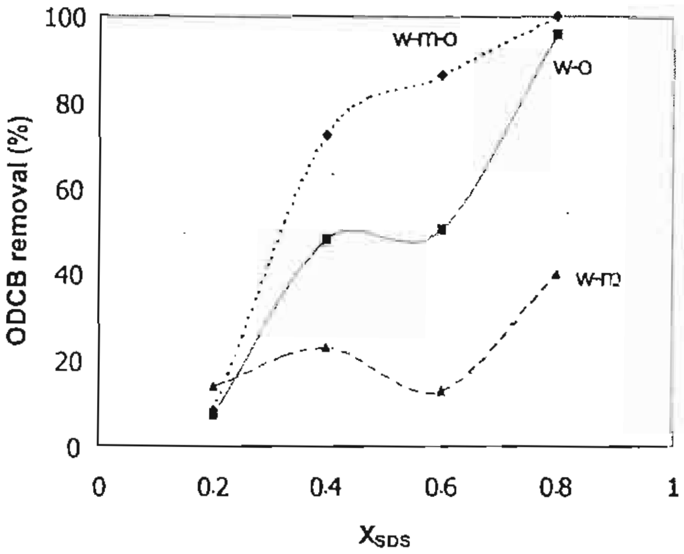

Figure 14. Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, without NaCl, initial oil:water ratio of 1:1, and 120 min aeration time.

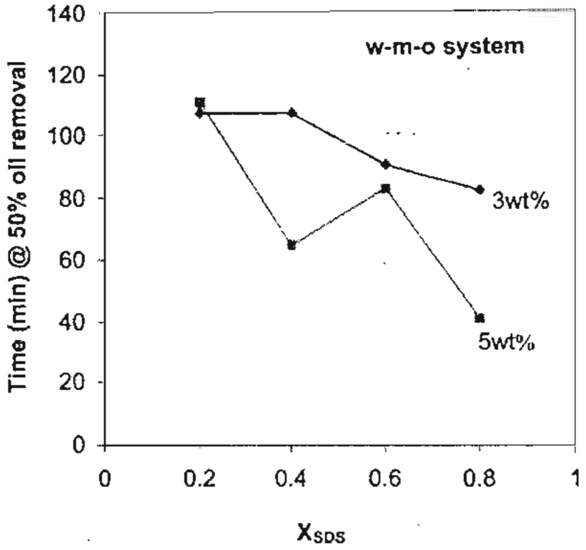

Figure 15. Comparison of time required to achieve 50% ODCB removal of w-m-o system at different fraction of SDS.

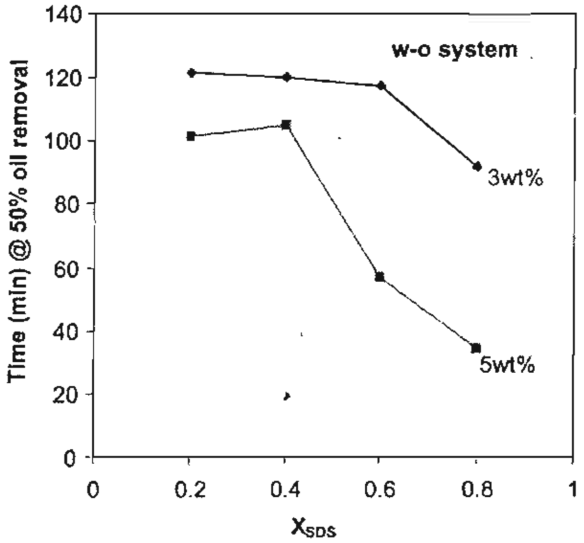

Figure 16. Comparison of time required to achieve 50% ODCB removal of w-o system at different fraction of SDS.

fraction of SDS on removal time for 50% oil removal in w-m-o and w-o system, respectively. To achieve 50% oil removal, the higher the weight fraction of SDS is, the shorter the operating time required. This is because more foam is produced at a higher weight fraction of SDS as shown in Fig. 13. For both w-m-o and w-o systems, 5 wt% initial mixed surfactant concentration requires a shorter time for 50% oil removal than 3 wt% initial mixed surfactant concentration does due to the higher amount of foam generated in the 5 wt% system.

From this result, it is obvious that oil removal efficiency depends upon both some characteristics in Winsor Type III microemulsion regime and the amount of foam volume produced.

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Ethylbenzene Removal by Froth Flotation Under Conditions of Middle-Phase Microemulsion Formation II: Effects of Air Flow Rate, Oil-to-Water Ratio, and Equilibration Time

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Abstract: Dihexyl sulfosuccinate (aerosol MA or AMA) was used to prepare microemulsion solutions in a study of the froth flotation process in batch mode to remove emulsified ethylbenzene from water. Oil removal, surfactant removal, and enrichment ratio were used to evaluate the performance of froth flotation. In this study, the effects of air flow rate, oil-to-water ratio, and equilibration time were investigated. A very high air flow rate was found to create more turbulence in the froth flotation column, resulting in low oil removal. As the oil-to-water ratio decreases, the enrichment ratio increases, whereas the oil removal slightly decreases. The froth flotation column with a feed solution in which the oil and water had been allowed to equilibrate was found to yield much higher ethylbenzene removal than that with a nonequilibrium feed solution. When the feed solution was agitated for 40 minutes to induce a state closer to equilibrium than with no mixing, the ethylbenzene removal was nearly as high as that with the equilibrium feed solution.

Keywords: Froth flotation, microemulsion, air flow rate

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INTRODUCTION

Froth flotation can be utilized in a variety of separation processes (1–5). Froth flotation is widely used in the area of mineral processing (6). However, it can also be used for wastewater treatment (7) as is studied here. In previous work (8), it was found experimentally that the highest removal of emulsified ortho-dichlorobenzene corresponded to the formation of a Winsor Type III microemulsion in the oil-water system in which an excess oil phase and excess water phase are in equilibrium with a "middle-phase", which is a microemulsion containing almost all the system surfactant. Chavadej et al. (9) concluded that most of the removed oil (ortho-dichlorobenzene) came from the excess oil phase rather than from the middle phase in the Winsor Type III microemulsion. In a continuation of our work, the relationship of the ultra-low interfacial tension characteristic of Winsor Type III microemulsions and the oil removal efficiency in a flotation column was studied and presented in Part I of this series of papers (10) with ethylbenzene as the oil. It was revealed that the ultra-low interfacial tension was not a sole factor causing the high effectiveness of froth flotation; foam formation and foam stability were also shown to be important parameters. The importance of foam stability was also observed by Carre et al. (12).

In many previous studies of froth flotation to remove emulsified oil from water, an initial oil-to-water ratio of 1:1 was used (9, 13, 14). This is because microemulsion phase studies are traditionally carried out at this initial oil-to-water ratio. However, wastewater with emulsified oil typically has lower oil-to-water ratios (6, 15). Therefore, the effect of initial oil-to-water ratio is investigated in this study. Previous studies from our group have correlated froth flotation efficiency to equilibrium phase behavior of oil/water systems (8–10, 13). However, equilibration of microemulsion systems can be very slow, in extreme cases taking months. Since actual wastewaters will not have time to equilibrate, the effect of equilibration time is investigated here, as well as the effect of agitation during equilibration. Finally, the effect of air flow rate is discussed in this paper.

EXPERIMENTAL SECTION

Materials

Ethylbenzene with 98% purity from Fluka Company was used as emulsified oil in this work. Dihexyl sulfosuccinate (aerosol MA or AMA) with 80% purity from CYTEX Corporation, Los Angeles, CA was used as surfactant here. Analytical grade sodium chloride (NaCl) was obtained from Aldrich Chemical Company, Inc. Deionized water was used in all experiments. All chemicals were used as received.

Methodology

The surfactant concentration and salinity are expressed as percent by weight based on the aqueous solution in this study. Figure 1 depicts the schematic diagram of the experimental froth flotation system used in this study. The system consisted of a glass cylindrical column with 5-cm inside diameter and 120-cm height and operated in a batch mode. Filtered air was introduced into the bottom of the column with various flow rates through a sintered glass disk, having pore size diameters about 16–40 μm.

Microemulsions formed with 0.3 wt% AMA and 3 wt% NaCl was selected for froth flotation experiments since these systems can exhibit low oil/water interfacial tensions (IFT) and form a Winsor Type III microemulsion (10). Interfacial tension was measured with a spinning drop tensiometer (Krüss, GmbH model). To study effect of equilibration time, different systems having three equilibration times were prepared for flotation experiments. For a nonequilibrium system, 750 mL of sample solution with various oil-to-water ratios was immediately transferred to the froth flotation column after mixing. For an "induced" equilibrium system, another 750 mL of sample solution with an 1:1 of oil-to-water ratio was agitated by using a mechanical stirrer at 2000 rpm for 40 minutes using a stirrer at 800 rpm before being introduced to the flotation column. For the equilibrium system, 750 mL of sample solution with an oil-to-water ratio of 1:1 was kept in an incubator at 30°C for 1

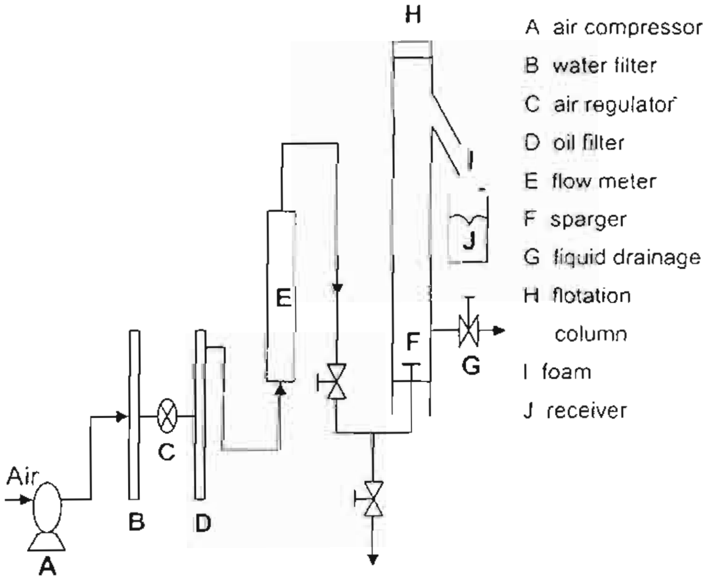

Figure 1. Schematic diagram of the froth flotation system.

month, which was shown to be long enough to reach equilibrium before being used in the flotation experiments. After the solution was transferred into the column, air was introduced to the column at various flow rates. The foam overflown from the column was collected over different time intervals and each froth was broken to analyze concentrations of ethylbenzene in the collapsed froth. Moreover, the solution remaining in the column was collected at the same interval of time for analysis of ethylbenzene and AMA concentrations. The experiments were stopped when no foam was overflowing from the column. To analyze the concentration of ethylbenzene, a GC-Headspace (Perkin Elmer) was used whereas the titration method, ASTM D1681-92, 1997, was employed to analyze the concentration of surfactant.

To measure foamability and foam stability, 250 mL of sample containing desired amounts of ethylbenzene and AMA was transferred to the same column used in the froth flotation experiment. The filtered air was introduced through the solution at flow rates of 100, 130, 150, and 200 mL/min until the foam height in the column was constant. The time required for the foam volume to collapse by half was recorded. For this experiment, the air flow rate could not exceed 200 mL/min because foam overflowed from the column. All froth flotation as well as foamability and foam stability experiments were carried out at room temperature (25–27°C).

RESULTS AND DISCUSSION

In this study, wt% is based upon the aqueous system consisting of water, salt, and surfactant (not including oil). In this paper, IFT is referred to the interfacial tension between excess oil and excess water phases. Foamability is defined as a ratio of maximum foam height to initial solution height, whereas foam stability ($t_{1/2}$) is the time required for the foam volume to collapse to half of the maximum height.

Effect of Oil-to-Water Ratio on IFT

The phase behavior of the ethylbenzene system having different AMA and NaCl concentrations was presented in Part I of this series (10). Therefore, only the effect of oil-to-water ratio upon phase behavior is discussed here. The system having a minimum IFT (at optimum salinity) at an oil-to-water ratio of 1:1 was selected to determine the effect of oil-to-water ratio on IFT. As shown in Fig. 2, IFT is in the same order of magnitude when the oil-to-water ratio increases from 1:19 to 1:1. This finding is beneficial to froth flotation operation, since oil-to-water ratios in industrial wastewaters are often much less than those in microemulsion phase behavior experiments where an oil-to-water ratio is traditionally set at unity.

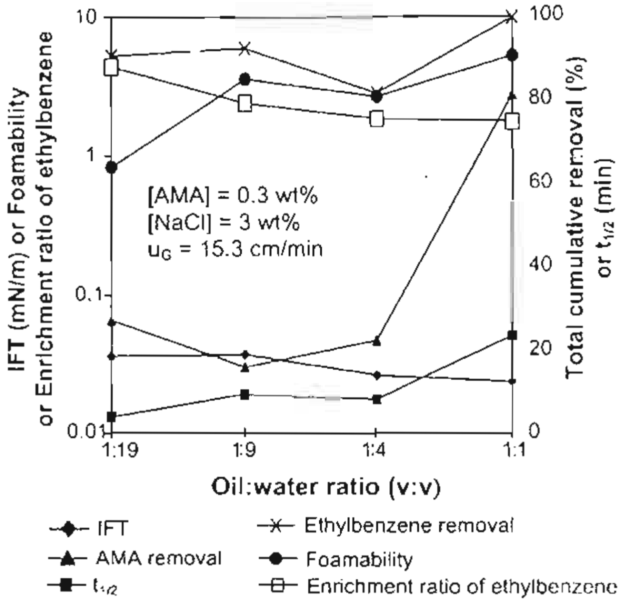

Figure 2. Effect of oil-to-water on process parameters.

Foam Formation and Foam Stability

From Fig. 2, both foamability and foam stability increase slightly with increasing ratio of oil-to-water. At a low oil-to-water ratio, the viscosity of the total solution is also low, resulting in a higher drainage rate of water from foam lamellae. Therefore, foam rupture occurs easily. In case of a high oil-to-water ratio, the high oil content in solution leads to high resistance to oil movement within the restricted volume of the Plateau borders. Since the oil drops in the Plateau borders drain slower than the surrounding aqueous phase, they get trapped in the Plateau borders due to high viscosity. The confined structure of the Plateau borders basically squeezes the oil drops into the close-packed configuration, so the area available for the flow of the water out of the Plateau borders decreases. Foam drainage is slowed down, resulting in a higher foam stability when oil-to-water ratio increases (11). Air flow rate is one of the vital parameters in dispersed-air flotation systems including froth flotation. In this paper, superficial velocity (u_G), which is a volumetric air flow rate divided by the cross-sectional area of the flotation column, is reported instead of a volumetric air flow rate. From Fig. 3, as expected, increasing u_G increases foam formation monotonically because there are more bubbles passing through the solution. Zouboulis, Lazaridis, and Zamboulis (5) also observed that a higher air flow rate resulted in a greater amount of foam generated. Both ethylbenzene and AMA removals will be discussed in detail in the next section.

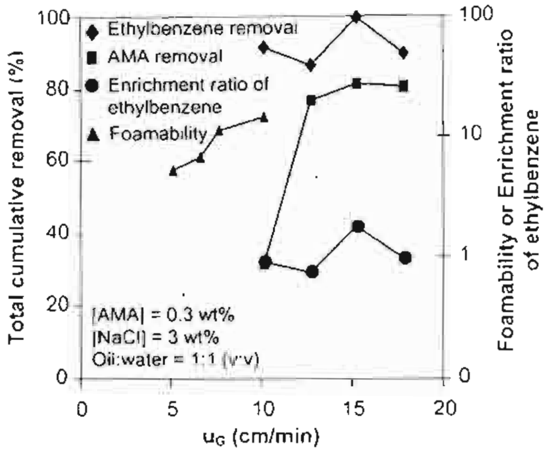

Figure 3. Effect of superficial air velocity on process parameters.

Froth Flotation Performance

Concentrations of 0.3 wt% AMA and 3 wt% NaCl were selected for froth flotation experiments since the system offers an ultra-low interfacial tension (0.052 mN/m) at a low AMA concentration (10).

Removal of Ethylbenzene and Surfactant

The effects of oil-to-water ratio on IFT, total cumulative ethylbenzene removal, total cumulative AMA removal, enrichment ratio of ethylbenzene, foamability, and foam stability are shown in Fig. 2. The total cumulative ethylbenzene removal (as a percentage) exhibits a minimum with increasing oil-to-water ratio. The percent removal of surfactant also exhibits a minimum at a certain oil-to-water ratio (1:9), although a different ratio (1:4) from the minimum ethylbenzene removal was observed. The highest enrichment ratio of ethylbenzene corresponds to the lowest oil-to-water ratio. This is because the solution viscosity increases with increasing oil-to-water ratio, leading to lower water drainage rate from foam lamellae. The foamability and foam stability monotonically increase and IFT monotonically decreases with increasing oil-to-water ratio. There is a substantial increase in ethylbenzene removal, AMA removal, and foamability as oil-to-water ratio increases from 1:4 to 1:1. These results are rather surprising in that much more total oil is removed as oil-to-water ratio increases as the fraction removed even increases. This is associated with substantially increasing AMA removal, which is caused by substantially increasing foamability and modestly decreasing IFT.

Figure 3 shows the effects of u_G on total cumulative ethylbenzene removal, total cumulative AMA removal, enrichment ratio of ethylbenzene, and foamability. The total cumulative ethylbenzene removal is not much affected by u_G. An increase in u_G leads to more bubbles passing through the solution (16), which would tend to increase oil removal. However, a very high u_G affects the flow pattern in the solution, and the circulation velocity induced by the bubble swarm rising through the column is responsible for the turbulence at the froth/collection zone interface (16), resulting in ethylbenzene adsorbed in the froth being partly entrained back into the solution. These two contradictory effects approximately cancel each other, resulting in little effect of u_G on oil removal. Unlike ethylbenzene removal, u_G causes an increase in AMA removal, especially in the range of u_G from 10.2 to 12.7 cm/min. However, AMA removal seems to reach a plateau when u_G is greater than 12.7 cm/min. This is because some froth is dissolved back into the solution because of the turbulent flow pattern in the solution at high u_G. The enrichment ratio of ethylbenzene is lower than 1 when u_G is lower than 15.3 cm/min. When enrichment ratio is equal to or less than unity, no separation is achieved: i.e., the oil is not enriched in the collapsed foam relative to the solution.

Since equilibration in microemulsion systems can be very slow in some cases (months), and much shorter oil/water equilibration times are practical in actual wastewater treatment systems, we have investigated the effect of contact or equilibration time once the oil, water, and surfactant are mixed together. Three cases are considered: the nonequilibrium system where the solution is immediately transferred to the flotation column after mixing, the induced equilibrium system where the solution is intensely agitated after mixing, and equilibrium systems that are equilibrated for a month. Table 1 shows IFT, total cumulative ethylbenzene removal, total cumulative AMA removal, enrichment ratio of ethylbenzene, and foam flow rate for these three systems. An aqueous solution containing 0.3 wt% AMA and 3 wt% NaCl was selected to form microemulsions with ethylbenzene at an oil-to-water ratio of 1:1 in this study because it provides an ultra-low interfacial

Table 1. Effect of equilibration conditions on process parameters

System	IFT (mN/m)	Total cumulative ethylbenzene removal (%)	Total cumulative AMA removal (%)	Enrichment ratio of ethylbenzene	Foam flow rate (mL/min)
Non-equilibrium	2.388	40.59	82.94	1.76	1.34
Induced equilibrium	0.674	87.79	64.39	1.11	2.23
Equilibrium	0.052	99.29	63.18	1.18	3.59

tension with a middle phase microemulsion (10). As shown in Table 1, the highest ethylbenzene removal is achieved with the equilibrium system, associated with the highest foam flow rate and lower IFT. It is interesting to note that the induced equilibrium system gave an ethylbenzene removal much higher than the nonequilibrium system, but lower than the equilibrium system. The results indicate that a short period of time (40 minutes in this study) of vigorous agitation is long enough to move the system substantially towards its equilibrium state. Unlike ethylbenzene removal, AMA removal in the nonequilibrium system is much higher than those of the other two systems. This is because in both the induced equilibrium and equilibrium systems, a large fraction of surfactant is present in a bicontinuous structure in the middle phase compared to the nonequilibrium system. The surfactant molecules in the bicontinuous structure are not well transferred to the foam, so the surfactant removal in overhead froth is much lower for equilibrium than the nonequilibrium system. In addition, a large fraction of surfactant in bicontinuous structures in both induced equilibrium and equilibrium systems helps to retard the water drainage rate from foam lamellae, resulting in lower enrichment ratios of ethylbenzene. It is somewhat surprising that lower AMA removal corresponds to higher oil removal, implying that as long as enough surfactant is being removed to generate sufficient foam, decreasing the IFT can improve oil removal despite lower surfactant removal.

Dynamics of Flotation

Dynamic froth flotation results are shown in Figs. 4–8. The dynamic removal of ethylbenzene and AMA as a function of oil-to-water ratio are shown in Figs. 4 and 5, respectively. As shown in Fig. 4, ethylbenzene removal is not a monotonic function of oil-to-water ratio with the order changing with time. Despite a lack of systematic variation in ethylbenzene removal with oil-to-water ratio, this variable can have a large influence. For example, at 90 minutes, ethylbenzene removal arises from 55.71% to 91.14% as the oil-to-water ratio varies from 1:4 to 1:1. From Fig. 5, the 1:1 oil-to-water ratio yields a substantially higher AMA removal fraction than lower ratios with the 1:4 to 1:19 ratios not showing a systematic trend. The lack of a clear correlation between AMA removal and ethylbenzene removal as previously noted is confirmed in these dynamic studies.

From Figs. 6 and 7, while superficial air velocity can have a substantial effect on both ethylbenzene and AMA removal, there is a lack of systematic trends as u_G increases.

For the observation of the effect of the equilibration condition on dynamic ethylbenzene removal (Fig. 8), the nonequilibrium system has a much lower ethylbenzene removal as compared to the equilibrium and induced-equilibrium systems, which showed similar ethylbenzene removal

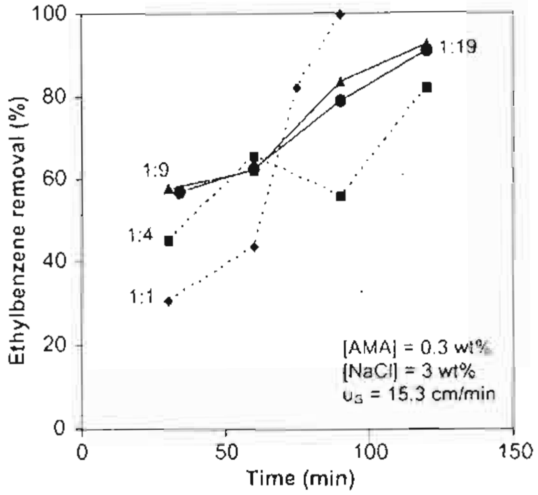

Figure 4. Dynamic removal efficiency of ethylbenzene at different oil-to-water ratios (1:1, 1:4, 1:9, and 1:19 v:v).

characteristics. Practically, vigorous agitation can move the Winsor Type III microemulsion system toward equilibrium and high oil removal efficiency without the very long equilibration times required in quiescent systems. Clearly, this pre-equilibration step is key to an economic process using the microemulsion approach and deserves further study.

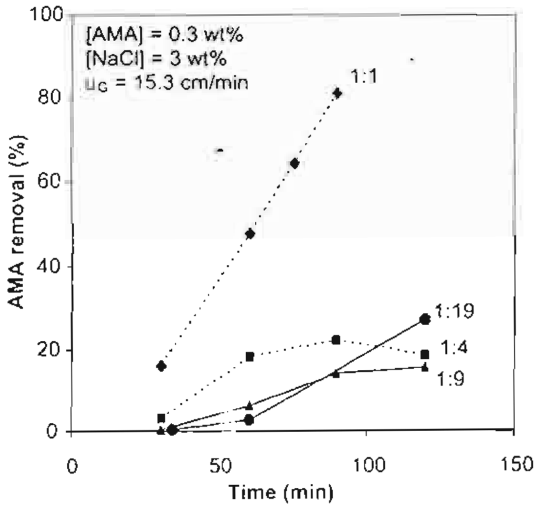

Figure 5. Dynamic removal efficiency of AMA at different oil-to-water ratios (1:1, 1:4, 1:9, and 1:19 v/v).

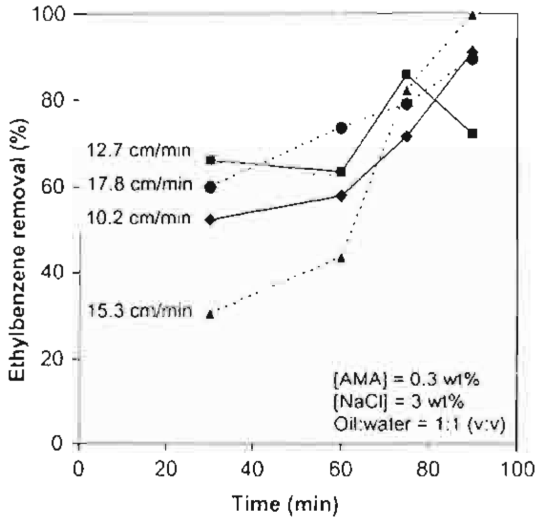

Figure 6. Dynamic removal efficiency of ethylbenzene at different superficial air velocities.

CONCLUSIONS

In this study, the performance of froth flotation is indicated by oil removal, enrichment ratio, and surfactant removal. The effects of operating variables in the flotation column such as superficial velocity, oil-to-water ratio, and

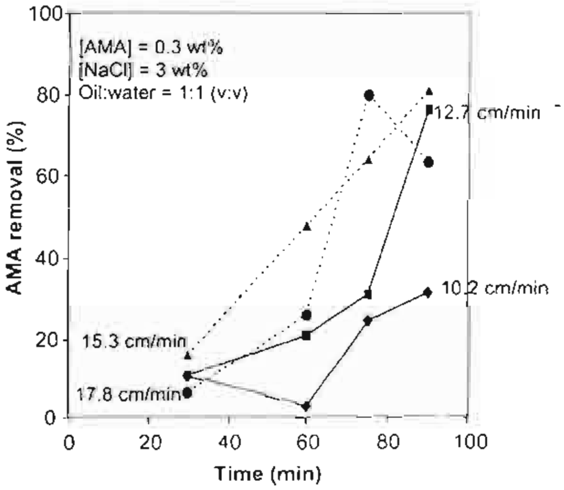

Figure 7. Dynamic removal efficiency of AMA at different superficial air velocities.

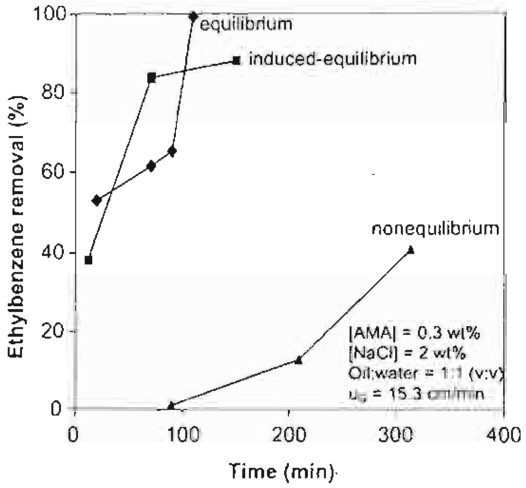

Figure 8. Dynamic removal efficiency of ethylbenzene for different equilibration conditions.

equilibration time were investigated systematically. The superficial velocity used in froth flotation operations should be optimized to obtain the proper balance between the foam production rate and the water back-entrainment rate in order to achieve the maximum performance of froth flotation. As oil-to-water ratio decreases, the enrichment ratio of ethylbenzene increases, but oil removal slightly decreases. In addition, to apply this research to real applications, agitation of the solution for only 40 minutes (induced equilibrium) before being transferred to the froth flotation was found to yield ethylbenzene removal almost as high as an equilibrated system.

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Ethylbenzene Removal by Froth Flotation Under Conditions of Middle-Phase Microemulsion Formation I: Interfacial Tension, Foamability, and Foam Stability

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Abstract: The objective of this study was to investigate the relationship of the froth flotation performance in removal of emulsified ethylbenzene in water with microemulsion formation and with foam formation characteristics. The surfactant used was dihexyl sulfosuccinate (Aerosol MA or AMA) which can form microemulsions with ethylbenzene. The systems studied were designed to form Winsor Type III microemulsions with ethylbenzene, which generally correspond to ultra-low interfacial tensions between oil and water phases. By varying the surfactant concentration, NaCl concentration, and oil-to-water ratio, it was found that the lowest interfacial tension was

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obtained at 1 wt% AMA and 3 wt% NaCl, while the interfacial tension was not substantially influenced by the oil-to-water ratio. The highest oil removal was achieved in froth flotation with 0.3 wt% AMA and 3 wt% NaCl. No separation was experienced when the NaCl concentration exceeded 4 wt% due to the poor foamability of the froth formed under these conditions. Therefore, these results demonstrate that both interfacial tension and foam characteristics influence the efficiency of oil removal in the froth flotation process.

Keywords: Froth flotation, microemulsion, interfacial tension, foamability, foam stability

INTRODUCTION

Flotation processes are useful for separation of various species such as ore, emulsified oil, and various products that are extracted from an aqueous medium, and can be used for product recovery or for wastewater treatment (1–3). There are two main types of froth flotation: dissolved air flotation and induced air flotation (4). The dissolved and induced air flotation processes have been used for many years in the separation of suspended solids, oils, greases, and fibers from wastewaters (5). In induced air flotation, air is introduced at the bottom of a froth flotation column. Emulsified oils can co-adsorb at the air-water interface and be carried over the top of the column. Surfactants play an important role in the froth flotation by inducing foam formation, reducing the coalescence rate of bubbles within the liquid phase, and increasing the retention time of bubbles in the column (6). Two advantages of froth flotation over other conventional separation processes include simplicity of operation and low operational cost. As a result, substantial research has been carried out to develop froth flotation as a waste treatment process (7–16). In this study, the froth flotation technique was implemented in batch mode to remove emulsified ethylbenzene from water; the ethylbenzene concentration is far above its solubility in water.

Ethylbenzene is a colorless organic liquid with a sweet and gasoline-like odor. It is widely used as a solvent and also found in a variety of products in the chemical industry. The USA and Canada limit the amount of ethylbenzene in wastewaters to between 2.4 and 5 μg/L (17). Ethylbenzene may be found in industrial discharges or leakage of underground storage tanks. The relevant routes for ethylbenzene exposure are through oral intake and inhalation, and it can damage the liver of humans.

From our previous work (6, 18, 19), the relationship between the type of microemulsion and the efficiency of oil removal has been investigated, and the maximum oil removal was found to correspond to the formation of a Winsor Type III microemulsion. However, the mechanism of this relationship has not been fully understood. It is known that a Winsor Type III microemulsion has unique characteristics of ultra-low interfacial tension and high solubilization.

Chavadej et al. (19) reported that most of the oil removed in the froth flotation column came from the excess oil phase rather than from the middle phase microemulsion always present in Type III systems. That work also showed the relationship between high oil removal and ultra-low interfacial tension in a Winsor Type III microemulsion—the presence of a middle phase microemulsion is coincidental to oil removal.

Depending upon the application, the presence of foam can be either undesirable or preferable. Foam can cause operational problems in many processes such as sewage treatment, coating applications, and crude oil processing (20). However, in some processes, such as fire fighting and froth flotation, foams are critical to successful process performance. Foam is simply produced by introducing air beneath the liquid surface (21). The two-sided aqueous films separating discrete gas bubbles are called lamellae. As liquid drains out of the lamellae, the foam is eventually destroyed. As a result, foam is unstable thermodynamically (20, 21).

Foams can be classified into three classes: unstable foams; metastable foams; and solid foams. Unstable foams remain for a very short time and collapse rapidly due to the thinning of the lamellae by pressure gradient between the lamellae and the plateau triangle regions and water drainage by gravitational forces (20). Metastable foams possess a persistence or degree of stability ranging from a few seconds to months. Added surfactants stabilize foams by retarding the loss or drainage of liquid from the lamellae. In addition, the foams produced can be disrupted by many factors including dust particles, vibration, evaporation, and pressure change (20). The last class of foams is solid foams, which are mechanically rigid due to an irreversible chemical process during foam formation (20). Sometimes foams only refer to the situation where the lamellae are liquid, so "solid foams" would be considered as sponges. In this study, we are interested in metastable foams.

Carre et al. (22) suggested that one of the key criteria for the success of a flotation operation is to produce a stable froth. Apart from the ultra-low interfacial tension in the Winsor Type III region, it is hypothesized that the following factors influence oil removal in the froth flotation process: the amount of oil attached to the froth, foamability (the rate of foam formation), and foam stability. The objective of this work is to probe the importance of oil/water interfacial tensions, foamability, and foam stability in froth flotation of ethylbenzene.

EXPERIMENTAL SECTION

Materials

Ethylbenzene (98% purity), obtained from Fluka Company, was used as the model oil in this study. The surfactants studied were as follows: di-1, 3-dimethylbutyl sulfosuccinate (Aerosol MA or AMA) with 80% in aqueous solution containing a maximum of 5% isopropanol in the solution supplied by CYTEX corporation, Los Angeles; sodium bis-2-ethylhexylsulfosuccinate (Aerosol-OT or AOT) with 98% purity from Fluka Company; and mono- and di-hexadecyl diphenyloxide disulfonate sodium salt (Dowfax 8390 or DPDS) in 36% solution from Dow Company, Midland, Michigan. Analytical purity grade sodium chloride (NaCl) from Aldrich Chemical Company Inc. was used as electrolyte in this work. All chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

Methodology

There were three experimental parts in this research work. The first part was to study microemulsion phase behavior of the aqueous solutions with ethylbenzene. The second part was to investigate foamability and foam stability. The third part of this work was to study the efficiency of froth flotation. In all experiments, the surfactant and electrolyte concentrations are expressed in weight percentage (wt%) per volume of the aqueous solution comprising water, surfactant, and salt (not including oil).

To investigate the phase behavior of microemulsions, 5 mL of homogeneous aqueous solution, prepared at various surfactant and NaCl concentrations, was mixed with 5 mL of ethylbenzene in a vial and sealed with a screw cap. The vials were shaken every day for 3 days, and then allowed to equilibrate at a constant temperature of 30°C in a water bath for 1 month to reach equilibrium, which was verified by the invariant height of each phase. The interfacial tensions between equilibrated excess oil and excess water phases were measured by a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg).

A schematic diagram of the froth flotation unit used in this work is shown in Fig. 1. A glass cylindrical column with 5 cm internal diameter and 120 cm height was used as the froth flotation column. A 250 mL sample containing a given surfactant concentration and an oil to water ratio of 1:1 was transferred to the column. Filtered air was introduced at the bottom of the column through the solution at a constant flow rate of 100 mL/min until the foam height in the column was constant. The maximum foam height was then measured. Then the filtered air was stopped, and the time required for the foam volume to collapse to one-half of the maximum height was recorded to quantify foam stability.

In order to better understand the froth flotation process, froth flotation experiment was conducted in the same column. A 750 mL sample with an initial oil:water ratio of 1:1 and various surfactant and NaCl concentrations was prepared, equilibrated at 30°C for 1 month in the incubator, and finally transferred to the froth flotation column. The ratio of oil to

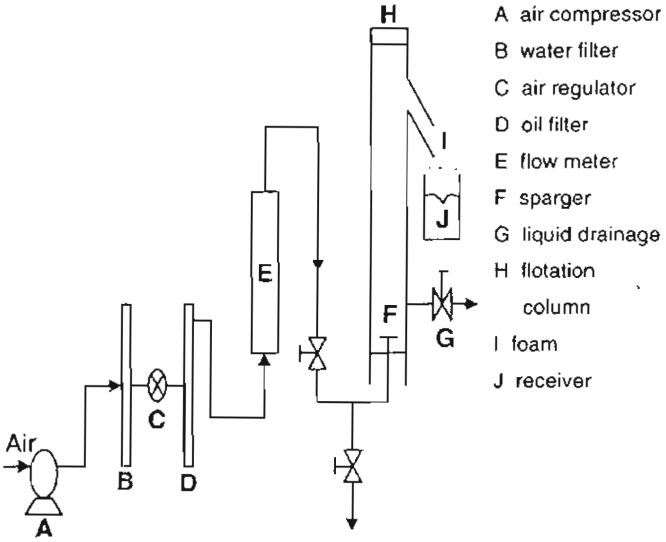

Figure 1. Schematic diagram of the froth flotation apparatus.

water of 1:1 was investigated in this work because microemulsion phase studies are traditionally carried out at this ratio. Filtered air was introduced at the bottom of the column at a constant flow rate of 300 mL/min through a sintered glass disk having pore size diameters of about 16–40 μm. The air flow rate of 300 mL/min was selected in this work because it provided appropriate amount of foam in the overhead froth. However, the effect of air flow rate on froth flotation operation was investigated in the next study in this series. The foam collected in the receiver (J in Fig. 1) over a period of time was broken by freezing with subsequent ethylbenzene analysis. Moreover, the solution in the column was sampled at the same time interval as foam collected for analysis of ethylbenzene and surfactant concentrations. All experiments were stopped when solution surfactant concentrations became low enough that no more foam came overhead from the column. All experiments of froth flotation operation, foamability, and foam stability were conducted at a room temperature of about 25–27°C.

RESULTS AND DISCUSSION

In this study, wt% is based upon the aqueous system consisting of water, salt, and surfactant. Foamability, which is ability of surfactant solution to form foam, is defined as the ratio of maximum foam height to initial solution height whereas foam stability ($t_{1/2}$), which is ability of foam to remain in the column, is the time required for the foam to collapse to 50% of the maximum height.

Phase Behavior

To form Winsor Type III microemulsions with ethylbenzene, multiple surfactant systems (e.g., AMA, AOT, and the mixture of AOT and DPDS) were tested systematically. For conditions used in this study, only AMA or mixtures of AOT and DPDS could form middle phase microemulsions (Winsor Type III) with ethylbenzene as indicated by the presence of three phases of excess oil, excess water, and middle phases. In operating froth flotation with the mixture of AOT and DPDS, the foam generated was not able to reach the overflow outlet of the column, indicating poor foamability and foam stability. Consequently, only results from the AMA system are reported here. The phase behavior of ethylbenzene with the mixture of AOT and DPDS is not shown here but is available elsewhere (23).

The effect of AMA surfactant concentration on interfacial tension (IFT) is shown in Fig. 2. Winsor Type III microemulsions are formed at AMA concentrations above 0.3 wt% as indicated by the presence of three phases at equilibrium: excess water phase; excess oil phase; and a middle

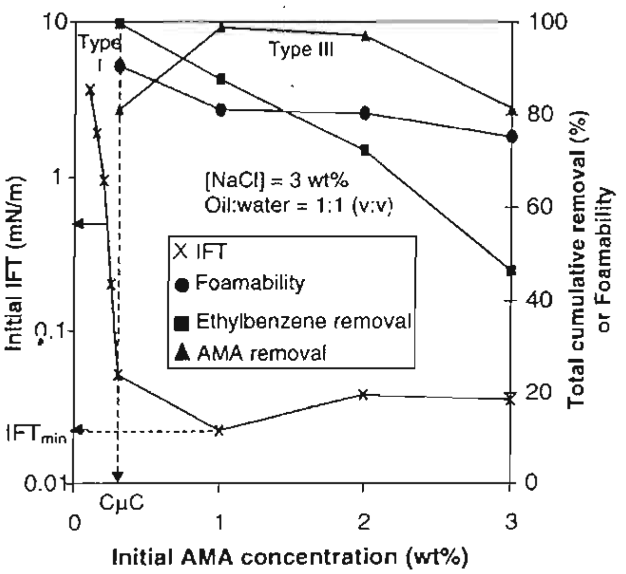

Figure 2. Effect of initial AMA concentration on process parameters.

phase. The shape of the IFT curves in Fig. 2 is typical of systems that transition from micellar solutions to optimum microemulsions (24). The surfactant concentration where the first microemulsion "droplet" is formed and ultra-low IFT is reached is called a critical microemulsion concentration (CµC) (24); in this case, the CµC is 0.3 wt% AMA. The CµC also corresponds to the Type I to Type III transition concentration. At an AMA concentration of 1 wt%, the minimum observed value of IFT was obtained. At this IFT minimum, the surfactant is balanced between water and oil solubility and can form a bicontinuous structure in the middle phase, leading to high oil and water solubilization in this phase corresponding to the minimum IFT value (25). However, as shown in Fig. 2, the IFT increases slightly when the AMA concentration is greater than 1 wt%, a trend that has been reported before and seems to be linked to strong surfactant – surfactant interactions (26).

The lowest AMA concentration which can form a Winsor Type III microemulsion (CµC = 0.3 wt%) was selected to determine the effect of salinity on IFT. The effect of NaCl concentration on IFT and other process parameters are shown in Fig. 3. The minimum IFT is observed at approximately 3 wt% NaCl: this is known as the optimum salinity. The changes of IFT vs. electrolyte concentration in Fig. 3 are typical of Winsor Type I–III–II transition. Systems with 2 wt% or less NaCl show Type I microemulsion systems (oil–swollen

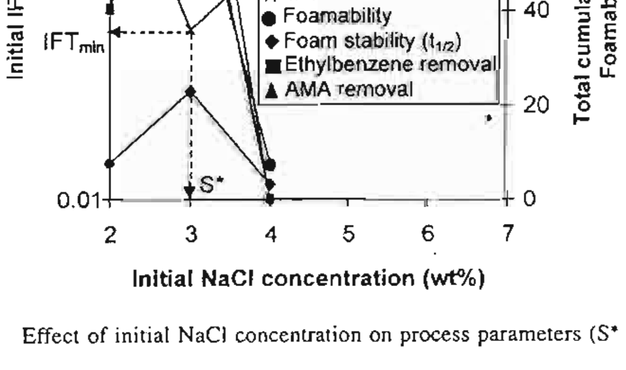

Figure 3. Effect of initial NaCl concentration on process parameters (S* = optimal salinity).

micelles) and systems with 4 wt% NaCl or more show Type II systems (reverse micelles); at intermediate salinity values, a Type III system is observed.

Foam Formation and Foam Stability

In froth flotation, both the rate of foam formation and the stability of the generated foam are extremely crucial for good separation. Figure 2 shows that increasing the AMA concentration decreases foamability. This is because enhanced viscosity of the continuous phase is an important factor in coalescence of bubbles (27). At a low surfactant concentration, the solution viscosity is low. Therefore, the diffusion rate of surfactant to the newly created interface, which occurs during the bubble generation, is fast enough to be adsorbed at the bubble interface. With the absence of further diffusion of surfactant from bulk solution to the interface, the action of the interface elasticity can restore the bubble size by the Gibbs-Marangoni effect (28). This result is consistent with the explanation of Marinhardt (29) that foam of low viscosity is claimed to propagate more easily than foam of high viscosity.

In typical foam situations, a surfactant accumulates at the oil/water interface, and as the water drains, it tends to form a metastable lamellae phase which imposes a near zero curvature to the surfactant molecules. The equilibrium state is a highly curved micellar solution. When the surfactant is formulated to form a Type III microemulsion system, the equilibrium net curvature of the surfactant film approaches zero (30). It is reasonable to imagine that when foam is produced in these microemulsion systems, instead of forming a lamellae phase, a film of near zero curvature is formed. The hypothesis that "microemulsion films" are formed instead of "lamellae films" is corroborated by the fact that not only the surfactant, but also the oil is removed during the froth flotation process, as indicated in Figs. 2 and 3.

While microemulsion films can satisfy the zero curvature conditions for the surfactant molecules, they are still under the influence of "drainage" effects imposed by the Laplace pressure, and because of that they are still metastable phases, but with longer half time than curved microemulsion systems (Type I and II).

Froth Flotation

To achieve good separation as well as an acceptable degree of treatment in running a froth flotation process, treated wastewater has to contain very low concentrations of both oil and surfactant. Hence, the overhead froth should have high concentrations of both oil and surfactant. In this study, parameters used to indicate the performance of froth flotation are oil removal, surfactant removal, and enrichment ratio of oil. An enrichment ratio of oil is defined as a ratio of concentration of oil in the collapsed froth to a concentration of oil in the initial solution. The enrichment ratio of oil must be greater than unity if separation has been achieved.

Maximum Removal of Ethylbenzene and Surfactant

Figure 2 shows the effects of surfactant concentration on total cumulative ethylbenzene removal, total cumulative AMA removal, initial IFT, and foamability. Since the surfactant concentration progressively decreases with time during the froth flotation and foamability experiments, the "initial" AMA concentration is used to characterize those experiments. The total cumulative AMA removal and total cumulative ethylbenzene removal are calculated based on the end of the flotation operation when the froth no longer flows overhead. The AMA removal is highest (nearly 100%) at the CμC level of AMA. However, the ethylbenzene removal decreases monotonically as the AMA concentration further increases, a trend that can be attributed to foamability.

Figure 3 shows the effects of initial NaCl concentration on total cumulative ethylbenzene removal, total cumulative AMA removal, initial IFT, foamability, and foam stability. All flotation experiments were carried out at initial conditions in the Winsor Type III region. In this case, unlike Fig. 2, the highest total cumulative ethylbenzene removal corresponded to not only the minimum IFT, but also to maxima in both foamability and foam stability. At 4% NaCl and above, no recovery of ethylbenzene or AMA occurred since the froth never reached the overhead outlet. This salinity also corresponds to a sharp decrease in foamability and foam stability even though the IFT was still quite low. Unlike ethylbenzene, total cumulative AMA removal is nearly constant with increasing salinity until the 4 wt% NaCl concentration is reached where froth stability is catastrophically low.

Enrichment Ratios and Dynamics of Flotation

Figure 4 shows the ethylbenzene enrichment ratio as a function of AMA concentration at 2 wt% and 3 wt% salinities. At an AMA concentration above 2 wt%, an ethylbenzene enrichment ratio of less than unity is observed—the oil is depleted instead of enriched in the froth. The separation is worthless in this region despite total cumulative oil removal of nearly 50% at the AMA concentration of 3 wt%. The highest enrichment ratio occurs at the AMA concentration corresponding to the minimum IFT (i.e., at lower AMA concentrations). The salinity with lower IFT and higher foamability and foam stability has slightly higher ethylbenzene enrichment ratio (1.76 at 3 wt% NaCl vs. 1.34 at 2 wt% NaCl) before froth collapse prevented a

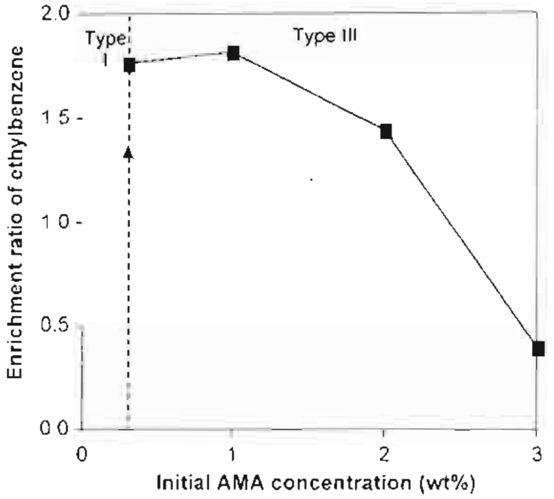

Figure 4. Effect of initial AMA concentration on enrichment ratio of ethylbenzene at 2 wt% NaCl (▲) and 3 wt% NaCl (■).

separation at still higher NaCl concentrations. As the initial AMA concentration increases, the foam wetness and foam production rate reach a minimum (Fig. 5) while ethylbenzene enrichment ratio tends to decrease, as shown in Fig. 4.

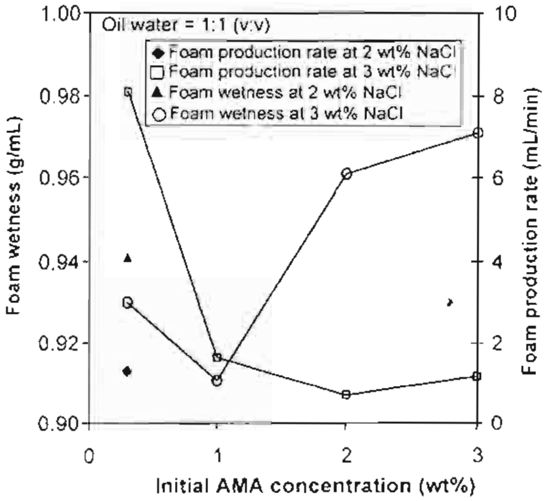

Figure 5. Effect of initial AMA concentration on foam wetness and foam production rate.

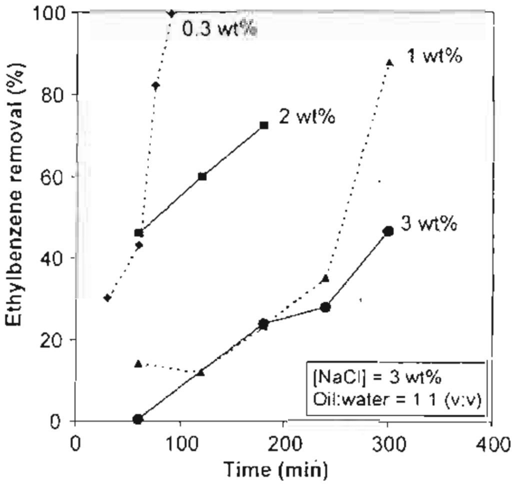

Figure 6. Dynamic removal efficiency of ethylbenzene at different initial AMA concentrations.

Dynamic froth flotation results (effect of operating time in the batch experiment) are shown in Figs. 6–10. Figures 6 and 7 show the effect of initial AMA concentration on dynamic ethylbenzene removal and dynamic AMA removal, respectively. The system having 0.3 wt% AMA concentration

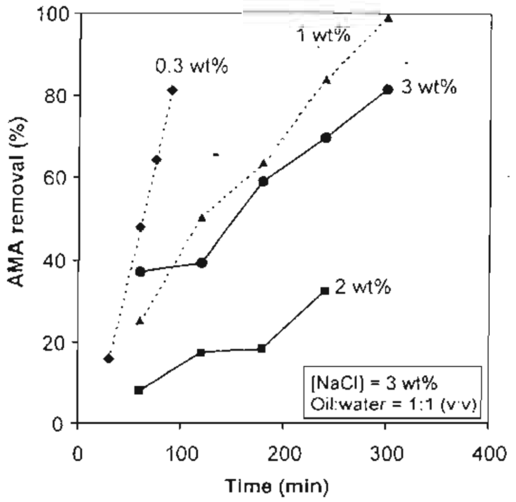

Figure 7. Dynamic removal efficiency of AMA at different initial AMA concentrations.

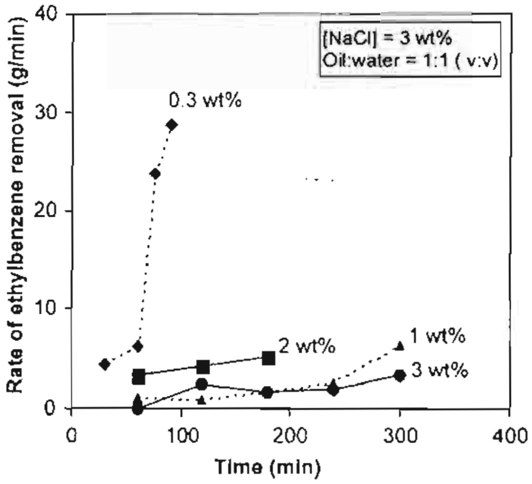

Figure 8. Rate of ethylbenzene removal at different initial AMA concentrations.

seems to be a very good condition for ethylbenzene removal because nearly 100% of ethylbenzene is removed within the shortest time due to the highest foam production rate. Even though at the beginning of operation, the ethylbenzene removal from a 2 wt% AMA concentration solution is higher than that from a 1 wt% AMA concentration solution, the total cumulative ethylbenzene removal from the latter is higher than that from the former

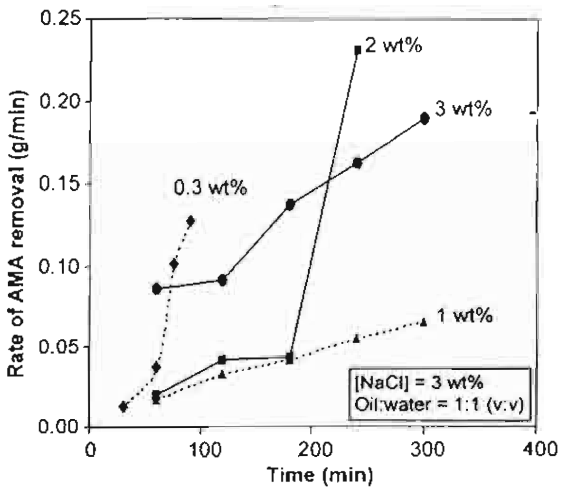

Figure 9. Rate of AMA removal at different initial AMA concentrations.

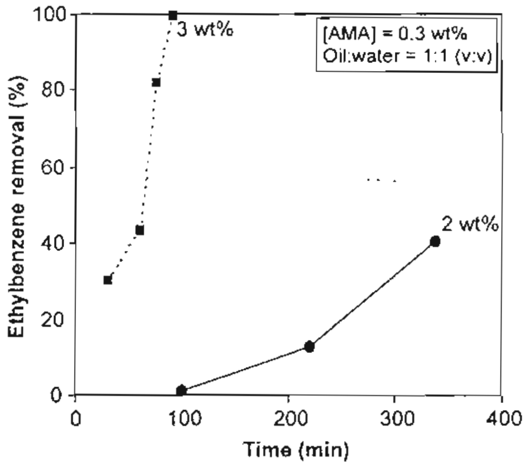

Figure 10. Dynamic removal efficiency of ethylbenzene at two different NaCl concentrations.

because the rate of ethylbenzene removal of the latter increases with time (Fig. 8). The AMA removal shows this same trend except at 2 wt% initial AMA where removal is lowest. This is because the rate of AMA removal at 2 wt% AMA, as shown in Fig. 9, is not high enough in the first 3 h. This is because the fact that the foam production rate is lowest for this system.

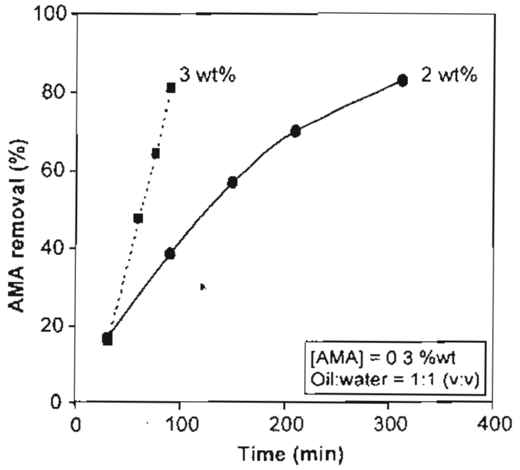

Figure 11. Dynamic removal efficiency of surfactant at two different NaCl concentrations.

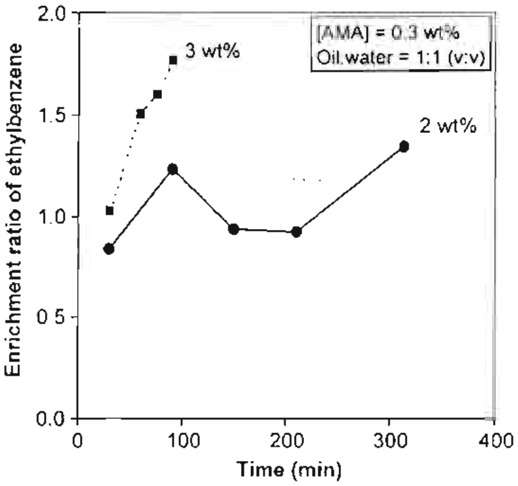

Figure 12. Enrichment ratio of ethylbenzene as a function of time at two different NaCl concentrations.

From Figs. 10–12, the ethylbenzene removal, the AMA removal, and ethylbenzene enrichment ratio at 3 wt% NaCl is higher than that at 2 wt% NaCl. This is because the rates of both ethylbenzene and AMA removal at 3 wt% NaCl correspond to the foam production rate (Fig. 5) which is much higher than those rates for 2 wt% salt as shown in Figs. 13–14.

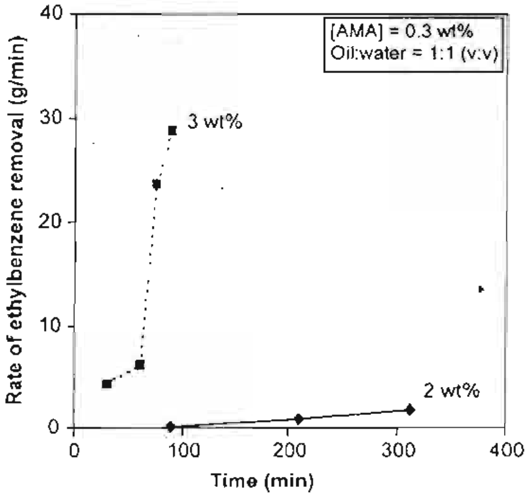

Figure 13. Rate of ethylbenzene removal at two different NaCl concentrations.

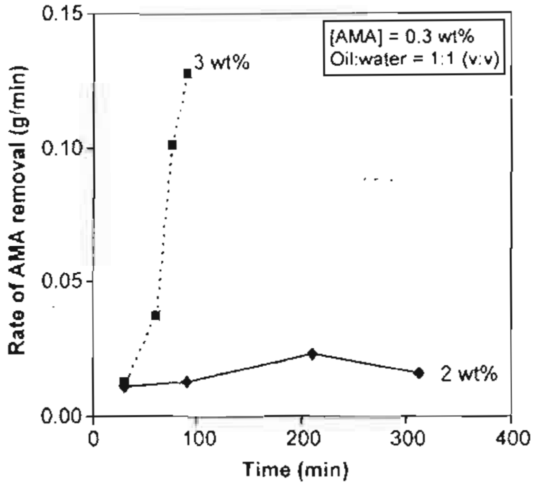

Figure 14. Rate of AMA removal at two different NaCl concentrations.

CONCLUSIONS

In our previous froth flotation work with ortho-dichlorobenzene (18), we concluded that oil removal increases with decreasing IFT. For this work with ethylbenzene, we have studied foam characteristics in more detail and have found that foam formation and stability can also have profound effects on oil removal. There are conditions where the frothing is so unfavorable that no froth comes overhead and no separation occurs even though IFT values can be ultralow. An important conclusion of this work is that both low IFT and good frothing are necessary for efficient separation. In Part II of this series, we examine the effect of oil-to-water ratio, air flow rate, and equilibration time on the froth flotation performance.

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DIESEL REMOVAL BY FROTH FLOTATION UNDER LOW INTERFACIAL TENSION CONDITIONS I: FOAM CHARACTERISTICS, COALESCENCE TIME AND EQUILIBRATION TIME

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ABSTRACT

Froth flotation is a surfactant-based separation process which is suitable for treating dilute wastewaters. In this technique, there are several advantages such as low space requirements, high removal efficiency, flexibility for various pollutants at different scales, and low cost. To achieve high performance for the froth flotation operation, the combination of ultra-low interfacial tensions between excess oil and excess water phases and high foam production rates, as well as high stability of the foam produced, must be attained. To obtain the ultra-low interfacial tensions, a Winsor Type III microemulsion or middle phase has to be formed. In this study, branched alcohol propoxylate sulfate sodium salt with 14 – 15 carbon number and 4 PO groups (Alfoterra 145 – 4PO) was used to form microemulsions with diesel. From the results of this work, an increase in surfactant concentration decreased interfacial tension (IFT), and increased foam stability. To obtain the minimum interfacial tension (IFT) in the region of a Winsor Type III microemulsion, the addition of 5 wt% NaCl was needed. However, this optimum salinity does not result in effective froth flotation due to poor foam characteristics. The results indicate that both IFT and foam characteristics should be optimized to achieve high efficiency of oil removal in a froth flotation operation. Unlike the previously-studied ethylbenzene system, agitation of the solution before introduction into the flotation column yielded the lowest diesel removal efficiency because of the poor foam characteristics compared to either unagitated systems or systems allowed to equilibrate for one month.

Key words: Microemulsion, Froth flotation, Foam formation, Foam stability, Diesel removal

INTRODUCTION

In many countries, including Thailand, diesel consumption is much higher than gasoline consumption. This is because diesel provides more energy per unit volume than gasoline (1). In the US and Latin America, diesel is used primarily for the transportation of goods. Moreover, in Europe, Japan, and elsewhere, diesel is a significant source of energy for personal transportation (2). The demand for diesel is forecasted to grow faster than the demand for other fuels in general. Therefore, the contamination of groundwater by diesel leakage from gas stations or underground storage tanks is of increasing concern. Since many components in diesel have low water solubility, diesel oil has been found to be present as an oil-in-water emulsion in polluted water.

Froth flotation is the technique investigated in this work to remove the emulsified diesel oil from water. Froth flotation has been widely used for decades to separate a desired ore from unwanted substrates in mineral processing (3). Moreover, nowadays, the froth flotation technique is widely employed in wastewater treatment applications (4 – 5) and in paper deinking processes (6 – 7). There are two main types of froth flotation: dissolved and induced air flotation. In the latter, which was employed in the present study, filtered air is bubbled into the solution through a sintered glass disk. Droplets of emulsified oil can co-adsorb at the bubble surfaces, and then rise to the top of the column to form a foam or froth. However, the stability of these bubble-droplet aggregates is generally low, leading to a lower separation efficiency. To achieve a higher separation efficiency in traditional froth flotation, a proper type of surfactant with an optimum concentration is introduced into the solution to stabilize the foam (8). Chang et al. (9) reported that the surfactant added had to be adjusted at an appropriate concentration to obtain high foam stability. As described in previous work (10 – 13), our approach is to generate conditions in the flotation column corresponding to ultra-low interfacial tensions between the oil and water phases through microemulsion formation by adding appropriate surfactants while still needing to maintain good foam stability in order to maximize the removal efficiency of several types of oils.

In previous work (10), the maximum oil removal was found to correspond to the formation of Winsor Type III microemulsion for ortho-dichlorobenzene. Later, Chavadej *et al.* (11) found that most of the oil removed from the column during the flotation operation came from the excess oil phase rather than the middle phase (phase rich in oil, water and surfactant) in Winsor Type III microemulsion systems with ortho-dichlorobenzene. After that, Yanatatsaneejit *et al.* (12) found that the ultra-low oil-water interfacial tension characteristic of a Winsor Type III microemulsion was not the only factor affecting the performance of froth flotation, but foam stability was also crucial to achieving a high flotation efficiency for ethylbenzene removal. In addition, Yanatatsaneejit *et al.* (13) reported the effect of equilibration time on the performance of froth flotation. For the ethylbenzene system, the highest performance of froth flotation was achieved when the microemulsion system was allowed to equilibrate prior to flotation. Interestingly, pre-mixing of the solution for 40 min (called induced-equilibrium) was found to provide a high performance of froth flotation. In this present work, the performance of froth flotation to remove diesel from water was correlated with interfacial tension and foam characteristics. In addition, the coalescence between oil droplets was hypothesized to be a key factor in the separation, and so the coalescence time between oil droplets was independently measured in this work.

EXPERIMENTAL SECTION

Materials

The model oil used in this study is a commercial grade diesel obtained from the Petroleum Authority of Thailand (PTT). A branched alcohol propoxylate sulfate sodium salt with 14 to 15 carbons in the alkyl chain, and 4 propylene oxides ($C_{14-15}(PO)_4SO_4$), trade name Alfoterra 145-4PO where PO represents propylene oxide, an anionic surfactant which is an experimental (not yet commercially available) surfactant specially synthesized by Sasol Company (formerly Condea Vista Company), Rosebank, South Africa, was used in this study. Analytical purity grade sodium chloride (NaCl) from Aldrich Chemical Company Inc. was used as the electrolyte in this work. All chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

Methodology

This work is divided into four parts. The first part was to study the microemulsion phase behavior of aqueous solutions containing different $C_{14-15}(PO)_4SO_4$ concentrations with diesel. The second part was to investigate the foamability and foam stability under different conditions. The coalescence between oil droplets was studied in the third part. The fourth part was the investigation of the oil separation efficiency of froth flotation in a batch flotation column. In all experiments, the surfactant and electrolyte concentrations are expressed in weight percentage (wt%) per volume of the aqueous solution consisting of water, surfactant, and electrolyte.
To investigate the phase behavior of microemulsions, 5 mL of a homogeneous aqueous solution, prepared at various surfactant and NaCl concentrations, was mixed with 5 mL of diesel in a vial

sealed with a screw cap. These vials were shaken every day for 3 days, and then allowed to equilibrate at a constant temperature of 30°C in an incubator for 1 month to reach equilibrium, which was verified by the invariant height of each phase. The height of each phase was measured by using a cathetometer with a precision of 0.01 mm. The interfacial tension (IFT) between equilibrated excess oil and excess water phases was measured by a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg).

A schematic of the froth flotation unit used in this work is shown in Figure 1. A glass cylindrical column with 5 cm internal diameter and 120 cm height was used as the froth flotation column. A 750 mL sample with different initial oil-to-water ratios and various surfactant and NaCl concentrations which had been equilibrated at 30°C for 1 month in the incubator, was transferred to the froth flotation column. Filtered air at a flow rate of 300 mL/min was introduced at the bottom of the column through a sintered glass disk having pore size diameters of about 16 – 40 μm. The generated air bubbles rose through the solution to the top of the column. The foam collected in the receiver over a period of time was broken by freezing for diesel concentration analysis. Moreover, the solution in the column was sampled at the same time interval as the foam collected for analysis of residual diesel and surfactant concentrations. All experiments were terminated when no more foam came overhead from the column, i.e. the stage at which the surfactant concentration in the solution became too low to generate sufficient foam to reach the overhead weir.

In order to obtain a better understanding about the phenomena of the froth flotation process, foamability and foam stability experiments were conducted independently in the same flotation column. A 250 mL sample containing a given surfactant and NaCl concentrations and an oil-to-water ratio of 1:1 was transferred to the column. Filtered air was introduced at the bottom of the column through the solution at a constant flow rate of 100 mL/min until the maximum foam height in the column was achieved. This maximum foam height was used to indicate foamability. Then, the air injection was ceased and the time required for the foam volume to collapse to half of the maximum height was recorded to quantify foam stability. All experiments of froth flotation operation, foamability, and foam stability were conducted at a room temperature of about 25 – 27°C. The ratio of maximum foam height to initial solution height is considered as foamability while foam stability ($t_{1/2}$) is defined as the time required for the foam to collapse to half the maximum foam height.

To investigate the coalescence time between oil droplets, an aqueous solution having different surfactant and NaCl concentrations was mixed with diesel in a vial at various oil-to-water ratios. After that, this mixture was gently shaken for 1 minute. The intensity of light generated from a Light Emitting Diode (LED) having a wavelength of 568 nm passing through the solution in the vial was measured at various times by a photo sensitive detector until reaching a constant value. In this research, the time that the light intensity begins to reach a plateau is defined as the coalescence time between oil droplets. The plateau light intensity indicates that the coalescence between oil droplets is completed. The measurement of the coalescence time was also conducted at a room temperature of about 25 – 27°C.

RESULTS AND DISCUSSION

To gain a better understanding of the mechanism of the froth flotation process, all results obtained from the four experimental parts are presented in the same graph in order to determine the correlation of all process parameters. Figure 2 shows the proposed mechanism of oil separation in the froth flotation operation which consists of four sequential steps. Firstly, air bubbles are generated within the liquid solution by introducing air into the bottom of the flotation column. In this step, oil droplets adhere to the surface of the air bubbles. In the second step, as the air bubbles rise in the solution, the formation of an oil film on the surface of the air bubbles visually appears. The thickness of the oil film should be great enough to achieve a high oil removal; thus the coalescence between oil droplets has to be maximized. The third step is the rising of bubbles (with attached oil droplets) to the top of the column. High stability of the air bubbles covered by an oil film is required in this step. The fourth step is the air bubbles emerging from the liquid phase to form froth. To operate froth flotation successfully, high stability of the froth is needed to obtain a dry foam with a high oil content. In this work, all important parameters including interfacial tensions obtained from the phase behavior study, foam stability and foamability obtained from the foam characteristic study, and oil droplet coalescence time are simultaneously analyzed to correlate to the efficiency of the froth flotation separation.

Phase Behavior

According to previous work, interfacial tension (IFT) is one of the major factors affecting the performance of the froth flotation operation (12 – 13). As shown in Figure 3, at 3 wt% NaCl concentration, increasing surfactant concentration decreases the IFT monotonically between excess oil and excess water phases, presumably because of the increasing adsorption of surfactant at the oil/water interface (14). However, if the surfactant concentration exceeded 0.15 wt%, stable macroemulsions were found to form, causing the oil/water separation to be too slow for equilibration of the phases to be practically obtainable.

As shown in Figure 4, at a fixed $C_{14-15}(PO)_4SO_4$ concentration of 0.10 wt%, a minimum IFT is observed at 5 wt% NaCl. For anionic surfactants, a minimum in IFT with varying salinity is commonly observed and is known as the optimum salinity; this effect has been discussed in our previous study of the relationship between the microemulsion phase behavior and froth flotation performance of ethylbenzene (12).

Figure 5 shows the insignificant effect of oil-to-water ratio on IFT at 0.1 wt% $C_{14-15}(PO)_4SO_4$ concentration and 3 wt% NaCl concentration, which is consistent with the ethylbenzene (with different surfactant systems) results (13). Since oil-to-water ratios in practical froth flotation operations can be quite different from those used in traditional phase studies (of 1:1 v/v), this lack of sensitivity on oil-to-water ratio justifies the use of phase studies to guide the design and operation of flotation for real wastewater, which generally has very low ratios of oil-to-water.

Foam Characteristics

As described in previous work (12 – 13), the removal efficiency of oil in a froth flotation operation is improved by adjusting the system to have both higher foamability and foam stability. The effects of $C_{14-15}(PO)_4SO_4$ concentration on both foam stability and foamability are illustrated in Figure 3. Both foam stability and foamability reached the maximum at 0.1% surfactant concentration.

From Figure 4, at 0.1 wt% $C_{14-15}(PO)_4SO_4$, foamability reaches a maximum at 3 wt% NaCl while foam stability decreases with increasing NaCl concentration over the range studied. As shown in

Figure 5, both foamability and foam stability tend to increase slightly with increasing oil-to-water ratio, consistent with the results of the ethylbenzene system (13). In systems with anionic surfactant, salt, and oil, there are a number of factors affecting foamability and foam stability, including Gibbs-Marangoni effects, surfactant viscosity, viscosity in film lamellae, packing of surfactant monolayer at the air-water interface, and bridging of foam lamellae by oil droplets, to name a few. Therefore, explanations of these effects of surfactant and salt concentration and oil-to-water ratio would be largely speculative without much more detailed studies.

Figure 6 shows the effect of air superficial velocity (u_G) on foam characteristics of the system, having an $C_{14-15}(PO_4)SO_4$ concentration of 0.10 wt%, a NaCl concentration of 3 wt%, and an oil-to-water ratio of 1:1. As shown in Figure 6, the foam stability is strongly affected by u_G; the foam stability decreases substantially with increasing u_G. This is because at a higher u_G, the velocity of the bubble swarm rising through the column is higher, leading to increasing coalescence between air bubbles. However, in the case of foamability, the foam formation is proportional to u_G because the number of bubbles increases when u_G increases. In this studied system, above a u_G of 15 cm/min, the observation of foam characteristics was not able to be obtained because foam did overflow from the flotation column.

Coalescence of Oil Droplets

The coalescence time between oil droplets is expected to be one of the major parameters affecting the performance of froth flotation since there should be a difference between floating many small droplets vs. a few large drops. The coalescence time increases with increasing C_{14-}

$_{15}(PO)_4SO_4$ concentration, as shown in Figure 3. The coalescence time first generally increases and then decreases with increasing salinity, and reaches a maximum at 3% NaCl, as seen in Figure 4. Figure 5 shows the effect of oil to water ratio on the coalescence time. There are several important factors affecting coalescence rates and their complex interaction makes the prediction of the effects of operation variables difficult. Increasing viscosity tends to increase coalescence times (15) (decrease coalescence rates), probably explaining the effects of surfactant concentration and oil-to-water ratio. Decreasing IFT reduces the decrease in system free energy upon the loss of interfacial area upon coalescence, tending to decrease coalescence times. Interfacial tension gradients also tend to decrease as IFT decreases, reducing Gibbs-Marangoni effects which help stabilize the thin aqueous film between oil droplets, which tends to decrease coalescence times also. Increasing salinity compresses the electrical double layer, reducing electrical repulsion between the oil droplets (which have induced charge due to the adsorbed anionic surfactant), also tending to reduce coalescence time. Increasing salinity could also cause denser packing of the surfactant molecules, increasing interfacial viscosity, tending to increase coalescence rates. The complex interaction between these effects results in the maximum in coalescence time with salinity, as seen in Figure 4. The effects of salinity on the coalescence rates for emulsions have been discussed in literature (16).

Evaluation and Correlation of Froth Flotation Performance

As in previous work (12), the three terms of oil removal, surfactant removal, and enrichment ratio of oil are used as the performance parameters of froth flotation operation. In this work, the enrichment ratio of diesel is defined as the diesel concentration in the collapsed froth to the diesel concentration in the initial feed as an indication of selectivity of diesel removal compared to water. Therefore, to achieve any separation, the enrichment ratio of diesel has to be higher than unity.

Removal of diesel and surfactant

Figure 3 shows the effects of $C_{14-15}(PO)_4SO_4$ concentration on IFT, total cumulative diesel removal, total cumulative $C_{14-15}(PO)_4SO_4$ removal, foamability, foam stability, and coalescence time between oil droplets. Similar to the ethylbenzene system (12), the total cumulative diesel removal is the highest at the $C_{14-15}(PO)_4SO_4$ concentration corresponding to the maximum foamability and the maximum foam stability, but not the minimum IFT. The same trend is observed for total cumulative $C_{14-15}(PO)_4SO_4$ removal. Both diesel and $C_{14-15}(PO)_4SO_4$ removal was found experimentally not to correlate to the coalescence time between oil droplets.

The interfacial tension (IFT), total cumulative diesel removal, total cumulative $C_{14-15}(PO)_4SO_4$ removal, foamability, foam stability, and coalescence time between oil droplets as a function of NaCl concentration are shown in Figure 4. Enough foam could not be generated to overflow the flotation column when the NaCl concentration was greater than 3 wt%, resulting in no diesel or surfactant removal above 3 wt% NaCl. Between 2 and 3 wt% NaCl, the removal of diesel and surfactant was found to be almost constant.

Figure 5 shows IFT, total cumulative diesel removal, total cumulative $C_{14-15}(PO)_4SO_4$ removal, foamability, foam stability, and coalescence time as a function of oil-to-water ratio. Similar to the previous work (13), the removal efficiency of oil is not significantly affected by the oil-to-water ratio, whereas the surfactant removal reached the minimum value at 1:4 ratio for the diesel system, but 1:9 ratio for the ethylbenzene system (13). The variables most affected by oil-to-water ratio are coalescence time, which increases dramatically as the oil-to-water ratio approaches 1:1, and the enrichment ratio of diesel, which approaches unity (no selectivity for oil removal vs. water) as the oil-to-water ratio approaches 1:1. At extremely high oil loading in the wastewater, the froth flotation technique is not effective, which is expected. It is important to note that the IFT is almost independent of oil-to-water ratio since microemulsion phase studies used to equilibrate oil/water/microemulsion phases prior to measurement of the IFT are typically performed at an initial oil-to-water ratio of unity, whereas oily wastewater typically has an oil-to-water ratio much lower. It means that IFT values in this study are relevant to real wastewater having a low oil-to-water ratio.

The effects of superficial velocity (u_G) on total cumulative diesel removal, total cumulative $C_{14-15}(PO)_4SO_4$ removal, foamability, and foam stability are shown in Figure 6. The highest removal efficiency of diesel corresponded to the u_G which had the highest foamability but relatively low foam stability. This is because the number of bubbles passing through the solution increases rapidly with increasing u_G, leading to a higher foam production rate. The results indicate that under the studied conditions, the effect of foamability is more significant than that of foam stability on the diesel removal. In contrast, the total cumulative $C_{14-15}(PO)_4SO_4$ removal was not significantly affected by u_G, even though the volume of foam generated increased. This is due to some of the surfactant being entrained back into the solution since the circulation velocity of the bubble swarms is higher at a higher u_G.

Table 1 shows the effects of equilibrium condition on IFT, total cumulative diesel removal, total cumulative $C_{14-15}(PO)_4SO_4$ removal, foamability, and foam stability. For the equilibrium system, the total cumulative diesel removal, foamability, and foam stability, were the highest as expected. It is interesting to note that the total cumulative diesel removal from the non-equilibrium system was very close to that of the equilibrium system. Unlike the ethylbenzene system (13), the diesel removal of the induced-equilibrium system was found to have the lowest oil removal because both foamability and foam stability were extremely low. The induced-equilibrium system also gave the lowest $C_{14-15}(PO)_4SO_4$ removal, again not consistent with the previous work on ethylbenzene (13). In contrast with the results of the diesel removal, the maximum $C_{14-15}(PO)_4SO_4$ removal was found for the non-equilibrium system.

From a practical viewpoint, these results lead to the important and counterintuitive conclusion that no agitation may be preferable to agitation for a short time for the diesel/water mixture. Of course, real wastewater will have emulsified oil in contact with the water for some time before treatment, so optimum contact time will need to be determined for the specific stream of interest. Since different trends have been observed for the two oils studied (diesel and ethylbenzene), results may be highly dependent on oil structure.

Mechanistically, a hypothesis to explain the results is that when mixing for 40 minutes, the emulsion droplet size may be reduced, leading to a greater oil/water interface area and more surfactant adsorbed at this interface. The resulting lower surfactant concentration in the bulk aqueous phase leads to higher oil/water interfacial tension, lower foamability, and lower stability, leading to lower diesel and surfactant removal. When the system equilibrates, the surfactant primarily incorporates itself into the microemulsion phase and ultralow IFT values are observed. The equilibrium system gives a high diesel removal, but low surfactant removal as compared to the non-equilibrium system. Most of the oil being removed comes from the excess oil phase and not from the microemulsion phase, as has been deduced in previous work for dichlorobenzene under equilibrium conditions (11).

Enrichment ratio of diesel

The enrichment ratio of diesel as a function of $C_{14-15}(PO)_4SO_4$ concentration is shown in Figure 3. As the $C_{14-15}(PO)_4SO_4$ concentration increases, the enrichment ratio of diesel is almost constant. Actually, increasing surfactant concentration should decrease the enrichment ratio of oil because of several aspects such as thicker foam lamellae causing higher water content in foam lamellae, and higher viscosity of the solution leading to a lower drainage rate of water from the foam lamellae. However, the amount of oil in the froth also increases with increasing surfactant concentration due to more hydrophobic regions in the froth.

From Figure 4, the diesel enrichment ratio increases as the NaCl concentration increases from 2 to 3 wt%. A possible explanation is that the repulsive force between the head groups of the anionic surfactant at the opposite site of the foam lamellae decreases with increasing NaCl concentration, resulting in a thinner foam lamellae, resulting in a lower amount of water carried over with the foam, leading to a higher enrichment ratio of diesel. The enrichment ratio of diesel reaches a maximum at a 1:4 oil-to-water ratio. It is expected that the diesel enrichment ratio would increase with increasing oil-to-water ratio, but the mild maximum observed here is due to increasing solution viscosity at high oil to water ratio, causing slower water drainage from the foam lamellae. From Figure 6, we can see that the superficial air velocity has no significant effect on enrichment ratio while Table 1 shows that equilibration conditions have little effect.

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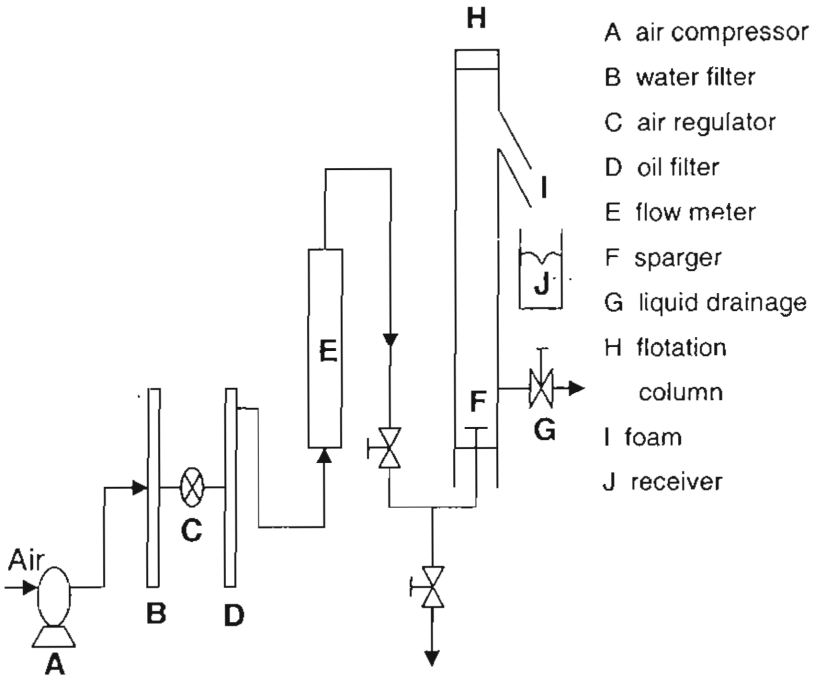

Figure 1. Schematic of the froth flotation apparatus

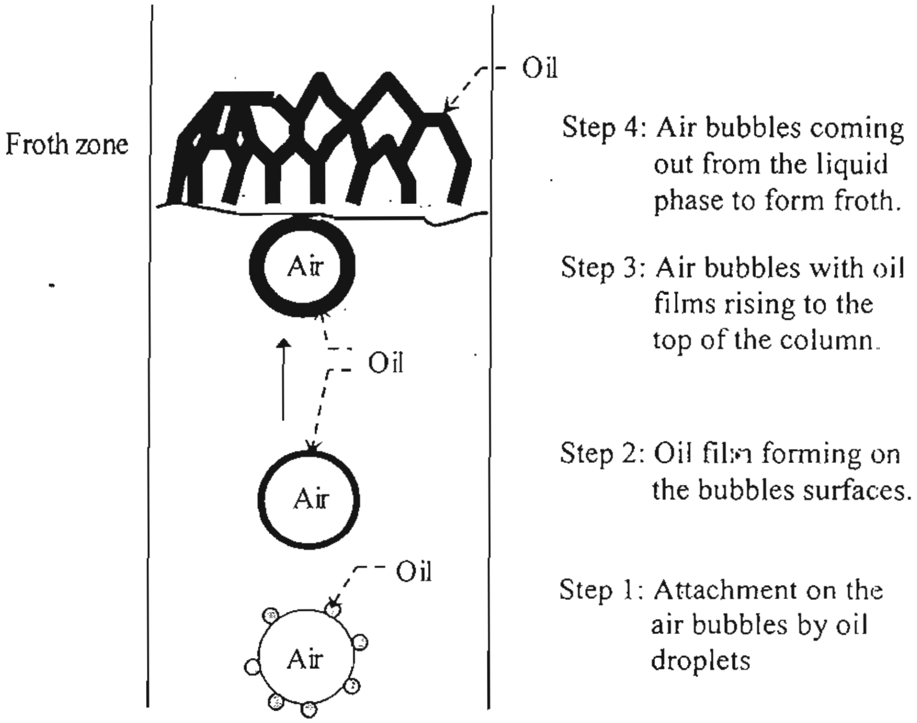

Figure 2. Proposed mechanism in froth flotation operation

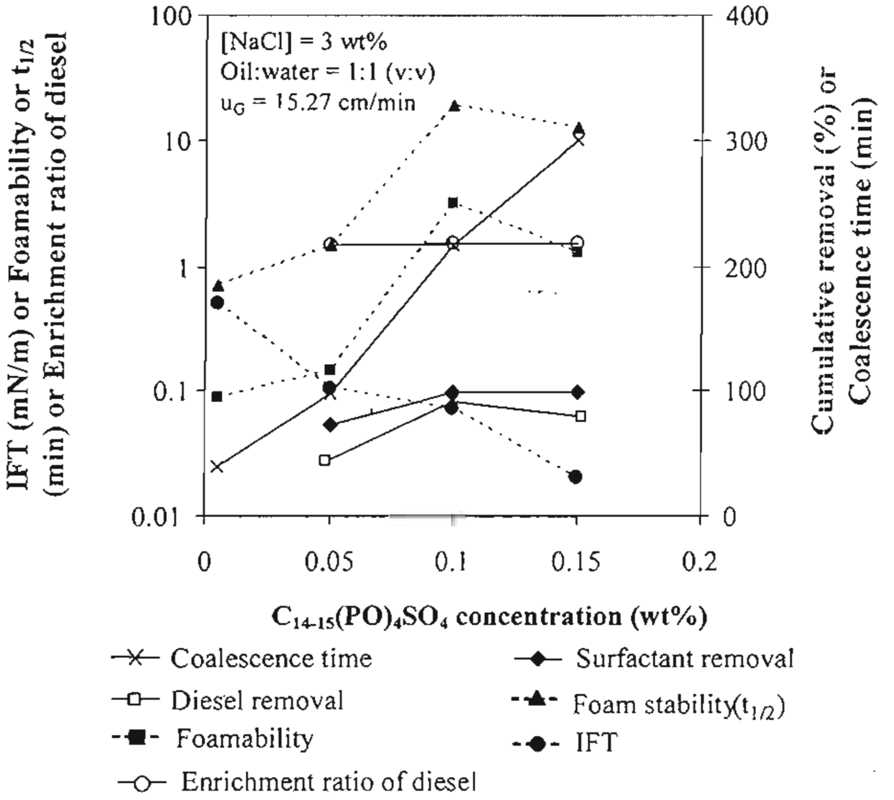

Figure 3. Effect of surfactant concentration on process parameters

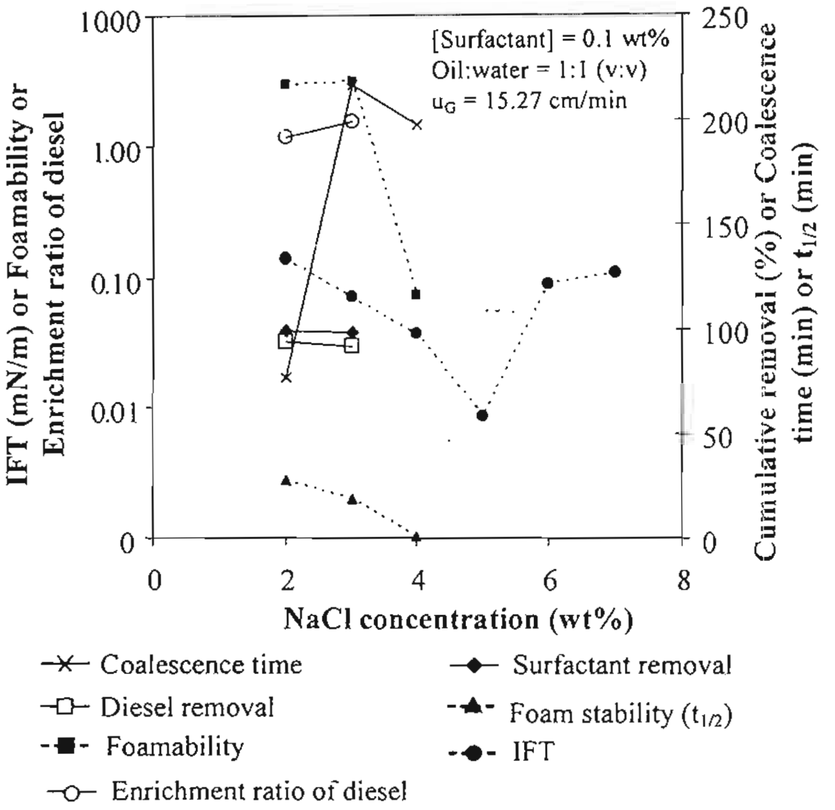

Figure 4. Effect of NaCl concentration on process parameters

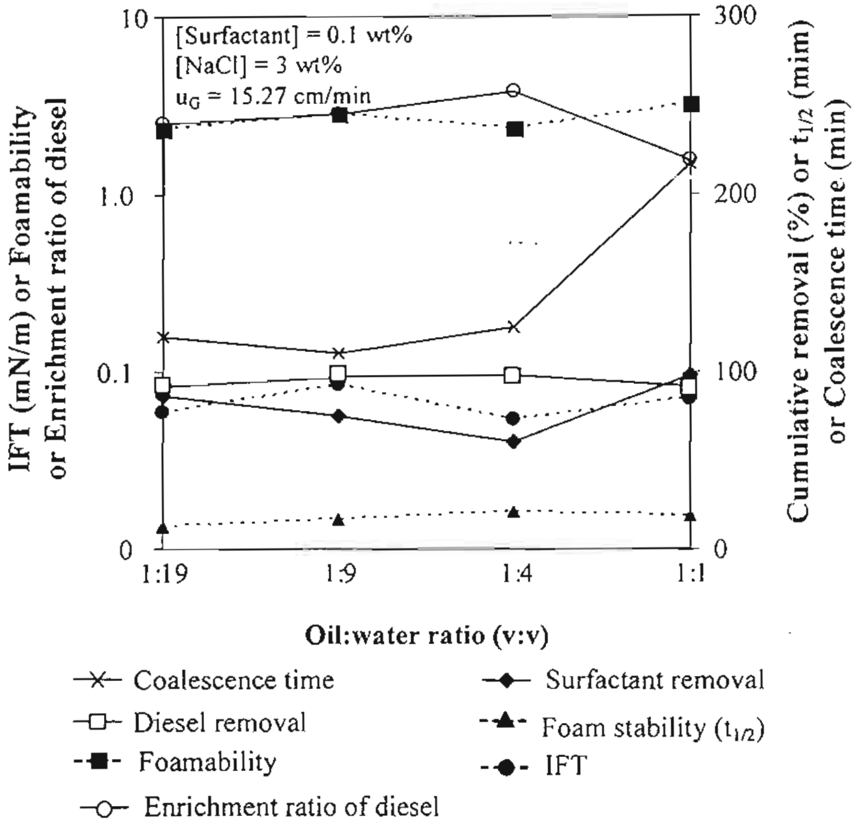

Figure 5. Effect of oil-to-water ratio on process

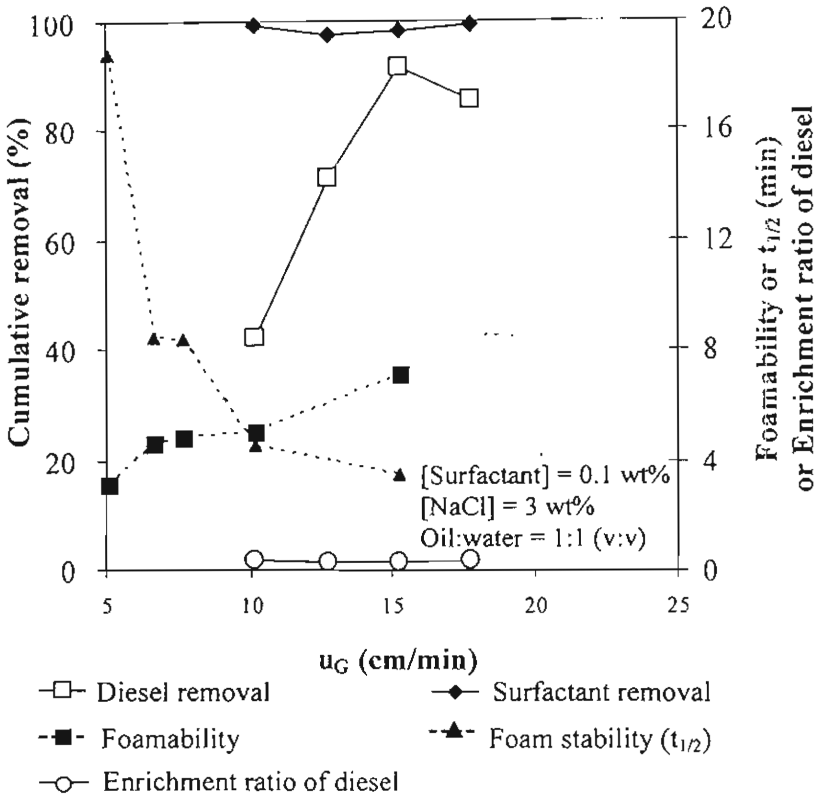

Figure 6. Effect of superficial air velocity on process parameters

Table 1 Effect of equilibration condition on process parameters at a fixed surfactant concentration of 0.10 wt%, a NaCl concentration of 3 wt%, and an oil-to-water ratio of 1:1

System	IFT (mN/m)	Total cumulative removal (%)		Enrichment ratio of diesel	Foamability	$t_{1/2}$ (min)
		Diesel	Surfactant			
Non-equilibrium (no premixing)	0.109	91.54	98.30	1.53	3.13	18.82
Induced-equilibrium (40 min mixing)	0.159	54.46	46.89	1.62	0.11	0.87
Equilibrium (1 month storage)	0.036	96.86	74.06	1.53	3.21	20.03

DIESEL REMOVAL BY FROTH FLOTATION UNDER LOW INTERFACIAL TENSION CONDITIONS II: CONTINUOUS MODE OF OPERATION

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ABSTRACT

Froth flotation is a surfactant-based separation process which is suitable for separating emulsified oils from wastewaters. The objective of this study was to investigate the relationship between interfacial tension (IFT) and foam characteristics and the efficiency of diesel removal from water in a continuous froth flotation column. The effects of operational parameters including surfactant concentration, salinity, oil to water ratio, air flux, foam height and hydraulic retention time (HRT) on the oil removal were investigated in the continuous mode of froth flotation operation and compared to the batch operation results. Form the batch results, the maximum diesel removal (approximately 98%) was achieved at 0.3 wt% of branched alcohol propoxylate sulfate sodium salt surfactant ($C_{14\text{-}15}(PO)_4SO_4$), 3 wt% NaCl, and an oil to water ratio of 1:4. For the continuous system used in the present study, having only $C_{14\text{-}15}(PO)_5SO_4$ present in the solution yielded such poor foam characteristics that a stable froth which overflowed the flotation column could not be produced, so an addition of sodium dodecyl sulfate (SDS) as a frother was used to improve the foam stability. From the results of both batch and continuous modes of froth flotation operation, the maximum oil removal efficiency of the froth flotation process were found not to correspond to the minimum IFT of the system, indicating that the ultralow IFT alone cannot be used as a sole criterion for optimizing the froth flotation process. Foam formation, stability, and production rate were found to be crucial parameters to the froth flotation efficiency. The continuous froth flotation system with 0.1 wt% $C_{14-15}(PO)_5SO_4$, 0.5 wt% SDS, 4 wt% NaCl, an oil to water ratio of 1:19 was found to yield a highest diesel removal of 96% with a hydraulic retention time of 60 minutes.

INTRODUCTION

Diesel is an important transportation fuel because based upon volume, it possesses a higher power output than gasoline. It is anticipated that diesel demand and utilization will still rise substantially in the next few decades (1). Because of its widespread usage and appearance in several industrial processes such as metal manufacture and machining as well as petroleum refinery plant, diesel is often found in wastewaters (2). Hence, it is of interest to develop an high efficiency process with low cost and simplicity in operation for removing diesel as well as other oils from wastewaters before discharging into the environment.

Froth flotation is a surfactant-based separation process (3, 4, 5). It was first used in ore processing, and it has been pointed out to be a promising technique for oily wastewater treatment (4-7, 10, 12, 13, 15, 16, 18). Froth flotation processes are suitable for treating wastewaters containing suspended solids as well as oils in both emulsion and undissolved forms since it has several advantages including rapid operation, low space requirement for equipment set-up, high efficiency of removal, flexibility of application to various pollutants at various scales, and low cost of operation (8).

In a froth flotation operation, a proper type and concentration of surfactant is first added into an oily wastewater, and air is introduced into the system in order to generate fine bubbles. The surfactant added tends to adsorb preferentially at the air/water interface with the hydrophillic part or head groups in the water and the hydrophobic part or tail groups in the air. As a result, oil will concentrate at the bubble surfaces while they rise through the solution to form foam or froth at the top of the flotation cell which is continuously skimmed off. As known, the formation of stable bubble particle aggregates is required in the froth flotation operation to achieve a high separation efficiency (9).

From our previous work (10), the maximum oil removal was found to correspond to the ultralow interfacial tension (IFT) condition when the system was in the Winsor Type III microemulsion region. This is the initial point of our research group to continue studying the relationship between the Winsor Type III microemulsion and the forth flotation efficiency with different types of oils because a microemulsion has superior characteristics such as relatively large interfacial area, high solubilization capacity, and ultralow IFT (11). Later, Chavadej *et al.* (12) found that the most oil removed during the froth flotation operation came from the excess oil phase rather than the middle phase in the Winsor Type III microemulsion system. This proves that it is the ultralow IFT corresponding to the Winsor Type III microemulsion which is responsible for efficient flotation; formation of a third phase (middle phase) under this condition is coincidental to oil removal. Recently, Yanatatsaneejit *et al.* (13) found that ethylbenzene removal from water by froth flotation was efficient only when both low IFT and good frothing are present. The importance of foam stability was also observed by Carre *et al.* (14). Moreover, Yanatatsaneejit *et al.* (15) proposed four sequential steps in the mechanism of oil removal by froth flotation. Firstly, air bubbles are generated through the liquid solution and oil droplets adhere on the surface of the air bubbles. The second step is the formation of oil films on the surfaces of the air bubbles while the air bubbles are rising through the solution. The third step is the rising of the air bubbles with attached oil films to the top of the solution. The fourth step is the emerging of air bubbles from the liquid phase to form froth. In both third and fourth steps, high stability of the air bubbles covered by oil films is necessary. For a successful separation, high stability of the froth is needed to yield dry foam with a high oil content. Foamability or foam formation and foam stability influences the foam production rate which needs to be sufficient for a good separation, no matter how well the oil attaches to air bubbles rising through solution. Yanatatsaneejit *et al.* (16) correlated the performance of batch froth flotaion to remove diesel from water with the system IFT, foam characteristics, and coalescence time between oil droplets.

As mentioned before, all studies of froth flotation including our group's previous works (10, 12, 13, 15, 16) were operated in a batch mode whereas large quantities of industrial wastewaters are more efficiently treated by continuous, steady-state processes. Hence, we have developed a continuous froth flotation process for treating oily wastewaters In this work, the relationship between the system IFT and foam characteristics and the efficiency of diesel removal from water by the continuous froth flotation was investigated using the surfactant mixture $C_{14-15}(PO)_5SO_4$ and SDS. The mixed surfactants were employed in order to achieve a low IFT as well as high foamability and high foam stability. The effects of all operational parameters (concentration of surfactant, salinity, oil to water ratio, air flux, foam height, and hydraulic retention time, HRT) on flotation efficiency were also investigated systematically.

EXPERIMENTAL SECTION

Materials

Two types of surfactants were used in this work, a branched alcohol propoxylate sulfate, sodium salt ($C_{14-15}(PO)_5SO_4$), and sodium dodecylsulfate (SDS). $C_{14-15}(PO)_5SO_4$ (Alfoterra) with purity of 28.7% in the liquid form which was supplied by Sasol North America Inc., Texas, USA is an extended anionic surfactant having 14-15 carbon atoms and 5 groups of propylene oxide (PO) which provides a high hydrophobicity with sulfate as a hydrophilic group. SDS which was obtained from Carlo Erba Reagenti with purity in the range of 94-98 % is an anionic surfactant with a negatively-charged sulfate head group and alkyl chain length of twelve carbon units. Diesel oil was selected as a model contaminant oil was purchased from PTT Public Co., Ltd (Thailand). Analytical grade of sodium chloride (NaCl) with 99% purity was obtained from Labscan Asia Co., Ltd. All chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

Methodology

This work consisted of three main parts. The first part was to study the equilibrium microemulsion formation of diesel with aqueous solutions of varying surfactant concentrations. For the second part, continuous froth flotation experiments were conducted at various surfactant concentrations, NaCl concentrations, oil to water ratios, air fluxes, foam heights, and hydraulic retention times (HRT). The last part was to determine foam characteristics.

Microemulsion Formation

A quantity of 5 mL of diesel was added in a series of vials containing 5 mL of a surfactant solution having different surfactant concentrations and salinities. After that, each vial was shaken gently by hand for 1 min and then equilibrated in a temperature-controlled incubator (BINDER, KB400/E2) at 30 °C until the system reached equilibrium. The equilibrium state was considered to be attained when the volume of each phase of the microemulsion system was invariant. The measurement of phase height was conducted by using a cathetometer, model TC-II from Titan Tool Supply, Inc. attached to a digimatic height gauge, model 192-631, obtained from Mituyo with ± 0.002 mm in accuracy. The interfacial tension (IFT) between diesel and various surfactant solutions was measured using a spinning drop tensiometer (SITE 04, Kruss GmbH, Hamburg).

In order to verify the existence of microemulsion type for the diesel system for a very low surfactant concentration, well-mixed solution samples were measured for conductivity using a conductivity meter (EUTECH INSTRUMENTS, CON11&CON110) at room temperature (26±1°C). A high conductivity indicates a Winsor Type I or III microemulsion while a low value implies a Winsor Type II microemulsions (17)

Froth Flotation Experiments

Figure 1 shows the schematic diagram of a continuous froth flotation apparatus used in this study. The froth flotation apparatus consisted of a glass cylindrical column with 5 cm inside diameter and 120 cm height and operated in a continuous mode. Compressed air was first filtered to remove all particles, water and oil before entering the flotation column. The flow rate of the filtered air was regulated by a mass flow controller (AALBORG, GFC171S). The filtered air was introduced into the bottom of the column through a sinter glass disk with pore size diameter of about 16-40 μm. A well-mixed solution, with different surfactant concentrations was fed continuously with a desired flow rate into the froth flotation column by using a peristaltic pump (Masterflex, easy-load II). The level of the solution in the column was adjusted by a three-way flexible outlet tube in order to vary the foam height. The air bubbles ascending through the solution in the column was to generate foam or froth. The foam overflow from the column was collected in a foam receiver, and then the collapsed froth was analyzed for diesel and surfactant concentrations in the froth at 10 minutes time intervals. In addition, effluent samples were also collected for analysis of diesel concentrations and total surfactant concentrations by using the methylene chloride extraction method (18) and titration method with methylene blue chloride (19), respectively. All froth flotation experiments were carried out at room temperature of 26 ± 1 °C. Each experiment was run until the system reached steady state. The steady state was justified when the concentrations of diesel in the froth and effluent samples became relatively invariant. The reported data obtained under steady state conditions were averaged to evaluate the process performance.

Measurement of Foam Characteristics

The experiments were conducted in a glass cylindrical tube having the same inside diameter of the flotation column. A quantity of 250 mL of the solution sample with different initial oil to water ratios, and various surfactant, and NaCl concentratons was transferred to the column. After that, filtered air at a constant flux of 5.1 cm/min was introduced into the bottom of the column though a sintered glass disc to generate fine bubbles through the solution. When for each run, the maximum foam height was achieved and recorded, the filtered air was then terminated. The ratio of maximum foam height to initial solution height is defined as foamability while the time required for the foam volume collapsed by half of the maximum foam height is used to quantify foam stability ($t_{1/2}$). All experiments were also carried out at room temperature (26 ± 1 °C).

RESULTS AND DISCUSSION

In all experiments, the surfactant and NaCl concentrations are expressed in weight percentage (wt%) per volume of the aqueous phase consisting of water, salt, and surfactants (not including oil).

Phase Behavior and IFT

A low or ultralow oil/ water IFT can greatly enhance the performance of froth flotation as mentioned in our previous studies (10, 12, 13, 15, 16). The use of extended surfactants can form microemulsion with a variety of oils without added alcohol at room temperature (20, 21). Hence, $C_{14-15}(PO)_5SO_4$ was selected to form micromulsion with diesel in the present study. Figure 2 shows the fish diagram of the diesel/water microemulsion system which was obtained by varying both salt and surfactant concentrations at an oil-to-water ratio of 1:1. For a given surfactant concentration in the range of 0.1-10 wt%, an increase in salinity, known as salt scan, results in phase transformation from Winsor Type I to Type III and Type II microemulsions (22). At a very high surfactant concentration above 10%, a single microemulsion phase known as Winsor Type IV was present. It is of interest to know a minimum surfactant concentration to exhibit a Winsor Type III microemulsion which is known as the critical microemulsion concentration (CμC) (23). From the fish diagram as shown in Figure 2, the CμC is about 0.1 wt% of $C_{14-15}(PO)_5SO_4$ in the range of 3-5 wt% of NaCl. As known, Winsor Type III microemulsion possesses an ultralow IFT which is considered as a primary criterion for a success of the froth flotation operation to remove oil from water (13).

Figure 3 depicts the phase diagram and the oil/water IFT as a function of surfactant concentration at a water-to-oil ratio of 1:1. For the pure $C_{14-15}(PO)_5SO_4$ system, the phase transformation from a Winsor Type I to Winsor Type III microemulsions appeared when the $C_{14-15}(PO)_5SO_4$ concentration was greater than 0.1 wt%. The system IFT was in the ultralow range (10^{-1}-10^{-2} mN/m) (23, 24) corresponding to the presence of a Winsor Type III microemulsion. The results indicate that $C_{14-15}(PO)_5SO_4$, an extended anionic surfactant, can promote a Winsor Type III microemulsion but interestingly the volume of middle phase was found to be relatively small for the diesel system in the study.

This CμC value (0.1 wt% $C_{14-15}(PO)_5SO_4$) was first selected as a base condition to run froth flotation experiments. It was found that with $C_{14-15}(PO)_5SO_4$ alone , the system was not able to generate stable foams to reach the foam outlet at the top of the column. Hence, SDS was added as a foam booster to improve the foam stability. Hence, the experiments of microemulsion formation with the mixed surfactants (SDS and $C_{14-15}(PO)_5SO_4$) were carried out. For the phase study of the mixed surfactants, the SDS concentration was varied at the optimum concentrations of 0.1 wt% $C_{14-15}(PO)_5SO_4$ and 3 wt% NaCl and an oil-to-water ratio of 1:19 was used instead of 1:1 as is generally used in most of phase studies since most of real waste waters normally contain oil contents much lower than 1:1. Figure 4 shows the fish diagram of diesel with the mixed surfactants. The CμC value (0.6 wt%) of the mixed surfactants was found to be much higher than that (0.1 wt%) of the pure $C_{14-15}(PO)_5SO_4$. This is because SDS is very hydrophilic (high HLB number). Thus, the addition of SDS simply increases the hydrophile-lipophile balance (HLB), so it is difficult to form a Winsor Type III microemulsion with diesel, high hydrophobic oil.

However, a Winsor Type III microemulsion can be obtained by selecting a suitable amount of total surfactant concentration and electrolyte concentration. As shown in Figure 4, for any given total surfactant concentration greater 0.6 wt%, the phase transformation from Winsor I to Type III and Type II microemulsion is achieved by increasing salinity.

The CμC value of 0.1 wt% $C_{14-15}(PO)_5SO_4$ for the pure $C_{14-15}(PO)_5SO_4$ system was used to study the phase diagram of the mixed surfactants by varying SDS concentration. Figure 5 shows the phase height and the system IFT as a fuction of SDS concentration. From the result, the addition of SDS caused the shift from a Winsor Type I microemulsion to a Winsor Type II microemulsion as well as to increase the system IFT. Interestingly, under the studied conditions, an addition of SDS resulted in a substantial increase in the IFT but a middle phase could not be formed. The adding SDS directly replaces the $C_{14-15}(PO)_5SO_4$ adsorbing onto the water/diesel interface, so the amount of $C_{14-15}(PO)_5SO_4$ adsorbing onto the water/diesel interface decreases with increasing SDS. Consequently, the system IFT increases with increasing SDS concentration since SDS can reduce IFT much less than $C_{14-15}(PO)_5SO_4$. As mentioned eariler, the pure $C_{14-15}(PO)_5SO_4$ system could not be used to operate froth flotation because the foam produced possessed a poor foam stability. Consequently, SDS was considered to improve the foam stability of the studied system. In order to conduct further studies, an SDS concentration of 0.5 wt% was selected since the system had a considerably low IFT (around 1 mN/m) which is believed to be low enough to run froth flotation experiments.

For an ionic surfactant system, an addition of salt can facilitate the phase transformation from a Winsor Type I microemulsion toward a Winsor Type III and then Winsor Type II microemulsions (11). In addition, the effect of salinity is important to know because most waste waters generally contain a certain amount of salts. From Figure 6, as the NaCl concentration increases from 2 to 4 wt%, the system IFT decreases almost linearly. This is because the repulsive force between the anionic head groups of both $C_{14-15}(PO)_5SO_4$ and SDS decreases when the NaCl concentration increases, leading to an increase in the surfactant adsorption at the oil/water interface. As a result, the system IFT decreases with increasing salinity. The explanation of the effect of NaCl concentration on IFT and phase behavior was already discussed in our previous work of ethylbenzene (13). The effect of NaCl on foam characteristics will be discussed in the next section.

Since the NaCl concentration of 4 wt% provides the lowest IFT and reasonably high foamability and foam stability as shown in Figure 6, 4 wt% of NaCl was selected to determine the effect of oil to water ratio on the IFT. Figure 7 illustrates the system IFT as a function of oil to water ratio at 0.1 wt% $C_{14-15}(PO)_5SO_4$, 0.5 wt% SDS and 4 wt% NaCl. In the studied range of oil to water ratio, the system IFT seemed to be independent on the oil to water ratio. This is because each oil to water ratio contains almost the same amount of surfactants adsorbing onto the oil/water interface. The explanation about the effect of oil to water ratio on IFT also was discussed in our previous work (13). Generally, the oil to water ratios in real waste water streams are much lower and different from those used in the traditional phase studies (1:1 volume/volume). Interestingly, this robust property that the system IFT is not sensitive with the oil to water ratio is very useful in design and operation of a froth flotation unit.

Based upon our previous results of batch froth flotation experiments with different types of oils (10, 12, 13, 15, 16), it has been pointed out that the oil removal is governed by both IFT and foam characteristics. Therefore, both data of IFT and foam characteristics should be discussed prior to the froth flotation results.

Foam Characteristics

As described in our previous works (13, 15, 16), foam characteristics which are foamability and foam stability significantly affect the oil removal efficiency in froth flotation operation. The higher the foamability and the foam stability, the higher the oil removal should be obtained.

As known, most real waste waters are not well mixed. Unlike the batch mode of operation (16), a continuous froth flotation unit is needed to agitate a feed solution before fed into the froth flotation column in order to obtain the uniform composition of the feed solution. Hence, in this study, the effect of premixing on foam characteristics was investigated. For the premixed system, the feed solution was agitated at 2,000 rpm for 1 hour before transferred into the froth flotation column. Figure 8 shows foamability and foam stability as a function of $C_{14-15}(PO)_5SO_4$ concentration with and without premixings. When the $C_{14-15}(PO)_5SO_4$ concentration is less than 0.5 wt%, the nonpremixed system had higher foam stability and foamability than the premixed system. However, at a $C_{14\text{-}15}(PO)_5SO_4$ concentration greater than 0.5 wt%, both systems had similar foamability and foam stability. For both systems of with and without premixings, the lowest foamability and foam stability were found at 0.1 wt% $C_{14\text{-}15}(PO)_5SO_4$ which corresponds to the lowest IFT as shown in Figure 3. Hence, 0.1 wt% of $C_{14\text{-}15}(PO)_5SO_4$ was selected for running froth flotation experiments. Based on the present results, the effect of premixings plays insignificant role on both foamability and foam stability. However, the premixing was still needed for running the continuous froth flotation unit to ensure the homogenity of feed solution. From the preliminary results of froth flotation experiments, the use of $C_{14\text{-}15}(PO)_5SO_4$ alone was found to produce foam with low foam stability, so the foam produced could not reach the outlet at the top of the column. This is because its structure of the high molecular mass alcohols has the antifoaming property (25). In addition, the branched-chain tail of $C_{14\text{-}15}(PO)_5SO_4$ possesses a larger diameter of tail group than a normal anionic surfactant's one, which tends to adsorp difficultly on the foam lamellae. Hence, the repulsive force between the two layers of the lamellae decreases, resulting in decreasing the foam stability. Again, a foam booster was required to overcome this problem.

The effects of adding SDS on both foamability and foam stability are shown in Figure 9. Both foamability and foam stability tend to increase with increasing SDS concentration. Interestingly, the effect of adding SDS is much more pronounced on the foam stability than on the foamability. According to the preferential adsorption of the surfactants at the air/water interface, an increase in SDS concentration results in increasing a foam production rate. Meanwhile, the more the surfactant adsorbing on the foam surface, the higher repulsive force between the two layers of the foam lamellae is, leading to an increase in foam stability.

Figure 10 shows the effect of NaCl concentration on foam characteristics. When the NaCl concentration increased from 2 to 3 wt%, the foamability increased drastically but the foam stability increased slightly. However, both foamability and foam stability decrease substantially when the NaCl concentration further increased from 3 to 5 wt%. The results of both foam stability and foamability can be explained that an increase in NaCl decreases the repulsive force between the head groups of the surfactants. As a result, the amount of surfactants adsorbing on the air/water interface increases, leading to more foam to be produced. An increase in surfactant adsorbing on the foam lamellae also increases the repulsive force between the two layers of the lamellae, leading to improving the foam stability. However, if the amount of adding NaCl is too high (greater than 3 wt%), both foamability and foam stability were found to decrease. At a very high NaCl concentration, it simply reduces the repulsive force between the two layers of foam lamellae because of the neutralization effect by the sodium counterion. As a result, foam can break easily.

The effect of oil to water ratio on foam characteristics is illustrated in Figure 11. From the results, the effect of oil to water ratio was not pronounced on both foamability and foam stability. This is because any oil to water ratio has almost the same amount of surfactants adsorbing on the foam lamellae.

Figure 12 illustrates the effect of air flux on foam characteristics. The foamability increased almost linearly with increasing air flux because increasing air flux simply produces a higher quantity of air bubbles passing through the solution. Zouboulis *et al.* (26) also found that a higher air flux caused a larger amount of foam created. For a low air flux lower than 12.73 cm/min, the foam stability was found to be independent on the air flux. However, the foam stability of the system decreased significantly with increasing air flux from 12.73 to 15.27 cm/min because the circulation velocity induced by the bubble swarm rising through the column causes the turbulence at the froth/collection zone, leading to foam collapsed. The similar results of the batch study were also reported (16). From the results, it is suggested that the air flux has to be optimized to get the maximum foam stability.

Froth Flotation Performance

Both removal and enrichment ratio of diesel are significant parameters to evaluate the performance of froth flotation process. Generally, high oil removal efficiency is a vital requirement for an effective froth flotation operation. If both oil and water are present in the froth with the same proportions as those in the influent, the separation of oil from water does not occur. Hence, for effective separation, the concentration of oil in the overhead froth has to be much higher than that in the feed. Consequently, in this study, both removal and enrichment ratio of diesel are used to evaluate the separation efficiency of the continuous froth flotation system. The diesel removal is calculated based on the mass difference of diesel in feed and in effluent. The enrichment ratio of diesel is defined as the ratio of a concentration of diesel in the overhead froth to that in the feed solution. The higher the enrichment ratio, the better the separation efficiency is. From the results of the batch froth flotation experiment, the optimum concentrations of $C_{14-15}(PO)_4SO_4$ and NaCl to achieve the maximum separation were found at 0.3 and 3 wt%, respectively (16). However, as mentioned before, under these conditions, the continuous froth flotation unit used in this study was not able to produce stable foam to reach the outlet at the top of the column since the single surfactant system with $C_{14-15}(PO)_5SO_4$ possessed very poor foam stability. To overcome this problem, SDS was added as a foam booster to the feed solution to obtain stable froth. In order to optimize the froth flotation operation, froth flotation experiments were carried out by varying all process parameters, surfactant concentration, salinity, oil to water ratio, air flux, foam height and hydraulic retention time (HRT).

Effect of adding SDS

Figure 9 shows the effect of adding SDS on the process performance of continuous froth flotation. At a fixed $C_{14-15}(PO)_5SO_4$ concentration of 0.1 wt%, the maximum diesel removal was achieved at 0.5 wt% of SDS. However, unlike the effect of surfactant concentration in the batch study (16), the trend of diesel removal as a function of SDS concentration is the same as that of the foamability. The diesel removal increases with increasing IFT and the maximum diesel removal does not correspond to the minimum IFT. This result also confirms that the foam characteristics are an important factor affecting the removal efficiency which is in good agreement with our previous work (16).

As described before, the enrichment ratio of diesel is another crucial parameter to indicate the froth flotation efficiency. As the SDS concentration increased from 0.1 wt% to 0.5 wt%, the enrichment ratio of diesel slightly decreased. This is because that SDS can enhance both foamability and foam stability. Consequently, the foam becomes more stability as well as holds a more water content. At 0.5 wt% of SDS, the system had the lowest enrichment ratio of diesel. When the SDS concentration further increased to 0.7 wt% and 1 wt%, the diesel enrichment ratio slightly increased. The result can be explained that at very high surfactant concentrations, increasing surfactant concentration leads to increasing both foamability and foam stability as well as increasing hydrophobic region, so the amount of oil content in the foam increases. The combined effect of both increasing amounts of diesel and water in the foam lamellae leads to the insignificant change in the enrichment ratio of diesel with respect to the SDS concentration. Conclusively, the enrichment ratio of diesel tends to increase slightly with increasing concentration of SDS in the studied range. This result is similar to the ethylbenzene results from our previous work (13). The enrichment ratio of surfactants decreased slightly with increasing SDS concentration. Interestingly, the surfactant enrichment ratio was found to be slightly higher than unity for the studied concentration range of SDS, confirming that the surfactants adsorb preferentially at the air/water interface.

Effect of NaCl concentration

It has been known that salinity is one of operational parameters, affecting froth flotation operation. Figure 10 shows the effect of NaCl concentration on the process parameters of continuous froth flotation operated at 0.1 wt% of $C_{14-15}(PO)_5SO_4$ and 0.5 wt% of SDS. The removal of diesel increased with increasing NaCl concentration in the studied range but the system IFT decreased. Both foamability and foam stability firstly increased with increasing NaCl from 2 to 3 wt%. After that, they decreased with increasing NaCl concentration, indicating that increasing NaCl results in more diesel attaching to the foam. This is because increasing NaCl directly decreases the repulsive force between the negative charged heads of the surfactants, leading to more surfactants adsorbing on the foam lamellae. As a result, both foamability and foam stability increase, which, in turn, the diesel removal increases. Moreover, the increasing surfactant adsorption at the lamellae simply increases the hydrophobic region, which, in turn, can adsorb more diesel. The maximum diesel removal was found at 4 wt% NaCl. Beyond the NaCl concentration of 4 %, the system could not produce stable froth to reach the outlet at the top of the column since the system has poor foamability and foam stability. The effect of adding NaCl on foamability and foam stability has already explained in the section of foam characteristics. An increase in the NaCl concentration from 2 to 4 wt% increased the enrichment ratio of diesel. Similar to the diesel removal, the diesel enrichment ratio was the highest at 4 wt% NaCl. This is again because NaCl reduces the repulsive force between the anionic head groups of the surfactants, so more diesel can attach to the foam. The present results of the continuous froth flotation system are in good agreement with our previous work in the batch mode (16).

Both the removal and the enrichment ratio of surfactants increased slightly with increasing NaCl concentration from 2 to 3 wt%. With increasing NaCl concentration beyond 3 wt%, the removal and the enrichment ratio of surfactants decreased which correspond to the foamability and foam stability results.

Effect of oil to water ratio

Most available work on froth flotation (13, 15, 16) involved 1:1 oil to water ratio but in real applications, a volume ratio of emulsified oil-to-waste water is much lower than 1:1. Consequently, in this work, the effect of oil loading on the performance of froth flotation was investigated by varying the oil-to-water ratio, 1:199, 1:99, 1:19, and 1:9 at 0.1 wt% $C_{14-15}(PO)_5SO_4$, 0.5 wt% SDS, and 4 wt% NaCl. Figure 11 shows the diesel removal efficiency as a function of oil-to-water ratio. Similar to our previous works of the batch froth flotation (13, 16), the efficiency of the oil removal of the continuous froth flotation was not affected significantly by changing the oil-to-water ratio in feed. However, the trend of oil removal was found to correspond to the foam production rate as well as the foamability and the foam stability. Interestingly, the highest enrichment ratio of diesel was found at 1:19 oil-to-water ratio. This is because at the oil-to-water ratio of 1:19, the system had the lowest foam production rate as well as the lowest foamability and foam stability, leading to the highest amount of water to be entrained back to the solution. However, the changing of oil-to-water ratio does not affect significantly both removal and enrichment ratio of surfactants in the studied conditions. The trends of both removal and enrichment ratio of surfactants were found to correspond to the foamability, foam stability and foam production rate of the system. A lower foam production rate indicates more foam collapsed, resulting in a higher amount of surfactants to be entrained back into the solution. As a result, the removal and enrichment ratio of surfactants decrease.

Effect of air flux

Figure 12 depicts the effect of air flux on the process performance of the continuous froth flotation system. The diesel removal was not affected significantly by increasing the air flux in the range of 7.64 to 10.18 cm/min while the foamability and the foam production rate of the system increased almost linearly. However, at an air flux higher than 12.73 cm/min, the diesel removal decreased remarkably with increasing air flux. Interestingly, the trend of the diesel removal was similar to that of the foam stability. The result indicates that the diesel removal is mainly governed by the foams stability of the system which is different from the batch result which the diesel removal was found to correspond to the foamability (16). The difference of the results can be explained that, for the batch system, all parameters especially diesel and surfactant concentrations vary during the operation while they are invariant in the continuous system. The higher the air flux, the lower enrichment ratio of diesel was obtained. This can be explained that a higher air flux simply produces more bubbles passing through the solution, resulting in both higher foamability and foam production rate, and a shorter time for water drainage. Hence, a larger amount of water can be carried with the foam produced to the top of the column, resulting in decreasing the enrichment ratio of diesel. Unlike the batch forth flotation operation in our previous work (16), the diesel enrichment ratio was not significantly affected by the air flux. For an air flux in the range of 7.64 to 12.73 cm/min, the surfactant removal was almost constant but at an air flux greater than 12.73 cm/min, the surfactant removal decreased with increasing air flux. It is interesting to point out that there is the similar trend of the removals of diesel and surfactants was observed. The same explanation can be used to describe the surfactant removal results. The enrichment ratio of surfactants decreased slightly as the air flux increased. The higher the air flux, the higher foam production rate and foamability were observed, leading to a high amount of water to be carried over into the collapsed froth. As a result, the enrichment ratio of surfactants decreases with increasing air flux.

Effect of foam height

Foam height is also a crucial parameter, affecting the performance of continuous froth flotation operation. Figure 13 illustrates the effect of foam height on all process parameters. The diesel removal decreased slightly when the foam height increased. It can be explained that the foam production rate decreased with increasing foam height. The lower the quantity of foam produced, the lower amount of diesel is removed. In contrast, the enrichment ratio of diesel increased as the foam height increased because the foam produced has a longer holding time to allow more water drainage from the foam. Hence, the foam produced contains a lower amount of water or a higher enrichment ratio of diesel. The surfactant removal decreased but the enrichment ratio of surfactants slightly increased as the foam height increased. This is because a high foam height leads to a low foam production rate. The same explanation for the removal and the enrichment ratio of diesel can be used to descript for the case of the surfactants. A foam height of 26 cm was selected for further studies because the system has the highest diesel and surfactant removals.

Effect of HRT

Hydraulic retention time (HRT) is an important parameter for a design of continuous froth flotation columns. The term of HRT is expressed as the holding liquid volume in the froth flotation column divided by a feed flow rate. Figure 14 shows the effect of HRT on all process parameters of the continuous froth flotation unit operated under the optimum conditions. The diesel removal increased slightly when the HRT increased. This is because a higher HRT represents a longer residence time of diesel in the flotation column to be adsorbed and coalesced themselves with the rising air bubbles. As a result, a higher amount of diesel can be carried by the foam produced to the top of the column and a higher diesel removal is obtained. In this study, the highest diesel removal (96 %) is achieved at 60 min HRT as compared to 98 % for the batch system of our previous study. The enrichment ratio of diesel increased slightly with increasing HRT. When considering the foam production rate result, it decreased as the HRT increased. It can be explained that the total amount of surfactant entering the flotation column increased with decreasing HRT. The surfactant removal increased with the increasing of HRT from 22 to 40 min but the surfactant removal reached the plateau region when the HRT was greater than 40 min. The similar trend of the enrichment ratio of surfactants was found in the studied range of HRT. The same explanation for the enrichment ratio of diesel can be used to describe for the case of surfactants.

CONCLUSIONS

From this work, quantitative removal of diesel oil can be achieved by the continuous froth flotation. The foamability and foam stability were found to be more important than the system IFT to achieve a high oil removal in both the batch and continuous modes of froth flotation operation. Both foamability and foam stability were found to be reduced by premixing. To succeed the separation of continuous froth flotation, an addition of SDS was added to enhance the foam stability of the pure $C_{14\text{-}15}(PO)_5SO_4$ system. Both enrichment ratio and removal of diesel increased with increasing NaCl concentration in the studied range since the system IFT decreases. The performance of the continuous froth flotation unit was not affected significantly by changing the oil to water ratio in feed. An increase in foam height resulted in increasing the enrichment ratio of diesel but the oil removal was almost invariant. An increase in air flux decreased significantly the enrichment ratio of diesel but had a little effect on the oil removal efficiency. Similar to our previous batch studies (15, 16), the air flux has to be optimized to get a maximum diesel removal efficiency. Increasing HRT increased the oil removal and reached the maximum at a very high HRT. Under the optimum conditions, 0.1 wt% $C_{14\text{-}15}(PO)_5SO_4$, 0.5 wt% SDS, 4 wt% NaCl, an oil to water ratio of 1:19, a foam height of 26 cm, an air flux of 12.73 cm/min, and a HRT of 60 min, the maximum oil removal of 95.72 % was achieved.

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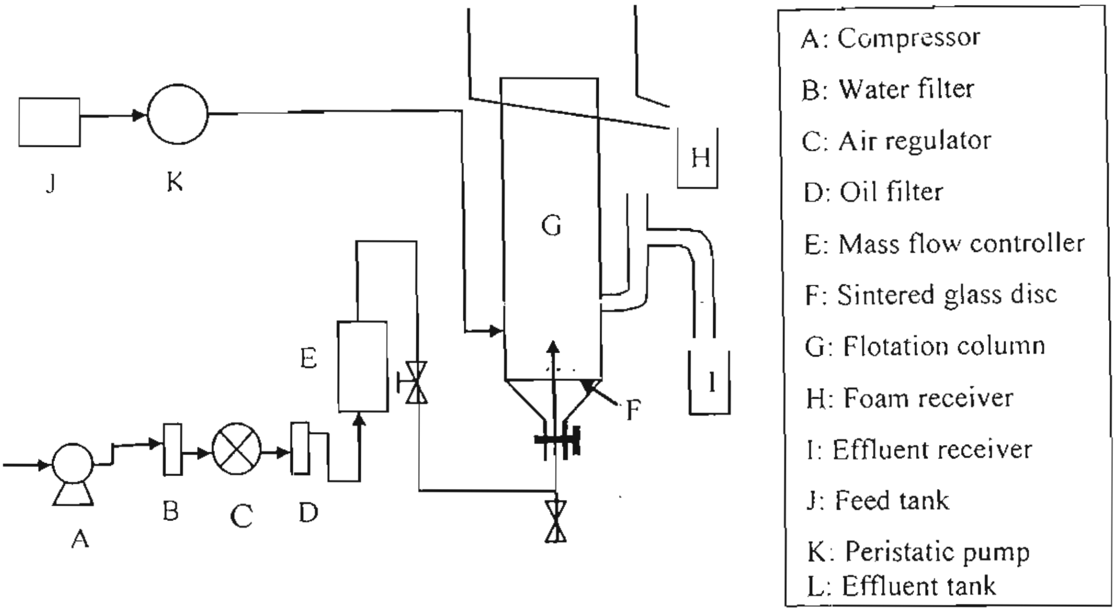

Figure 1. Schematic diagram of the froth flotation apparatus with a continuous mode of operation

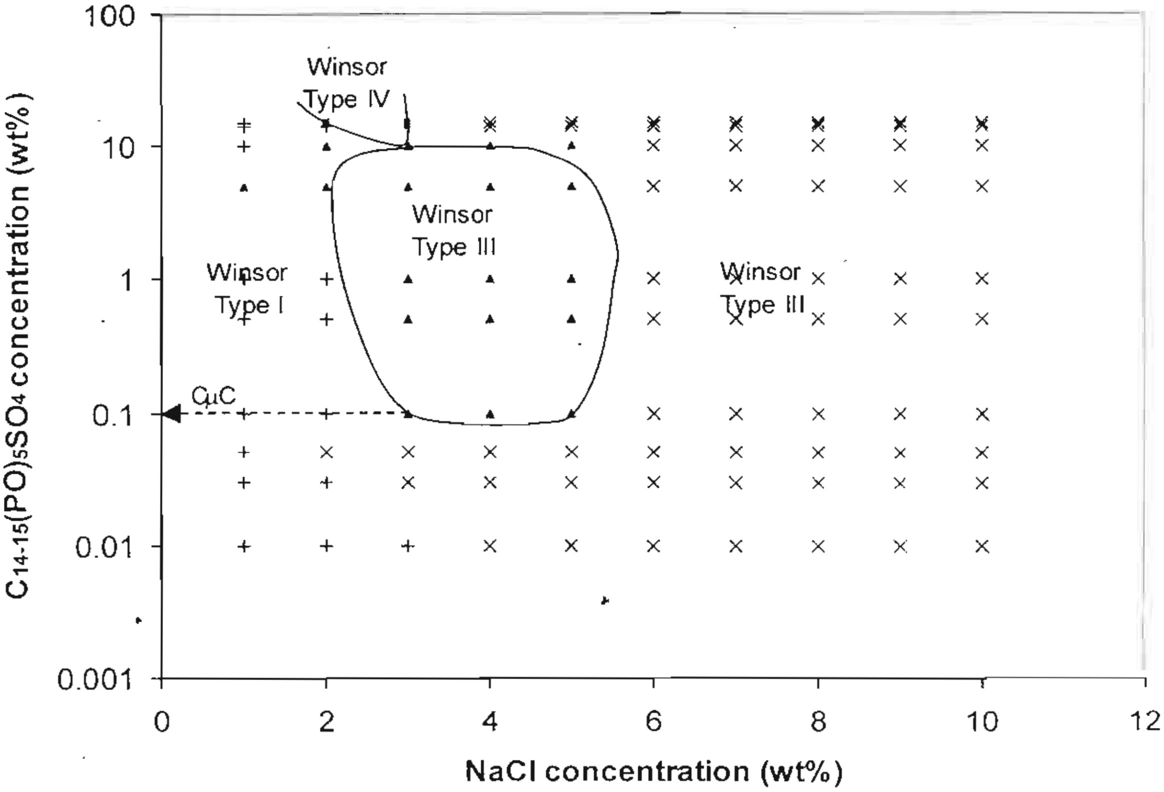

Figure 2. Fish diagram of single surfactant system ($C_{14-15}(PO)_5SO_4$) at an oil to water ratio of 1:1 (+ Type I, x Type II, and ▲Type III)

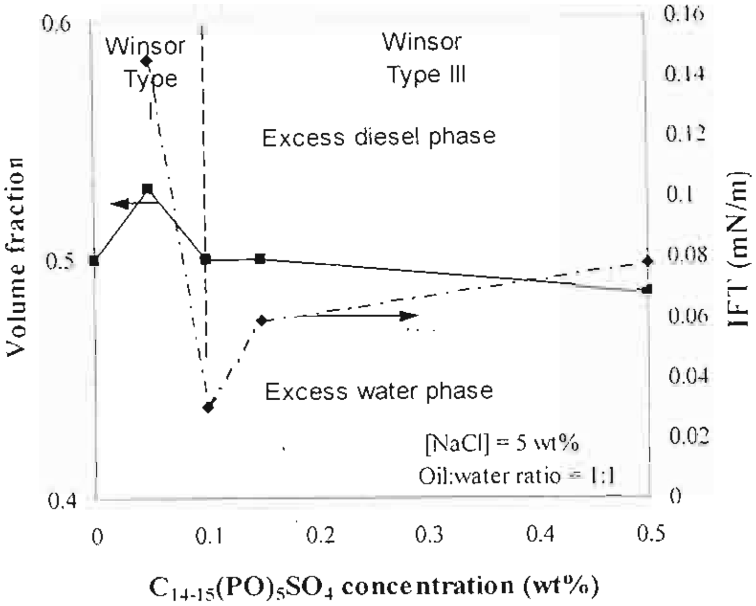

Figure 3. Phase diagram and IFT as a function of $C_{14-15}(PO)_5SO_4$ concentration for diesel system

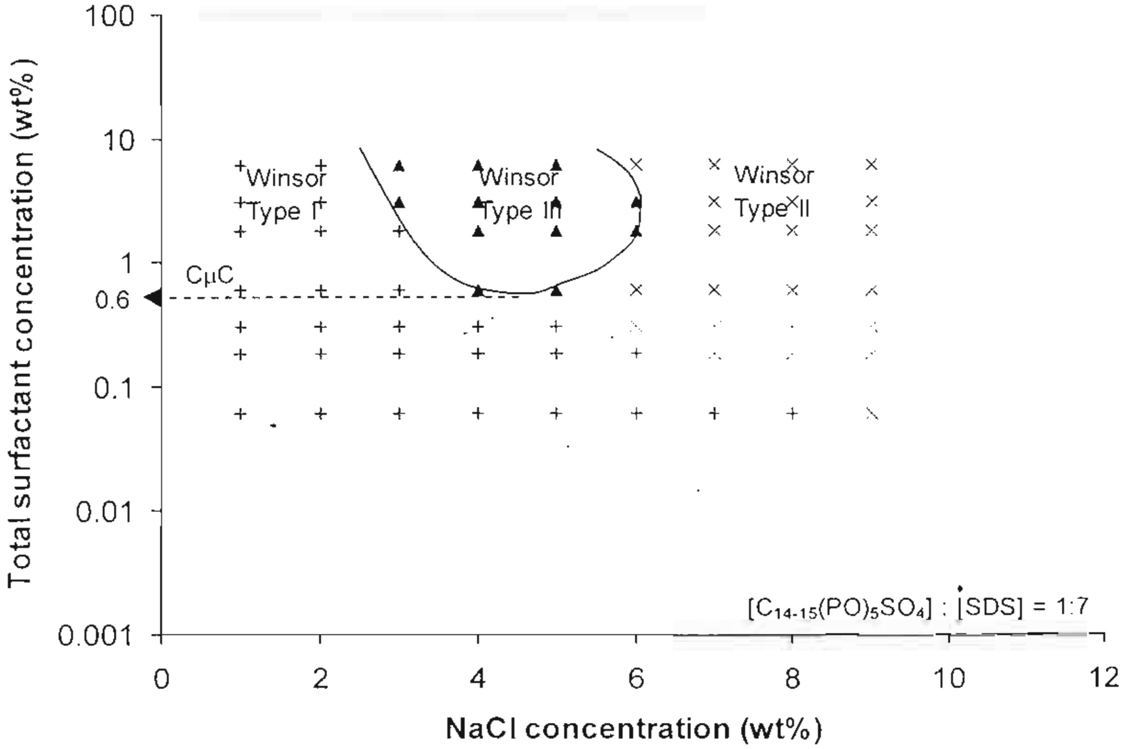

Figure 4. Fish diagram of mixed surfactant system between $C_{14-15}(PO)_5SO_4$ and SDS at an oil to water ratio of 1:1 (+ Type I, × Type II, and ▲ Type III)

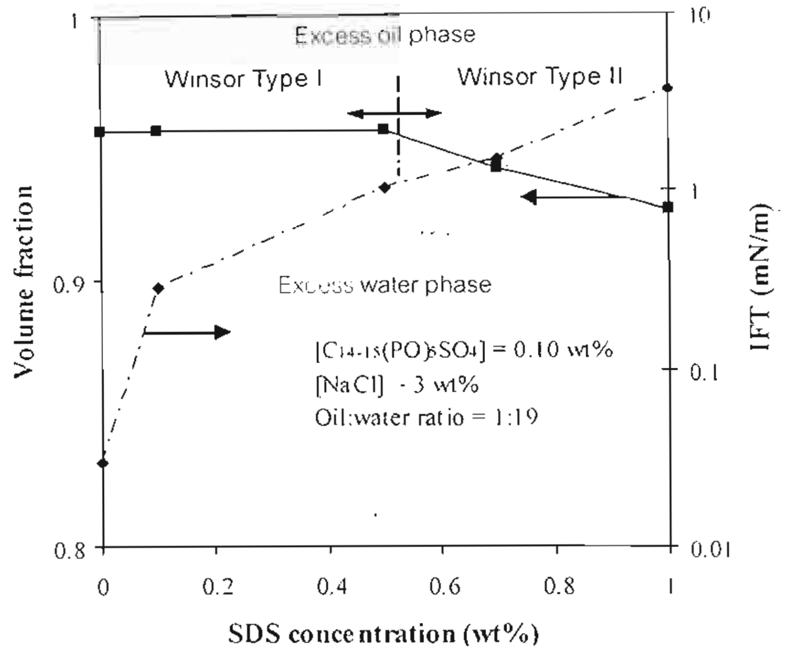

Figure 5. Phase diagram and IFT of the mixed surfactant system as a function of SDS

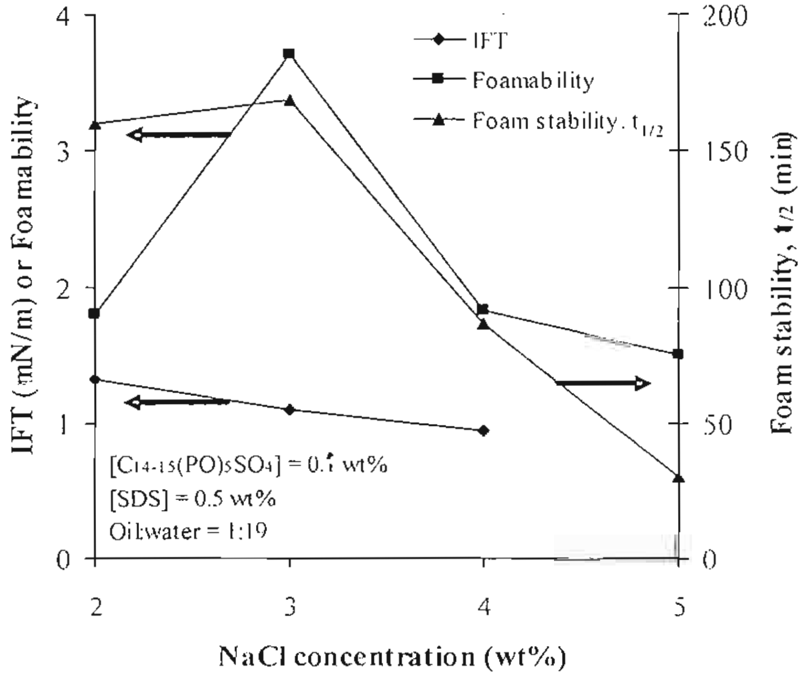

Figure 6. IFT, foamability and foam stability of the mixed surfactant system as a function of salinity

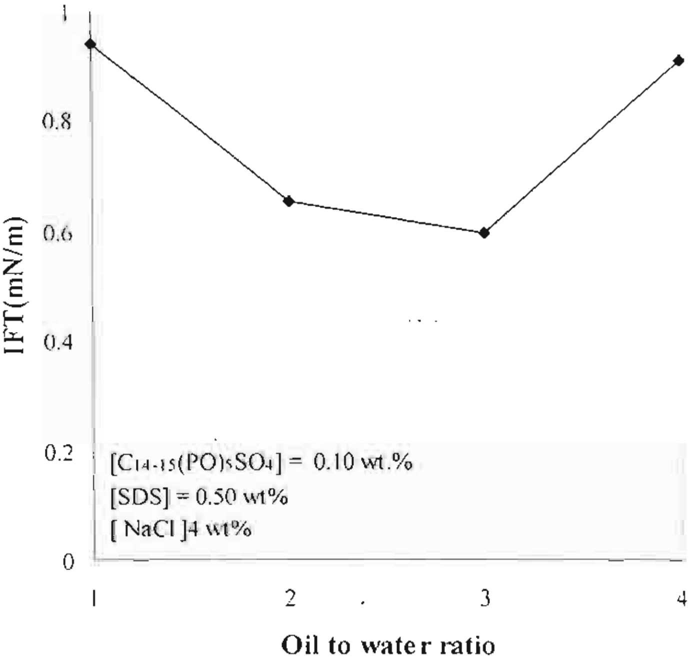

Figure 7. IFT of the mixed surfactant system as a function of oil to water ratio

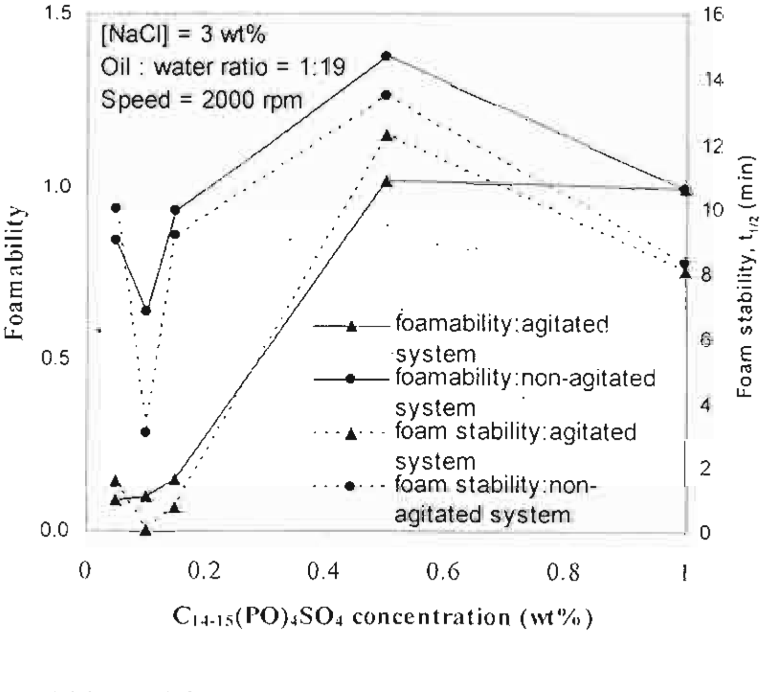

Figure 8. Foamability and foam stability (without added SDS) at different $C_{14-15}(PO)_5$ SO_4 concentrations with and without premixings

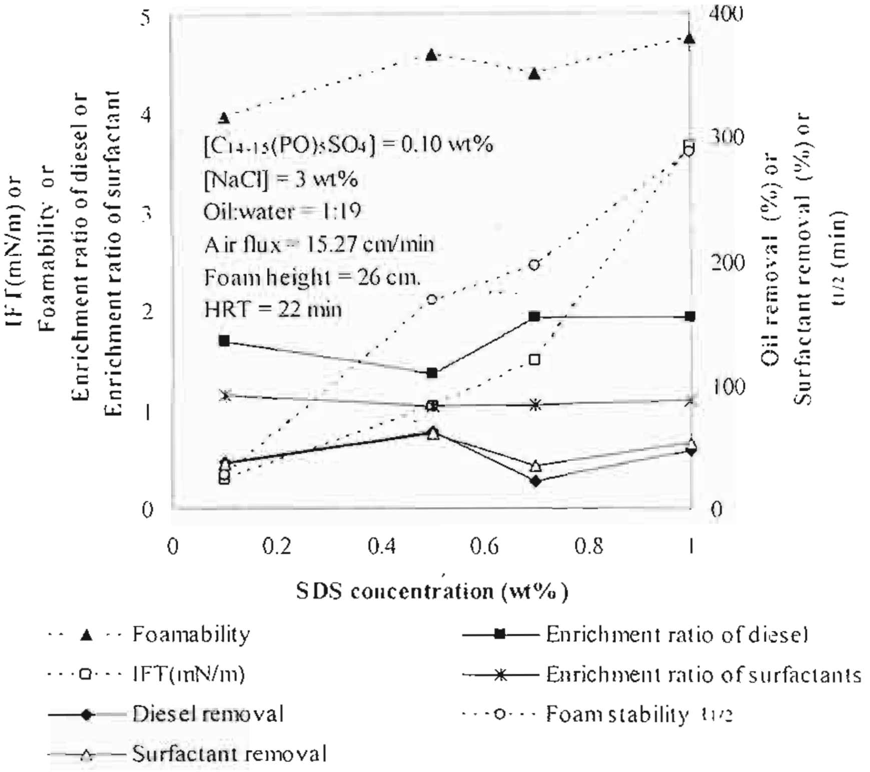

Figure 9. Effect of adding SDS on process parameters of continuous froth flotation

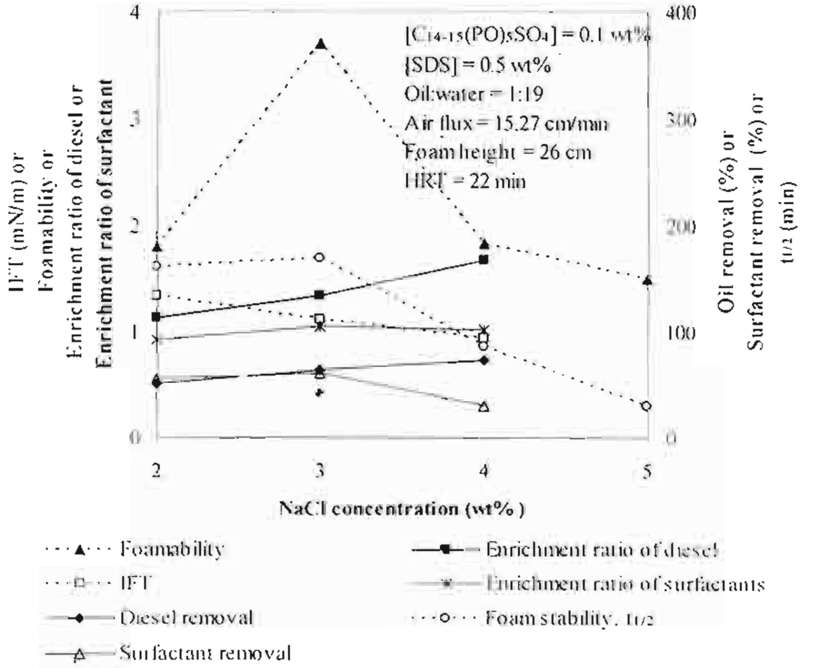

Figure 10. Effect of NaCl concentration on process parameters of continuous froth flotation

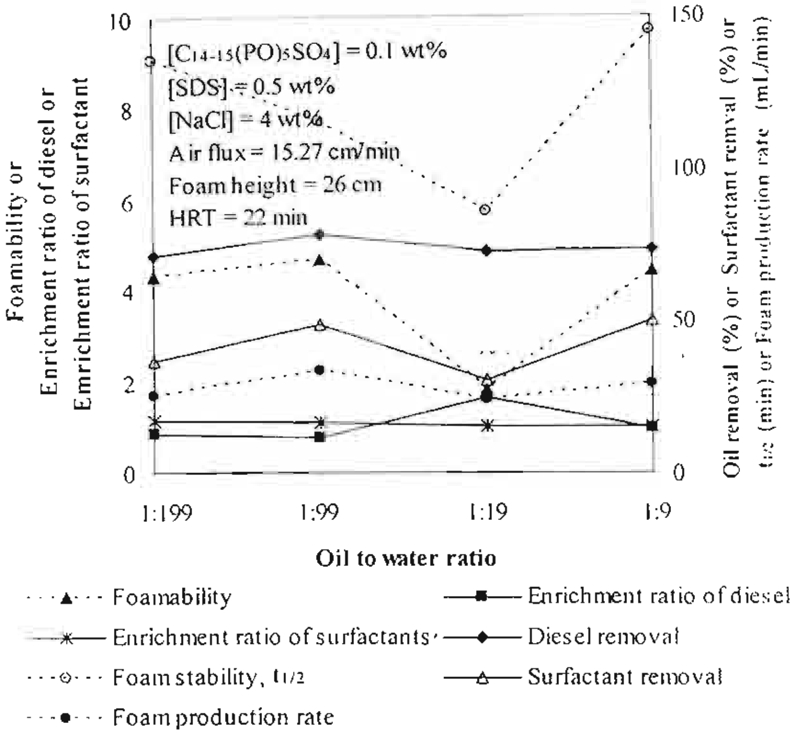

Figure 11. Effect of oil to water ratio on process parameters of continuous froth flotation

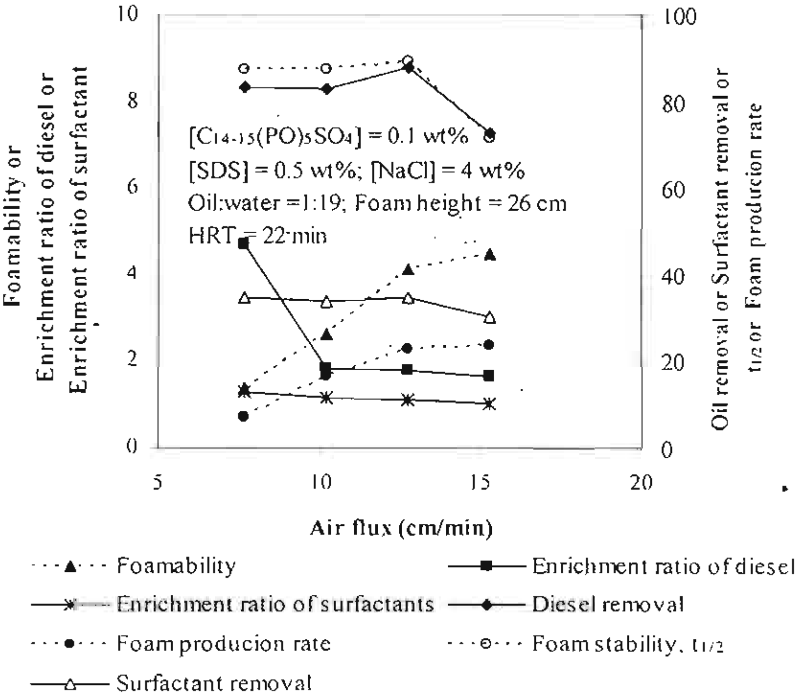

Figure 12. Effect of air flux on process parameters of continuous froth flotation

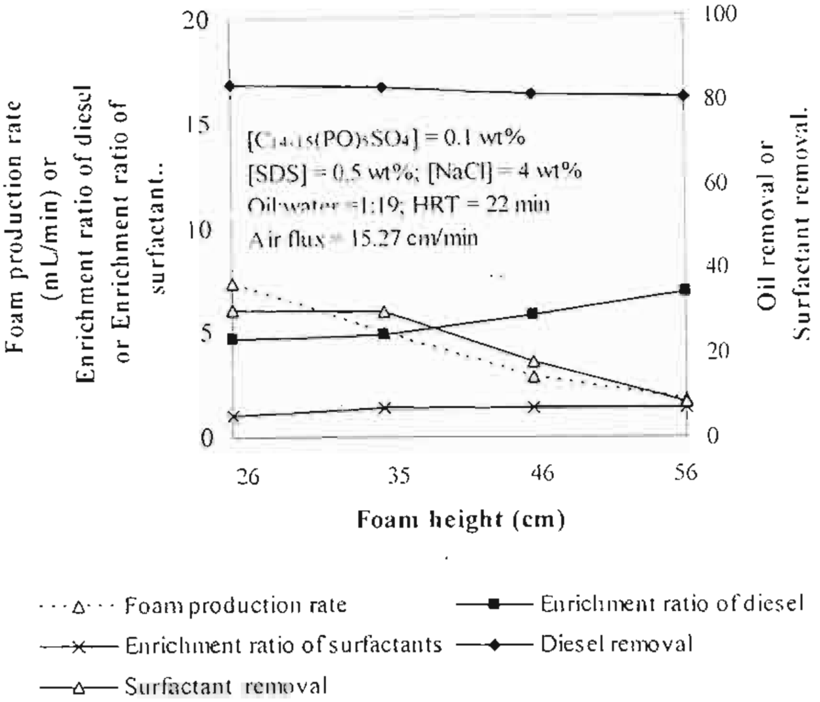

Figure 13. Effect of foam height on process parameters of continuous froth flotation

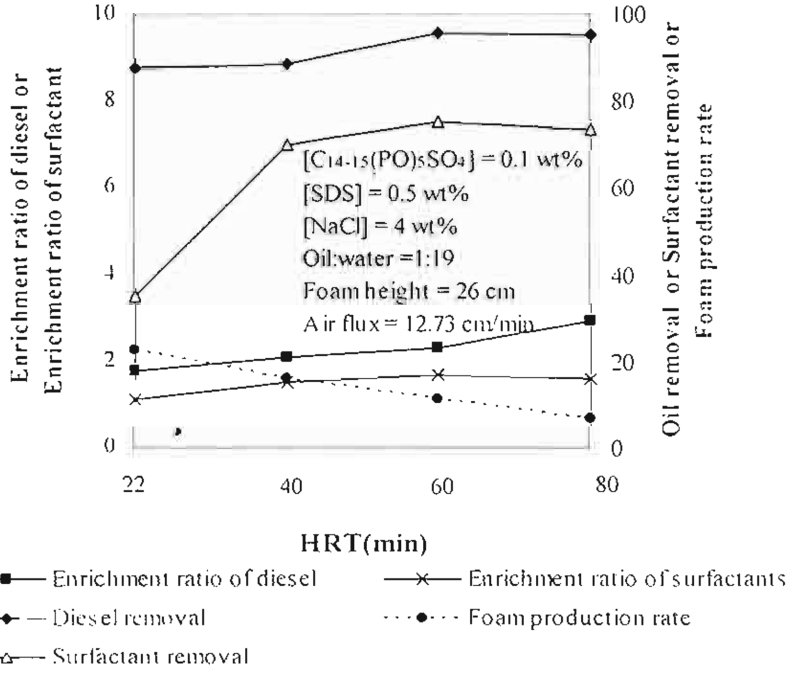

Figure 14. Effect of HRT on process parameters of continuous froth flotation

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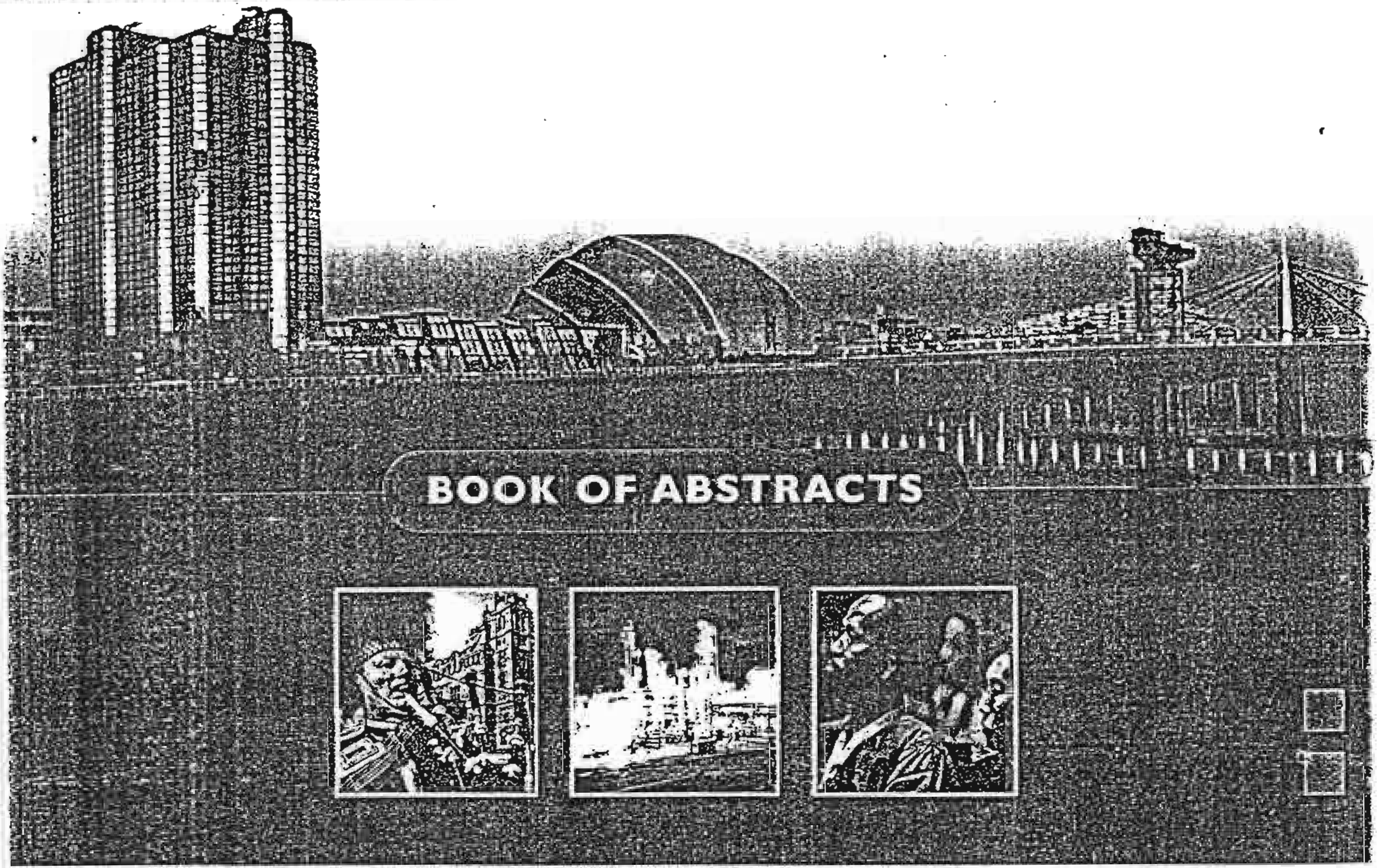

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Removal of Diesel in Froth Flotation Operation: Comparison between Batch and Continuous Modes of Operation

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ABSTRACT

Froth flotation is one of the surfactant based separation processes. Nowadays, it is widely applied to wastewater treatment because it has several advantages such as low cost. To achieve higher performance for froth flotation operation, the combination of ultra-low interfacial tensions between oil and water and stable foam production must be achieved. In this study, branched alcohol propoxylate sulfate sodium salt with 14 – 15 carbon and 4 PO groups (Alfoterra 145 – 4PO) was used to form microemulsions with diesel. The effects of surfactant concentration, salinity, and oil to water ratio on performance of the froth flotation in both batch and continuous modes of operations were studied. The maximum diesel removal (around 98%) in batch mode was achieved at 0.3 wt% Alfoterra, 3 wt% NaCl, and an oil to water ratio of 1:4. However, in the continuous mode of operation, only Alfoterra present in the solution yielded very poor foam characteristics because solution was continuously agitated during the operation. Then, an addition of sodium dodecyl sulfate (SDS) as a frother was employed to improve the foam stability in order to produce stable froth for the success of froth flotation operation. The system with 0.1 wt% Alfoterra, 0.5 wt% SDS, 4 wt% NaCl, and 1:19 of oil:water ratio yielded the maximum diesel removal of 90.37% corresponding to 49 minutes of residence time.

Keywords: Froth Flotation, ultra-low interfacial tensions, Foam characteristics, Diesel

INTRODUCTION

Diesel is one of the most important transportation fuels because diesel engines posses more thermally-efficient than gasoline engines do. It is anticipated that diesel demand and utilization will still rise substantially in the next few decades (1). Besides its widespread usage in several industrial processes such as metal manufacture and machining as well as petroleum refinery plant, diesel is often found in several wastewaters (2). Hence, it is necessary to get rid of diesel from wastewaters before discharging into public waters.

In this work, froth flotation was focused to remove diesel from water. Firstly, froth flotation was first utilized to separate a desired ore from unwanted substrates in the mineral processing processes (3). Moreover, nowadays, froth flotation technique has been widely employed in wastewater treatment application (4 – 5), and also in paper deinking process (6 – 7). There are 2 main types of froth flotation which are dissolved and induced air flotation. The induced air flotation was focused in this work. In the latter type of froth flotation, filtered air is introduced into the solution through a sintered glass disk. Air bubbles generated in the solution are a key for successful separation. Droplets of emulsified oil which have hydrophobic surfaces can co-adsorb at the bubble surfaces, which are also hydrophobic, and then rise to the top of the column to form foam called froth. However, the stability of these bubble-droplet aggregates is generally low leading to lower separation efficiency. To achieve higher separation efficiency, a proper type of surfactant with an optimum concentration is added into the solution to stabilize foam (8). Cheng *et al.* (9) reported that the surfactant added should be adjusted at an appropriate concentration to maintain high foam stability.

To achieve high oil separation efficiency in froth flotation operation, a proper amount of surfactant added into the solution is a crucial issue. In our previous work (10), it has been found that the maximum oil removal corresponds to the formation of Winsor type III microemulsion. This seems to be a starting point of our group to further investigate the relationship between the froth flotation efficiency and a Winsor type III microemulsion. Later, Chavadej *et al.* (11) investigated what was the main source of oil removed from flotation column. They found that the most oil removed from the column during flotation operation came from the excess oil phase rather than the middle phase in the Winsor type III microemulsion system. After that, Yanatatsaneejit *et al.* (12) hypothesized that the maximum oil removal was achieved because of the ultra-low interfacial tension characteristic in a Winsor type III microemulsion. Interestingly, they found that ultra-low interfacial tension is not only a factor affecting the performance of froth flotation but also foam characteristics are also important on flotation efficiency. In this work, the performance of froth flotation to remove diesel from water was correlated with interfacial tension and foam characteristics in both batch and continuous flotation operation.

EXPERIMENTAL SECTION

Materials

A model oil used in this study is a commercial grade of diesel obtained from the Petroleum Authority of Thailand (PTT). A branched alcohol propoxylate sulfate sodium salt (Alfoterra 145 – 4PO), an anionic surfactant which is an experimental (not yet commercially available) surfactant specially synthesized by Sasol Company (formerly Condea Vista Company), Rosebank, South Africa and sodium dodecylsulfate (SDS), an anionic surfactant obtained from Carlo Erba Reagenti with purity in the range of 94 – 98% were used in this study. Analytical purity grade sodium salt (NaCl) from Aldrich Chemical Company Inc. was used as electrolyte in this work. All Chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

Methodology

This work can be divided into three parts. The first part was to study microemulsion phase behavior of aqueous solutions containing different surfactant concentrations with diesel. The second part was to investigate the foam characteristics which are foamability and foam stability. The last part was the investigation of the efficiency of froth flotation. In all experiments, the surfactant and electrolyte concentrations are expressed in weight percentage (wt%) per volume of the aqueous solution consisting of water, surfactant, and electrolyte.

To investigate the phase behavior of microemulsion, 5 mL of homogeneous aqueous solution, prepared at various surfactant and NaCl concentrations, was mixed with 5 mL of diesel in a vial sealed with a screw cap. These vials were shaken every day for 3 days, and then allowed to equilibrate at a constant temperature of 30°C in an incubator for 1 month, which was verified by the invariant height of each phase. The interfacial tensions between equilibrated excess oil and excess water phases were measured by a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg).

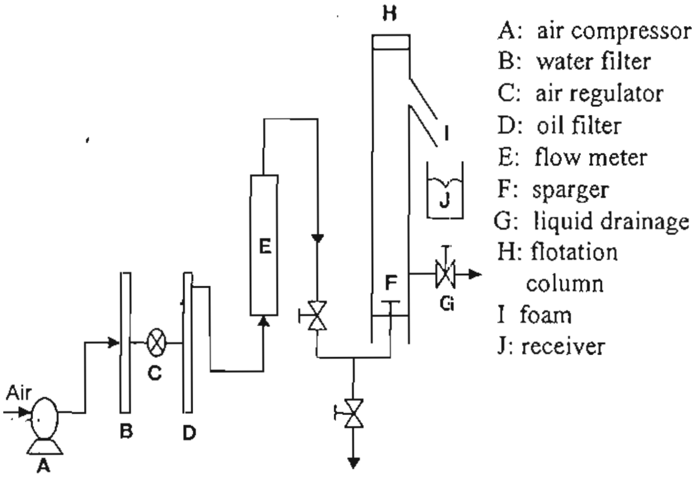

Figure1. Schematic diagram of the batch froth flotation apparatus

A schematic diagram of the froth flotation unit in batch and continuous mode of operation used in this work are shown in Figures 1 and 2, respectively. A glass cylindrical column with 5 cm internal diameter and 120 cm height was used as the froth flotation column. In batch mode of operation, a 750 mL sample with different initial oil:water ratios and various surfactant and NaCl concentrations which had been equilibrated at 30°C for 1 month in the incubator, was transferred to the flotation column. Filtered air at a flow rate of 300 mL/min was introduced at the bottom of the column through a sintered glass disk having pore size diameters about 16 – 40 μm. The foam collected in the receiver over a period of time was broken by freezing to analyze diesel concentration. Moreover, the solution in the column was sampled at the same time interval as the foam collected for analysis of untreated diesel and remained surfactant concentrations. For batch mode of operation, all experiments were stopped when no more foam came overhead from the column as a result of too low surfactant concentrations in the solution. In continuous mode of operation, a well mixed solution consisting of surfactant, water, and diesel under microemulsion condition was continuously transferred to the column via a peristatic pump (Masterflex, easy-load II). The level of solution in the column was adjusted by a three-way flexible tube. The generated air bubbles rose through the solution to the top of the column. The system was run to reach steady state before taking samples of froth produced and effluent for analysis of both surfactant and diesel concentrations. The steady state was justified by the invariant concentrations in froth and effluent.

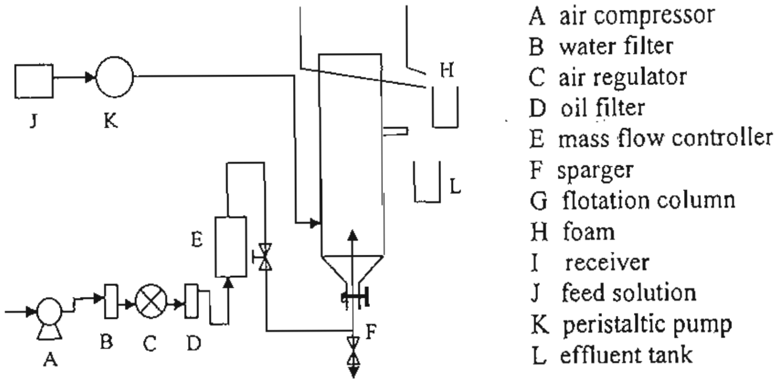

Figure 2. Schematic diagram of the continuous froth flotation apparatus

In order to obtain a better understanding about the phenomena in the froth flotation process, foamability and foam stability experiments were conducted in a glass column having 5 cm inside diameter and 120 cm height. A 250 mL sample containing a given surfactant and NaCl concentrations was transferred to the column. Filtered air was introduced at the bottom of the column through the solution at a constant flow rate of 100 mL/min until the maximum foam height in the column was achieved. The maximum foam height was then measured. After that the filtered air was stopped introducing to the column, and the time required for the foam volume to collapse to half of the maximum height was recorded to quantify foam stability. All experiments of froth flotation operation, foamability, and foam stability were conducted at room temperature of about 25 – 27°C. The ratio of maximum foam height to initial solution height is considered as foamability while foam stability ($t_{1/2}$) is defined as the time required for the foam to collapse to the half of the maximum foam height.

RESULTS AND DISCUSSION

Phase Behavior

Interfacial tension (IFT) is one of the major factors affecting the performance of froth flotation operation (12, 13). Figure 3 shows the effect of Alfoterra concentration on IFT value. At 3 wt% NaCl concentration, increasing Alfoterra 145 – 4PO concentration decreased the IFT between excess oil and excess water phases because a number of surfactant at the interface increases corresponding to the decrease of the IFT (14). However, Alfoterra 145 – 4PO concentration cannot be increased to more than 0.15 wt% because liquid crystal is formed. As a result, the optimum surfactant concentration was not achieved in this study. However from the previous work (11), it was found that most of oil removed from flotation column came from the excess oil phase instead of the middle phase. Therefore, in this study, an ultra-low interfacial tension (i.e. 10^{-2} mN/m) region was focused rather than the presence of the middle phase.

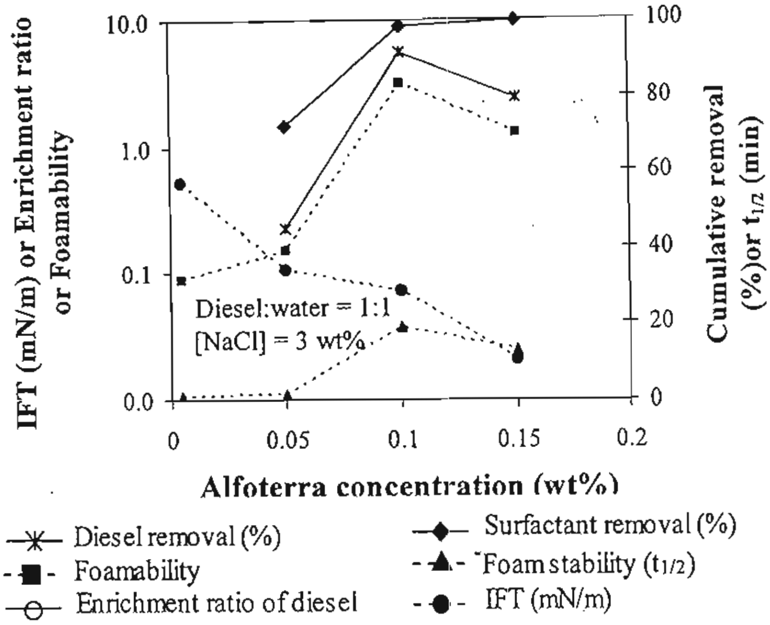

Figure 3. Effect of Alfoterra concentration on process parameters in batch operation

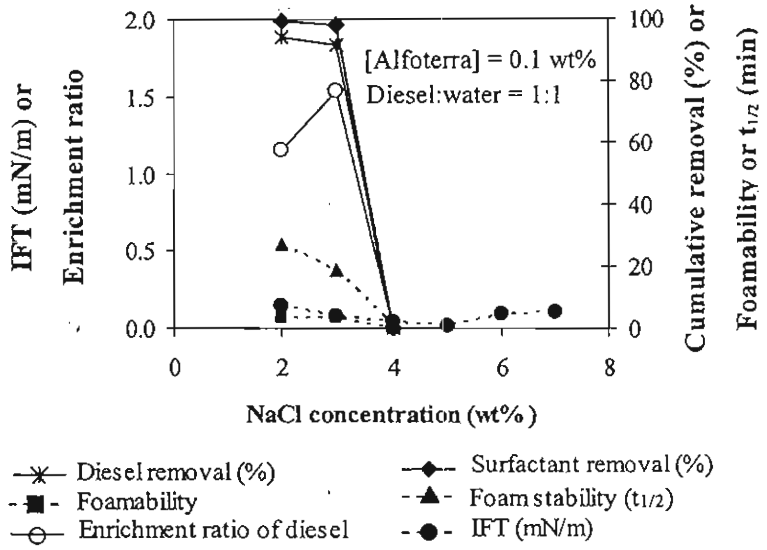

Figure 4. Effect of NaCl concentration on process parameters in batch operation

For the observation of the effect of NaCl concentration on IFT, at a fixed Alfoterra concentration of 0.10 wt%, the minimum IFT was found at 5 wt% NaCl (Figure 4). The explanation of the effect of NaCl concentration on IFT was already discussed in our previous work of ethylbenzene (12).

Foam Characteristics

As described in our previous works (12, 13), removal efficiency of oil in froth flotation operation is also influenced by foam characteristics (foamability and foam stability). The effects of Alfoterra 145 – 4PO concentration on both foamability and foam stability are illustrated in Figure 3. The foam stability tended to increase with increasing Alfoterra 145 – 4PO concentration because more surfactant molecules adsorb at the surface of air bubbles. Therefore, the repulsive force between surfactants increases with increasing surfactant concentration as a result that the foam stability increases. In addition, when the Alfoterra concentration increased from 0.005 to 0.10 wt%, the foamability increased. However, the foamability decreased when the surfactant concentration further increased to 0.15 wt%. At low surfactant concentrations, the foamability increases with increasing Alfoterra concentration because the foam stability increases. When the Alfoterra concentration further increases, however, the thicker foam lamellae causes more water content, resulting in a decline of foamability.

For the effect of NaCl concentration on foam characteristics, the descent of foam stability appears when NaCl concentration increases as shown in Figure 4. Perhaps because the negative charge of surfactant is bounded by the positive charge of Na^+, and so the repulsive force between the head groups of surfactant in the lamellae decreases. The thickness of the lamellae between two air bubbles becomes thinner until the critical thickness is reached resulting in coalescence of these bubbles. In case of foamability as a function of NaCl concentration, the foamability increased when the NaCl concentration increased from 2 to 3 wt%. However, further increasing NaCl concentration to 4 wt% substantially decreases the foamability as shown in Figure 4. Increasing NaCl concentration from 2 to 4 wt% causes lower interfacial tensions. Therefore, the system with 3 wt% NaCl needs a lower energy to form air bubbles within the liquid solution comparing to that with 2 wt% NaCl; so foams in 3 wt% NaCl system are easily formed. However, the foamability of 4 wt% NaCl system is lower than those of 2 and 3 wt% NaCl systems because the foam stability of 4 wt% NaCl is lower even though the IFT of 4 wt% NaCl is much lower than those of 2 and 3 wt% NaCl. Consequently, to achieve high foamability, both of the interfacial tensions and foam stability have to be optimized.

Froth Flotation Performance: Batch Operation

As described in the previous work (12), three parameters which are oil removal, surfactant removal, and enrichment ratio of oil are defined as the performance parameters of froth flotation operation. In this work, enrichment ratio of diesel is defined as the diesel concentration in the collapsed froth to the diesel concentration in the initial feed. Therefore, to achieve the separation, the enrichment ratio of diesel has to be higher than unity.

Figure 3 shows the effect of Alfoterra concentration on IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability, foam stability, and enrichment ratio of diesel. Similar to ethylbenzene system (12), the total cumulative diesel removal was found to be the highest at the Alfoterra concentration corresponding to the maximum foamability and the maximum foam stability but not the minimum IFT. This result implies that IFT is not the sole factor affecting the performance of froth flotation. Basically, IFT should be reduced to a critical value to enhance the amount of oil attached with foam. However, for system having IFT lower than the critical value, the effect of foam characteristics on the performance of froth flotation becomes dominant. For the observation of the diesel enrichment ratio, it is not significantly affected by Alfoterra concentration. Actually, increasing surfactant concentration should decrease the enrichment ratio of oil because of several aspects such as thicker foam lamellae causing higher water content in foam lamellae, and higher viscosity of solution leading to lower drainage rate of water from foam lamellae. However, the amount of oil content in the froth increases with increasing surfactant concentration due to the more hydrophobic region in the froth. Thus, the effect of Alfoterra concentration on the diesel enrichment ratio is not explicit.

IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability, foam stability, and enrichment ratio of diesel as a function of NaCl concentration are depicted in Figure 4. The maximum diesel and Alfoterra removal corresponds to the highest foam stability. Similar to the effect of Alfoterra concentration, the lowest IFT does not yield the maximum removal of both diesel and Alfoterra. From Figure 4, the removal of diesel or Alfoterra is not significantly affected by NaCl concentration in the range of 2 to 3 wt% due to the trade-off between foamability and foam stability. However, at a NaCl concentration above 3 wt%, the NaCl concentration substantially affected the removal efficiency since both foamability and foam stability are extremely low. Enrichment ratio of diesel increased when NaCl concentration increased from 2 to 3 wt%. This is because the repulsive force between the head groups of anionic surfactant at the opposite site of the foam lamellae decreases, resulting in a thinner foam lamellae. Therefore, at 3 wt% NaCl, a lower amount of water can be carried over with foam to the top of the column, leading to a higher enrichment ratio of diesel.

Froth Flotation Performance: Continuous Operation

From batch mode of operation, the optimum concentrations of Alfoterra and NaCl to achieve the maximum separation efficiency were found at 0.1 and 3 wt%, respectively. However, in the continuous system, foam characteristics of solution having only Alfoterra surfactant were found experimentally to be extremely low, leading to no separation. To overcome this problem, SDS was added to the solution to promote foam characteristics as a frother.

Figure 5 shows the effect of SDS concentration on IFT, diesel removal, surfactant removal, foamability, foam stability, and enrichment ratio of diesel. At a fixed Alfoterra concentration of 0.1 wt%, the maximum diesel and surfactant removals were achieved at 0.5 wt% SDS. Unlike the effect of surfactant concentration in batch mode of operation, the trend of diesel and surfactant removals as a function of SDS concentration is the same as that of foamability even though the lowest IFT was not achieved at this condition. This result also confirms that the foam characteristics are a crucial parameter affecting the removal efficiency. The enrichment ratio of diesel tended to increase with increasing concentration of SDS in the studied range. This result is similar to the result from our previous work (12).

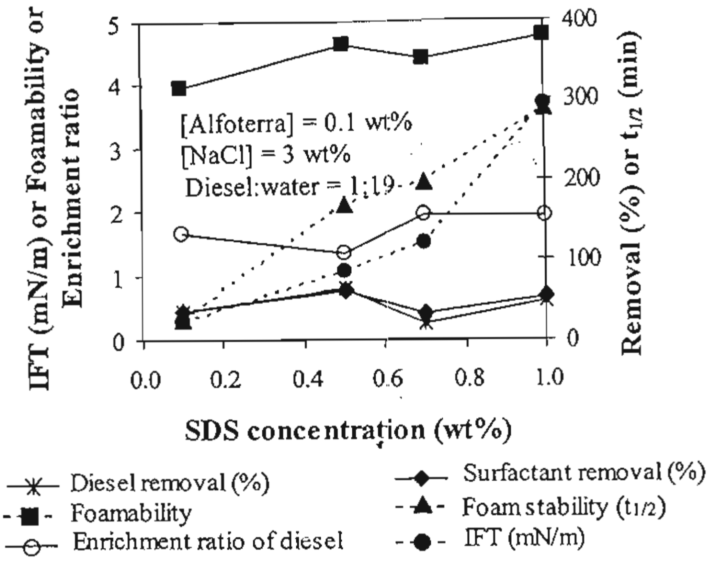

Figure 5. Effect of SDS concentration on process parameters in continuous operation

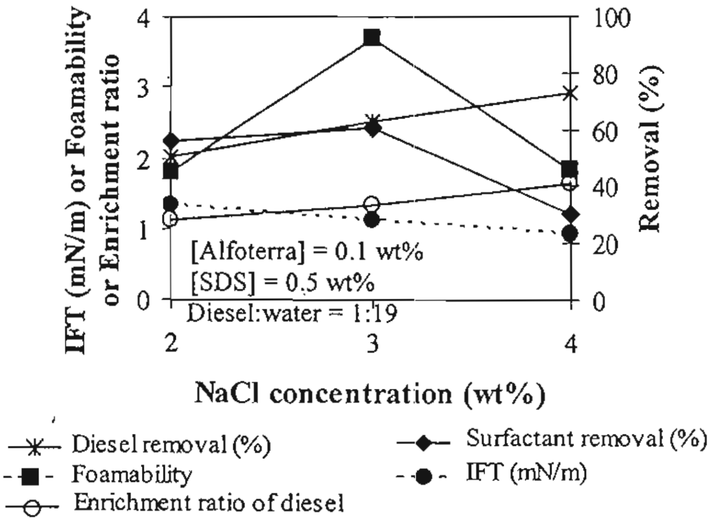

Figure 6. Effect of NaCl concentration on process parameters in continuous operation

The effects of NaCl concentration on IFT, diesel removal, surfactant removal, foamability, foam stability, and enrichment ratio of diesel are illustrated in Figure 6. The maximum diesel removal was achieved at NaCl concentration corresponding to the minimum IFT but not the maximum foamability. However, for the observation of surfactant concentration as a function of salinity, the maximum surfactant removal corresponds to the maximum foamability of the system as expected. Similar to the diesel removal, the diesel enrichment ratio was the highest at 4 wt% NaCl. Therefore, it can be concluded that both IFT and foamability of system influence the performance of froth flotation in both batch and continuous mode of operation.

CONCLUSIONS

In this study, the process performance of froth flotation in both batch and continuous mode of operation was correlated with IFT and foam characteristics. From the results in this work, the foam characteristics have profound effect on oil removal apart from the system IFT. In addition, foam characteristics can be suppressed by agiating solution for a long time in continuous mode of operation. Therefore, some frother can be added to the solution to enhance foam stability of the system. In batch mode of operation, the optimum condition to achieve the maximum removal efficiency is 0.3 wt% Alfoterra, 3 wt% NaCl, and 1:4 oil:water ratio. In continuous mode of operation, SDS was added to the solution to improve foam stability. The maximum diesel removal was achieved at 0.1 wt% Alfoterra, 0.5 wt% SDS, 4 wt% NaCl, and 1:19 oil:water ratio.

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PROGRAM & ABSTRACTS

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Diesel Removal by Continuous Froth Flotation : Effects of Ultralow Interfacial Tension and Foam Characteristics

On-line Number 589

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ABSTRACT

Froth flotation is one of the surfactant-based separation processes which is suitable for treating dilute oily wastewaters. The objective of this study was to investigate the relationship between ultralow interfacial tension (IFT) and the efficiency of diesel removal from wastewater by continuous froth flotation technique. Branched alcohol propoxylate sulfate, sodium salt (Alfoterra 145-5PO) and sodium dodecyl sulfate (SDS) were used for both microemulsion formation and froth flotation studies. Surfactant concentration, salinity, and oil to water ratio were varied in the microemulsion formation experiment in order to determine the compositions required to obtain ultralow IFT. The effects of surfactant concentration, salinity, and HRT on the oil removal were investigated. From the results, the oil removal efficiency of the froth flotation process did not correspond to the minimum IFT of the system indicating that the ultralow IFT alone cannot be used as a sole criterion for froth flotation operation. Foam stability was revealed to be another crucial factor in the froth flotation operation. The system with 0.1 wt% Alfoterra, 0.5 wt% SDS, 4 wt% NaCl, an oil:water ratio of 1:19, an air flow rate of 0.15 L/min, a foam height of 26 cm, and a HRT of 49 min gave the maximum oil removal (90.37 %).

KEYWORDS

Froth flotation, Diesel removal, Microemulsion, Ultralow IFT

INTRODUCTION

Diesel is one of the most important transportation fuels because diesel engines possess more thermally-efficient than gasoline engines. It is anticipated that diesel demand and utilization will still rise substantially in the next few decades (Song *et al.*, 2000). Besides its widespread usage in several industrial processes such as metal manufacture and machining as well as petroleum refinery plant, diesel is often found in several wastewaters (Patterson, 1975). Hence, it is necessary to get rid of diesel from wastewaters before discharging into public water.

Froth flotation is one of surfactant-based separation processes (Scamehorn and Harwell, 2000). It has been widely used in ore processing, but now being pointed out to be a promising technique to solve oily wastewater problems. Froth flotation process is suitable for dilute wastewater treatment because it has several advantages including rapid operation, low space requirement for equipment set-up, high efficiency of removal, flexibility of application to various pollutants at various scales, and low cost (Choi *et al.*, 1996).

In froth flotation operation, a surfactant is first added into an oily wastewater, and gas is introduced into the system in order to generate fine bubbles. At the air/water interface, the surfactant tends to adsorb with the hydrophillic or head groups in the water and the hydrophobic or tail groups in the air. The oil tends to attach at the air bubbles while they ascend through solution and are concentrated as foam or froth at the top of the flotation cell which is generally skimmed off. As a result, the formation of stable bubble particle aggregates is required in the froth flotation operation to enhance separation efficiency (Freund and Dobius, 1995).

A mixture of diesel, water and surfactants in the form of microemulsion was prepared as studied wastewater since a microemulsion has superior characteristics such as ultralow IFT, relatively large interfacial area and large solubilization capacity (Bourrel and Schechter, 1988). It has been known that the lower the interfacial tension of Winsor Type III microemulsion, the higher the efficiency of removal which is related to froth flotation efficiency (Pondsatabodee *et al.*, 1998). These properties render microemulsion intriguing from a fundamental point of view and versatile for industrial applications. Thus, microemulsion was applied in the froth flotation technique in this work. The formation of microemulsion with diesel oil was investigated in order to find out the ultralow IFT which is the first criteria for selecting what surfactant system is suitable for froth flotation operation (Withayapanyanon, 2003).

This study investigated the relationship between the efficiency of continuous froth flotation and the ultralow IFT of diesel in wastewater. Alfoterra 145-5PO (branched alcohol propoxylate sulfate, sodium salt) and SDS (sodium dodecyl sulfate) were used as surfactants to form Winsor Type III microemulsion or the middle phase with diesel. The effects of surfactant concentration, NaCl concentration, and oil to water ratio on the ultralow IFT of diesel was studied. After that, continuous froth flotation experiments were performed to investigate the efficiency of diesel removal from wastewater using mixed surfactants of Alfoterra 145-5PO and SDS that provided the ultralow IFT as well as the good performance on foamability and foam stability. Effects of oil/water ratio, concentration of surfactant, salinity, and hydraulic retention time (HRT) on flotation efficiency were also investigated.

MATERIALS AND METHODS

Chemical and Substance

Two types of surfactants were used in this work, branched alcohol propoxylate sulfate, sodium salt (Alfoterra 145-5PO Sulfate), and sodium dodecylsulfate (SDS). Alfoterra 145-5PO Sulfate with purity of 28.7% was supplied in the liquid form by Sasol North America Inc., Texas, USA. Alfoterra 145-5PO Sulfate is an anionic surfactant with a negatively charged sulfate head group. SDS was purchased from Carlo Erba Reagenti with purity in the range of 94-98 %. SDS is an anionic surfactant with a negatively charged sulfate head group and alkyl chain length of twelve carbon units. The general properties of the studied surfactants are shown in Table 1.

Table 3.1 General properties of studied surfactants

Surfactant	Molecular weight	Chemical Formula
Alfoterra 145-5PO Sulfate	595	$C_{16}H_{32}(C_3H_6O)_5SO_4Na$
SDS	288	$CH_3(CH_2)_{11}OSO_3Na$

Diesel was selected as a model oil contaminant in this research work. It was purchased from PTT Public Co., Ltd. Diesel is a complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon number predominantly in the range of C9-C20 and having a boiling point in the range of approximately 163-357 °C.

Analytical grade of sodium chloride (NaCl) was used as an electrolyte and obtained from Labscan Asia Co., Ltd. with purity of 99%.

All chemicals were used as received without further purification.

Microemulsion Formation

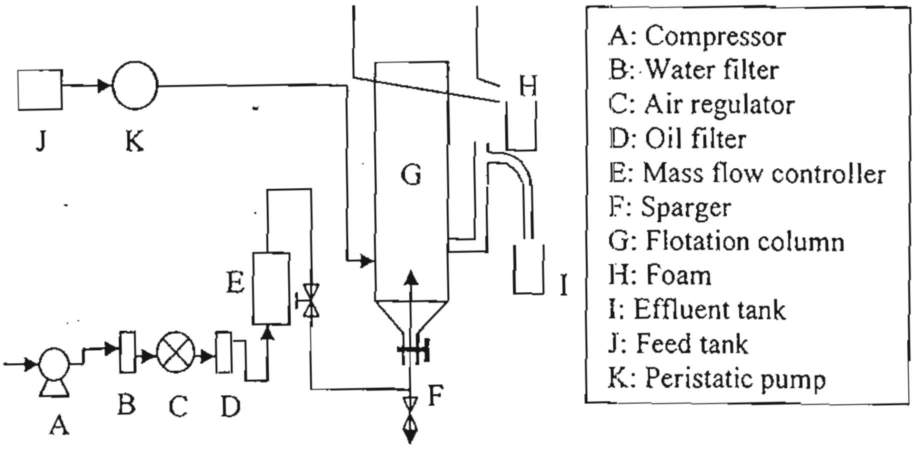


Figure 1. Schematic diagram of the froth flotation apparatus in a continuous mode of operation

Aqueous surfactant solution prepared at different surfactant concentrations and salinities was added in vials. 5 ml of diesel was added in a series of vials containing 5 ml of surfactant solution containing different surfactant concentrations and salinities. Surfactant concentration an salinity were expressed as percent by weight based on aqueous solution. After that, each vial was shaken gently by hand for 1 min and then equilibrated in a temperature-controlled incubator (BINDER, KB400/E2) at 30 °C until the system reached equilibrium. The equilibrium state was justified by observing that the volume of each phase of microemulsion remained constant. The measurement of phase height was conducted by using a cathetometer, model TC-II from Titan Tool Supply, Inc. attached to a digimatic height gauge, model 192-631, obtained from Mituyo with 0.002 mm in accuracy. The interfacial tension between each phase was measured by a spinning drop tensiometer (SITE 04, Kruss GmbH, Hamburg).

Froth Flotation Experiment

Figure 1 shows the schematic diagram of froth flotation apparatus used in this study. The froth flotation apparatus consisted of a glass cylindrical column with 5 cm inside diameter and 120 cm height and operated in a continuous mode. Compressed air was first filtered to remove all particles and oil and then passed through a water filter. The flow rate of the filtered air was regulated by a mass flow controller (AALBORG, GFC171S) before it was introduced into the bottom of the column through a sinter glass disk with pore size diameters about 16-40 μm. A well-mixed solution, which is composed of surfactant, water, and oil under microemulsion condition was fed continuously with a desired flow rate into the froth flotation column by using a peristatic pump (Masterflex, easy-load II). The level of solution in the column was adjusted by a three-way flexible tube in order to vary the foam height. The air bubbles ascended through the solution generated foam. The foam overflown from the column was collected. After that, the froth was collapsed to analyze diesel concentrations in the froth. In addition, effluent samples were also collected for analysis of diesel and surfactant concentrations by using the methylene chloride extraction method and titration method with methylene blue chloride, respectively. All experiments of the forth flotation were carried out at room temperature of 25-27 °C.

RESULTS AND DISCUSSION

In this study, wt% is based upon the aqueous system consisting of water, salt, and surfactant. Foamability is defined as the ratio of maximum foam height to initial solution height whereas foam stability ($t_{1/2}$) is the time required for the foam to collapse a half of the maximum height. Enrichment ratio is defined as the concentration of diesel in the collapsed froth divided by concentration of diesel in the feed.

Microemulsion Formation

The microemulsion formation of diesel with Alfoterra shows only two obvious phases, which were the excess water and excess oil phases. The layer of the middle phase (Winsor Type III microemulsion) was very thin, and it could not be clearly observed visually. Consequently, the measurement of the phase transformation became difficult to identify whether the system had a middle phase or not. Hence, the phase diagram of diesel with Alfoterra is not shown here. The IFT of the system was measured by the spinning drop tensiometer to examine the existence of Winsor Type III microemulsions. Figure 2 shows IFT as a function of Alfoterra concentration, The minimum IFT was found with 0.10 wt% Alfoterra. Figure 3 illustrates the IFT as a function of salinity scan at 0.1 wt% Alfoterra and an oil:water ratio of 1:1. The result shows that the minimum IFT occurs at 5 wt% NaCl concentration. According to the result from the effe2ct of agitation of single surfactant (Alfoterra) concentration on performance of froth flotation as will be shown later, it was found that the oil removal decreased as the solution was further agitated. Consequently, adding SDS as another frother to the solution is desirable because it provides good foamability and foam stability. The system consists of Alfoterra at 0.1 wt% and NaCl at 3 wt%, SDS concentration was varied from 0.1, 0.5, 0.7, and 1 wt%. The reason that 3 wt% of NaCl was used instead of 5 wt% NaCl is because foamability and foam stability at high NaCl concentration of the system are very poor because the repulsive force between the anionic head groups decreases when the NaCl concentration increases leading to a board foam lamella and high water content in a foam lamella. Hence, foam can break easily and froth flotation cannot be achieved. As shown in Figure 4, increasing the SDS concentration increases the IFT and the minimum IFT appears at 0.1 wt% of SDS.

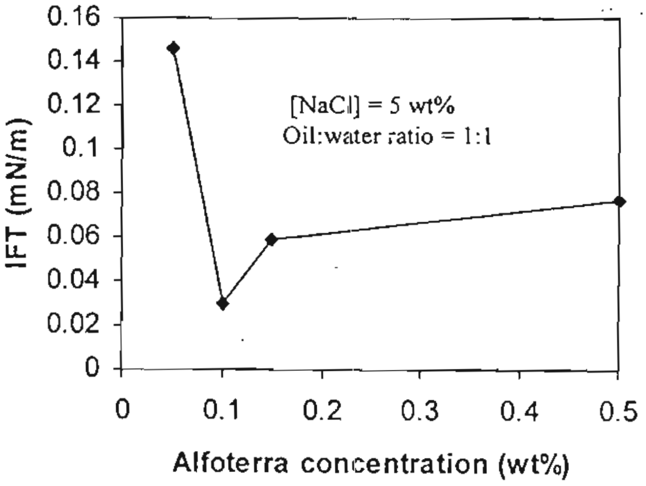


Figure 2. IFT as a function of Alfoterra concentration at 5 wt% NaCl with oil:water ratio = 1:1 (v:v)

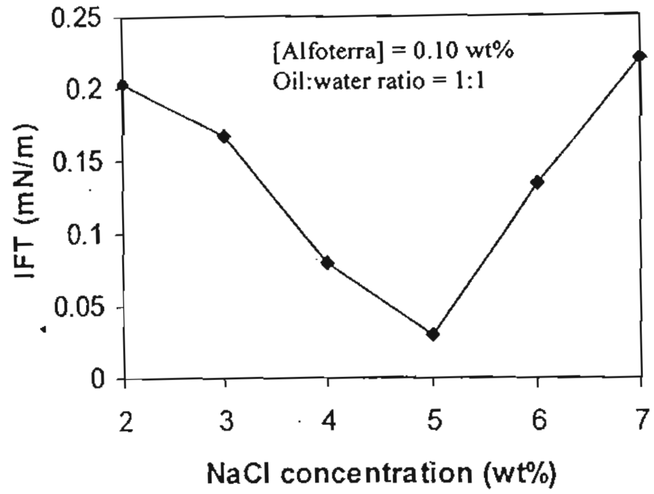


Figure 3. IFT as a function of salinity at 0.1 wt% of Alfoterra, oil:water ratio = 1:1 (v:v)

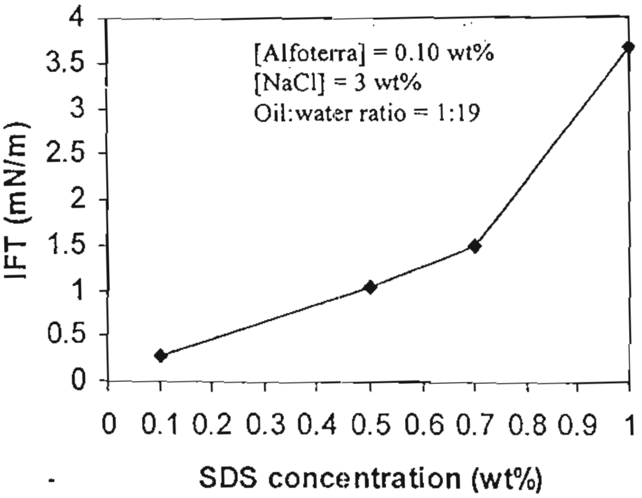


Figure 4. IFT as a function of mixed surfactant concentration at 0.1 wt% Alfoterra, 3 wt% NaCl, oil:water ratio = 1:19

Froth Flotation Results

Effect of single and mixed surfactant system

Figure 5 shows that the oil removal decreases with time of the froth flotation unit in batch mode of operation. This is because as the solution is agitated longer, foam stability decreases due to the decrease in the oil droplet size, but still higher than 2-10 μm which is the range of droplet size providing a high foam stability results in the decreasing of oil removal. Because of the speed of mixing between the surfactant solution and diesel oil used in this research is 2000 rpm, but the speed that can reduce the oil droplet size to 2-10 μm is between 5000-10000 rpm (Jarudilokkul *et al.*, 2003). The dependence of stability on the oil drop size can be explained by the oil accumulation mechanism. The small droplets tend to accumulate in the plateau borders of foam lamella at a lesser extent owing to their size and buoyancy force; therefore, they have less resistance for the movement in the plateau borders of foam lamella (Schramm, 1992). Consequently, they are less likely to be trapped within the plateau borders. As the drop size decreases, the accumulation of oil decreases. Nevertheless, the viscosity of emulsions increases rapidly with decreasing of the drop size under the range of 1-2 μm due to the interaction between the oil drops becomes significant. Hence, in the presence of very fine emulsion, the liquid drainage is much slower, and thus the foam stability is much greater. The foam stability can be increased by having small oil drop size in the range of 1-2 μm. This phenomena can be explained by the effect of size of droplets effect of size of droplets as mentioned before. However, reducing size of oil droplets into the range of 1-2 μm is very difficult and not commercially practical. Hence, an addition of a frother to the solution was selected to solve this problem. Figure 6 compares the foam stability of agitated-solution and non-agitated solution of the system with different Alfoterra concentrations. The non-agitated system was found to provide higher foam stability than that of the agitated-system. As shown in Figure 7, the maximum oil removal is at 0.5 wt% SDS. This can be explained by using the result of foamability as shown in Figure 8. Hence, this system was selected to study effects of other parameters.

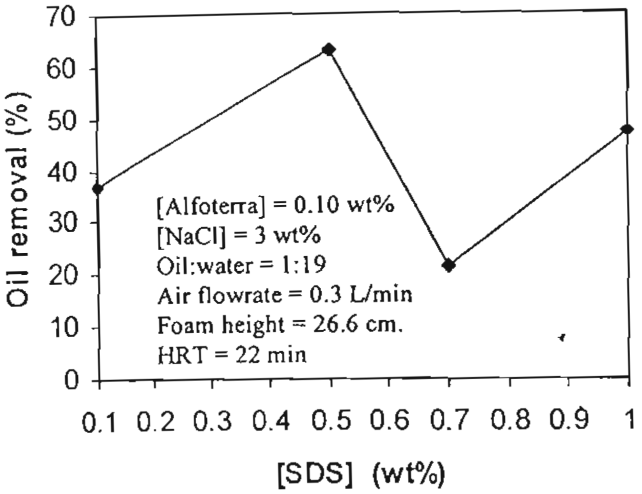


Figure 7. Oil removal efficiency of mixed surfactant system at different SDS concentrations

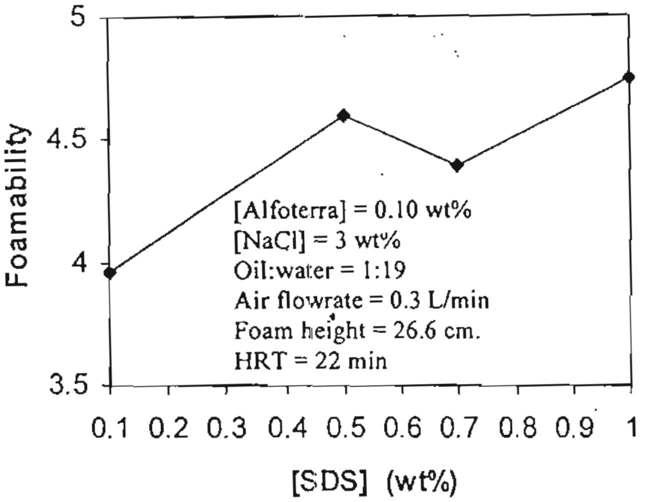
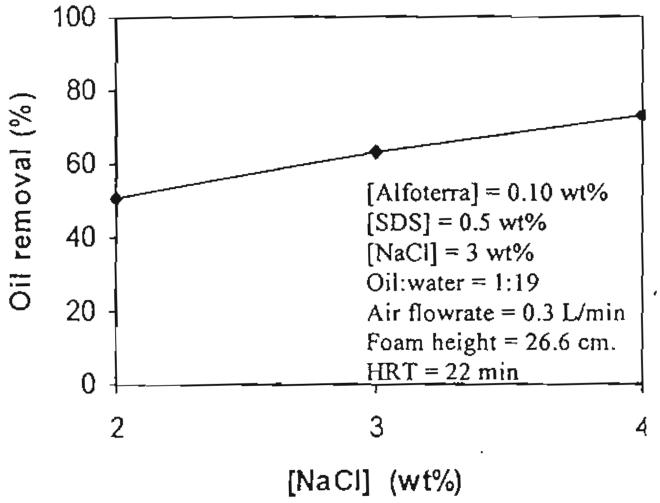
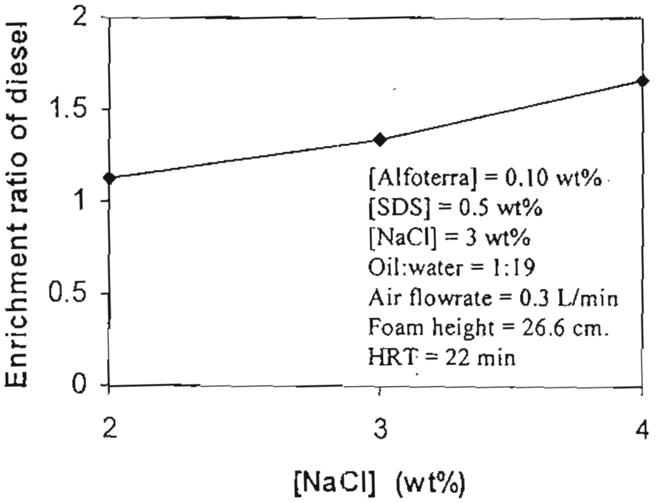


Figure 8. Foamability of mixed surfactant system at different SDS concentrations

Effect of NaCl concentration





The effect of NaCl concentration on the operation of froth flotation was carried out by varying NaCl concen

Figure 9. Removal efficiency of diesel at different NaCl concentrations

Figure 10. Enrichment ratio of diesel at different NaCl concentrations

The effect of NaCl concentration on the operation of froth flotation was carried out by varying NaCl concentration at 0.1 wt% Alfoterra and 0.5 wt% SDS. Figure 9 shows that an increase in the NaCl concentration from 2 to 4 wt% results in increasing oil removal. This is because the repulsive force between the anionic head groups decreases when the NaCl concentration increases. Consequently, the hydrophobic characteristics of the foam surface increase resulting in increasing amount of oil attached to the foam. A part from the removal efficiency the separation efficiency of the froth flotation can be indicated by the enrichment ratio. Figure 10 illustrates the effect of NaCl concentration on the enrichment ratio. It shows that an increase in the NaCl concentration from 2 to 4 wt% increases the enrichment ratio of diesel. This is because NaCl reduces the repulsive force between the anionic head groups of the surfactant so foam lamella becomes thinner leading to lower water content in the foam and higher oil content.

Effect of oil to water ratio

Most available work on froth flotation involves 1:1 oil to water ratio (Chavadej *et al.*, 2003, Feng *et al.*, 2000). Practically, a ratio of emulsified oil to wastewater is much less than 1:1. Consequently, in this work, the effect of oil loading on the performance of froth flotation was investigated by varying the oil to water ratio at 0.1 wt% Alfoterra, 0.5 wt% SDS, and 4 wt% NaCl. As illustrated in Figure 11, the effect of oil to water ratio on diesel removal corresponds to the result of foam production rate as shown in Figure 12. This is because with a high foam production rate, the drainage rate of water in the foam lamella decreases resulting in decreasing back-entrainment of oil content into the solution in the column leading to a high oil removal. It was found that the oil to water ratio does not affect significantly on the oil removal efficiency. Figure 13 shows the effect of oil to water ratio on the enrichment ratio of diesel. The enrichment ratio decreases slightly when the oil to water ratio increases from 1:199 to 1:99. This is because at an oil to water ratio of 1:99, the foam production rate is increased resulting wetter foam than a low oil to water ratio of 1:199. As a result, the collapsed foam contains a high amount of water leading to a lower enrichment ratio of

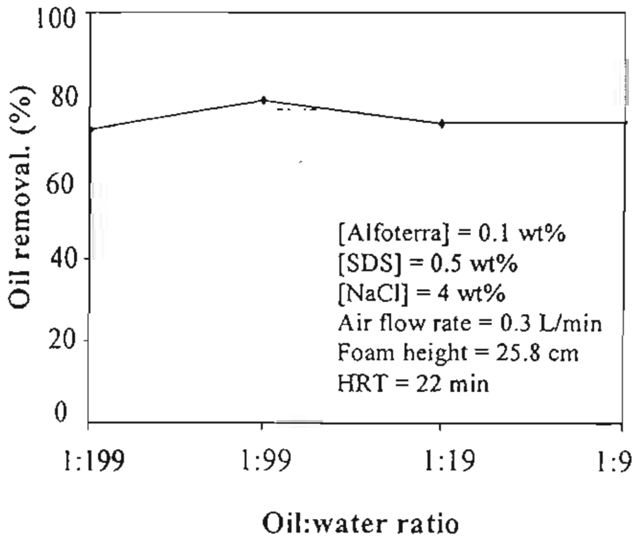


Figure 11. Removal efficiency of diesel at different feed NaCl concentrations

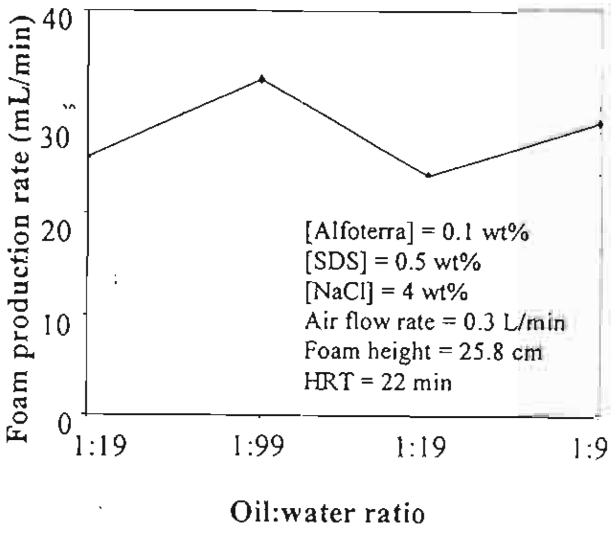
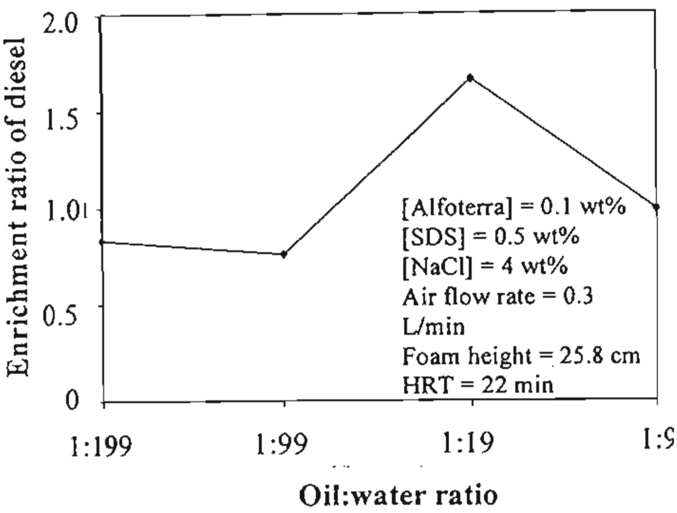


Figure 12. Foam production rate of system at different feed oil to water ratios



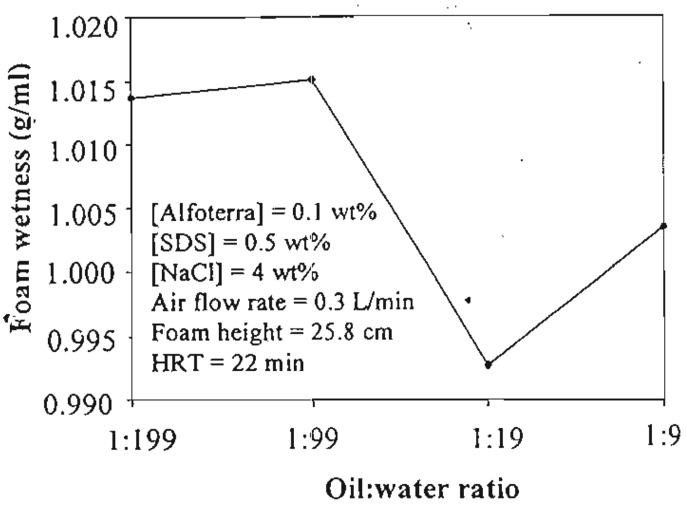
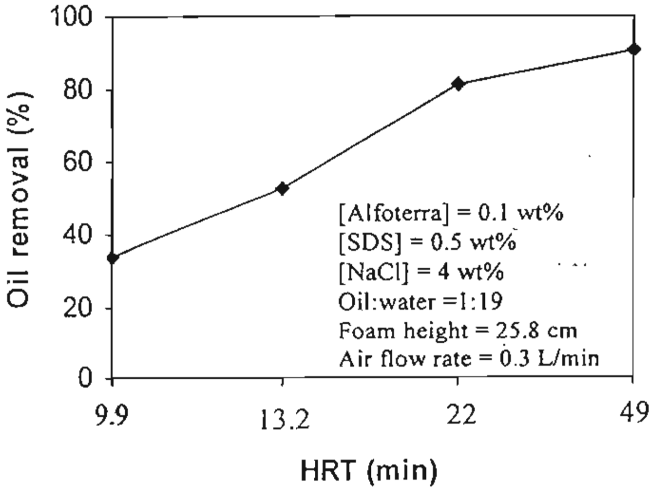


Figure 13. Enrichment ratio of diesel of system at different feed oil to water ratios

Figure 14. Foam wetness of system at different feed oil to water ratios

diesel. After that, when an oil to water ratio is further increased to 1:19, the enrichment ratio of oil increases substantially because at the system has the smaller amount of surfactant leading to the narrower foam lamella. When an oil to water ratio is further increased to 1:9, the enrichment ratio of diesel decreases again. The explanation is still the same as described before. As expected, the profile of foam wetness (see Figure 14) is the opposite trend of the enrichment ratio of diesel. The higher foam wetness, the higher water content is or the lower oil content is.

Effect of hydraulic retention time (HRT)



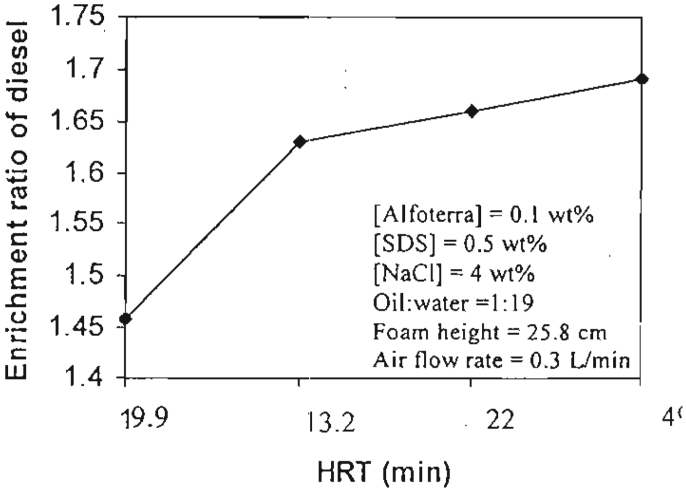


Figure 15. Removal efficiency of diesel at different HRTs

Figure 16. Enrichment ratio of diesel at different HRTs

From Figure 15, the oil removal increases when HRT increases. This is because a higher HRT gives a longer residence time for the solution to contact with air bubbles. As a result, a higher amount of oil can be carried on to the top of the column and a higher oil removal is obtained. In this work, the maximum oil removal is up to 90.37 % at a HRT of 49 min. As shown in Figure 16, the enrichment ratio of oil increases as HRT increases because a high HRT represents a lower feed flow rate resulting in longer time for oil to stay in the column as well as more time to be contacted and attached to the air bubbles and the froth at the top of the column. Therefore, the collapsed froth contains a higher amount of oil and a lower water content with increasing HRT.

CONCLUSIONS

From this work, foamability is another factor that affects on oil removal efficiency. Adding small amount of salt can enhance a froth flotation efficiency, but a high amount of salt deteriorate the foam stability. Oil to water ratio is not affected significantly on oil removal efficiency. This may be due to the same solubilization power of each sytem because it contains nearly the same Alfoterra and SDS concentration as well as NaCl concentration. Moreover, an increase in HRT increases the oil separation efficiency. The system with 0.1 wt% Alfoterra, 0.5 wt% SDS, 4 wt% NaCl, an oil:water ratio of 1:19, an air flow rate of 0.15 L/min, a foam height of 26 cm, and a HRT of 49 min gave the maximum oil removal (90.37 %).

ACKNOWLEDGMENTS

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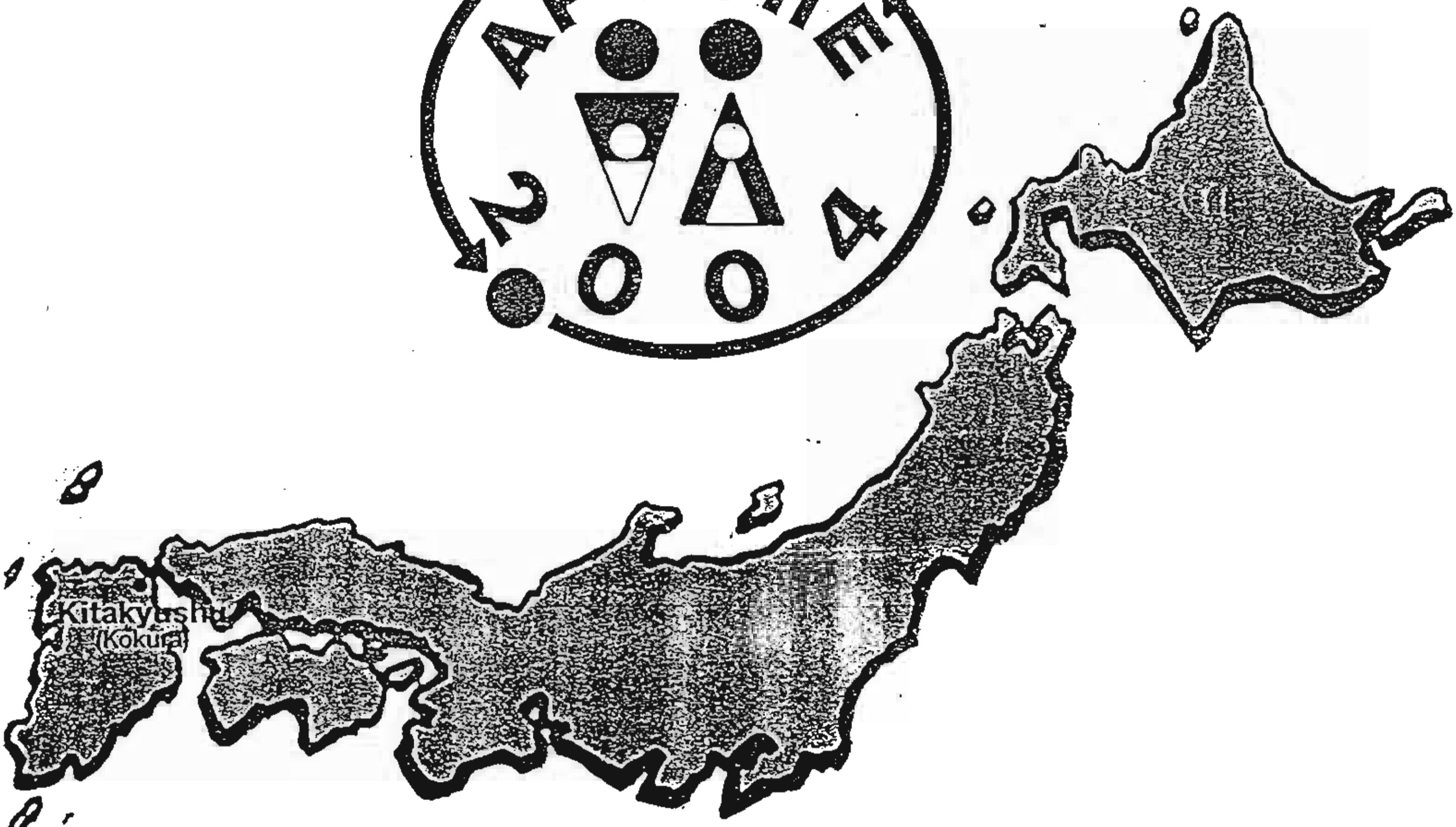

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Surfactant Recovery from Aqueous Phase Using Multi-Stage Foam Fractionation

On-line Number 980

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ABSTRACT

Surfactants are widely found in many products such as detergent, cosmetics, shampoo and drugs. As environmental regulations tightened, there is increasing concern about reducing the surfactant concentration in effluent streams. Foam fractionation is the direct and continuous treatment which would allow for the reuse of both water and surfactant. In this study, two multi-stage foam fractionators with different tray spacing were set up to investigate the recovery of cetylpyridium chloride (CPC), a cationic surfactant, from aqueous solution. Effects of several important variables, including surfactant feed concentration and flow rate, air flow rate, foam height, number of trays and recycle position ratio, were systematically studied. It can be seen from the results that increasing air flow rate and surfactant concentration resulted in lowering enrichment ratio but increasingly % surfactant recovery. Effect of foam height on surfactant recovery was not as significant as it was on the enrichment ratio. With increasing feed flow rate, both enrichment ratio and surfactant recovery decreased. On a contrary, increasing number of trays was found to enhance both enrichment ratio and recovery. Lastly, changing recycle position was shown to have more impact on the column performance than changing the recycle ratio or tray spacing.

KEYWORD

Foam Fractionation / Surfactant recovery

INTRODUCTION

Surfactants appear in the effluent wastewater from a number of industries such as textile, pulp and paper, food processing and detergent manufacturing. As environmental regulations tightened, there has been growing concern about reducing the surfactant concentration in aqueous streams. In addition, surfactant-based separation processes have gained increasing interest in the remediation of wastewater and ground water in recent years (Scamehorn and Harwell, 1992). In these processes, surfactants are added to remove toxic pollutants from the waste streams. Consequently, the resultant effluent streams often contain

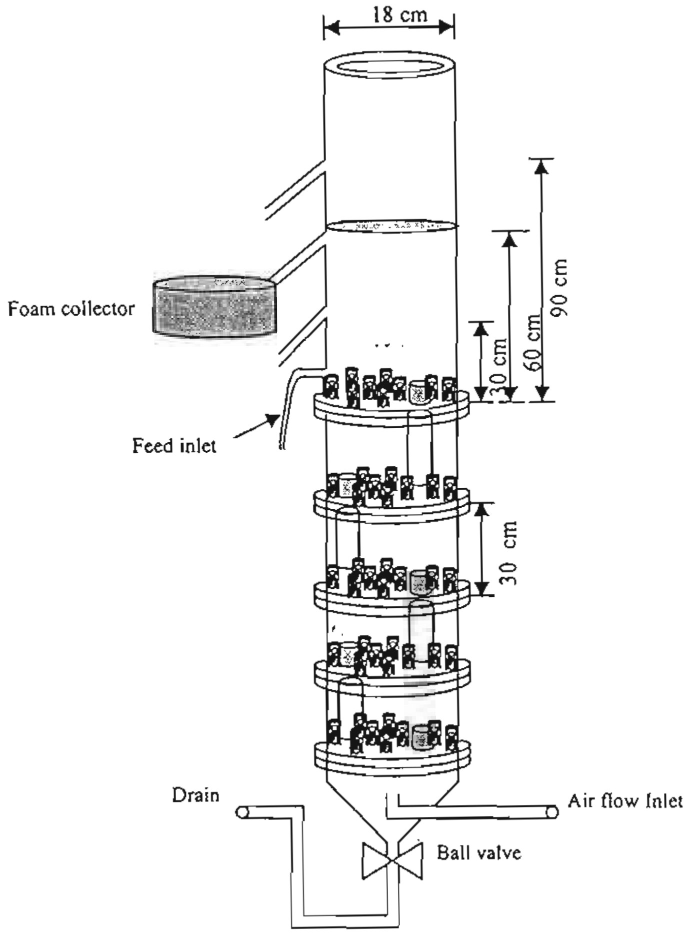


Figure 1 Schematic Diagram of a Multi-Stage Foam Fractionation Column

The compressed air was introduced at the bottom tray. Foamate at the top of the column was collected at three different foam height of 30, 60 and 90 cm from the liquid surface of the top tray.The foam was collected, frozen, thawed and then weighted to get the collapsed foamate volume.

The surfactant separation efficiency of the foam fractionation system was studied under steady state conditions. Steady state was insured when all measured parameters were invariant with time. After steady state was achieved, samples of the outlet stream and foam were taken for analysis and measurement. All experimental runs were performed at room temperature (25-27°C).

In each experiment, volumetric foam production rate (l/min.m^2), foam wetness (grams of foam solution/L of foam), and the surfactant concentration (g/l) in the collapsed foam solution were measured. The concentrations of CPC in collapsed foams, feed solutions and effluents were measured by an UV visible spectrophotometer at wavelength of 260 nm.

The critical micelle concentration (CMC) of CPC was also measured experimentally by plotting the specific surface tension versus surfactant concentration showing an abrupt change in slope.

RESULTS AND DISCUSSION

The multistage foam fractionator used in this study was first put through a series of tests in order to check when steady state could be established. Operating under the base conditions, the foam fractionation unit showed to reach steady state within approximately 6 hours. After this period of time, the surfactant concentration measured in each tray from the sampling port became constant, meaning that the steady state was established.

After the steady state was established, effects of several parameters on the separation efficiency of the multistage fractionator operated in a continuous mode were studied and evaluated in terms of surfactant recovery (%) and enrichment ratio as shown below:

$$\text{Surfactant Recovery (\%)} = \frac{(C_i - C_e) \cdot 100}{C_i}$$

$$\text{Enrichment Ratio} = C_f / C_i$$

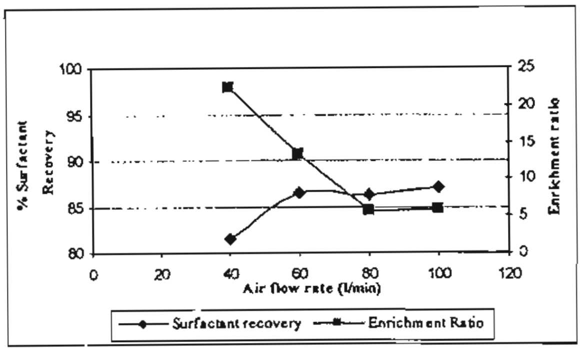
Where C_i and C_e are surfactant concentrations (mg/L) in the influent and effluent streams, respectively, and C_f is a surfactant concentration in the collapsed foam.

Effect of Air Flow Rate

From Figure 2, it can be seen that increasing air flow rate results in a reduction in the enrichment ratio but it leads to an increase in % surfactant recovery. An increase in the air flow rate increases the interfacial area between gas and liquid or the mass transfer area, thus increases the surfactant recovery. However, increasing air flow rate tends to generate wet foam which contains a lower amount of surfactant, resulting in a lower enrichment ratio.

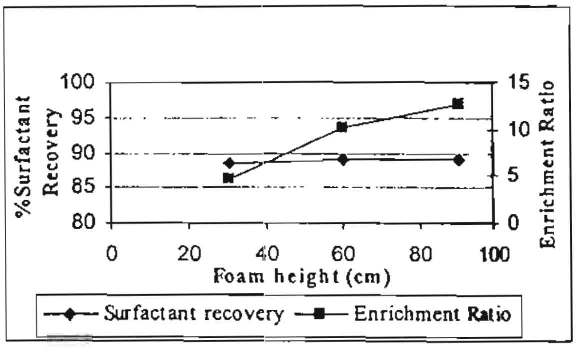
Effect of Foam Height

Effect of the foam height in the foam fractionation column was studied by varying a distance between the surface of liquid in the highest tray and the foam draw-off pipe. From Figure 3, it can be seen that increasing foam height results in an increase in the enrichment ratio but has little effect on the surfactant recovery. Increasing foam height leads to a longer foam residence time, which allows more drainage of the liquid in the films. Thus, the concentration of the adsorbed surfactant molecules increases as foam height increases, resulting in a higher enrichment ratio. On a contrary, within the range of foam heights investigated here, the effect of foam height on the surfactant recovery was not as significant as observed with the enrichment ratio.



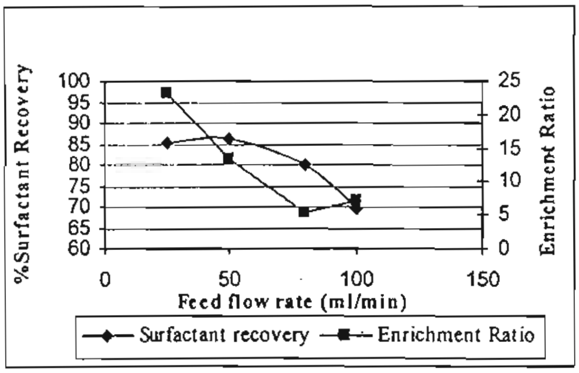
Conditions: [CPC] = 0.25 CMC; feed flow rate = 50 ml/min; foam height = 30 cm; tray spacing =15 cm and number of tray =5

Figure 2 Effects of air flow rate on surfactant recovery and enrichment ratio.



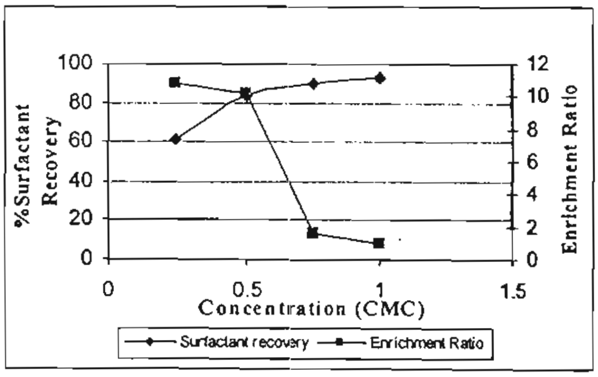
Conditions: [CPC] = 1 CMC; Air flow rate = 40 L/min; Feed flow rate = 25 ml/min; tray spacing =30 cm and No. of tray =5

Figure 3 Effects of foam height on surfactant recovery and enrichment ratio.



Conditions: [CPC] = 0.25 CMC; Air flow rate = 60 L/min; foam height = 30 cm; tray spacing = 15 cm and No. of tray = 5

Figure 4 Effects of feed flow rate on surfactant recovery and enrichment ratio.



Conditions: [CPC] = 0.5 CMC; Air flow rate =40 L/min; Feed flow rate = 50 ml/min; foam height = 30 cm; and tray spacing = 30 cm

Figure 5 Influence of CPC concentration in feed on surfactant recovery and enrichment ratio.

Effect of Liquid Feed Flow Rate

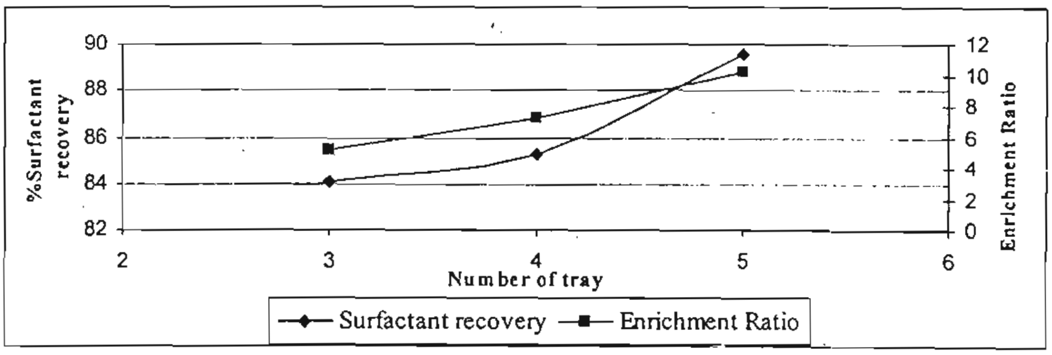
From Figure 4, it shows that increasing feed flow rate results in a decrease in both enrichment ratio and surfactant recovery. The decrease in the enrichment ratio and surfactant recovery upon increasing feed flow rate may attribute to a shorter residence time at a higher liquid flow rate. As a result, considerable amount of surfactant still remains in the liquid which drains out of the column and the surfactant becomes more concentrated at the higher trays.

Effect of Feed Concentration

. The surfactant concentration in the feed solution was varied in the range of 25-100% of the CMC of CPC. From Figure 5, increasing surfactant concentration from 0.25 CMC to 1 CMC results in a drastical decrease in the enrichment ratio. In contrast, within the same range of the surfactant feed concentration, the surfactant recovery increases slightly. A higher surfactant concentration in the thin liquid film in the foam lamellae may make this liquid more stable as well as causes an increase in surface viscosity and surface concentration, leading to a decrease in the rate of film drainage, thus causing the surfactant to quickly go out off the column. On the other hand, foam that formed over a fluid with a low surfactant concentration is less stable and results in a much higher enrichment ratio than that formed over high-surfactant fluid. The foam formed over a fluid with a higher concentration is characterized by smaller, more stable bubbles.

Effect of Number of Trays

From Figure 6, it can be seen that increasing number of trays from 3 to 5 results in an increase in both enrichment ratio and surfactant recovery. Under the conditions studied, the highest % surfactant recovery of 90 % and enrichment ratio of 10 were achieved when 5 trays were used. This is due to the fact that increasing number of trays provides a longer residence time and, consequently, allowing the surfactant to become more concentrated in foam as well as a higher surfactant recovery. The present study is in good agreement with the previous result (Boonyasuwat et.al, 2003)



Conditions: Air flow rate =50 L/min; feed flow rate = 50 ml/min; foam height = 60 cm; tray spacing = 30 cm and number of trays =3

Figure 6 Influence of Number of tray on surfactant recovery and enrichment ratio

Effect of Recycle Position and Recycle Ratio

From Table 2 it can be seen that the change in recycle position and recycle ratio of the effluent had only little effect on both surfactant recovery. However, slight increase in the enrichment ratio was observed when the recycle feed was fed into the trays at higher position (trays 4 and 5). Therefore the effect of recycle ratio was further studied by using 3 different ratios (3/1, 1/1, and 1/3). It can still be seen that no significant change was observed upon varying the recycle ratio. The results suggested that the recycle feed position and recycle ratio may not have much effect on this small column.

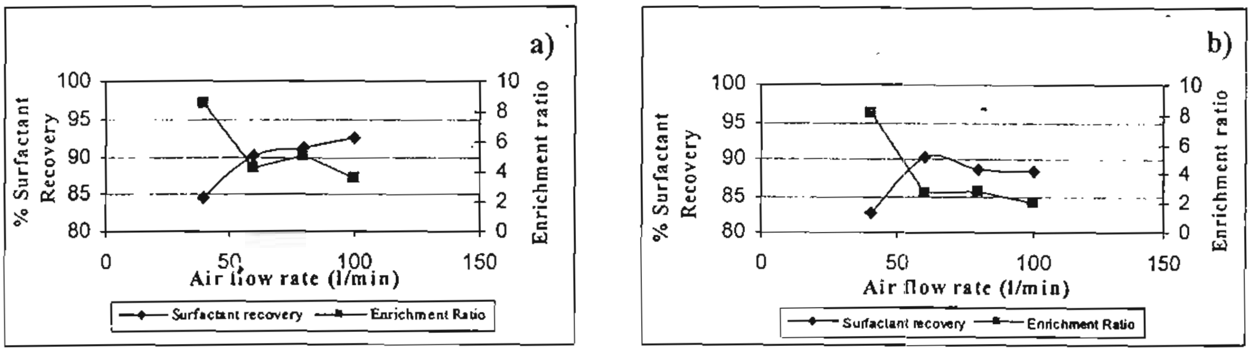
Table 2 Effect of recycle ratio and recycle position on surfactant recovery and enrichment ratio.

Condition: [CPC] = 0.50 CMC air flow rate =40 L/min; feed flow rate = 50 ml/min; foam height = 30 cm; tray spacing = 15 cm; and number. of tray =5

Recycle Position	No recycle		Recycle					
	% Surfactant Recovery	Enrichment Ratio	Recycle/Feed = 1:1		Recycle/Feed = 1:2		Recycle/Feed = 3:1	
			% Surfactant Recovery	Enrichment Ratio	% Surfactant Recovery	Enrichment Ratio	% Surfactant Recovery	Enrichment Ratio
tray5	88.99	7.66	84.33	12.16	85.31	9.62	88.62	9.53
tray4	89.12	10.44	83.76	14.18	88.69	13.24	86.54	11.24
tray3	88.47	9.99	81.78	12.15	87.56	10.29	87.65	9.11
tray2	88.62	11.11	84.53	9.32	87.23	9.85	82.62	12.54
tray1	87.75	9.54	84.46	11.53	84.29	10.35	86.81	10.89

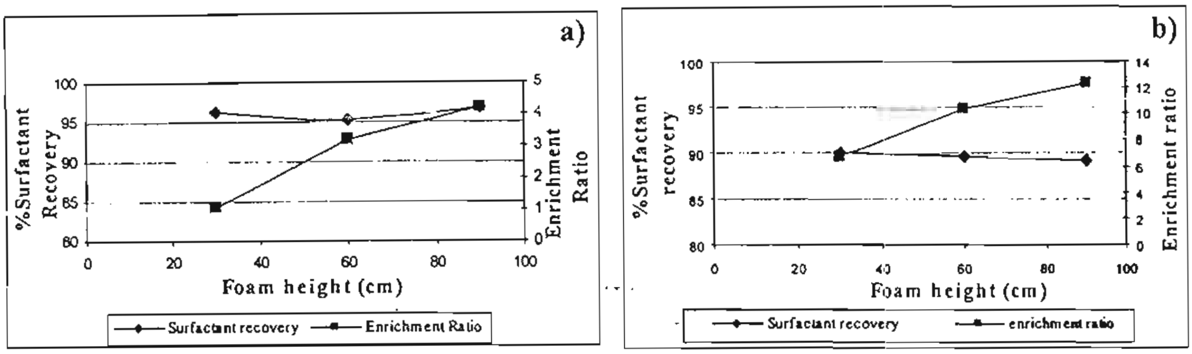
Effect of Tray Spacing

The results observed from Figure 7-11 indicated that under the conditions studied increasing tray spacing from 15 cm to 30 cm did not show any significant effect on the performance of the multistage foam fractionation in terms of both surfactant recovery and enrichment ratio. Very similar results and comparable values of surfactant recovery (%) and enrichment ration were obtained from the two columns using different tray spacing. This may be due to the limited size and dimension of the column which might not large enough to see the effect. In addition, the number of bubble caps on each tray may be too few which limited the extent of the mass transfer occurred in the column.



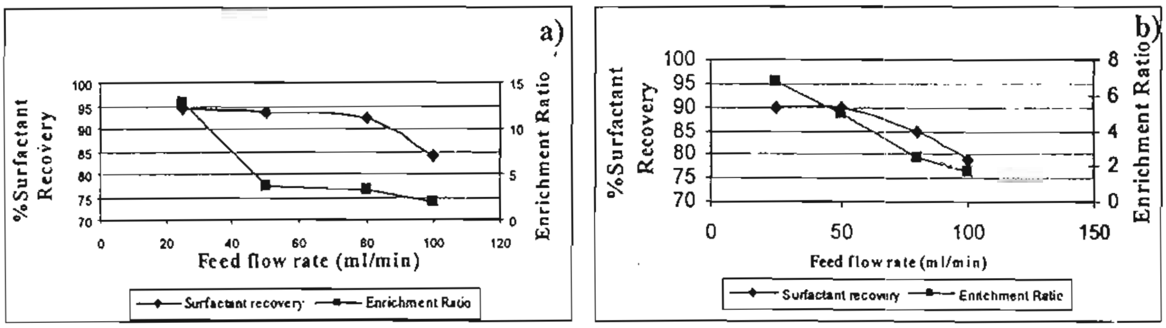
Conditions: [CPC] = 0.5 CMC; Feed flow rate = 50 ml/min; Foam height= 30 cm, and No. of tray = 5

Figure 7 Effects of superficial air velocity on surfactant recovery and enrichment ratio. a) 15 cm tray spacing b) 30 cm tray spacing



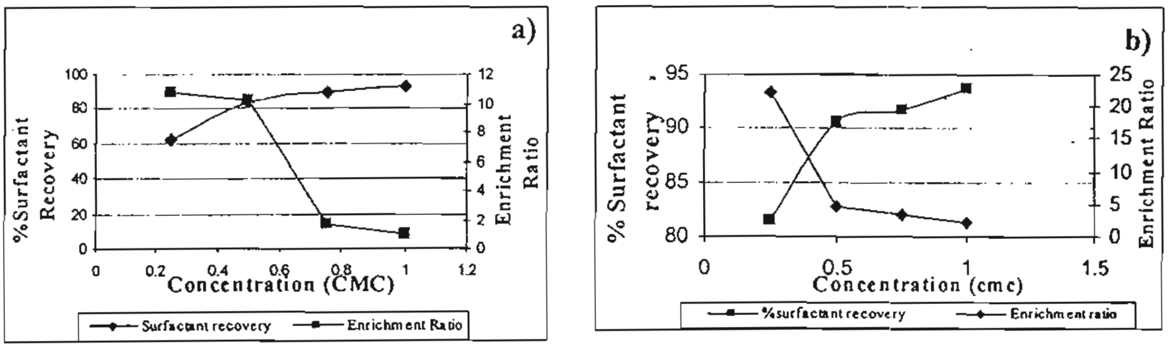
Conditions: [CPC] = 0.75 CMC; Air flow rate = 60 L/min; Feed flow rate = 50 ml/min and No. of tray =5

Figure 8 Effects of foam height on surfactant recovery and enrichment ratio a) 15 cm tray spacing b) 30 cm tray spacing



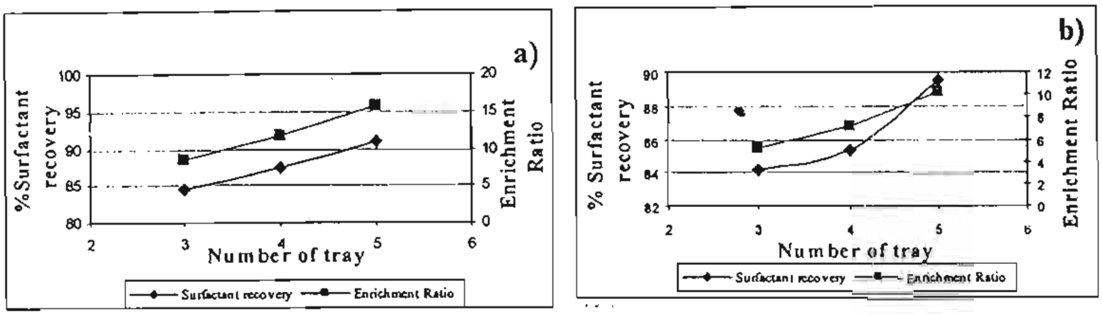
Conditions: [CPC] = 0.75 CMC; Air flow rate = 40 L/min; foam height = 30 cm and No. of tray = 5

Figure 9 Effects of feed flow rate on surfactant recovery and enrichment ratio a) 15 cm tray spacing b) 30 cm tray spacing



Conditions: Air flow rate =40 L/min; Feed flow rate = 50 ml/min; foam height = 30 cm and No. of tray =5

Figure 10 Effects of CPC concentration on surfactant recovery and enrichment ratio a) 15 cm tray spacing b) 30 cm tray spacing



Conditions: [CPC] = 0.5 CMC; Air flow rate =40 L/min; Feed flow rate = 50 ml/min and foam height = 60 cm

Figure 11 Effects of Number of tray on surfactant recovery and enrichment ratio
a) 15 cm tray spacing b) 30 cm tray spacing

CONCLUSIONS

The influence of the system parameters can be concluded as follows:

1. Increasing liquid feed flow rate results in both decreases in the enrichment ratio and % surfactant recovery.
2. An increase in air flow rate results in a reduction in the enrichment ratio but the surfactant recovery increases.
3. The efficiency of surfactant recovery does not change with increasing foam height but has more positive impact on the enrichment ratio.
4. The efficiency of surfactant recovery increases with surfactant feed liquid concentration but enrichment ratio decreases as feed liquid surfactant concentration increases.
5. With increasing number of trays both surfactant recovery and enrichment ratio are increased.

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PROGRAM & ABSTRACTS

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Separation of Carbon Black from Silica by Froth Flotation Technique as an Approach for Single-Walled Carbon Nanotubes Purification

On-line Number 884

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ABSTRACT

To produce single-walled carbon nanotubes (SWNT) by catalytic decomposition of carbon-containing molecules on silica support, as-prepared SWNT are grown on the surface of catalyst support. A very high purity of SWNT is required in various specific applications. Therefore, a purification step is considerably important in commercial production of SWNT. The conventional method for purifying SWNT is chemical treatment with acid or base. However, drawbacks of chemical treatment are toxicity, high cost, and the structural change of purified SWNT. To purify SWNT, froth flotation was focused as a better technique to separate SWNT from the spent catalysts. In this research, carbon black was used as model for investigation of effect of various parameters in froth flotation operation on purity and recovery of carbon. Nonionic surfactant was founded to be superior to ionic surfactants in the separation process between carbon and silica because both of silica and carbon are negatively charged. Effects of surfactant concentration, carbon loading, air flow rate, and foam height were investigated in this work.

KEYWORDS

froth flotation, purification, carbon nanotubes, surfactant

INTRODUCTION

Since single-walled carbon nanotubes were first discovered in 1993 (Ijima, et al., 1993, and Bethune, et al., 1993), they have captured attention from researchers worldwide because they exhibit many unique and exceptional physical and chemical properties that can be extended to several potential applications (Yakobson, et al., 1997).

In the present, SWNT are produced by 3 main methods: arc discharge (Bethune, et al., 1993), pulsed laser vaporization (Guo, et al., 1995), and catalytic decomposition of carbon-containing molecules (Kitiyanan, et al., 2000). Among these techniques, the catalytic method has been considered as a promising approach for large-scale production at a relatively low cost. However, in some processes that use silica as a catalytic support, it is difficult to separate as-prepared SWNT from the spent catalyst. Therefore, purification might be one of the important concerns that limit the scaling up to commercial scale. Currently, the conventional method to separate SWNT from silica support is chemical treatment by using concentrated HF or concentrated NaOH (Matarredona, et al., 2003). After that, membrane extraction is utilized to recover purified SWNT. However, both chemical treatment and membrane extraction display some negative impacts such as toxicity, high operating cost, and structural change of purified SWNT. Therefore, this work focused on applying froth flotation as an alternative separation process for SWNT purification.

Froth flotation is one of the surfactant based separation processes (Fuerstenau, et al., 1989) which is widely used in several applications. The schematic of froth flotation process is shown in Figure 1. In froth flotation operation, surfactant is added to the solution to promote the separation while air is sparged into the solution through sintered glass disk because air bubbles are used as a mean of separation in this technique (Zouboulis, et al., 1994). Hydrophobic particles such as SWNT could be carried by generated air bubbles to the top of the column. There are several advantages of flotation operation such as rapid operation, low space requirement, high removal efficiency, and low cost of operation (Choi, et al., 1996). Therefore, in this work, froth flotation was focused to separate SWNT from catalytic support because its advantage is superior to the conventional purification methods.

In fact, the as-prepared SWNT are grown on the surface of catalytic support, it needs some additional steps to break the interaction between SWNT and catalytic support before operated in froth flotation. In this study, the step of breaking the SWNT-support interaction has been neglected. To investigate the appropriate conditions in froth flotation operation for SWNT purification, physical blending between carbon black and silica was used as a model at the starting point of novel algorithm for SWNT purification.

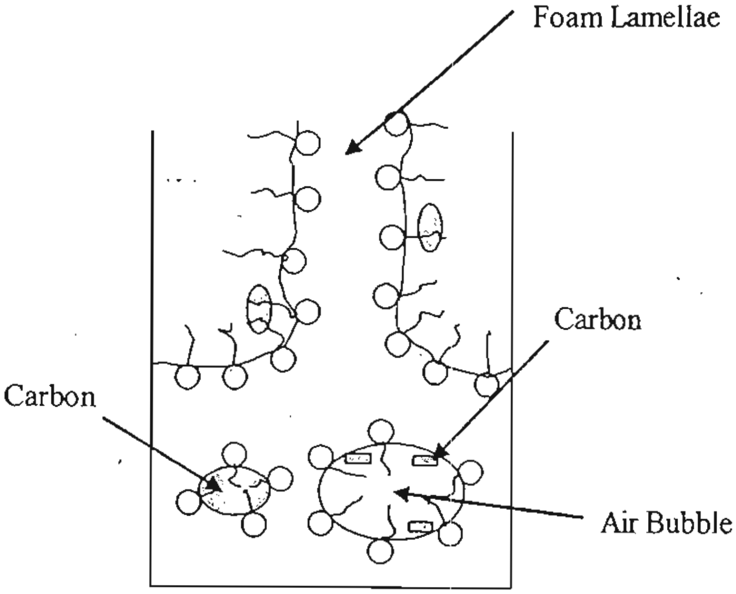


Figure 1. Schematic of the froth flotation process

MATERIALS AND METHODS

Carbon black type 400R having average particle size of 0.24 µm was supplied from Cabot Company. The as-received carbon black was rinsed with deionized water, centrifuged and dried to remove impurities before use. Surfonic L24-7, containing linear alcohol ethoxylate with seven-mole ethoxylate of linear, primary 12 – 14 carbon number alcohol, nonionic surfactant was obtained from Huntsman Company, USA. The surfactant was used as received. Deionized water was used in all experiments.

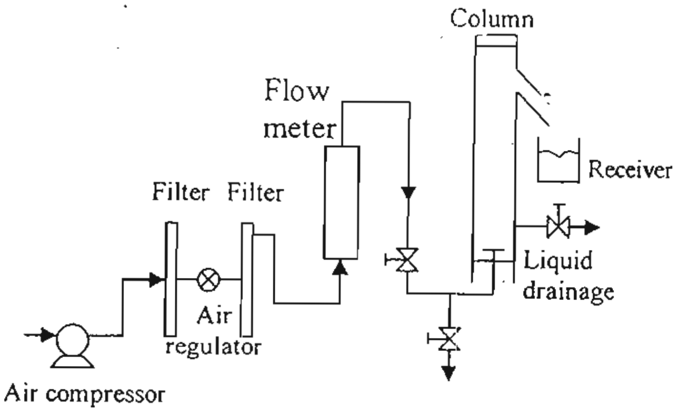


Figure 2. Schematic diagram of the froth flotation apparatus

The schematic diagram of flotation apparatus used in this work is shown in Figure 2. Flotation column is a glass column with 3.8 cm of inside diameter and 120 cm in length. Filtered air was introduced at the bottom of the column at constant flow rate of 200 mL/min through a sintered glass disk having pore size diameters about 16 – 40 μm. However, the air flow rate can be varied from 150 to 300 mL/min for investigation of the effect of air flow rate. The effects of surfactant concentrations ranging from 0.25 - 1 CMC (82.1 μM) were also observed. Foam was collected at the top of the column and then broken for analysis. All of flotation experiments were performed at room temperature (25-27° C). Deionized water was used to wash surfactant out of carbon-containing solid in the overhead froth. After that, the weight of the solid after dried in the oven at 110° C and after heated in the presence of air at 700° C was recorded and used to evaluate the purity and recovery of carbon black.

RESULTS AND DISCUSSION

To purify SWNT by using froth flotation technique, many parameters such as concentration of surfactant, and air flow rate should be first investigated. Since there are other additional parameters affecting the purification of the as-produced SWNT such as the interaction between SWNT and catalyst support, carbon black was utilized to represent SWNT after the interaction with the support is broken and to investigate the appropriate operating conditions in flotation column. In this research, purity of carbon is defined as a weight percentage of carbon on total solid (carbon and silica) in the overhead froth, while recovery is a weight percentage of carbon in the overhead froth on carbon in the initial feed.

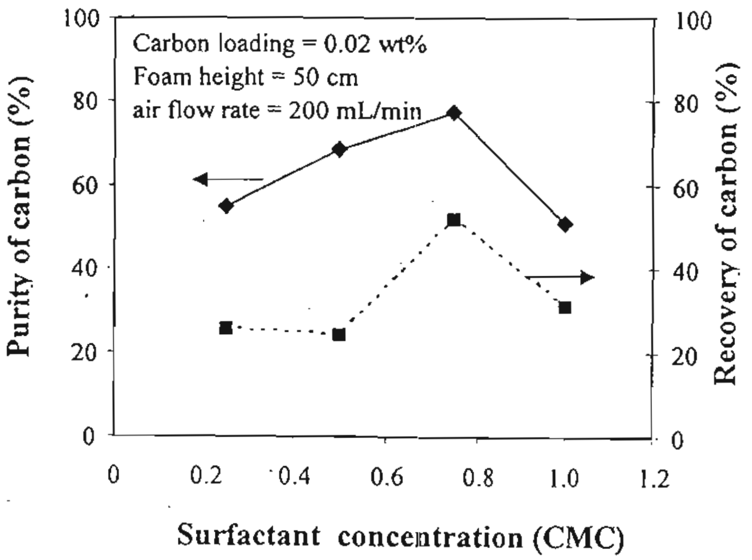
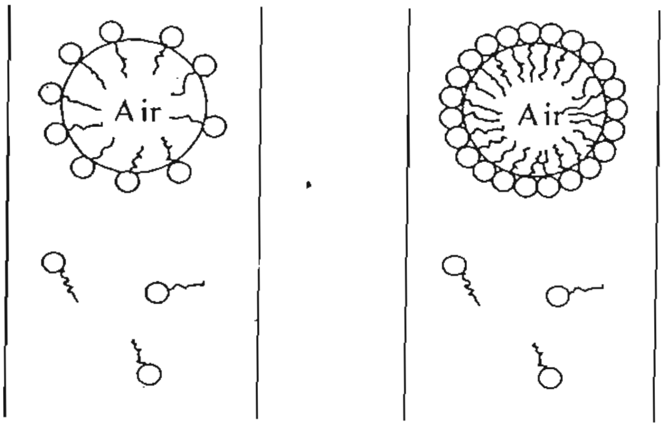


Figure 3. Effect of surfactant concentration on separation efficiency (1 CMC=82.1 μM)

Effect of surfactant concentration

Figure 3 depicts the purity and recovery of carbon as a function of surfactant concentration. At below CMC, as surfactant concentration increases, the separation efficiency increases due to more surfactant monomers adsorbed on the bubble surface as demonstrated in Figure 4. At a lower surfactant concentration, a small number of surfactant monomers adsorbed on bubble surface leads to lower solubilization power for co-adsorption of carbon on the air bubbles than that of a higher surfactant concentration. Therefore, the recovery of carbon is significantly dropped when



Low [surfactant] High [surfactant]

Figure 4. Schematic of froth flotation process at surfactant concentration below CMC

surfactant concentration is decreased. For the purity of carbon, at a low surfactant concentration, the steric effect from surfactant is also low. Hence, silica has higher possibility to be co-adsorbed on the bubble surface resulting in depressing the purity of carbon. However, increasing surfactant concentration beyond CMC descends both purity and recovery of carbon. This may be because micelles are formed in the solution leading to decreasing in a number of surfactant monomers on the air bubbles as demonstrated in Figure 5.

Effect of carbon loading

Figure 6 shows the effect of carbon loading on purity and recovery of carbon. From the result, the recovery of carbon decreases while the purity of carbon is almost constant, when carbon loading increases. In this investigation, surfactant concentration was kept constant to yield a constant surface concentration of surfactant on the bubbles. As a result, recovery of carbon decreases when more carbon is added into the solution.

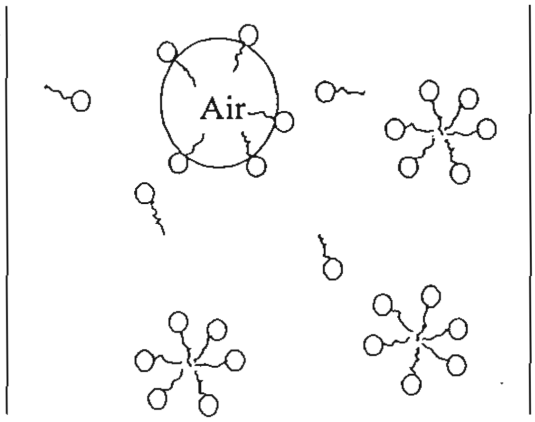


Figure 5. Schametic of froth flotation of CMC

Effect of air flow rate

The effects of air flow rate on purity and recovery of carbon are shown in Figure 7. Both purity and recovery decrease when air flow rate increases. Typically, the efficiency of the separation is expected to be improved when air flow rate increases due to more bubbles in the solution. However, as air flow rate increases, not only a number of bubbles passing through the solution, but also flow pattern in the column is altered. A very high air flow rate leads to severe circulation velocity in the solution; so some portion of carbon adsorbing on the bubble surface is dissolved back into the solution. Therefore, the lower the air flow rate, the better the separation efficiency is. However,

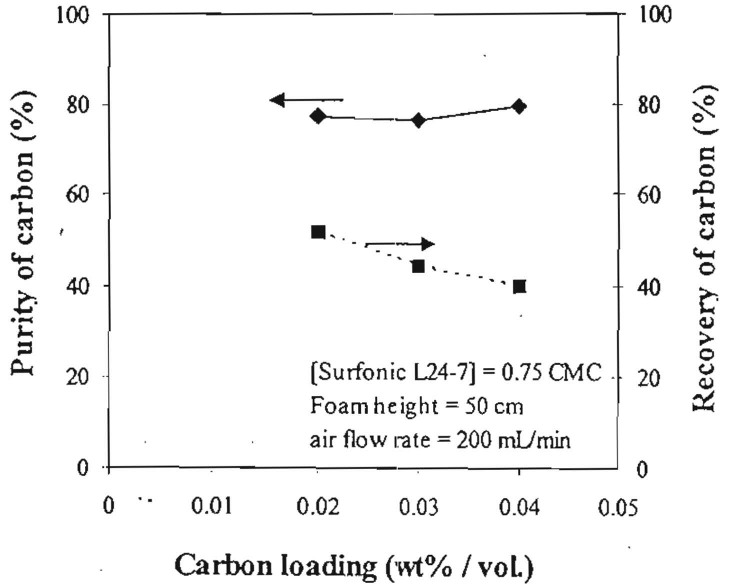


Figure 6. Effect of carbon loading on separation efficiency

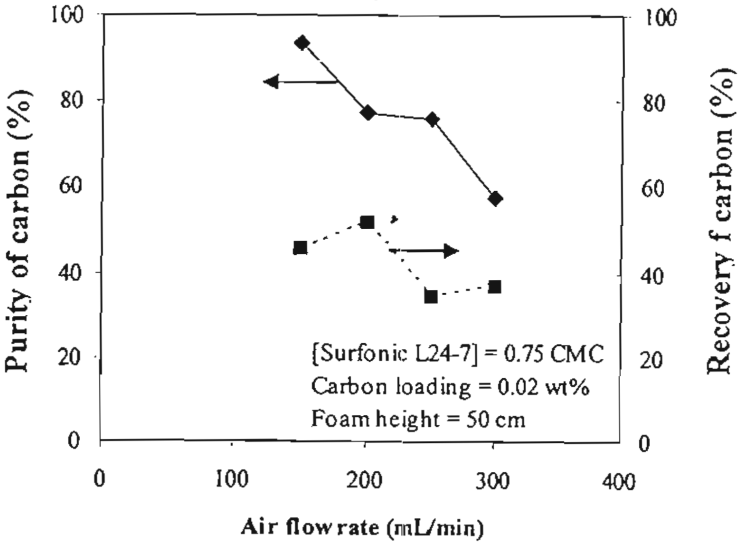


Figure 7. Effect of air flow rate on separation efficiency

in this study, air flow rate cannot be reduced to lower than 150 mL/min because no foam overflows from the column.

Effect of foam height

The separation efficiency as a function of foam height is shown in Figure 8. The purity of carbon increases from around 80 to 90% when foam height increases within the range of studied. As the foam height increases, foam has a longer retention time to stay in the froth zone before it overflows from the column. Hence, silica that has been carried to the foam lamellae is possible to be drained out of foam lamellae due to the gravitational force resulting in the improvement of purity. For the recovery of carbon, the maximum recovery was observed at a foam height of 50 cm. At a lower foam height, carbon has longer residence time to move from the bottom of the column to the froth zone because of the higher solution level. Therefore, some portion of carbon could be entrained back to the solution as a result of fluid circulation in the column. However, the recovery is decreased with further increasing foam height or decreasing solution height, because the residence time of carbon in the froth zone increases. Consequently, to achieve the maximum separation efficiency, foam height should be optimized.

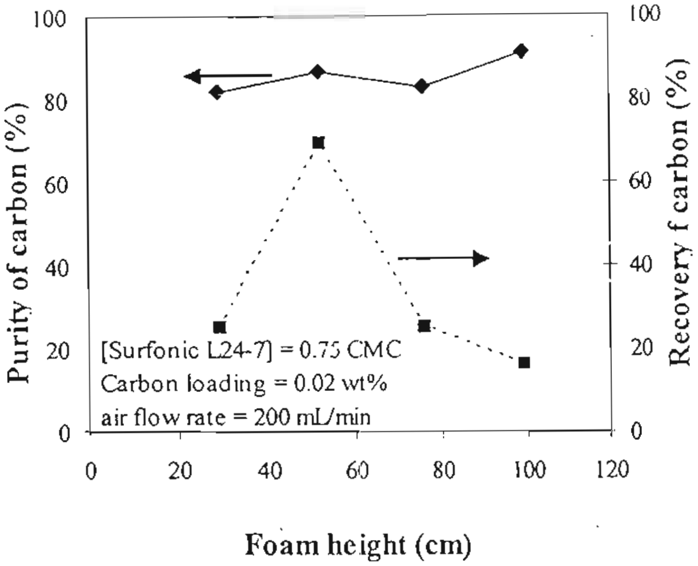


Figure 8. Effect of foam height on separation efficiency

CONCLUSIONS

In this study, the novel technique which is froth flotation operation for purification of single-walled carbon nanotubes was introduced. However, to focus only on the important parameters in froth flotation technique without effect of interaction between SWNT and catalytic support, carbon black which is physically blended with silica was used in this work as a model for purification. To achieve high separation efficiency, surfactant concentration should be lower than 1 CMC whereas a lower air flow rate yields a higher separation efficiency. Moreover, foam height should be optimized while carbon loading does not significantly affect the separation efficiency.

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PROGRAM & ABSTRACTS

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Effect of Interfacial Tension and Foam Characteristics on Diesel Removal in Froth Flotation Operation

On-line Number 256

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ABSTRACT

Froth flotation is one of surfactant based separation processes which is suitable for dilute wastewater treatment. There are several advantages such as low space requirement, high removal efficiency, flexibility for various pollutants at different scales, and low cost. To achieve high performance for froth flotation, the combination of ultra-low interfacial tensions between oil and water and stable foam production must be achieved. To get the ultra-low interfacial tensions, Winsor type's III microemulsion or middle phase has to be formed. In this study, branched alcohol propoxylate sulfate sodium salt with 14 – 15 carbon and 4 PO groups (Alfoterra 145 – 4PO) was used to form microemulsion formation with diesel. The effects of surfactant concentration and NaCl concentration on phase study, foam characteristics, and performance of froth flotation operation were investigated in this work. An increase in surfactant concentration decreases interfacial tension (IFT), but increases foam stability. For the effect of NaCl concentration, the minimum IFT was achieved at 5 wt% NaCl. However, this optimum salinity cannot be operated in froth flotation experiment due to poor foam characteristics. Therefore, both IFT and foam characteristics should be optimized to achieve high efficiency of froth flotation.

KEYWORDS

Froth Flotation, ultra-low interfacial tension, Foam characteristics, Microemulsion with diesel

INTRODUCTION

In the presence, a number of vehicles have been increasing rapidly affecting the amount of fuel usage. Diesel comsumption seems is much higher than gasoline consumption. This may be because diesel provides more energy per unit volume than gasoline does (State Home Page, April 2004). In United State and Latin America, diesel is used primarily for the transportation of goods. However, In Europe, Japan, and elsewhere, diesel is a significant source of energy for personal transportation (UPO Home Page, April 2004). The demand for diesel is forecasted to grow faster than the demand for energy in general. Therefore, diesel has high possibility to contaminate in water by leakage from gas station or underground storage tank.

To remove diesel from water, froth flotation is focused in this work. Firstly, froth flotation was utilized to separate the desired ore from unwanted substrates in the mineral processing process (Yarar, 1997). However, nowadays, froth flotation technique is widely employed in wastewater treatment application (Nabih, et al., 2003 and Walcarius, et al., 2001), and also in paper deinking processes (Zhu, et al., 1998 and Moon, et al., 1998). There are 2 main types of froth flotation which are dissolved air flotation and induced air flotation. In this work, induced air flotation was focused. Filtered air is introduced into the solution through sintered glass disk. Air bubbles generated in the solution are keys for successful separation. Droplets of emulsified oil which have hydrophobic surfaces can co-adsorb at the bubble surfaces which are also hydrophobic and can rise to the froth zone (air/bubble interface) with air bubbles. However, the stability of these bubble-droplet aggregations is low since pure liquid cannot form foam (Rosen, 1989) leading to lower separation efficiency. To achieve higher separation efficiency, surfactant is added into the solution because surfactant can stabilize foam. Chang et al. (Chang, et al., 2000) reported that the surfactant concentration should be adjusted to maintain the foam stability.

To achieve high separation efficiency, a proper amount of surfactant added into the solution is needed. In previous work (Pondstabodee, et al., 1998), it was found that the maximum oil removal corresponds to the formation of Winsor Type III microemulsion. This seems to be starting point of our group to further investigate the relationship between froth flotation and Winsor Type III microemulsion. Therefore later, Chavadej *et al.* (2004) investigated the main source of oil removed from flotation column. They found that most oils removed from the column came from excess oil phase rather than middle phase in Winsor Type III microemulsion. After that, Yanatatsaneejit *et al.* (2004) hypothesized that the maximum oil removal was achieved because of the ultra-low interfacial tension characteristic in Winsor Type III microemulsion. However, they found that interfacial tension is not the sole factor affecting the performance of froth flotation, foam characteristics are also important on flotation efficiency. In this work, the performance of froth flotation to remove diesel from wastewater as function of interfacial tension and foam characteristics was investigated systematically.

MATERIALS AND METHODS

The model oil in this study was commercial grade of diesel obtained from The Petroleum Authority of Thailand (PTT). The studied surfactant was branched alcohol propoxylate sulfate sodium salt (Alfoterra 145-4PO) which is not yet commercially available. It is specially synthesized by Sasol Company (formerly Condea Vista Company), Rosebank, South Africa. Analytical purity grade sodium chloride (NaCl) from Aldrich Chemical Company Inc. was used as electrolyte in this work. All chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

To investigate the phase behavior of microemulsions, 5 mL of homogeneous aqueous solution, prepared at various surfactant concentrations and NaCl concentrations, was mixed with 5 mL of diesel in a vial sealed with a screw cap. The vials were shaken every day for 3 days, and then allowed to equilibrate at a constant temperature of 30°C in a water bath for 1 month to reach equilibrium, which was verified by the invariant height of each phase. The interfacial tensions between equilibrated excess oil and excess water phases were measured by a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg).

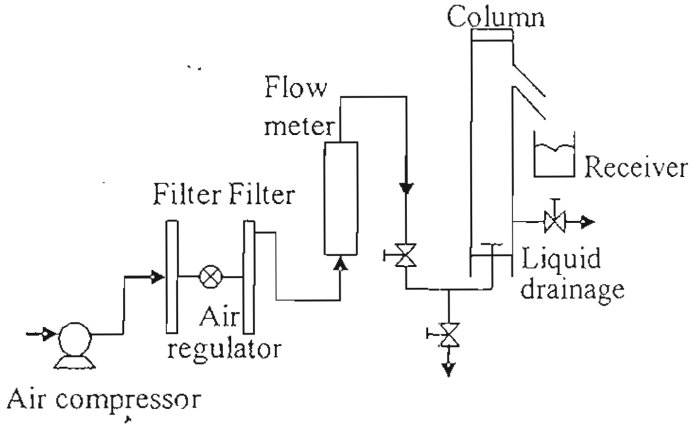

Figure 1. Schematic diagram of the froth flotation apparatus

A schematic diagram of the froth flotation unit used in this work is shown in Figure 1. A glass cylindrical column with 5 cm internal diameter and 120 cm height was used as the froth flotation column. A 750 mL sample with an initial oil:water ratio of 1:1 and various surfactant and NaCl concentrations which had been equilibrated at 30°C for 1 month in the incubator, was transferred to the froth flotation column. Filtered air at a flow rate of 300 mL/min was introduced at the bottom of the column through a sintered glass disk having pore size diameters about 16 – 40 μm. The generated air bubbles rose through the solution to the top of the column. The foam collected in the receiver over a period of time was broken by freezing for diesel concentration analysis. Moreover, the solution in the column was sampled at the same time interval as the foam collected for analysis of diesel and surfactant concentrations. All experiments were stopped when solution surfactant concentrations became too low that no more foam came overhead from the column.

In order to obtain a better understanding about the phenomena in the froth flotation process, foamability and foam stability experiments were conducted in the same flotation column. A 250 mL sample containing a given surfactant concentration and an oil to water ratio of 1:1 was transferred to the column. Filtered air was introduced at the bottom of the column through the solution at a constant flowrate of 100 mL/min until the maximum foam height in the column was achieved. The maximum foam height was then measured. Then the filtered air was stopped introducing to the column, and the time required for the foam volume to collapse to half of the maximum height was recorded to quantify foam stability. All experiments of froth flotation operation, foamability, and foam stability were conducted at a room temperature of about 25 – 27° C.

RESULTS AND DISCUSSION

In this study, wt% is based upon the aqueous system consisting of water, salt, and surfactant. The ratio of maximum foam height to initial solution height is considered as foamability while foam stability ($t_{1/2}$) is defined as the time required for the foam to collapse to half of the maximum height.

Phase behavior study

Interfacial tensions (IFT) is one of the major factors affecting the performance of froth flotation operation. To achieve high separation efficiency, a reduction of the system IFT is required. Figure 2 shows the effect of initial surfactant concentration on IFT value. At 3 wt% NaCl concentration, increasing Alfoterra 145 – 4PO concentration decreases IFT between oil and water because a number of micelles increases whereas IFT is vise versa (Huh, 1983). However, Alfoterra 145 – 4PO concentration cannot be increased to more than 0.15 wt% because macroemulsion is formed rather than microemulsion. As a result, the optimum surfactant concentration in a range of ultralow IFT (less than 10^{-2} mN/m) was not achieved.

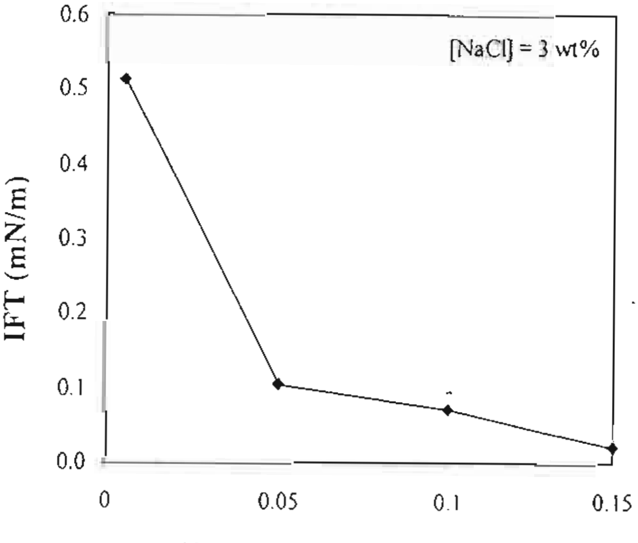

Figure 2. Effect of surfactant concentration on IFT

The Alfoterra 145 – 4PO concentration of 0.1 wt% was selected to elucidate the effect of NaCl concentration on IFT. As shown in Figure 3, the minimum IFT was achieved at 5 wt% NaCl. The explanation of the effect of NaCl concentration on IFT was already discussed in our previous work of ethylbenzene (Yanatatsaneejit, et al. 2004a).

Foam characteristics

As described in previous work (Yanatatsaneejit, et al. 2004a and Yanatatsaneejit, et al. 2004b), removal efficiency of oil in froth flotation operation is also influenced by foam characteristic (foam formation and foam stability). Therefore, the higher the foamability and the foam stability, the higher the oil removal should be obtained. Figure 4 shows the effects of Alfoterra 145 – 4PO concentration on foam stability and foamability. Foam stability tends to increase with increasing Alfoterra 145 – 4PO concentration because more surfactants adsorb at the surface of air bubbles. Therefore, the repulsive force between surfactants increases, and foam stability also increases. In addition, when Alfoterra 145 – 4PO concentration increases from 0.005 to 0.10 wt%, foamability increases. However, foamability decreases when the surfactant concentration further increases to 0.15 wt%. At low Alfoterra 145 – 4PO concentrations, formability increases with Alfoterra 145 – 4PO concentration because foam stability increases. However, when Alfoterra 145 – 4PO concentration further increases greater than 0.1%, a thicker foam lamellae is formed causing a higher water content in the foam. As a result, foamability decreases.

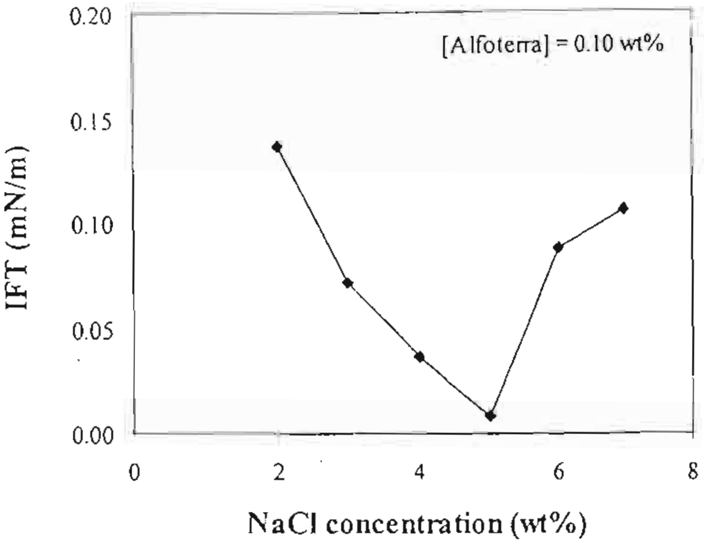

Figure 3. Effect of NaCl concentration on IFT

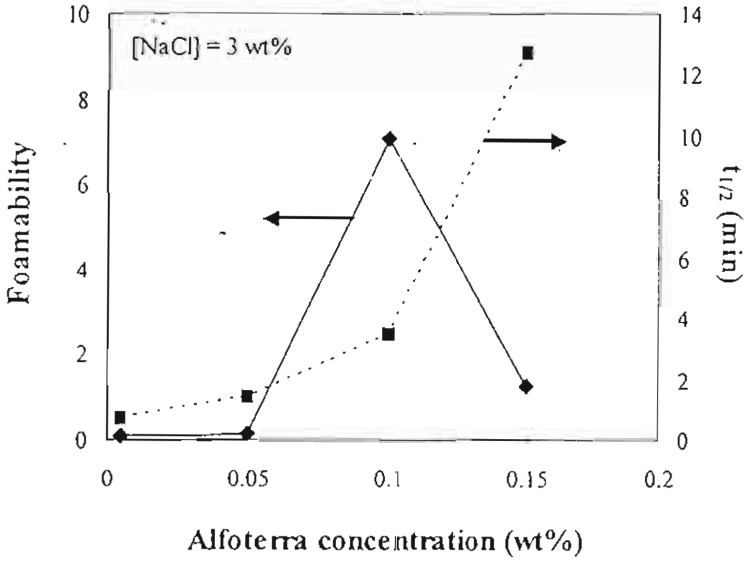

Figure 4. Effect of surfactant concentration on foamability and foam stability ($t_{1/2}$)

For the effect of NaCl concentration on foam characteristics, the descent of foam stability was observed when NaCl concentration increases as shown in Figure 5. This is because the negative charge of surfactant is neutralized by the positive charge of NaCl, causing decreasing repulsive force between head groups of surfactant. The distance between two bubbles becomes closer until the critical distance is reached resulting in coalescence of these bubbles. In case of foamability, it increases rapidly when NaCl concentration increases from 2 to 3 wt%. However, farther increasing NaCl concentration to 4 wt% substantially decreases foamability. Increasing NaCl concentration from 2 to 4 wt% causes lower interfacial tensions as in Figure 3. Therefore, at 3 wt% NaCl, the system needs less energy to form air bubbles within the liquid solution than 2 wt% NaCl does and so foams are easily formed in 3 wt% NaCl system as compared to those in 2 wt% NaCl system. However, even though the interfacial tensions of 4 wt% NaCl is much lower than that of 2 and 3 wt% NaCl, but foamability of 4 wt% NaCl is the lowest because foam stability of 4 wt% NaCl is the lowest. Consequently, to achieve high foamability, both of the interfacial tensions and foam stability have to be optimized.

Froth flotation

As shown in the previous work (Yanatatsaneejit, et al. 2004a), three parameters which are oil removal, surfactant removal, and enrichment ratio of oil are defined as the performance of froth flotation. Figure 6 shows the effect of Alfoterra concentration on IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability and foam stability. Similar to ethylbenzene system (Yanatatsaneejit, et al. 2004a), the total cumulative diesel removal is the highest at the Alfoterra concentration corresponding to the maximum foamability and foam stability but not the minimum IFT. The similar result of the Alfoterra removal was also found. This result implies that IFT is not the sole factor affecting performance of froth flotation. Actually, IFT should be reduced to the critical value to enhance the amount of oil attached with foam. However, for system having IFT lower than the critical value, the effect of foam characteristic on the performance of flotation is dominant.

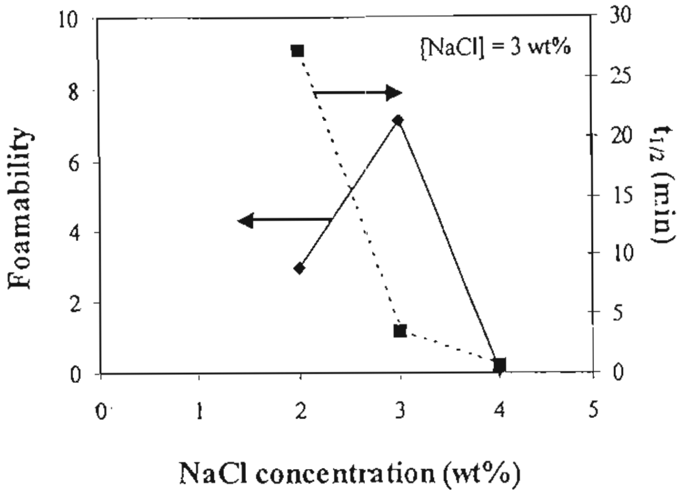

Figure 5. Effect of NaCl concentration on foamability and foam stability ($t_{1/2}$)

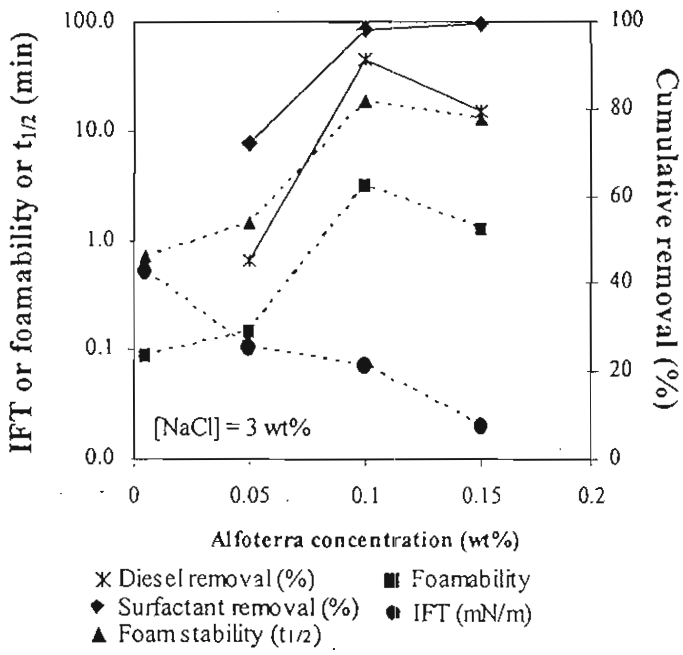

Figure 6. Effect of surfactant concentration on process parameters

IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability, and foam stability as function of NaCl concentration are depicted in Figure 7. The maximum diesel and Alfoterra removals correspond to the highest foam stability. From Figure 7, the removal efficiencies of diesel and Alfoterra are not significantly affected by NaCl concentration in the range of 2 to 3 wt%. This is because the trade-off between foamability and foam stability. However, at NaCl concentration above 3 wt%, NaCl concentration substantially affects the removal efficiency since both foamability and foam stability are extremely low. From the effect of both Alfoterra concentration and NaCl concentration, foam characteristics and IFT seem to be principal parameters affecting the performance of froth flotation

CONCLUSIONS

In this study, the induced air flotation was investigated to remove diesel from wastewater. There are 3 parts of experiment in this work which are phase behavior, foam characteristics, and froth flotation operation. The effects of surfactant and NaCl concentrations on all 3 parts were studied. The optimum surfactant concentration was not achieved in this work because macroemulsion was formed at high surfactant concentrations. The highest diesel removal corresponds to the maximum foamability and foam stability but not the minimum IFT. Therefore, it can be concluded that in froth flotation operation, IFT is not the sole factor to obtain good separation efficiency but foam characteristic have to be taken into consideration in froth flotation operation.

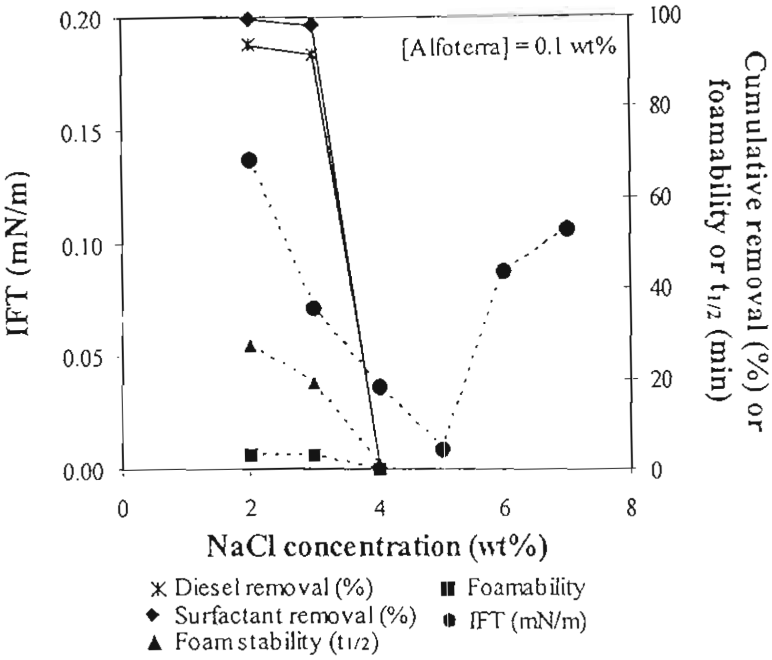

Figure 7. Effect of NaCl concentration on process parameters

ACKNOWLEDGEMENTS

The Thailand Research Fund is acknowledged for providing a Royal Golden Jubilee Ph.D. grant to Ms. Ummarawadee Yanatatsaneejit as well as providing a research grant under TRF Advanced Research Scholar. The Research Unit of Applied Surfactants for Separation and Pollution Control supported by the Ratchadapiseksompoch Fund from Chulalongkorn University and the Petroleum and Petrochemical Technology Consortium under the Minister of Education are also acknowledged for providing financial support and facilities, respectively. Financial support for this research was also received from the industrial sponsors of the Institute for Applied Surfactant Research including Akzo Nobel Chemicals Inc., Clorox Company, Colgate-Palmolive, Dial Corporation, Dow Chemical Company, Halliburton Services Corp., Huntsman Corporation, Kerr-McGee Corporation, Lubrizol Corporation, Phillips Petroleum Company, Pilot Chemical Company, Procter & Gamble Company, Schlumberger Technology Corp., Shell Chemical Company, and Unilever Inc. Sasol Company is also acknowledged for providing surfactant used in this study.

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TECHNICAL PROGRAM IN BRIEF

	Monday August 18, 2003	Tuesday August 19, 2003	Wednesday August 20, 2003	Thursday August 21, 2003
REGISTRATION	Foyer A 8:30-9:30			
(OWR)	Room A 9:30-10:00			
Plenary	Room A 10:00-10:40			
Workshop-I	Room A 11:00-17:40			
BioTech-I	Room B 11:00-12:40			
Separation-I	Room B 14:00-15:40			
BioTis	Room B 16:00-17:40			
BioTech-II		Room A 9:00-10:10		
Keynote		Room A 10:10-10:40		
Separation-II		Room B 9:00-10:40		
Microreactors-I		Room A 11:00-12:40		
Env. Tech.-I		Room B 11:00-12:40		
Energy-I		Room A 14:00-15:40		
Workshop-II		Room B 14:00-17:30		
Energy-II		Room A 16:00-17:40		
Microreactors-II			Room A 9:00-10:40	
Particle Tech.			Room B 9:00-10:40	
Chemical Reactor-I			Room A 11:00-12:40	
Env. Tech.-II			Room B 11:00-12:40	
Chemical Reactor-II			Room A 14:00-15:40	
Env. Tech.-III			Room B 14:00-15:40	
Catalysis			Room A 16:00-17:40	
Env. Tech.-IV			Room B 16:00-17:40	
Open Forum- Discussion			Room A 17:40-18:30	
Chemical Reactor-III				Room B 9:00-10:40
Uni. Lab Visit - Closing				University 11:00-12:40
Ref. Break (Morning)	10:40 – 11:00	10:40 – 11:00	10:40 – 11:00	10:40 – 11:00
Ref. Break (Afternoon)	15:40 – 16:00	15:40 – 16:00	15:40 – 16:00	
Lunches	12:40 - 14:00	12:40 - 14:00	12:40 - 14:00	
Welcoming Reception	19:30 - 22.30			
Symposium Banquet		19:30 – 22.30		

PROCESS INTENSIFICATION OF WASTEWATER TREATMENT THROUGH SECONDARY BIOMASS FILTRATION, Trond E. Bustnes, C. F. Kaminski and M. R. Mackley, University of Cambridge, UK (on page 68)

EFFECT OF MICROEMULSION FORMATION ON OILY WASTEWATER TREATMENT BY USING FROTH FLOTATION TECHNIQUE, U. Yanatatsaneejit, W. Phoochinda, P. Ratanarojanatam, S. Chavadej, and J.F. Scamehorn, Chulalongkorn University, Thailand, The U of Okl., USA (on page 69)

p-AZO-SUBSTITUTED CALIX[4]ARENES AS "PROTON-SWITCHABLE" EXTRACTANTS FOR DICHROMATE ANIONS, Hasalettin Deligöz, Mine Sulak Ak, Mustafa Tabakci and Mustafa Yılmaz, Pamukkale University, Turkey, Selçuk University, Turkey (on page 70)

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Chair:

14:00 – 15:40

FORMATION AND INTERFACIAL PROPERTIES OF WATER-IN-SUPERCRITICAL CO_2 MICROEMULSIONS WITH FLUORINATED SURFACTANTS, Masanobu Sagisaka, Satoshi Yoda, Yoshihiro Takebayashi, Katsuto Otake, Yukishige Kondo, Norio Yoshino, Hideki Sakai, Masahiko Abe, Tokyo University of Science; JAPAN, Institute for Green Technology, JAPAN (on page 71)

MORPHOLOGY EFFECT OF NANO-TITANIUM DIOXIDE PREPARED BY MICROEMULSION TECHNIQUE ON PHOTOCATALYTIC DECOMPOSITION OF PHENOL, T. Anukunprasert & C. Saiwan, Chulalongkorn University, Thailand (on page 72)

SORPTION OF COPPER AND NICKEL BY NATURAL HUMIC ACID OBTAINED FROM LIGNITES,G. Arslan, S. Cetin and E. Pehlivan, Selcuk University, Turkey (on page 73)

BIOSURFACTANT ENHANCED TREATMENT OF SOILS CONTAMINATED BY PETROLEUM OILS IN A PACKED COLUMN, Kingsley Urum, and Turgay Pekdemir, Heriot-Watt University, UK (on page 74)

15:40 – 16:00 Refreshment Break

→ Room B: **ENV. TECH.-IV**

Chair:

16:00 – 17:40

OILY SOIL DETERGENCY MECHANISM RELATED TO LOW INTERFACIAL TENSIONS IN MICROEMULSION FORMATION, C. Tongcumpou, E.J. Acosta, L.B.Quencer, A.F. Joseph, J. F. Scamehorn, D.A. Sabatini, S. Chavadej and N. Yanumet, Chulalongkorn University, Thailand, University of Oklahoma, USA, The Dow Chemical Company, USA (on page 75)

BIOSURFACTANT ENHANCED TREATMENT OF SOILS CONTAMINATED BY PETROLEUM OILS USING STIRRED TANK REACTORS, Kingsley Urum, and Turgay Pekdemir, Heriot-Watt University, UK (on page 76)

MECHANISM OF ANOMALOUS PHASE TRANSITION BEHAVIOR IN THE MIXED SURFACTANT SYSTEM, Hisanori Nakanishi, Koji Tsuchiya, Hideki Sakai, Masahiko Abe, Tokyo University of Science, Japan (on page 77)

LIGHT OIL REMOVAL FROM WASTEWATER BY MIDDLE PHASE MICROEMULSION AND FROTH FLOTATION, A. Witthayapanyanon, U. Yanatatsaneejit, J. F. Scamehorn, and S. Chavadej, Chulalongkorn University, Thailand, University of Oklahoma, USA (on page 78)

EFFECT OF MICROEMULSION FORMATION ON OILY WASTEWATER TREATMENT BY USING FROTH FLOTATION TECHNIQUE

U. Yanatatsaneejit[1], *W. Phoochinda*[1], *P. Ratanarojanatam*[1], *S. Chavadej*[1], *and J.F. Scamehorn*[2]

[1]The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand
[2]Institute for Applied Surfactant Research, The University of Oklahoma, Norman, Oklahoma 73019, USA

ABSTRACT

The relationship between phase behavior and efficiency of froth flotation of ortho-dichlorobenzene removal was investigated. In this work, high selectivity for oil compared to water in the overhead froth was demonstrated. In order to determine the source of removed oil, the froth flotation experiment was performed with three systems; excess water-middle phases (w-m), excess water-oil phases (w-o), and excess water-middle-excess oil phases (w-m-o). The results showed that most of the oil removed came from the excess oil phase in Winsor Type III.

INTRODUCTION

Nowadays, the presence of organic contaminants derived from the chemical industry found in wastewaters and groundwater is a major concern (1). Halogenated organic compounds are not only found in many wastewaters, but also appear extensively in groundwater and soil as a result of the improper designs of hazardous waste disposal facilities, accidental spills, and leakage of underground storage tanks (2).

Froth Flotation is widely used in several separation processes (3 – 12). In flotation operation, air is sparged into the solution, and the particles of solids or droplets of oils adhere to the rising air bubbles. These particles or droplets adhered to the air bubbles are concentrated in the foam or froth at the top of the flotation cell, and are finally skimmed off.

The surfactant added tends to strongly adsorb at the air-water interface with the hydrophobic or tail groups in the air and the hydrophilic or head groups in the water. The hydrophobic region formed by the tail groups of the surfactant is compatible for dissolved organic solutes which tend to co-adsorb at the bubble surface. Polar regions of the solute molecule can interact with the surfactant head groups, affecting solute adsorption at the air-water interface (13).

A microemulsion is described as a transparent or translucent system formed spontaneously upon mixing oil and water with a relatively large amount of an ionic surfactant (14). In this study, an anionic surfactant was used to mix with nonionic surfactant instead of a cosurfactant (e.g. an alcohol of medium chain length). There are four types of microemulsions classified by Winsor (15). Winsor Type III microemlsion, one of the types of microemulsions, was focused in this work because the previous work (3) showed that the maximum percentage of oil removal was achieved when Winsor Type III was present. When middle-phase microemulsion or Winsor Type III is formed, ultralow oil-water interfacial tension (i.e. 10^{-3} mN/m) is observed. The optimum salinity at which equal volumes of brine and oil are solubilized in the middle-phase microemulsion is known as an optimum condition in the enhanced oil recovery (3). This condition corresponds to the maximum solubilizing power of surfactant and the minimum of interfacial tension (16).

EXPERIMENT

Materials

Sodium dodecyl sulfate (SDS) and nonylphenol ethoxylate ($NP(EO)_{10}$) were used in this study. SDS supplied by Henkel Co. was a commercial grade with a purity at least 90%. $NP(EO)_{10}$ with 99.9% purity was supplied by ICI Australia Operations Pty Ltd. Otho-dichlorobenzene (ODCB) from Fisher Scientific Co., with 99% purity was used as emulsified oil. Sodium chloride (NaCl), analytical purity grade, was obtained from Aldrich Chemical Co. Deionized water was used in all of experiments.

Methodology

In both the microemulsion formation and the froth flotation experiments, the surfactant concentration and salinity were expressed as percent by weight of the overall system which comprised water, oil, surfactants, and NaCl. The experiments were conducted at 30°C.

Phase behavior experiments

To investigate the phase behavior, surfactant solutions were prepared with different concentrations of each surfactant and of salt in a water phase. Then 5 mL of this aqueous solution was mixed with 5 mL of ODCB in a vial and sealed with a screw cap. The series of samples with different surfactant concentrations and salinities were well mixed by shaking and kept in a constant temperature of 30°C until equilibrium was reached as indicated by invariant phase volumes. The equilibrium time was about 4 weeks. The height and appearance of each phase were measured and observed.

Froth flotation experiments

The froth flotation apparatus used in this study was consisted of a cylindrical glass column with 5 cm inside diameter and 70 cm height. A constant flowrate of 250 mL/min of filtered air was introduced into the bottom of the column through the sintered glass disk having pore diameters of 16 – 40 μm. One liter of well mixed solution at 5% total surfactant concentration and 1/1 of ODCB/water volume ratio was immediately transferred to the column to study the selectivity of oil to water in the overhead froth. To study the source of oil removed, after reaching equilibrium in water bath at 30°C for 1 month, the solution consisted of 5% total surfactant concentration and 1/1 of ODCB/water was separated into middle (m), excess oil (o), and excess water (w) phases. Three systems of w-m phases, w-o phases, and w-m-o phases were prepared by using 1/1 volume ratio in each system. The foam overflown from the column was collected over different time intervals. After that, the foam was broken for analysis of the concentration of ODCB by using HPLC with a UV detector. The schematic diagram of froth flotation operation is shown in Figure 1.

RESULTS AND DISCUSSION

For a mixed surfactant system, a weight fraction of SDS (X_{SDS}) is defined as a weight of SDS divided by the total weight of surfactants ($NP(EO)_{10}$ and SDS).

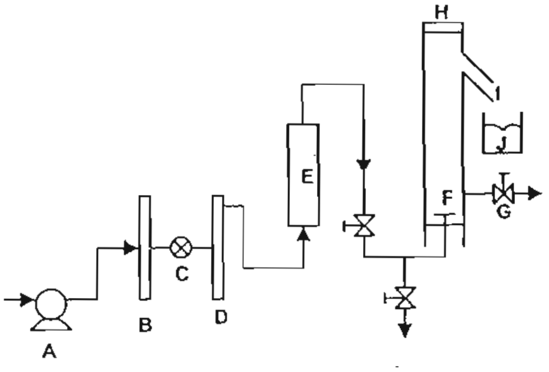
Phase Behavior

Effects of type and concentration of surfactant

As shown in Figure 2, volume of water phase and oil phase slightly increases and decreases, respectively when SDS concentration increases from 1% to 9%. SDS is more hydrophilic and so it mostly dissolves in water resulting in solubilizing oil in the water phase. Under the studied conditions, the middle phase was not formed in the SDS system, so this system is Winsor Type I microemulsion. Figure 3 shows Winsor Type III microemulsion, middle phase, appears when $NP(EO)_{10}$, nonionic surfactant, was used instead of SDS since $NP(EO)_{10}$ has a proper balance between hydrophobicity and hydrophilicity for the ODCB system. A maximum relative volume of the middle phase microemulsion was achieved at 7% of $NP(EO)_{10}$.

Effect of mixed surfactant composition

As shown in Figures 4-8 for any given total surfactant concentration, the volume fraction of middle phase microemulsion in the mixed surfactant system is higher than that in the single $NP(EO)_{10}$ system. The mixed surfactant system showed the synergistic effect on microemulsion formation. At low total surfactant concentrations, 1% and 3%, water was almost insolubilized in the middle phase microemulsion. Therefore, a minimum interfacial tension cannot be achieved under these conditions.



A air compressor	B water filter	C air regulator
D oil filter	E flow meter	F sparger
G liquid drainage	H flotation column	I foam
J receiver		

Fig.1. Schematic diagram of the froth flotation apparatus

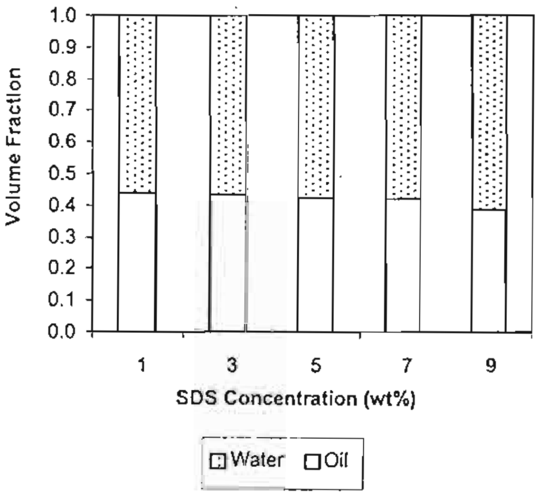


Fig.2. Volume fractions at different SDS concentrations with an initial ODCB/water volume ratio of 1/1

At a high total surfactant concentration of 5% and a SDS weight fraction of 0.5, approximately equal volumes of oil and water were solubilized in the middle phase, indicating a proper balance between hydrophobicity and hydrophilicity. However, at an extremely high total surfactant concentration of 7% or 9%, liquid crystal occurred (see Figures 7 and 8). As a result, 5% total surfactant concentration was selected for the froth flotation operation.

Froth Flotation Results

A total surfactant concentration of 5% with different SDS fractions was selected to run the froth flotation experiment because this system has the highest solubilization parameter for both oil and water as well as the lowest interfacial tension. Figures 9-11 show

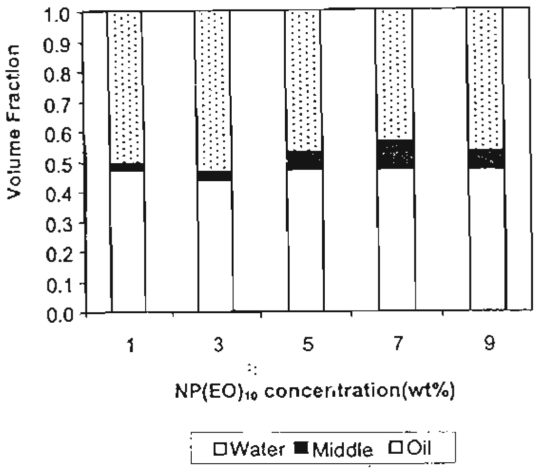


Fig.3. Volume fractions at different NP(EO)$_{10}$ concentrations with an initial ODCB/water volume ratio of 1/1

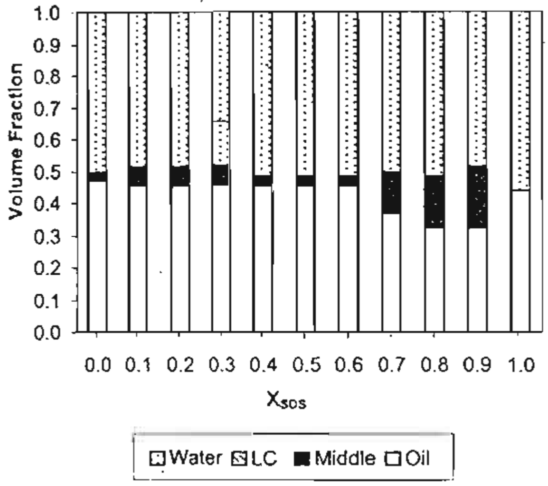


Fig.4. Volume fractions at different SDS fractions of 1% total surfactant concentration, and an initial ODCB/water volume ratio of 1/1

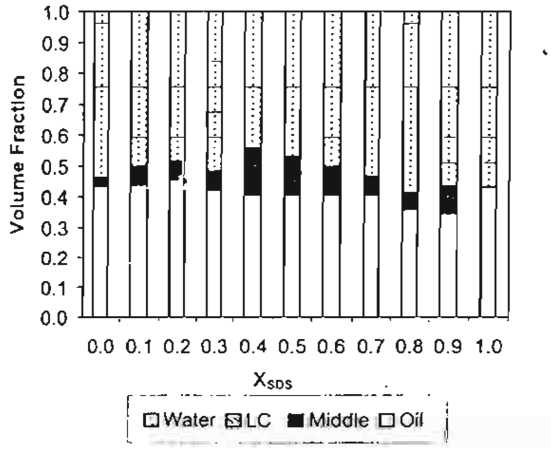


Fig.5. Volume fractions at different SDS fractions of 3% total surfactant concentration and an initial ODCB/water volume ratio of 1/1

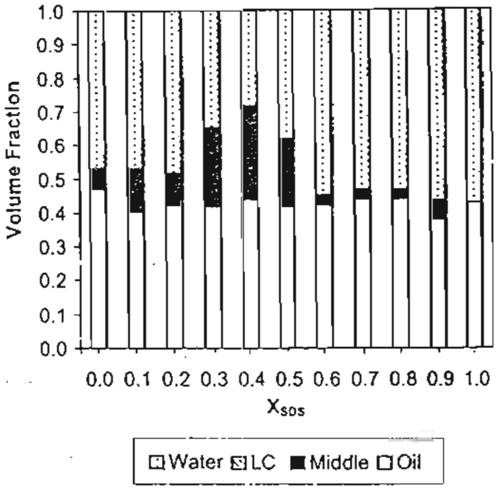


Fig.6. Volume fractions at different SDS fractions of 5% total surfactant concentration and an initial ODCB/water volume ratio of 1/1

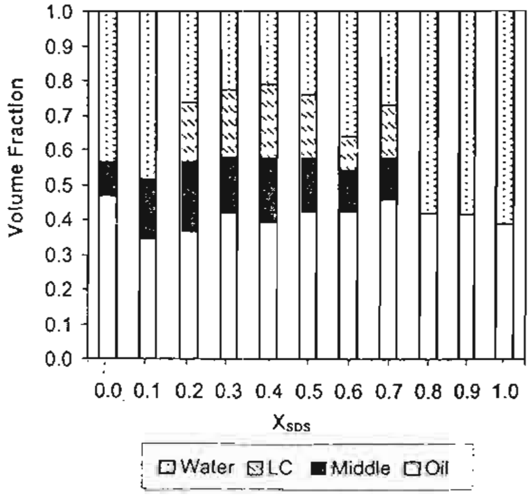


Fig.7. Volume fractions at different SDS fractions of 7% total surfactant concentration and an initial ODCB/water volume ratio of 1/1

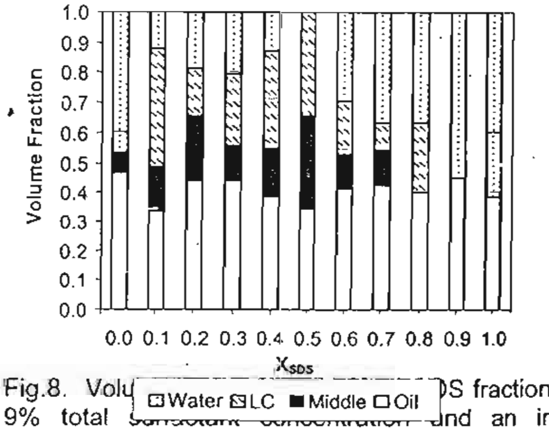


Fig.8. Volu S fractions of 9% total nd an initial ODCB/water volume ratio of 1/1

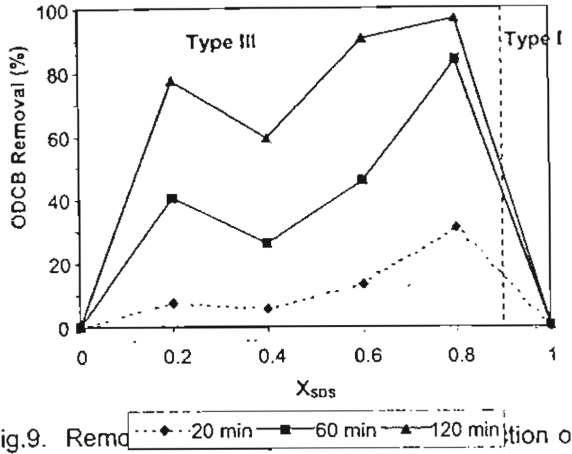


Fig.9. Rem tion of SDS fraction at different time of 5% total surfactant concentration and an initial ODCB/water volume ratio of 1/1

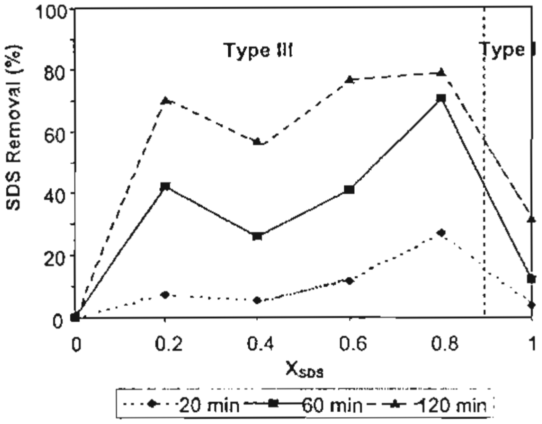


Fig.10. Removal efficiency of SDS as a function of SDS fraction at different times of 5% total surfactant concentration and an initial ODCB/water volume ratio of 1/1

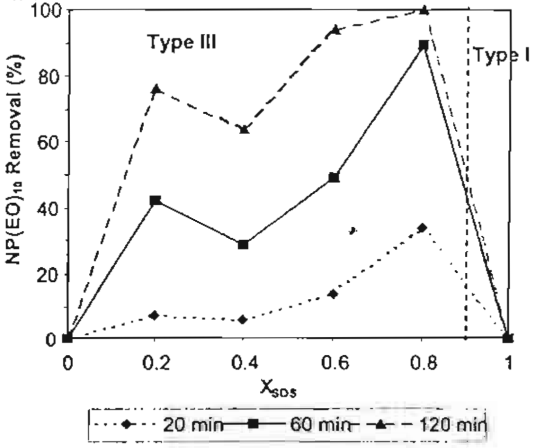


Fig.11. Removal efficiency of $NP(EO)_{10}$ as a function of SDS fraction at different times of 5% total surfactant concentration and an initial ODCB/water volume ratio of 1/1

the effect of SDS fraction on oil and surfactant removals for the system having 5% total surfactant concentration. In the Winsor Type III microemulsion region, increasing weight fraction of SDS tended to increase both oil and surfactant removals because the foam stability with anionic surfactants is generally higher than that with nonionic surfactants. The repulsive force among the head groups of anionic surfactant causes the foam more difficult to collapse as compared to foams formed by nonionic surfactants. In the Winsor Type III microemulsion regime, almost all ODCB and $NP(EO)_{10}$ can be removed from the solution as well as the maximum SDS removal of 80% after 120 minutes of operating time and at a SDS fraction of 0.8 as shown in Figures 9-11. This is because SDS is more hydrophilic than $NP(EO)_{10}$, and then SDS can adsorbs less at the air bubble-water interface than $NP(EO)_{10}$. Since the ultralow interfacial tension between oil and water can be observed in the Winsor Type III microemulsion regime, the maximum removals of ODCB, SDS, and $NP(EO)_{10}$ are expected to obtain in this region. An analogous behavior of oil and surfactant removals has been reported in the previous work (3). Hence, the stability of foam, as well as interfacial tension between liquid phases, are important in froth flotation operation. From the results of the phase study, the optimum condition is achieved at a SDS fraction of 0.5 as shown in Figure 6 while, as shown in Figure 9, the maximum ODCB removal is achieved at a SDS fraction of 0.8. This is because at a SDS fraction of 0.5, the system has low repulsive force between the head groups of surfactants leading to low foam stability compared to that at a SDS fraction of 0.8. From the results, it indicates that foam stability is also another important parameter that should be considered in flotation operation.

High efficiency of oil removal is not a sole factor for an effective flotation operation. The selectivity for oil compared to water in the overhead froth is also a vital factor for successive flotation. If oil and water are present in the overhead froth with the same proportion as in the feed solution, no separation of oil from water is achieved. The relative fractions of oil and of water in the foam phase at 5% total surfactant concentration and at 120 minute aeration time are shown in Figure 12. A higher selectivity for oil compared to water occurred in the Winsor Type III microemulsion regime not in the Winsor Type I microemulsion regime. This result supports the advantages of Winsor Type III microemulsion in flotation operation.

Under Winsor Type III microemulsion, the system consists of three phases of excess oil, excess water, and middle phases. It is very interesting to know what phase is a major source of oil removed. Hence, a solution with Winsor Type III microemulsion was separated then three systems: w-o phases, w-m phases, and w-m-o phases were prepared for flotation experiment. From Figures 13-14, ODCB removal from the w-o system is always higher than that from w-m system. The oil droplets in the Winsor Type III microemulsion phase are known in form of bilayer (17). The surface of the oil droplets in the middle phase becomes less hydrophobic than that in excess oil phase. Hence, the oil droplets in this middle phase are difficult to attach with the air bubbles as compared to those in the excess oil phase. Consequently, oil removal from the Winsor Type III microemulsion phase (middle phase) is lower than that from the excess oil phase.

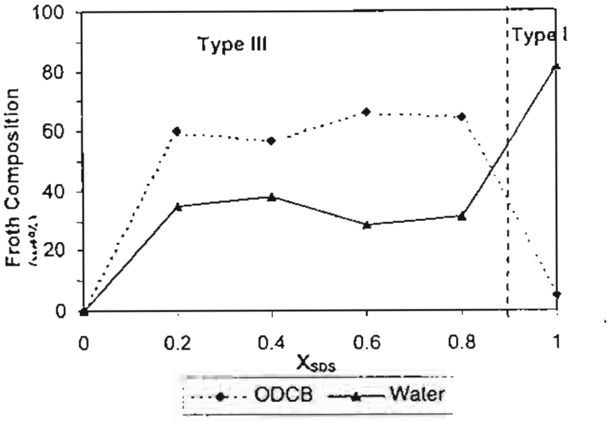


Fig.12. ODCB and water concentrations in foam fraction at different SDS fraction of 5% total surfactant concentration, an initial ODCB/water volume ratio of 1/1, and 120 min aeration time

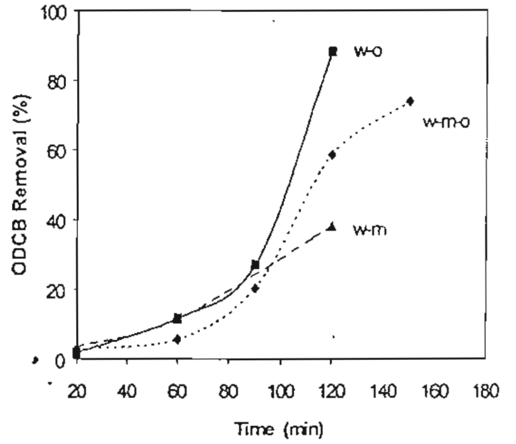


Fig.13. Comparison of ODCB removal of w-m, w-o, and w-m-o systems at different times of 5% total surfactant concentration, X_{SDS} of 0.2, and an initial ODCB/water volume ratio of 1/1

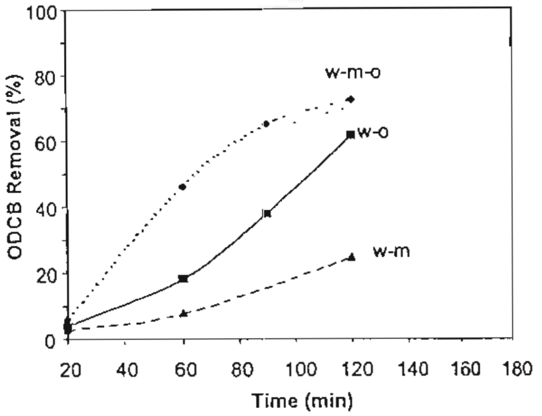


Fig.14. Comparison of ODCB removal of w-m, w-o, and w-m-o systems at different time of 5% total surfactant concentration, X_{SDS} of 0.4, and an initial ODCB/water volume ratio of 1/1

CONCLUSIONS

In previous work (3), the maximum oil removal from flotation process was observed under Winsor Type III microemulsion condition. Although, high oil removal is a necessary need for an effective flotation operation, but other factors should be also considered. From this work, for the system in Winsor Type III, more oil than water was indeed carried over with the foam. Then the separation between oil and water occurred in the overhead froth. To understand the mechanism of synergism between efficiency of flotation and Winsor Type III microemulsion, the source of oil removed was investigated. All studies in this work showed that most of oil removed in the overhead froth came from excess oil phase instead of middle phase.

ACKNOWLEDGEMENT

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PIM-1

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BIOMASS ENERGY

TECHNICAL PROGRAM IN BRIEF

	Monday August 18, 2003	Tuesday August 19, 2003	Wednesday August 20, 2003	Thursday August 21, 2003
REGISTRATION	Foyer A 8:30-9:30			
(OWR)	Room A 9:30-10:00			
Plenary	Room A 10:00-10:40			
Workshop-I	Room A 11:00-17:40			
BioTech-I	Room B 11:00-12:40			
Separation-I	Room B 14:00-15:40			
BioTis	Room B 16:00-17:40			
BioTech-II		Room A 9:00-10:10		
Keynote		Room A 10:10-10:40		
Separation-II		Room B 9:00-10:40		
Microreactors-I		Room A 11:00-12:40		
Env. Tech.-I		Room B 11:00-12:40		
Energy-I		Room A 14:00-15:40		
Workshop-II		Room B 14:00-17:30		
Energy-II		Room A 16:00-17:40		
Microreactors-II			Room A 9:00-10:40	
Particle Tech.			Room B 9:00-10:40	
Chemical Reactor-I			Room A 11:00-12:40	
Env. Tech.-II			Room B 11:00-12:40	
Chemical Reactor-II			Room A 14:00-15:40	
Env. Tech.-III			Room B 14:00-15:40	
Catalysis			Room A 16:00-17:40	
Env. Tech.-IV			Room B 16:00-17:40	
Open Forum- Discussion			Room A 17:40-18:30	
Chemical Reactor-III				Room B 9:00-10:40
Uni. Lab Visit - Closing				University 11:00-12:40
Ref. Break (Morning)	10:40 – 11:00	10:40 – 11:00	10:40 – 11:00	10:40 – 11:00
Ref. Break (Afternoon)	15:40 – 16:00	15:40 – 16:00	15:40 – 16:00	
Lunches	12:40 - 14:00	12:40 - 14:00	12:40 - 14:00	
Welcoming Reception	19:30 - 22.30			
Symposium Banquet		19:30 – 22.30		

PROCESS INTENSIFICATION OF WASTEWATER TREATMENT THROUGH SECONDARY BIOMASS FILTRATION, Trond E. Bustnes, C. F. Kaminski and M. R. Mackley, University of Cambridge, UK (on page 68)

EFFECT OF MICROEMULSION FORMATION ON OILY WASTEWATER TREATMENT BY USING FROTH FLOTATION TECHNIQUE, U. Yanatatsaneejit, W. Phoochinda, P. Ratanarojanatam, S. Chavadej, and J.F. Scamehorn, Chulalongkorn University, Thailand, The U of Okl., USA (on page 69)

p-AZO-SUBSTITUTED CALIX[4]ARENES AS "PROTON-SWITCHABLE" EXTRACTANTS FOR DICHROMATE ANIONS, Hasalettin Deligöz, Mine Sulak Ak, Mustafa Tabakci and Mustafa Yılmaz, Pamukkale University, Turkey, Selçuk University, Turkey (on page 70)

12:40 – 14:00 Lunch Break

→ Room B: **ENV. TECH.-III**

Chair:

14:00 – 15:40

FORMATION AND INTERFACIAL PROPERTIES OF WATER-IN-SUPERCRITICAL CO_2 MICROEMULSIONS WITH FLUORINATED SURFACTANTS, Masanobu Sagisaka, Satoshi Yoda, Yoshihiro Takebayashi, Katsuto Otake, Yukishige Kondo, Norio Yoshino, Hideki Sakai, Masahiko Abe, Tokyo University of Science; JAPAN, Institute for Green Technology, JAPAN (on page 71)

MORPHOLOGY EFFECT OF NANO-TITANIUM DIOXIDE PREPARED BY MICROEMULSION TECHNIQUE ON PHOTOCATALYTIC DECOMPOSITION OF PHENOL, T. Anukunprasert & C. Saiwan, Chulalongkorn University, Thailand (on page 72)

SORPTION OF COPPER AND NICKEL BY NATURAL HUMIC ACID OBTAINED FROM LIGNITES,G. Arslan, S. Cetin and E. Pehlivan, Selcuk University, Turkey (on page 73)

BIOSURFACTANT ENHANCED TREATMENT OF SOILS CONTAMINATED BY PETROLEUM OILS IN A PACKED COLUMN, Kingsley Urum, and Turgay Pekdemir, Heriot-Watt University, UK (on page 74)

15:40 – 16:00 Refreshment Break

→ Room B: **ENV. TECH.-IV**

Chair:

16:00 – 17:40

OILY SOIL DETERGENCY MECHANISM RELATED TO LOW INTERFACIAL TENSIONS IN MICROEMULSION FORMATION, C. Tongcumpou, E.J. Acosta, L.B.Quencer, A.F. Joseph, J. F. Scamehorn, D.A. Sabatini, S. Chavadej and N. Yanumet, Chulalongkorn University, Thailand, University of Oklahoma, USA, The Dow Chemical Company, USA (on page 75)

BIOSURFACTANT ENHANCED TREATMENT OF SOILS CONTAMINATED BY PETROLEUM OILS USING STIRRED TANK REACTORS, Kingsley Urum, and Turgay Pekdemir, Heriot-Watt University, UK (on page 76)

MECHANISM OF ANOMALOUS PHASE TRANSITION BEHAVIOR IN THE MIXED SURFACTANT SYSTEM, Hisanori Nakanishi; Koji Tsuchiya, Hideki Sakai, Masahiko Abe, Tokyo University of Science, Japan (on page 77)

LIGHT OIL REMOVAL FROM WASTEWATER BY MIDDLE PHASE MICROEMULSION AND FROTH FLOTATION, A. Witthayapanyanon, U. Yanatatsaneejit, J. F. Scamehorn, and S. Chavadej, Chulalongkorn University, Thailand, University of Oklahoma, USA (on page 78)

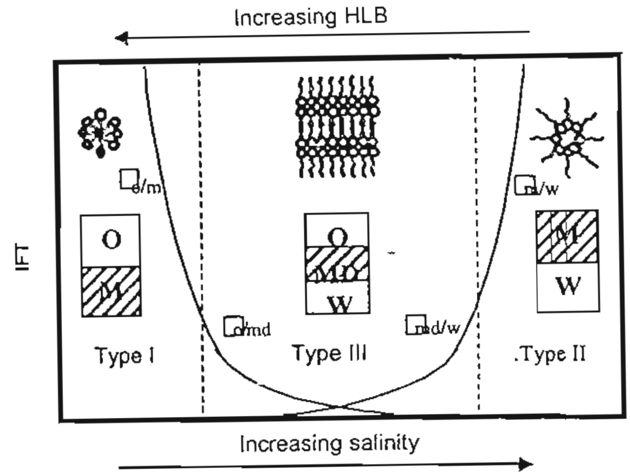

Fig.2. Relationship between phase behavior and IFT

objective of this work was to elucidate which character of type III microemulsion was responsible for oil separation in froth flotation operation.

EXPERIMENT

Materials

Sodium di-1,3-dimethylbutyl sulfosuccinate, AMA (80wt% in mixture of isopropanol and water) was supplied by CYTEX Corporation. Ethylbenzene (greater than 98% purrity) was selected as a light oil contaminant and purchased from Fluka Co. Sodium chloride (AR grade) was used as an electrolyte and purchased from Aldrich Chemical Company,Inc

Procedure

This experimental study was divided into two parts of microemulsion formation and froth flotation. All of the experiment, the concentrations of surfactant and electrolyte were expressed in weight percent of the aqueous solution.

For the microemulsion formation study, it was carried out in a series of 20-ml test tubes with screw caps. 5 ml of ethylbenzene (EB) and 5 ml of surfactant solution were added in flat bottom test tubes sealed with teflon screw caps. The surfactant solution contained different concentrations of AMA and NaCl. The mixed solution were well shaken and left in a water bath at 30 °C until equilibrium was reached (around 3 weeks). The heights of all phases formed were measured by using a cathetometer with 0.01 mm error. IFT of two phases at equilibrium was measured by using a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg).

In the froth flotation study, the experiment was conducted in a batch mode at room temperature (30°C). A schematic diagram of an apparatus used in this study is shown in Fig. 3. The flotation column was a cylindrical glass tube of 5 cm I.D., and 70 cm in height. Two sets of one liter of the well-mixed solution were prepared at desired conditions as equilibrium and non-equilibrium systems. For the non-equilibrium system, after mixing equal volumes of ethylbenzene and surfactant solution, the mixture was suddenly transferred into the column while for the equilibrium system, the mixture was kept in a water bath at 30 °C for 3 weeks before it was transferred to the column. In flotation operation, air bubbles rising through the solution in the column were created by introducing compressed air through a sintered glass disk (40-60μm pore size) at the bottom of the column. The foam overflowed from the column and was collected over a desired period of time. In addition, an induced equilibrium system by shaking the mixture for 40 minutes was also investigated in comparison to the equilibrium and non-equilibrium systems.

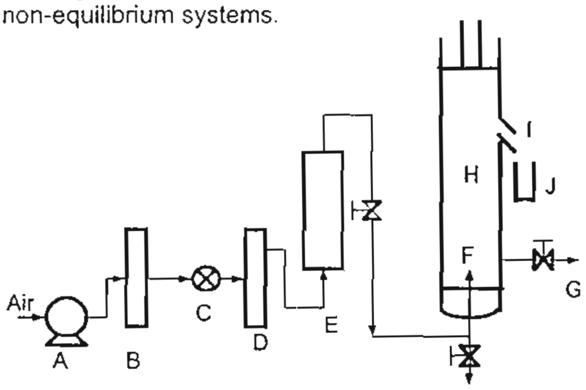

Fig.3. Schematic diagram of froth flotation apparatus (A-air compressor, B-water filter, C-air regulator, D-oil filter, E-flow meter, F-spager, GG-liquid drainage, H-flotation column, I-foam, and J-receiver).

The performance of froth flotation was determined by oil removal. The oil removal was calculated by the following formulation (1):

$$\text{Oil removal (\%)} = [(C_t - C_i)/C_i] \times 100 \qquad (1)$$

where C_t and C_i are the concentrations of oil (EB) in a solution at time t and zero, respectively. The concentration of ethylbenzene was determined by a GC-Headspace. The temperatures of the injector, oven, and detector were 150 °C, 100 °C, and 250 °C, respectively. A flow rate of N_2 carrier gas was fixed at 4 ml/min. The evaluation of all data was done with TCNavigator program.

RESULTS AND DISCUSSION

Microemulsion formation

In this experiment, low AMA concentrations were used to form microemulsion with ethylbenzene because of cost saving. The transformation of microemulsion's type of this system was achieved by salinity scan. As a result of low AMA concentrations, very small volumes of the middle phase were generated leading to difficulty in observing volume change of each phase. The phase behaviors of the studied system are not presented here since this work wants to emphasize the ultra low IFT of type III microemulsion. Fig. 4 shows IFT as a function of salinity at four different AMA concentrations.

From Fig. 4, a low IFT value is obtained in the salinity range of 2-4 % NaCl for various AMA concentrations of 0.3, 1, 2, and 3 %. The minimum IFT of each system was found around 3 % salt. At the optimum point found in the middle phase, IFT was around 10^{-2} mN/m and classified as an ultra-low IFT. The minimum IFT value of each AMA concentration is shown comparatively in Fig. 5. From the result, the lowest IFT was found at 1 % AMA but the minimum IFT value did not vary significantly with AMA concentration.

Froth Flotation Results

Effect of NaCl concentration

As shown in Fig. 6, for the non-equilibrium system at a constant surfactant concentration of 0.3%, dynamic EB removal of the system having 3 % NaCl is much higher than that of 2% NaCl. When the salinity was increased to 4 %, the separation was not achieved (no foam coming out from the column) even though the IFT at 4 % NaCl was significantly lower than 2 % NaCl. The higher the NaCl concentration, the lower the repulsive force between head groups of anionic surfactant is obtained. Consequently, the hydrophobic characteristic of foam surface increases leading to increase in oil attached to the air bubble. However, decreasing repulsive force decreases foam stability. Again, it can be explained that the foam stability becomes lower with increase salinity. Hence, the optimization between the hydrophobic characteristic of foam and the foam stability to obtain the maximum oil separation can be achieved by adjusting salinity.

For equilibrium system, the effect of NaCl concentration on oil removal is shown in Fig. 7. It was found that the system, which reached the equilibrium, used a shorter operation time and got a higher EB removal than the non-equilibrium system did. An increase in salinity decreased the oil removal as a result of salt effect.

Effect of surfactant concentration

From the phase behavior, type III microemulsion was formed at any AMA concentration and a minimum IFT was found at 3 % NaCl concentration. As mentioned before, a difference in surfactant concentration resulted in a different IFT value. Therefore, 0.3 to 3 % AMA concentrations were operated in froth flotation experiment to determine the relationship between IFT and froth flotation operation.

Fig. 8 showed the effect of AMA concentration on oil removal at different times. The highest oil removal

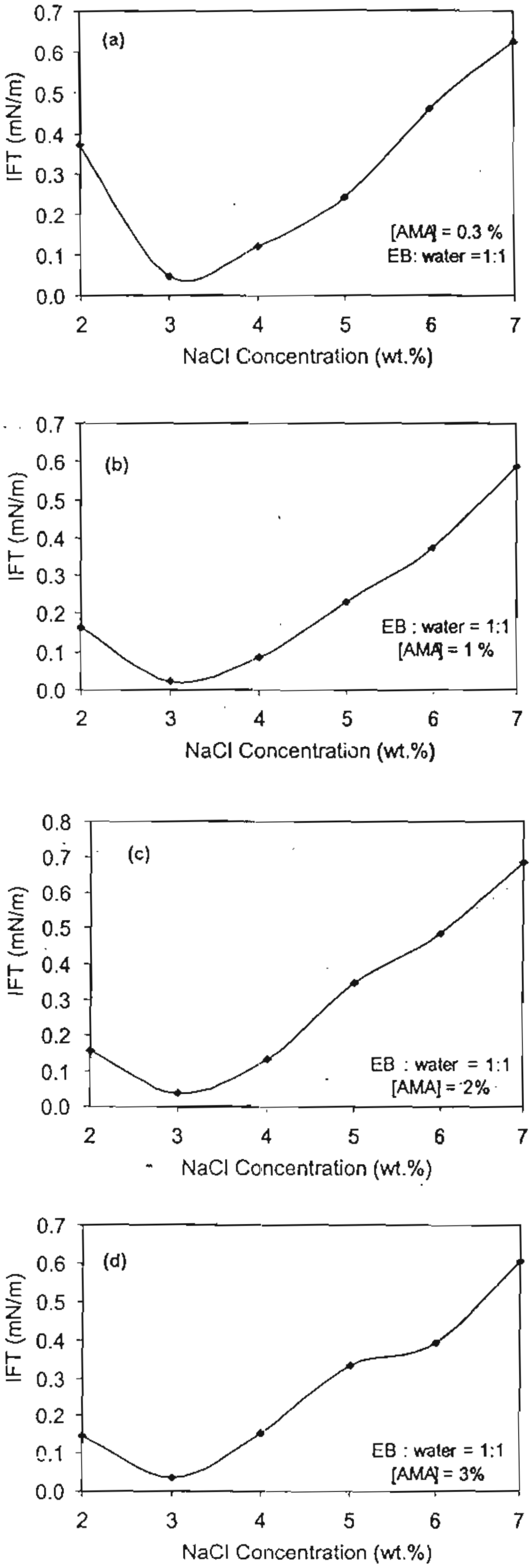

Fig.4. IFT of ethylbenzene-water system as a function of salinities at different AMA concentration

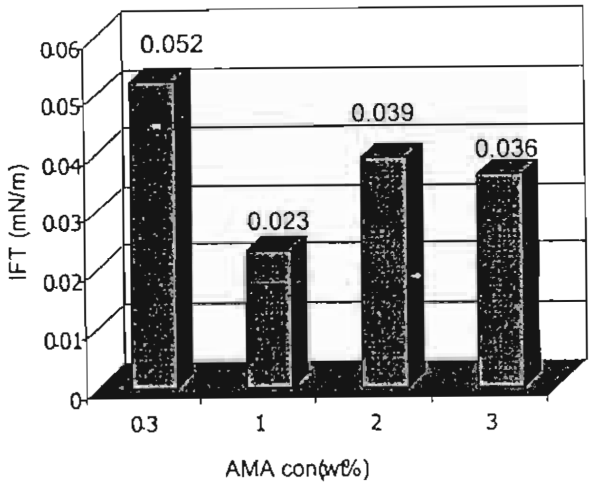

Fig.5. Comparison of Minimum IFT at different AMA concentrations with 3%NaCl concentration and an initial EB:water ratio = 1:1

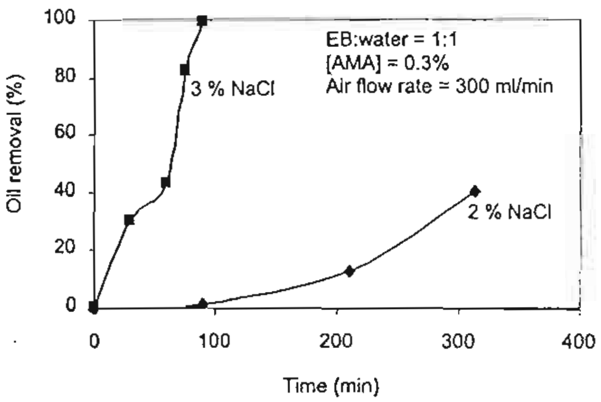

Fig.6. Dynamic removal efficiency of EB of non-equilibrium system at different NaCl concentration.

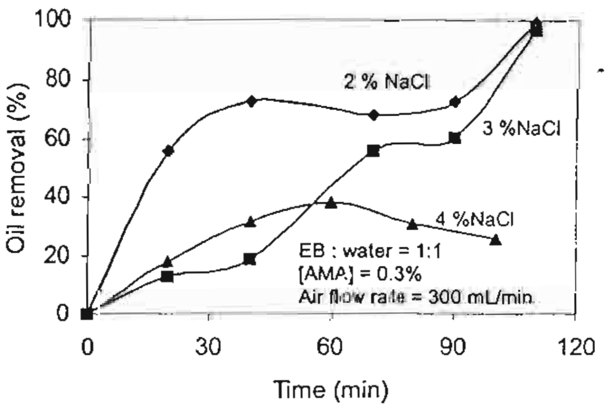

Fig.7. Dynamic removal efficiency of EB of equilibrium system at different NaCl concentration

was found in the system of 0.3 % AMA concentration with the shortest operation time when compared to other systems having higher AMA concentrations. This result deviates from the hypothesis that the maximum oil removal should be found at 1 %AMA due to the lowest IFT (0.023 mN/m). It can be explained that it may have other factors, which affect the operation of froth flotation. The foam ability and foam stability of froth are believed to involve the oil removal efficiency in froth flotation, which will be further studied in our future work.

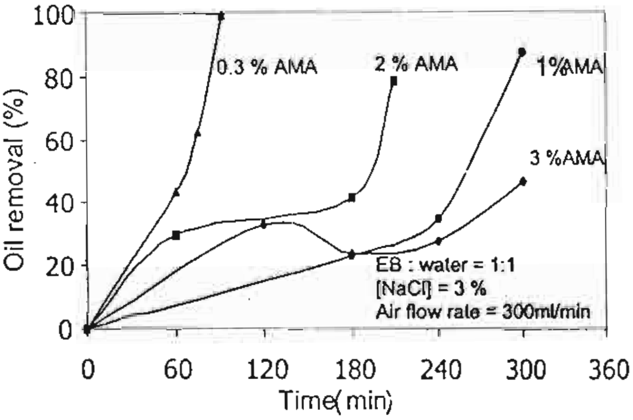

Fig.8. Dynamic removal efficiency of EB of non-equilibrium system at different AMA concentrations

Effect of equilibration time

As shown in Fig. 9, the oil removal of the non-equilibrium system is very much lower than those of both induced equilibrium and equilibrium systems. In addition, the non-equilibrium system took the longest operation time as compared to the other systems. It is because the foam production of the non-equilibrium system was lower than that of the induced equilibrium and the equilibrium systems as shown in Fig. 10. It is interesting to point out that to obtain a high oil removal efficiency, the system has to reach equilibrium. However, a well mixing with a short time may be sufficient to obtain a high oil removal efficiency as closed to that of the equilibrium system.

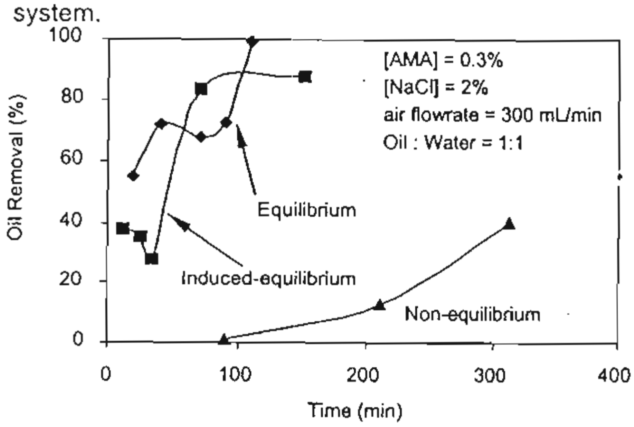

Fig.9. Effect of equilibration time on dynamic oil removal

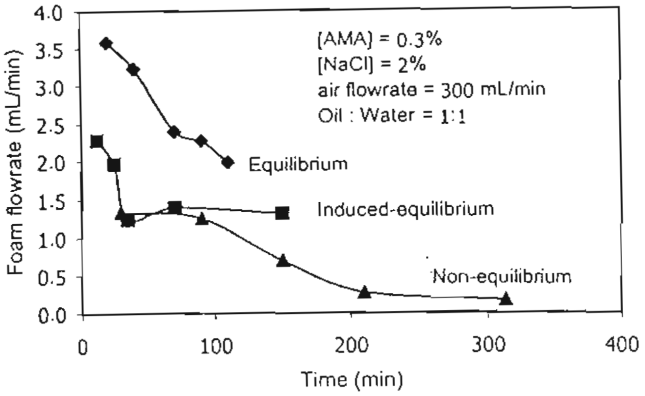

Fig.10. Effect of equilibration time on foam flow rate

CONCLUSIONS

This work has pointed out the ultra-low IFT enhancing the froth flotation efficiency. However, the result showed that the system providing the maximum oil removal did not correspond to the minimum IFT found in the middle phase obtained from the phase study. This result leads to a conclusion that the ultra-low IFT of a type III microemulsion is not a sole factor that affects flotation process. The equilibrium system was found to have a very much higher oil removal than that the non-equilibrium system. A short mixing time of 40 minute was long enough to move the system closed to its equilibrium. Foam stability and foam ability are other parameters should be taken into consideration for froth flotation operation.

NOMENCLATURE

AMA	sodium di-1,3-dimethylbuty sulfosuccinate
EB	ethylbenzene
GC	gas chromatography
HLB	hydrophilic-lipophilic balance
IFT	interfacial tension (mN/m)

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PRO 2: Processing and Applications of Specialty Oils

Joint session developed in conjunction with the Specialty Oils Applications Common Interest Group

Chairs: Nurhan T. Dunford, Oklahoma State University, USA; and Steve Gregory, Texas A&M University, USA

Room 2210A, Convention Center

1:55 **Opening Remarks.**

2:00 ***Salicornia bigelovii*: An Oilseed for Saline Agriculture.** F.J. Flider, Arcadia Biosciences/Seaphire International, USA.

2:20 **The Reintroduction of Castor as a Domestic Crop and the Uses of Castor Oil.** L. Browning, Castor Oil, Inc., USA.

2:40 **Pecan Oil—A Specialty Oil Opportunity.** T.O. Harwell, Prairie Harvest Farms, USA.

3:00 **Rice Bran "Emulsion" Extracts: Chemical and Functional Properties.** A. Proctor and M.A. Monsoor, Dept. of Food Science, University of Arkansas, USA.

3:20 **Tung Oil: Current Industrial Uses and Future Opportunities for Domestic and Foreign Production.** B. Hanson, Industrial Oil Products, USA.

3:40 **End.**

PCP 2: Current Research on Corn Protein Utilization

Chair: Milagros P. Hojilla-Evangelista, USDA, ARS, NCAUR, USA

Room 1204A, Convention Center

1:55 **Opening Remarks.**

2:00 **Current State and Challenges of Corn Products Research.** R. Shunk, National Corn Growers Association, USA.

2:20 **A New Method of Separating Ethanol Extracts of Corn.** L. Dickey and N. Parris, USDA, ARS, ERRC, USA.

2:40 **Improving Zein Films by Cross-linking.** J.W. Lawton, D.J Sessa, A. Biswas and J.L. Willett, USDA, ARS, NCAUR, USA.

3:00 **Adhesive Properties of Corn Zein Formulations or Glass Surfaces.** N. Parris and L. Dickey, ERRC, ARS, USDA USA.

3:20 **End.**

SOA 2: Processing and Applications of Specialty Oils

Joint session developed in conjunction with the Processing Division.

Chairs: Nurhan T. Dunford, Oklahoma State University, USA; and Steve Gregory, Texas A&M University, USA

Room 2210A, Convention Center

See Processing Division (PRO) above for programming.

S&D 2: Surfactants I

Chair: Jeffrey J. Scheibel, Procter & Gamble Company, USA

Room 1203B, Convention Center

1:55 **Opening Remarks.**

2:00 **Use of Cationic Surfactant to Remove Solvent-Based Ink from High-Density Polyethylene Surfaces.** J. Scamehorn D. Songsiri[2], J. Ellis[2], S. Osuwan[2] and S. Min[2], [1]Institute for Applie Surfactant Research, University of Oklahoma, USA, [2]Petroleum an Petrochemical College, Thailand.

2:20 **Kinetics of Surfactant Precipitation.** S. Soontravanic ***(Surfactant and Detergent Division Student Trave Award Winner)*** and J.F. Scamehorn, University of Oklahoma USA.

2:40 **New Alkylethersulfonates by Sulfoalkylation with AO Acid.** P. Berger, Oil Chem Technologies, Inc., USA.

3:00 **Novel Sulfonation Process of Fatty Acid Methyl Este Sulfonate (MES).** T. Nishio, S. Matoba, Y. Kimura, T. Ishikaw and I. Hama, Lion Corporation, Japan.

3:20 **Effect of Middle-Phase Microemulsion Formation or Ethylbenzene Removal by Using the Froth Flotatio Technique.** U. Yanatatsaneejit[1], A. Witthayapanyanon[1], S Chavadej[1], E.J. Acosta[2], J.F. Scamehorn[2] and D.A. Sabatini[2], [1]Th Petroleum and Petrochemical College, Chulalongkorn University Thailand, [2]University of Oklahoma, USA.

3:40 **Recent Advances in Structured Surfactant Technology** G.A. Smith[1], R. Smadi[1], P. Chadwick[2] and G. Holliday[3], [1]Huntsma Surface Sciences, USA, [2]Huntsman Surface Sciences, Europe [3]Huntsman Surface Sciences, Australia.

4:00 **End.**

Ether sulfonate surfactants prepared by the reaction of oxyalkylated alcohols, phenols and amines with olefin sulfonic acids of the structure shown will be discussed: R^1 [-(O-(R^2O)m-(R^3O)n-(R^4)]y where: R^1 = alkyl, alkenyl, amine, alkylamine, dialkylamine, trialkylamine, aromatic, polyaromatic, cycloalkane, cycloalkene, R^2 = C_2H_4 or C_3H_6 or C_4H_8, R^3 = C_2H_4 or C_3H_6 or C_4H_8, R^4 = linear or branched $C_7H_{14}SO_3X$ to $C_{30}H_{60}$ SO_3X when y =1, R^4 = linear or branched $C_7H_{14}SO_3X$ to $C_{30}H_{60}$ SO_3X or H when y>1 but at least one R4 must be linear or branched $C_7H_{14}SO_3X$ to $C_{30}H_{60}$ SO_3X, m ≥ 1, n ≥ 0, n + m = 1 to 30+, y ≥ 1, and X = alkali metal or alkaline earth metal or ammonium or amine. These novel ether sulfonate surfactants have excellent surfactant properties including low surface tensions and CMCs, excellent wetting and foaming characteristics as well as electrolyte, hard water, pH and temperature tolerance making them suitable for a variety of applications as surfactants. The unique reaction allows for the synthesis of mono-alkyl ether sulfonates, polyalkyl ether sulfonates such as anionic gemini surfactants and oligomer ether sulfonates such as those derived from alkylphenol/formaldehyde resins. The synthesis of these materials will be discussed as well as examples of their application as surfactants for detergents, stain repellents, water-soluble corrosion inhibitors, herbicides and enhanced oil recovery.

Novel Sulfonation Process of Fatty Acid Methyl Ester Sulfonate (MES). T. Nishio, S. Matoba, Y. Kimura, T. Ishikawa and I. Hama, Lion Corporation, Japan. *Contact:* Taku Nishio, Lion Corporation, 13-12, Hirai 7-chome, Edogawa-ku, Tokyo 132-0035, Japan.

Methyl ester sulfonate (MES) has a high detergency in hard water and an excellent biodegradability that is derived from renewable natural fats and oils. MES should become a cheaper alternative surfactant of linear alkylbenzene sulfonate (LAS). However, MES production technology is very problematic compared with other surfactant production technologies. The main problems in the production are MES's bad coloring (dark brown) and the generation of undesirable by-products such as disodium salt. In the conventional production process, manufacturers use acid bleaching in which methyl ester sulfonated acid is bleached with hydrogen peroxide under the existence of a large amount of methanol to suppress the hydrolysis of MES. This process is very complicated because additional systems of methanol recovery and an organic peroxide decomposition are necessary. Therefore, a novel MES process was developed. The technical points of this process are as follows. First, the acid color can be enhanced with the use of the color improving agents and methyl ester with a low iodine value. As a result of the improvement, neutralized paste bleaching that has a lower bleaching effect than acid bleaching can be used. Furthermore, the process becomes very simple, environmentally friendly, and basically safe because the methanol recovery system does not need to be used and no organic peroxide is generated. Second, a novel vessel sulfonation reactor can be developed instead of the film sulfonation reactor. This change will alllow the color improving agent to be used effectively. In this process, methyl ester with various carbon chain lengths can be used as raw materials. The MES compound can also be obtained for laundry detergent powder using a dry neutralization of low-color methyl ester sulfonated acid produced during this process.

Effect of Middle-Phase Microemulsion Formation on Ethylbenzene Removal by Using the Froth Flotation Technique. U. Yanatatsaneejit[1], A. Witthayapanyanon[1], S. Chavadej[1], E.J. Acosta[2], J.F. Scamehorn[2] and D.A. Sabatini[2], [1]The Petroleum and Petrochemical College, Chulalongkorn University, Thailand, [2]The University of Oklahoma, USA. *Contact:* Ummarawadee Yanatatsaneejit, Chulalongkorn University, 299/27 Soi Ladpraw 94, Ladpraw Road, Wanghonglang, Bangkok 10310, Thailand.

This study showed the relationship between surfactant phase behavior and efficiency of flotation of ethylbenzene in a continuous mode of operation. The phase behavior related to surfactant composition and salinity was performed with 3 anionic surfactants: sodium dihexyl sulfosuccinate (Aerosol MA), dioctyl sodium sulfosuccinate (Aerosol OT), and branched alcohol propoxylate sulfate sodium salt (Alfoterra). It was hypothesized that the maximum efficiency of froth flotation corresponds to the ultralow interfacial tensions between oil and water in the Winsor Type III microemulsion. Aerosol MA at 1 wt.% and 3 wt.% of NaCl exhibited the minimum interfacial tensions (2.2´ 10^{-2} dyne/cm). The effects of foam height, air flow rate, electrolyte concentration, equilibration time, and hydraulic retention time on the efficiency of froth flotation will be discussed.

Recent Advances in Structured Surfactant Technology. G.A. Smith[1], R. Smadi[1], P. Chadwick[2] and G. Holliday[3], [1]Huntsman Surface Sciences, USA, [2]Huntsman Surface Sciences, Europe, [3]Huntsman Surface Sciences, Australia. *Contact:* George Smith, Huntsman Surface Sciences, 7114 N. Lamar Blvd., Austin, Texas 78752, USA.

Structured surfactant technology (SST) is well established especially in Europe where liquid detergents do not need to be clear and isotropic. SST is capable of delivering actives which are incompatible in aqueous solution. In a structured liquid, the soluble surfactant system is salted out of aqueous solution as a suspended lamellar phase. The particle size is typically around 10 μm with a bilayer spacing around 50 A. The suspended surfactant spherulites interact to give rise to a yield stress that is capable of suspending insoluble particles such as STPP or zeolite. Recent work has identified other types of structured surfactant systems. In aqueous solution, sucrose has been used to structure surfactants. The resulting system is optically clear and highly birefringent under polarized liquid. The system is believed to be consist of a extended bilayer with spacing around 200 A. The spacing is large enough to appear optically transparent but still give rise to a yield stress capable of suspending insoluble ingredients. It has also been found that anhydrous structured surfactant systems are possible. Surfactants are dissolved in a suitable nonionic surfactant and then forced out of solution by ionic crosslinking. The anhydrous nature of the systems allows for the use of ingredients which are incompatible with water such as peroxygen bleaches. Performance of structured surfactant technology in laundry, liquid dish and hard surface cleaning has been examined. When properly formulated, structured systems shows better cleaning performance than conventional isotropic systems and do not require hydrotropes or other formulation aids.

Tuesday Morning

S&D 3: Surfactants II

Chair: Albert Joseph, Dow Chemical Co., USA

Study of Simultaneous Removal of an Organic Solute and a Metal Ion from Aqueous Solution by Surfactant/Polyelectrolyte Aggregates in Colloid-Enhanced Ultrafiltration. N. Komesvarakul[1] (Ralph H. Potts Memorial Fellowship Award Winner), L. Do[1], T. Nguyen[1], J.F. Scamehorn1 and H. Gecol[2], [1]The University of Oklahoma, USA, [2]University of Nevada, USA. *Contact:* Napaporn Komesvarakul, The University of Oklahoma, School of Chemical Engineering & Materials Science and Institute for Applied Surfactant Research, 100 E. Boyd, Energy Center, T-335, Norman, OK 73019, USA.

The colloid-enhanced ultrafiltration (CEUF) technique is used for the simultaneous removal of a phenolic solute and a metal ion; in this study specifically dichlorophenol (DCP) and Mg^{2+}. These compounds are often found in pulp and paper mill wastewater effluent. Surfactant/polymer mixtures with an excess of polyelectrolyte are used as colloid solutions forming net negatively charged complexes. The organic solute can solubilize in the surfactant/polymer aggregates and the metal ion can bind onto the aggregates. In this application of CEUF, the colloids are ultrafiltered from the solution with the solubilized chlorinated phenol pollutant and the bound metal ion. The effects of the metal concentration and polyelectrolyte concentration on the organic solute removal are discussed. Semiequilibrium dialysis is used to deter-

3 **Liquid Chromatography of Phospholipids Using Mixed Retention and Detection Modes.** N. Danielson, M. Wandstrat, A. Kijak, and J. Cox, Miami University, USA.

4 **Emulsifying Properties in Relation to the Quality of Egg Yolk Lecithin.** H. Narabe, Y. Shigematsu, and H. Kobayashi, Q.P. Corporation, Japan.

5 **Physicochemical Properties of Positively Charged Liposomes.** A. Inagaki, T. Ohkubo, H. Sakai, and M. Abe, Tokyo University of Science, Japan.

6 **Effect of Highly Purified Fatty Acids on Membrane Properties of Liposomes.** H. Sakai, H. Sasakura, T. Ohkubo, M. Suzuki, and M. Abe, Tokyo University of Science, Japan.

PRO-P: Processing Posters

Chair: F. Karaosmanoglu, Istanbul Technical University, Turkey.

1 **Preparation and Properties of Microcapsule by Using Electrocapillary Emulsification Method.** K. Tanaka, A. Nakayama, T. Kondo, H. Sakai, and M. Abe, Tokyo University of Science, Japan.

2 **Membrane Processing of Ethanol-Extracted Corn Oil.** J. Kwiatkowski and M. Cheryan, University of Illinois, USA.

3 **Effect of Physical Refining on Chemical and Sensory Attributes of Coconut Oil.** M. Torres-Gonzalez[1], O. Angulo-Guerrero[2], R. Oliart-Ros[2], and L. Medina-Juarez*[3], [1]Instituto Tecnologico de Colima, Mexico, [2]Instituto Tecnologico de Veracruz, Mexico, [3]Universidad de Sonora, Mexico.

4 **Modeling the Tocopherol Adsorption on Bleaching of Soybean Oil.** L. González-Tovar, J. Noriega-Rodríguez, J. Ortega-García, N. Gamez-Meza, and L. Medina-Juarez, Universidad de Sonora, Mexico.

5 **Hexane Removal from Oil Mixtures Using Liquid CO_2 and Analyzed via SFC.** S. Taylor and F. Eller, USDA, ARS, NCAUR, USA.

6 **Effect of Physical Refining on Quality of High-Oleic Safflower Oil Produced in Mexico.** J. Ortega-García, J. Noriega-Rodríguez, L. Medina-Juarez, N. Gamez-Meza, and O. Dennis*, Universidad de Sonora, Mexico.

7 **Column Fractionation of Canola Oil Deodorizer Distillate Using Supercritical Carbon Dioxide.** O. Guclu-Ustundag and F. Temelli*, University of Alberta, Canada.

8 **Phospholipid Molecular Species of Cottonseed Expander Oil.** M. Kuk and J. Blond, USDA, ARS, SRRC, USA.

9 **Kinetic Modelling of Glycerolysis in Supercritical Carbon Dioxide Media.** P. Moquin[1], F. Temelli[1], J. King[2], and M. Palcic[1], [1]University of Alberta, Canada, [2]Los Alamos National Laboratory, USA.

10 **How Chemical Interesterification Is Initiated: Nucleophilic Substitution or α-Proton Abstraction?** L. Liu, ConAgra Foods, Inc., USA.

11 **Impact of Impurities on Thermal Energy Storage Properties of Biobased Phase Change Materials.** S. Lopes and G. Suppes, University of Missouri at Columbia, USA.

12 **Influence of the Refining Process on Pesticides Residues Removal.** X. Page-Xatart-Pares, J. Laur, C. Birot, J. Arnaud, and F. Lacoste, ITERG, France.

13 **Hydrogenation of Vegetable Oils with Minimum *trans* and Saturated Fatty Acid Formation over Novel Generation of Pd-Catalysts.** A. Boulmerka ***(Processing Division Student Excellence Award Winner),*** J. Arul, and K. Belkacemi, Universite Laval, Canada.

14 **Removal of Organic Environmental Pollutants from Fish Oil by Short-Path Distillation.** H. Breivik[1] and O. Thorstad*[2], [1]Hydro Pronova a.s., Norway, [2]Pronova Biocare a.s., Norway.

15 **A Comparison of Commercial Nickel Catalysts Effects on *trans* Fatty Acids Formation during Hydrogenation of Soybean Oil and Optimization of Process.** H. Safafar[1], H Nikoopour[2], and M. Babaee[2], [1]ORDC, Iran, [2]National Nutrition and Food Technology Research Institute, Iran.

PCP-P: Protein and Co-Products Posters

Chair: M Hojilla-Evangelista, USDA, ARS, NCAUR, USA.

1 **The (-)-Gossypol-2,4-Pentanedione (1:2) Inclusion Complex.** M. Dowd[1] and E. Stevens[2], [1]USDA, ARS, SRRC, USA, [2]Dept. of Chemistry, University of New Orleans, USA.

2 **Effect of Hydrophilic Zein Films on the Growth of Tomato Plants and Evaporative Water Loss.** N. Parris and D. Douds USDA, ARS, ERRC, USA.

3 **Emulsification Capacity Properties of Protease-Modified Soy Protein Substrates.** S. Jung, P. Murphy, and L Johnson, Iowa State University, USA.

4 **Effect of Extraction Solvent on Composition of Oil and Meal Obtained from Cottonseed.** P. Wan, M. Dowd, and A Waggoner, USDA, ARS, SRRC, USA.

5 **Effects of Flour Sources on Acrylamide Formation and Oi Uptake in Fried Batters.** F. Shih, S. Boue, K. Daigle, and B. Shih USDA, ARS, SRRC, USA.

6 **Construction of Green Fluorescent Protein Fusion Protein to Investigate the Transduction Mechanism of TAT Protein Transduction Domain.** S. Liu, R. Fu, H. He, J. Chen, and P. Rao Fuzhou University, China.

7 **Lesquerella Fendleri Protein Fractionation and Properties** Y Wu, USDA, ARS, NCAUR, USA.

8 **Refunctionalization of EE Meals by Novel Means.** H. Wang L. Johnson and T. Wang, Iowa State University, USA.

9 **The Effect of Heat Treatment and pH on the Thermal and Rheological Properties of *Lupinus Albus* Flour Meal.** A Mohamed, S. Peterson, and G. Biresaw, USDA, ARS, NCAUR, USA.

S&D-P: Surfactants and Detergents Posters

Chair: M. Saint Victor, Cognis Corporation, USA.

1 **Phase Behaviors of Highly Purified Polyglycerine Fatty Aci Esters.** T. Nakamura[1], M Kikuchi[2], T. Ohkubo[2], and M. Abe[2], Hasegawa Co. Ltd., Japan, [2]Tokyo University of Science, Japan.

2 **Stabilization of Oil/Hydrophobic Polymer/Wate Surfactant-Free Emulsions with Heat Treatment.** T. Umeda K Kamogawa[2], T. Ohkubo[1], H Sakai[1], and M. Abe[1], [1]Toky University of Science, Japan, [2]Ministry of Education, Culture, Sport Science, and Technology Japan.

3 **Preparation of Emulsions with Hydrophobic Silic Particles as an Emulsifier.** K. Ikemoto, T. Ohkubo, M. Koishi, H Sakai, and M. Abe, Tokyo University of Science, Japan.

4 **Stabilization of Surfactant-Free Styrene Emulsions by th Addition of Hexadecane.** D. Tsutsui[1], K. Kamogawa[2], Ohkubo[1], H. Sakai[1], and M. Abe[1], [1]Tokyo University of Scienc Japan, [2]Ministry of Education, Culture, Sports, Science, an Technology, Japan.

5 **Solution Properties of a Novel Fluorinated Hybri Surfactant with a Sulfate Headgroup.** C. Sun, Y. Kondo, N Yoshino, T. Ohkubo, H. Sakai, and M Abe, Tokyo University Science, Japan.

6 **Light Oil Removal from Wastewater by Middle Phas Microemulsion and Froth Flotation.** A. Witthayapanyanon[1], Yanatatsaneejit[2], J. Scamehorn[1], D Sabatini[1], and S. Chavade [1]Oklahoma State University, USA, [2]Chulalongkorn University, Thailan

but also decreased interfacial tension between water and normal alkanes remarkably. By utilizing this advantage, we could spread the droplet of the hybrid surfactant aqueous solutions with larger density on the surface of benzene with lower density.

The aggregation behaviors of F8H3OS and F6H5OS in water have been investigated by light scattering and fluorescence spectrum measurements. The micelle size and aggregation number of F8H3OS were 2.8 nm and 30, respectively, which are smaller than those of normal hydrocarbon surfactants. For F6H5OS, surfactant molecules formed larger aggregates whose size is from 10 nm to 900 nm. Aggregation states of the hybrid surfactants in aqueous solutions were investigated in more details by fluorospectroscopy in which pyrene(Py) and fluorocarbon-substituted pyrene (PyCORf) were employed as probes of polarity in hydrophobic environment. Unlike hydrocarbon surfactants for which the fluorescence intensity ratio of the first (I1) and third band (I3) bands decreased dramatically at cmc and settle down to a plateau, the ratio of I1/I3 for the hybrid surfactant aqueous solutions decreased even at higher concentration (above the cmc), indicating that aggregation behaviors of the hybrid surfactants vary even at higher concentration range.

Furthermore, we have measured the diffusion coefficient of sucrose (Ds) in hybrid surfactant aqueous solutions by NMR: Two different values of Ds have been determined in F8H5OS solutions. Due to its high hydrophilicity, sucrose can not be solubilized in the hydrophobic core of micelles, so we think the different values of Ds in F6H5OS solutions indicated different diffusion rates of sucrose in the internal water phase of vesicles and the bulk solution. In other words, with increasing concentration, F6H5OS forms vesicles and some of sucrose molecules are incorporated in the internal water phase.

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Light Oil Removal from Wastewater by Middle Phase Microemulsion and Froth Flotation. A. Witthayapanyanon[1], U. Yanatatsaneejit[2], J. Scamehorn[3], D. Sabatini[3] and S. Chavadej[4], [1]Oklahoma State University, United States, [2]The Petroleum and Petrochemical College,Chulalongkorn University, Thailand, Thailand, [3]Oklahoma State University, United States, [4]The Petroleum and Petrochemical College, Chulalongkorn University, Thailand, Thailand. *Contact:* Anuradee Witthayapanyanon, Oklahoma State University, 202 W.Boyd St. Room 334, Norman, Oklahoma 73019-1024, United States.

Abstract: In the previous work (1-7), the maximum oil removal occured when type III microemulsion was formed. In order to elucidate which character of type III microemulsion was responsible for froth flotation. Ultra low interfacial tension (IFT) is focused in this work.Effect of surfactant concentration, electrolyte concentration and equilibration time on oil removal were investigated. These three effects linked between IFT and oil removal. The results showed that ultra low IFT enhanced the flotation efficiency. However, the system providing the maximum oil removal did not correspond to the minimum IFT found in the middle phase obtained from phase study. It led to conclude that ultra low IFT was not the sole significant factor in flotation operation. Foam stability and foam ability are other parameters that should be taken into consideration further.

Production of O/W Emulsions Stabilized by β-lactoglobulin-Pectin Membranes. D. Guzey, H. Kim and D. McClements, University of Massachusetts Amherst, United States. *Contact:* Demet Guzey, University of Massachusetts Amherst, Department of Food Science, Amherst, Massachusetts 01003, United States.

Abstract: Previously a novel technology was developed to produce O/W emulsions stabilized by chitosan-lecithin membranes (Ogawa *et al.*, 2003) and β-lactoglobulin-pectin membranes (Moreau *et al.*, 2003) using a two-stage process. The main driving force for adsorption of the polymer onto the primary emulsion droplets was reported as the electrostatic attraction between the charged groups on the polymer and the oppositely charged groups on the colloidal particle. In this study the optimum preparation conditions (pH, ionic strength, mechanical agitation) for biopolymer adsorption onto the droplets in primary emulsions to form kinetically stable secondary emulsions were investigated.

A primary emulsion was prepared by homogenizing 10 wt% corn oil with 90 wt% aqueous emulsifier solution (0.5 wt% β-lactoglobulin, pH 3 or 7) with a high-speed blender followed by 5 passes at 5000 psi through a two-stage high-pressure valve homogenizer. This emulsion was mixed with aqueous pectin solution (2 wt%, pH 3 or 7), NaCl solution and buffer solution to yield secondary emulsions with the composition of 5 wt% corn oil, 0.45 wt% β-lactoglobulin, 0.2 wt% pectin and 0 or 100 mM NaCl. The pH of the secondary emulsions was then adjusted to pHs ranging from 3 to 8. Primary and secondary emulsions were treated with ultrasound waves to disrupt any flocculated droplets (30 seconds at 20 kHz and 40% amplitude). Emulsions were then stored for 24 hours at ambient temperature prior to analysis. The zeta potential of emulsions was determined using a particle electrophoresis instrument. The particle size distribution of the emulsions was measured using a laser light scattering instrument. Creaming stability was reported as % Serum which is defined as the height of the serum layer divided by the height of the emulsion in a test tube.

Secondary emulsions were more stable than primary emulsions at intermediate pHs. Secondary emulsions prepared at pH 7 had smaller droplet diameters (0.35 to ~6 μm) than those prepared at pH 3 (0.42 to ~18 μm) across the whole pH range studied, and also had smaller diameters than the primary emulsions (0.35 to 13.6 μm). Ultrasound treatment reduced the droplet diameter of both primary and secondary emulsions and lowered the rate of creaming. The presence of salt screened the charges and thus the electrostatic interaction between biopolymers. Secondary emulsions were more stable to the presence of 100 mM NaCl at low pHs (3 to 4) than primary emulsions.

The results of this study show that stable emulsions can be prepared by engineering their interfacial membranes using the electrostatic interaction of natural biopolymers, especially at intermediate pHs where proteins normally fail to function. This technology can be utilized to produce emulsions containing functional ingredients encapsulated within biopolymer layers.

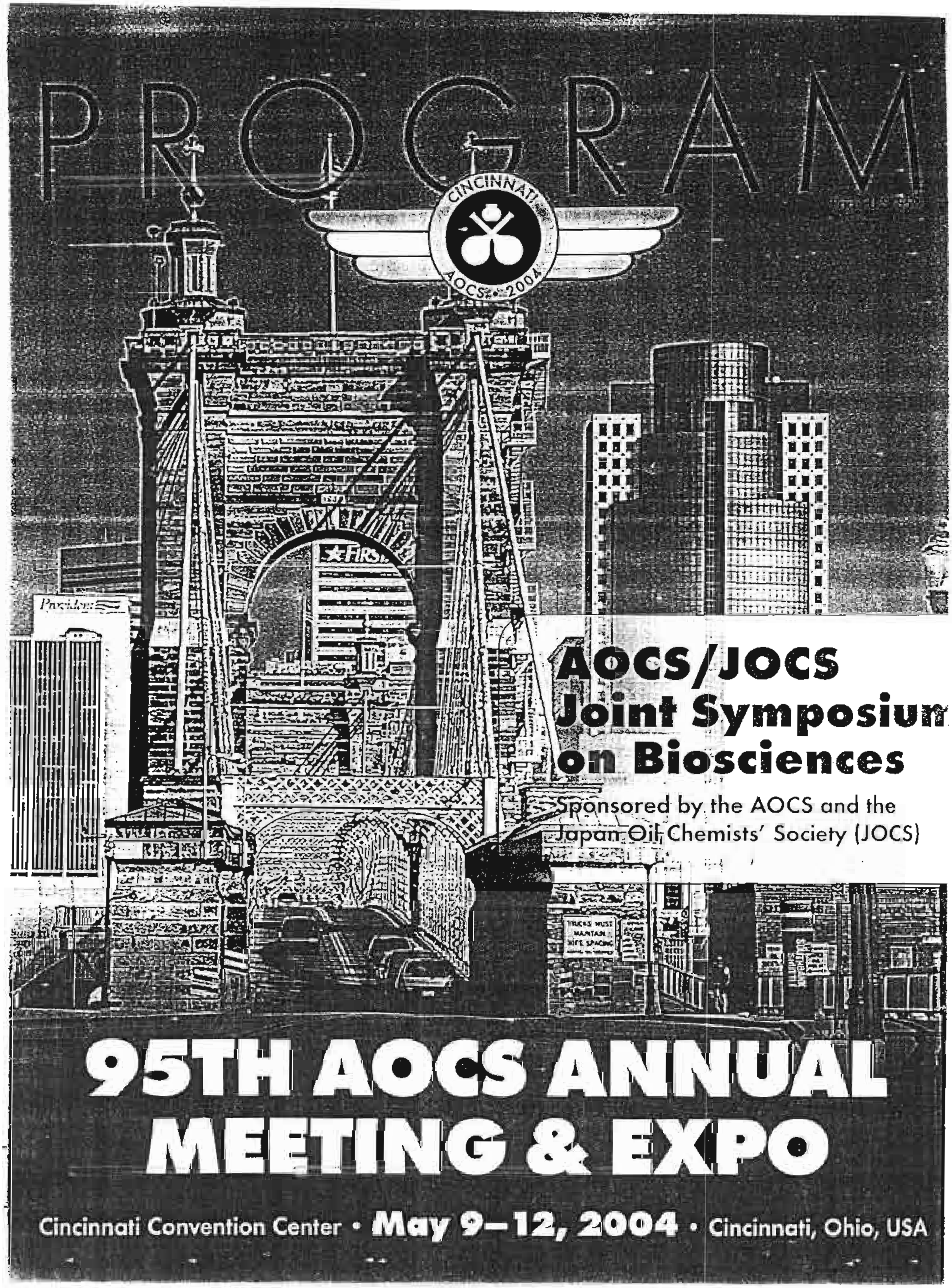
Application of Cationic Surfactant and Modified Silicone Combination System to Fabric Softener. J. Yokoyama, E. Hashimoto, H. Yamazaki, H. Miyasaka and T. Mukaiyama, LION Corporation, Japan. *Contact:* Jun Yokoyama, LION Corporation, 13-12, Hirai 7-chome, Edogawa-ku, Tokyo 132-0035, Japan.

Abstract: Silicones are well known as functional materials. Especially they have been used as lubrication materials to reduce the friction between fibers in the textile manufacturing industry. Though they are expected to provide high performances to domestic fabric softener, there are few products that contain silicone. So, we investigated the performances and the physicochemical properties of the new liquid fabric softeners that were formulated with modified silicone and cationic surfactant combination system. Polyoxyalkylene modified silicone (PMS) and dialkyl dimethyl ammonium chloride (DAA) were used in the experiments.

The softener showed high performances concerning softness, anti-staticity, wrinkle reduction, easy ironing, re-wettability and so on. From the adsorption experiment, PMS showed quite low adsorption ability by itself, but it was improved drastically under co-existence of DAA. The aggregation structure in the dispersion and the adsorbed structure onto a model surface were investigated by several methods such as DLS, ESR, AFM, XRD, DSC and so on. As the result, PMS was suggested to exist in the vesicle structure formed by DAA.

And we also conducted these experiments on triethanol amine origin esterquat (TEQ)/PMS combination system. As the result, TEQ /PMS combination showed smaller particle size and lower viscosity of the dispersion in comparison with DAA / PMS.

Removal of Toluene from Nonionic Surfactant Coacervate Phase from a Cloud Point Extraction by Vacuum Stripping. S. Kungsanant[1], B. Kitiyanan[1], S. Osuwan[1] and J. Scamehorn[2], [1]The



PROGRAM

AOCS/JOCS
Joint Symposiun
on Biosciences

Sponsored by the AOCS and the
Japan Oil Chemists' Society (JOCS)

95TH AOCS ANNUAL MEETING & EXPO

Cincinnati Convention Center • **May 9–12, 2004** • Cincinnati, Ohio, USA

Joint session developed in conjunction with the Specialty Oils Applications Common Interest Group.

PRO 4/SOA 4: Processing of Specialty Oils

Chairs: J.W. King, Los Alamos National Laboratory, USA; F.T. Orthoefer, Consultant, USA; and P.M. Sonkul, Mumbai University, India (Student Co-Chair).

Room 243, Convention Center

7:55 **Opening Remarks.**

8:00 **Biological Activity of Micronutrients in Vegetable Oils: Impact of Oil Processing.** R. Nicolosi[1] and F. Orthoefer[2], [1]American Society for Nutritional Sciences, USA, [2]Food Science and Technology, LLC, USA.

8:20 **High Phytosterol Oils from Corn Fiber and Barley.** R.A. Moreau[1], A.-M. Lampi[2], and K.B. Hicks[1], [1]USDA, ARS, ERRC, USA, [2]University of Helsinki, Finland.

8:40 **Hibiscus Seed Oil Compositions.** R.A. Holser[1] and G. Bost[2], [1]USDA, NCAUR, Food and Industrial Oils Research Group, USA, [2]The Village Botanica, Inc., USA.

9:00 **Nutraceutical Composition of Avocado Oil (Crude, Virgin and Refined) through the Operations for Its Industrial Production.** J. Simental[1,2], H. Escalona[2], and M. Estarrón[2], [1]Universidad de Guadalajara, Mexico, [2]Centro de Investigación y Asistencia en Tecnología y Diseño del Estado de Jalisco, Mexico.

9:20 **HPLC-ESI-MS/MS Analysis of Novel Brazilian Food Oils.** S. Segall[1], W. Artz[2], D. Raslan[1], V. Ferraz[1], and J. Takahashi[1], [1]Universidade Federal de Minas Gerais, Brazil, [2]University of Illinois, USA.

9:40 **Extraction and Processing of Nut-Oils and -Products Using Compressed Fluids.** J. King, Los Alamos National Laboratory, USA.

10:20 **End.**

PCP 4: Vegetable Proteins as Meat Analogs

Chairs: R. Shukla, Archer Daniels Midland Co., USA; and N. Parris, USDA, ARS, ERRC, USA.

Room 204, Convention Center

7:55 **Opening Remarks.**

8:00 **Contribution of Vegetable Proteins to Water-Holding and Texture of Meat Products.** T. Lanier, North Carolina State University, USA.

8:20 **High-Moisture Extrusion of Protein to Create Unique Meat Analogs.** R. Egbert and M. Matlock, Archer Daniels Midland Company, USA.

8:40 **A Review of Research on TSP from Extruded-Expelled Soybean Flour at Iowa State University.** D. Myers, Iowa State University, USA.

9:00 **High-Moisture Extruded Soy Proteins and Their Potential.** Y. Li, The Solae Company, USA.

9:20 **How to Make Soy Meat Analogs.** M. Riaz and M. Barron, Texas A&M University, USA.

9:40 **Break.**

10:00 **Soy Protein as Carbohydrate Replacement in Conventional Foods.** S. Rittmanic, Protient, Inc., USA.

10:20 **Novel Applications for Soy Proteins.** B. Govindarajan, Legacy Foods, USA.

10:40 **Textured Soy Protein—Field to Plate Technology.** W Wijeratne, Insta-Pro International, USA.

11:00 **Development of Meat Analog Using Peanut Flour and Soy Protein Isolate Mix.** B. Wang and E. Parmer Jr., Tuskegee University, USA.

11:20 **Development of Peanut-Based Meat Analogs.** I. Goktepe and M. Ahmedna, North Carolina A&T State University, USA.

11:40 **End.**

S&D 4: General Detergents

Chair: J. Shi, Procter & Gamble Co., USA.

Room 202, Convention Center

7:55 **Opening Remarks.**

8:00 **Industrial Home Laundry Closed Loop Cleaning Process.** J. Scamehorn[1], E. Tucker[1], H. Gecol[2], N. Komesvarakul[1], L. Serventi[1], K. Raney[3], and S. Capps[3], [1]The University of Oklahoma, USA, [2]University of Nevada at Reno, USA, [3]Shell Chemical LP, USA.

8:20 **E(quivalent) HLB? Emulsion Inversion Studies as a Tool for Surfactant Characterization.** I. Johansson and I. Voets, Akzo Nobel Surface Chemistry AB, Sweden.

8:40 **Polyetheramine Derivatives: Physical Chemical and Performance Properties.** G. Smith, Huntsman Surface Sciences, USA.

9:00 **Synergism of Cationic and Anionic Surfactant Mixtures with Asymmetric Head Groups.** A. Fuangswasdi[1], A. Charoensaeng[1], E. Acosta[2], S. Khoodhiar[1], K. Osathaphan[1], J. Scamehorn[2], and D. Sabatini[2], [1]Chulalongkorn University, Thailand, [2]University of Oklahoma, USA.

9:20 **Evaluation of Silicones for Fabric Mechanical Reinforcement.** B. Henault[1] and M. Severance[2*], [1]Dow Corning S.A., Belgium, [2]Dow Corning Corporation, USA.

9:40 **Break.**

10:00 **Softening Performance and Physicochemical Properties of Gemini-Type Cationic Surfactants and Their Complexes with Anionic Surfactants.** H. Imai, H. Miyasako, H. Konto, and M. Fujiwara, Lion Corporation, Japan.
10:20 **Stabilization of Cationic Polymers in Anionic Formulations.** M. Crossman, Alco Chemical, USA.
10:40 **Enzyme Stability in Liquid Detergent.** M. Stoner[1] ***(Ralph H. Potts Memorial Fellowship Award Winner)***, D. Dale[2], and T. Randolph[1], [1]University of Colorado, USA, [2]Genencor International, USA.
11:00 **Polymers for Improved Soil Removal.** H. Koch, Sasol, Germany.
11:20 **Absorption of Aqueous Aroma Chemicals on Fabric Substrates.** H. Liu[1], K. Obendorf[1], M. Leonard[2], T. Young[2], and M. Incorvia[2], [1]Cornell University, USA, [2]International Flavors & Fragrances, USA.
11:40 **Effect of Interfacial Tension and Foam Characteristics on Diesel Removal in Froth Flotation Operation.** U. Yanatatsaneejit[1] ***(Surfactants and Detergents Division Student Travel Award Winner)***, S. Chavadej[1], P. Rangsunvigit[1], and J. Scamehorn[2], [1]Chulalongkorn University, Thailand, [2]University of Oklahoma, USA.
12:00 **End.**

S&D 4.1: Claim Substantiation and Brand Building in Detergents

Chairs: N. Prieto and R. Deinhammer, Novozymes North America, Inc., USA.
Room 213, Convention Center

7:55 **Opening Remarks.**
8:00 **Building Brands through Technology Innovation.** R. Swift, Procter & Gamble Co., USA.
8:20 **Solving the Consumer Riddle Before We Are Asked.** M. Boe-Lee, N. Diaz, and H. Keiserman, Unilever Home & Personal Care-NA, USA.
8:40 **Developing Claims Benefits from Detergent Ingredient Innovations.** J. Houston, Colin A. Houston & Associates, Inc., USA.
9:00 **Brandbuilding with Enzymes.** S. Troff, Novozymes A/S, Denmark.
9:20 **A Lever, a Fulcrum, a Place to Stand—and Good Timing.** G. VanBuskirk, Clorox Services Company, USA.
9:40 **Advertising in 20 Minutes.** B. Cutler, Baker & Hostetler LLP, USA.
10:00 **Break.**
10:20 **Building Brands with Oxygen-Based Bleach Technology.** G. Reinhardt, Clariant GmbH, Germany.
10:40 **Launching a Car Care Revolution: Mr. Clean AutoDry.** P. Vinson, M. Kreuzer, B. Barger, J. Powell, and K. Kern, Procter & Gamble Co., USA.
11:00 **Performance Evaluation for Brand Building.** P. Sosis, Argeo Inc., USA.
11:20 **Sure It Cleans, but What Else Can It Do?** T. Germain, McIntyre Group, Ltd., USA.
11:40 **Brandbuilding in the Laundry Category.** T. Gatzulis, The Dial Corporation, USA.
12:00 **Panel Discussion.**
12:20 **End.**

Joint session developed in conjunction with the Processing Common Interest Group.

SOA 4/PRO 4: Processing of Specialty Oils

Chairs: J.W. King, Los Alamos National Laboratory, USA; and F.T Orthoefer, Consultant, USA.
Room 243

Please refer to PRO 4/SOA 4 Session above for programming.

WEDNESDAY AFTERNOON

AOCS/JOCS JOINT SYMPOSIUM ON BIOSCIENCES

BIO 5: Single-Cell Oils

Chairs: S. Shimizu, Kyoto University, Japan; and S. Bloomer, Land O'Lakes Inc., USA.
Room 200, Convention Center

1:55 **Opening Remarks.**
2:00 **Model Studies for the Production of Transgenic Single Cell Oils.** T. Aki[1], Y. Michinaka[1], T. Shimauchi[2], T. Nakajima[2], Kawamoto[1], S. Shigeta[1], and K. Ono, [1]Hiroshima University, Japa and [2]Idemitsu Technofine Co., Japan.
2:20 **A Perspective on Single-Cell Oil.** E. Hammond and B. Glat Iowa State University, USA.
3:00 **Polyunsaturated Fatty Acids Production by Labyrinthulids.** T. Nakahara, T. Yokochi, and Y. Kumon, Nation Institute of Advanced Industrial Science and Technology, Japan.
3:20 **The Development and Commercialization of PUFA-Ric SCO.** D. Kyle, Advanced BioNutrition Corporation, USA.
4:00 **Operation of n-4 and n-7 Pathways for th Polyunsaturated Fatty Acid Biosynthesis in a Mutant an Arachidonic Acid-Producing Fungus, *Mortierell alpina* 15-4.** E. Sakuradani, M. Naka, H. Kanamaru, Y. Ioka, Nojiri, J. Ogawa, and S. Shimizu, Division of Applied Life Science Graduate School of Agriculture, Kyoto University, Japan.
4:20 **Wax Ester Production from *n*-Alkanes by *Acinetobacter* s Strain M-1.** T. Ishige, Y. Sakai, and N. Kato*, Kyoto University, Japa
4:40 **Production and Applications of a Vegetarian Hig Quality DHA-Oil by Fermentation.** T. Kiy, Nutrinova Nutritio Specialties & Food Ingredients GmbH, Germany.
5:00 **End.**

EAT 5: General Edible Applications Technolog

Chair: G. List, USDA, ARS, NCAUR, USA.
Room 214, Convention Center

1:55 **Opening Remarks.**
2:00 **The Yield Stress and Elastic Modulus of a Fat and Thei Relationship to Structure.** A. Marangoni ***(Timothy L Mounts Award Winner)***, University of Guelph, Canada.
2:40 **Zero *trans* Margarine Oils Formulation by Chemic Esterification and Blending.** S. Mirzaee Ghazani, Margari Co., Iran.
3:00 **Adsorbent Treatment of Frying Oils and the Impact Health and Nutrition.** B. Cooke, The Dallas Group of Americ Inc., USA.
3:20 **End.**

Effect of Interfacial Tension and Foam Characteristics on Diesel Removal in Froth Flotation Operation. U. Yanatatsaneejit[1], S. Chavadej[1], P. Rangsunvigit[1] and J. Scamehorn[2], [1]Petroleum and Petrochemical College, Chulalongkorn University, Thailand, Thailand. [2]University of Oklahoma, United States. *Contact:* Ummarawadee Yanatatsaneejit, Petroleum and Petrochemical College, Chulalongkorn University, Thailand, Chula Soi 12, Phyathai Road, Pathumwan, Bangkok 10330, Thailand.

Abstract: Froth flotation is a surfactant-based separation process which can remove emulsified oil from water. There are several advantages such as low space requirement, high removal efficiency, flexibility for various pollutants at different scales, and low cost. To achieve higher performance for froth flotation, the combination of ultra-low oil–water interfacial tensions and stable foam production must be achieved. To get the ultra-low interfacial tensions, Winsor's type III microemulsion is formed in oily wastewater before transferred to the froth flotation cell. In this study, diesel fuel is used as the model oil and branched alcohol propoxylate sulfate sodium salt with 14–15 carbon hydrophobe and 4 PO groups (Alfoterra 145-4PO) are used as the surfactant. The effect of surfactant concentration, salinity, oil to water ratio, air flow rate, and equilibration time on performance of the froth flotation operation will be discussed.

Wednesday Morning

S&D 4.1: Claim Substantiation and Brand Building in Detergents

Chairs: R. Deinhammer and N. Prieto, Novozymes North America, Inc., USA.

Building Brands Through Technology Innovation. R. Swift, Procter & Gamble Company, United States. *Contact:* Ron Swift, Procter & Gamble Company, 5299 Spring Grove Ave., Cincinnati, Ohio 45217, United States.

Abstract: In the increasingly competitive world of branded products, the importance of technology fit with brand character is becoming more evident. It is no longer enough to offer a product upgrade that has a technical, claimable or even consumer noticeable benefit. In the environment of price and profit pressure, growing brands innovate with technologies that offer benefits specifically tuned to the product equity or the direction of the product equity. This benefit "tuning" offers greater differentiation in an effort to reduce commoditization of brands and categories.

Solving the Consumer Riddle Before We Are Asked. M. Bae-Lee, N. Diaz and H. Keiserman, Unilever Home & Personal Care–NA, United States. *Contact:* Myongsuk Bae-Lee, Unilever Home & Personal Care–NA, 45 River Rd, Edgewater, New Jersey 07020, United States.

Abstract: Unilever is a consumer packaged goods company dedicated to meeting the everyday needs of people everywhere. Connecting to the consumer is our passion. We are on a continuous quest to obtain the consumer insights that will guide product innovations that anticipate future consumer expectations. However, consumer insights are complicated and constantly changing, in part due to trends like cultural infusion and escalating product choices. Our challenge is to deliver products that consumers will feel connected to, be delighted with, and experience real benefits from. Predicting what consumers will want tomorrow is today's challenge.

Developing Claims Benefits from Detergent Ingredient Innovations. J. Houston, Colin A. Houston & Associates, Inc., United States. *Contact:* Joel Houston, Colin A. Houston & Associates, Inc., 20 Milltown Road, Brewster, New York 10509, United States.

Abstract: As detergents have developed, a series of technical achievements allowed product performance to accelerate and marketers found that performance claims enhanced sales effectively and differentiated products one from another. Early performance additives were FWA and protease enzymes. In the 1980's, tremendous attention was placed on low temperature oxygen based bleaches while in the nineties attention shifted to improved color and fabric care. This paper will examine the linkage between performance and product claims and look at where detergent claims are and where they appear to be headed.

Brand-Building with Enzymes. S. Traff, Novozymes A/S, Denmark. *Contact:* Stig Traff, Novozymes A/S, Smoermosevej 25, Bagsvaerd 2880, Denmark.

Abstract: A key challenge for the detergent industry is to push new innovations for their brands in order to build consumer preference and to counter the commoditization of products. This need is probably more out spelled today than ever before.

A great many parameters are involved in the detergent brand-building process. But very basically it is about identifying and delivering value to the specific brand and keeping the specific brand top-of-mind within the target group, in order to trigger the target group's initial purchase, trial and re-purchase.

Any detergent formulation contains some basic ingredients, but those basic ingredients are usually not the ones which differentiate one specific detergent from another at the consumer level. The ingredient specialties—like enzymes—play a key role in supporting detergent product innovation and brand differentiation.

Our prediction for the future is that new enzymes will continuously be core for generating novel claims and for efficient detergent brand-building. This presentation will exemplify the above by discussing some of the latest enzyme developments.

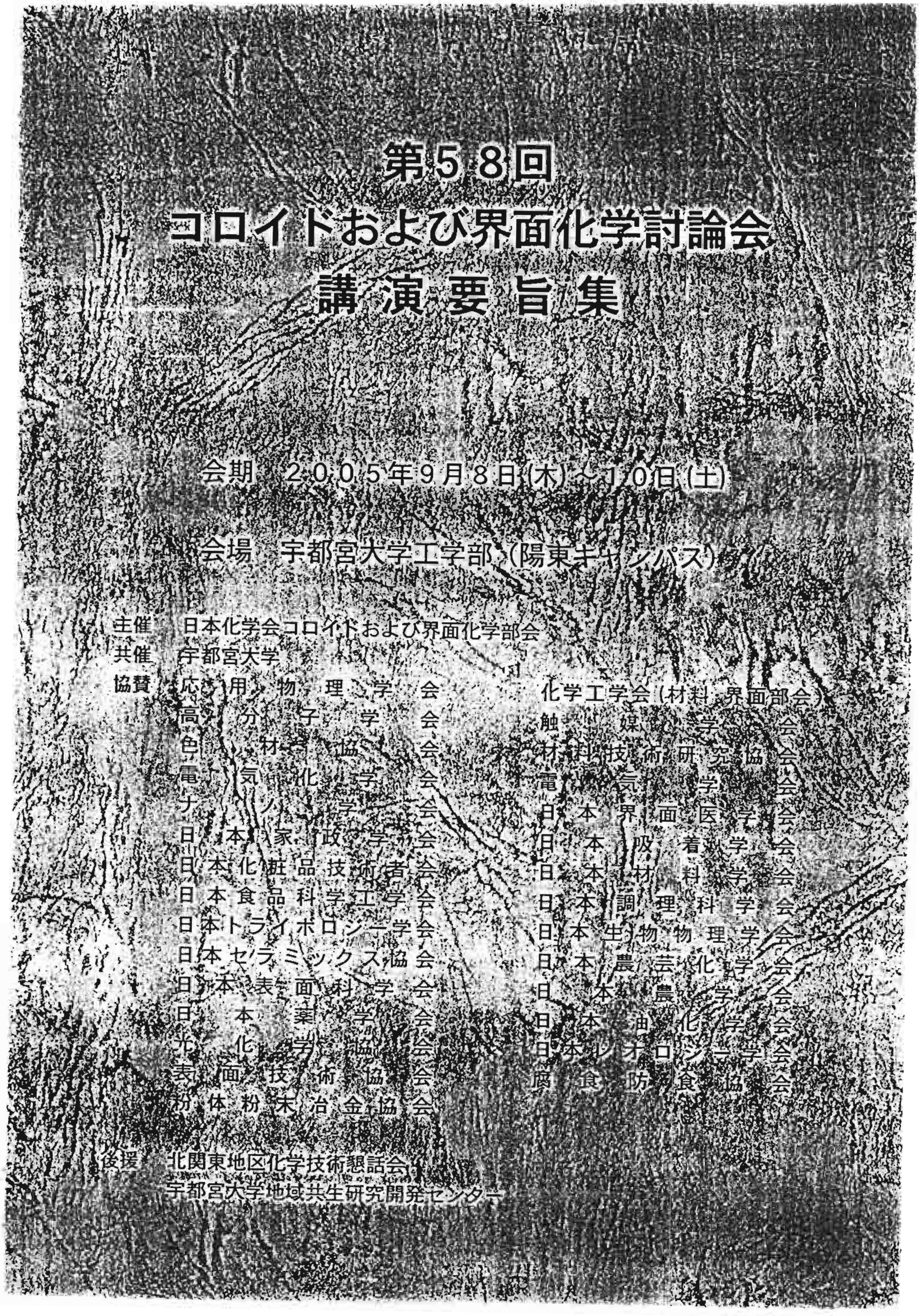
A Lever, a Fulcrum, a Place to Stand—and Good Timing. G. van Buskirk, Clorox Services Company, United States. *Contact:* Gregory van Buskirk, Clorox Services Company, 7200 Johnson Drive, Pleasanton, California 94506, United States.

Abstract: The prescription of Archimedes for being able to move the world neglected a key factor, which centuries later has been found by numerous product development companies to be vital—the significance of timing. The identification of key consumer needs, the ability to bring together the appropriate technology, and a key brand name on which to build the product have become the price of entry—and can be wasted for lack of good fortune. Is a product ahead of its time, lost in the crowd, or in the right place at the right time? What influence can seemingly disparate events have? Case histories will be presented, which illustrate the importance, in rewards and consequences, of this elusive factor.

Advertising in 20 Minutes. B. Cutler, Baker & Hostetler LLP, United States. *Contact:* Barry Cutler, Baker & Hostetler LLP, Suite 1100, 1050 Connecticut Avenue, N.W., Washington, District of Columbia 20036, United States.

Abstract: The use of truthful advertising is critical to fair competition in free markets. However, there are many misconceptions about advertising rules among marketers and lawyers alike. Many of these involve notions that advertising turns heavily on technicalities, such as that words that are strictly true are permitted, even if they create a misleading impression and that a consumer "testimonial" is legal so long as the speaker "really believes it." In fact, advertising law turns more on common sense and on determining what the "net impression" of the ad will be to the typical consumer. This presentation will cover, with examples, how to determine what the meaning of an ad is and how to determine what proof ("substantiation") is needed to prove that the ad claims are true.

Building Brands with Oxygen-Based Bleach Technology. G. Reinhardt, Clariant GmbH, Germany. *Contact:* Gerd Reinhardt, Clariant GmbH, Industriepark Hoechst, Frankfurt 65926, Germany.



第５８回
コロイドおよび界面化学討論会
講演要旨集

会期　２００５年９月８日（木）～１０日（土）

会場　宇都宮大学工学部（陽東キャンパス）

主催　日本化学会コロイドおよび界面化学部会
共催　宇都宮大学
協賛　応用物理学会
高分子学会
色材協会
電気化学会
ナノ学会
日本家政学会
日本化粧品技術者会
日本食品科学工学会
日本トライボロジー学会
日本セラミックス協会
日本表面科学会
日本薬学会
光化学協会
表面技術協会
粉体粉末冶金協会
化学工学会（材料・界面部会）
触媒学会
材料技術研究協会
電気学会
日本界面医学会
日本吸着学会
日本材料学会
日本調理科学会
日本生物物理学会
日本農芸化学会
日本農学会
日本油化学会
日本レオロジー学会
腐食防食協会

後援　北関東地区化学技術懇話会
宇都宮大学地域共生研究開発センター

第58回 コロイドおよび界面化学討論会
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Book of Abstracts
The 58th Divisional Meeting on Colloid and Interface Chemistry
Publication Data: 22 August, 2005
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2F05 カルボン酸リチウム長繊維／炭化水素集合体の安定性（産総研）○坂口　豁

2F06 陰イオン性界面活性剤ーシリカ前駆物質複合体の形成過程（横国大院環境情報）○平澤俊和・カルロス ロドリゲス・荒牧賢治・アルトロ ロペスキンテーラ・坂本一民・國枝博信

座長　荒牧　賢治（11:00－12:10）

2F07 コロイド粒子により誘起される界面活性剤メソ構造の形態変化（お茶大人間文化）○菅沼有希子・今井正幸・馬渡理奈

2F08 酸化チタン膜上におけるポルフィリンJ会合体の可逆的配向変化と円二色性（阪大院工）○藤井祐介・塚原保徳・和田雄二

2F09 【依頼講演】分子スイッチによるリポソームソーティングの制御（奈良先端大院物質創成科学）○大槻理志・佐々木善浩・菊池純一

9月10日(土)

分子集合体の科学と技術

座長　坂口　豁（9:00－10:00）

3F01 SDS-牛血清アルブミン複合体の段階的成長（岡山理大工）○渡辺えみ・森山佳子・金沢優子・竹田邦雄

3F02 両性と陰イオン性界面活性剤の混合系における牛血清アルブミンの構造変化（岡山理大工）○AZAIMA RAZALI・岩本千賀・塊場勝仁・森山佳子・竹田邦雄

3F03 オリゴ（p-フェニレンビニレン）とポリエチレンオキシドから成るT字型ロッド-コイル分子の合成と自己集合性（徳島大工）○原田俊彦・平賀範之・森　健・南川慶二・田中正己

座長　竹田邦雄（10:00－11:00）

3F04 荷電デンドリマー溶液における多体相互作用ー分子動力学シミュレーション（岐阜大工）○寺尾貴道

3F05 アルキル部構造異性を利用したポリ（N-アシルデヒドロアラニンアルキル）水溶液の相転移温度の精密制御（徳島大工）○福島　功・小林　徹・森　健・南川慶二・田中正己

3F06 互いに構造異性な α,α-ジアミドビニルポリマー水溶液の相転移に関する研究（徳島大院工）○別府　卓・森裕紀・森　健・南川慶二・田中正己

座長　尾関寿美男（11:00－12:00）

3F07 界面活性剤水溶液中における高分子層の表面挙動（東京都立大理）○吉田早苗・藤井政俊・加藤　直

3F08 混合非イオン界面活性剤固体が形成する水和ゲルの構造（横国大院環境情報）○弓場三彩子・池田直哲・佐藤高影・國枝博信

3F09 長鎖アミド誘導体の分子認識能とゲル化能（東理大工界面科研）○伊藤怜三・近藤剛史・河合武司

座長　河合武司（13:00－13:50）

3F10 【依頼講演】極限環境微生物の培養担体としての多孔質セルロース（海洋研究開発機構）○出口　茂・津留美紀子・辻井　薫・伊藤　進・掘越弘毅

3F11 新機能性 NIPA-PMDP ゲルの合成とキャラクタリゼーションおよびその機能（北大電子研）○厳　虎・辻井　薫

座長　出口　茂（13:50－14:30）

3F12 磁場下での化学架橋ゲルの挙動；膨潤度の増加と磁場誘起体積相転移（信大理）○大塚伊知郎・尾関寿美男

3F13 細胞間情報伝達物質の高分子ゲルシートへのトラップに基づくクオーラムセンシング制御（宇都宮大工）○加藤紀弘・諸星知広・田中　徹・中川翔太・池田　宰

ポスター発表

国際シンポジウム (International Symposium)

P001 What is the Stable Form of a Charged Bubble Suspended in Air? (Utsunomiya Univ., Japan) ○ IWASAKA, Tomomi・YONEMURA, Denjirou・YODA, Hidehiko・SUEZAKI, Yukio・KATO, Teiji

P002 Synthesis and Characterization of Rambutan-like Poly(methyl methacrylate)/Polyacrylonitrile Composite Latex Particles (Gunma Univ., Japan) ○SHI, Shan・KURODA, Shin-ichi・KUBOTA, Hitoshi

P003 Synthesis and Characterization of Polyelectrolyte Grafted Charged Colloidal Particles using Block Copolymer as an Emulsifier (Department of Polymer Chemistry, Graduate School of Engineering, Kyoto Univ., Japan) ○ MOHANTY, Sundar Priti・HARADA, Tamotsu・MATSUMOTO, Kozo・MATSUOKA, Hideki

P004 Recovery of Mixed Surfactants from Water using Multi-Stage Foam Fractionator (Petroleum and Petrochemical College, Chulalongkorn Univ., Thailand) ○ TRIROJ, Manutchanok・CHAVADEJ, Sumaeth・MALAKUL, Phomthong・SCAMEHORN, John

P005 Diesel Removal from Wastewater by Froth Flotation with Colloidal Gas Aphon (Petroleum and Petrochemical College, Chulalongkorn Univ., Thailand) ○ANGKATHUNYAKUL, Panita・CHAVADEJ, Sumaeth・RANGSUNVIGIT, Pramoch・SCAMEHORN, John

P006 Detergency of Oily Soil by Microemulsion at Low Salinity (Petroleum and Petrochemical College, Chulalongkorn Univ., Thailand) ○ RATCHATAWADKUL, Pantipa・CHAVADEJ, Sumaeth・KITIYANAN, Boonyarach・TONGCOMPOU, Chantra・SCAMEHORN, John

P007 Synthesis and Properties of a Novel Surfactant Modified with Cycloamylose (Tokyo University of Science, Japan) ○ WONGTRAKUL, Paveena・ICHIGE, Hidetoshi・OYAIZU, Kenichi・YUASA, Makoto・OHKUBO, Takahiro・SAKAI, Hideki・ABE, Masahiko

P008 Direct Observation of PFPE Lubricant Molecules by Cryo-AFM under Ultrahigh Vacuum (Utsunomiya Univ, Hitachi Ltd., Japan・JEOL) TORITA, Naoyuki・NAKAKAWAJI, Takayuki・AMO, Mina・IIMURA, Ken-ichi・KATO, Teiji・SATO, Tomoshige

P009 Interfacial Tension Studies of Crown Ethers at Air/Water and Hexane/Water Interfaces (Bu-Ali Sina Univ., Iran・Kyushu Univ.) ○ SAEID, Azizian・KASHIMOTO, Kaoru・MATSUDA, Takashi・ARATONO, Makoto

一般シンポジウム

P010 AOT 逆ミセルナノ液滴中における銅イオンの水和構造解析（東理大理工）○安藤一行・大久保貴広・酒井秀樹・阿部正彦

総合セッション

P011 超臨界二酸化炭素逆ミセルの会合形態に及ぼす温度/圧力/水添加量の影響（弘前大理工・東理大理工・日大理工・産総研）○鷲坂将伸・小池大輔・酒井秀樹・越智健二・吉澤　篤・阿部正彦・大竹勝人

P012 透明導電性ガラスの作成と色素増感太陽電池への応用（福島工専物質工）○黒澤雄樹・鈴木大将・酒巻健司

P013 高極性オイルを用いた界面化学的乳化（富士写真フイルム先進コア技術研）○西見大成

P014 規則性マクロ多孔体を有する白金金属粒子の調製法（産総研・コンパクト化学プロセス）○峯　英一・白井誠之

P015 原子間力顕微鏡によるマイカ表面上のタンパク質分子の吸着状態の観察（筑波大数理物質）○木村繁人・栗田忠史・寺島　浩・高野　薫

P016 生体環境下で機能するPEG/オリゴカチオン安定化クレイナノ粒子の調製と評価（筑波大学際物質科学研究セ）○佐藤嘉秀・山田嘉明・高橋唯仁・長崎幸夫

005

Diesel Removal from Wastewater by Froth Flotation with Colloidal Gas Aphon

Ms. Panita Angkatbunyakul*
Sumaeth Chavadej*, Pramoch Rangsunvigit*, and John F. Scamehorn**

** The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand*
*** Institute of Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma*

Froth flotation is a surfactant-based separation process suitable for treating dilute oily wastewater. From previous work, ultra low interfacial tension alone cannot be used as the sole criterion for froth flotation operation, as foam stability is also important in the process. In this work, it was hypothesized that foam stability can be enhanced by colloidal gas aphron (CGA). The objectives of this work were to study parameters affecting CGA formation and to determine the optimum conditions for maximum diesel removal in the froth flotation operation. Branched alcohol propoxylate sulfate sodium salt (Alfoterra 145-5PO) was used to form microemulsions with diesel oil. The effects of surfactant concentration, salinity, air flow rate, stirring time and stirring speed of CGA formation on foam characteristics and froth flotation performance were investigated. The CGA enhanced oil removal in the froth flotation operation because of higher foam stability and foam ability.

97th AOCS Annual Meeting & Expo

Abstracts

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column, preferably separating them within a single chromatographic run. To identify unknowns in complex sample, MS compatible chromatographic conditions are required. Although a variety of HPLC columns are available and have been used for surfactant analysis, none provide optimal separation for anionic, nonionic, cationic, and amphoteric surfactants under the same and MS compatible chromatographic conditions.

In this paper, chromatographic methods were developed to separate anionic, nonionic, cationic, and amphoteric surfactants on a single column, using a simple and MS compatible mobile phase system, and within a single chromatographic run. The stationary phase provides multimode separation mechanism, and exhibits ideal selectivity and excellent peak shapes for different types of surfactants. The mobile phase system consists of ammonium acetate and acetonitrile. It is found that mobile phase ionic strength and pH are two important parameters for method optimization. Surfactant analysis of a series of consumer products, including laundry detergents, fabric softeners, mouthwashes, liquid soaps, shampoos, will be demonstrated on this new column.

Removal of Aromatic Contaminants from Wastewater by Continuous Cloud Point Extraction in a Multi-Stage Rotating Disc Contactor. Phanphat Taechangam*[1], Somchai Osuwan[1], Thirasak Rirksomboon[1], and John Scamehorn[2], [1]*The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand*, [2]*Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma, USA*.

Cloud Point Extraction (CPE) has been successfully scaled up to continuously remove aromatic contaminants from a wastewater stream in a multi-stage rotating disc contactor (RDC). This work mainly focuses on the improvement in the efficiency of this cloud point extraction unit for toluene removal from the wastewater stream by using t-octylphenolpolyethoxylate nonionic surfactant. When the nonionic surfactant solution has a temperature higher than the certain temperature known as cloud point, phase separation occurs. The micellar rich phase, or coacervate phase, and the micellar dilute phase are formed. Toluene contained in the wastewater will solubilize into the surfactant micelles and concentrate in the coacervate phase during the phase separation so that the dilute phase containing less concentration of toluene can be released to the environment as treated water. In this contribution, the optimal condition has been determined by varying the wastewater and surfactant feed flow rates, rotating disc speed, and operating temperature. It was observed that up to 99% of toluene extraction can be accomplished at the following conditions: 18.2 ml/min of wastewater flow rate; 1.47 ml/min surfactant flow rate; 100 rpm rotating disc speed; 40°C operating temperature; and, 100 ppm of toluene concentration in the wastewater feed. However, the detailed study will be performed further to achieve the highest efficiency of the operating unit. The effect of concentrations of toluene in the wastewater feed on the cloud point extraction is discussed in this paper. It was found that the cloud point extraction performance decreased as the concentration of toluene in the wastewater feed increased. Finally, it was noted that the entrainment of surfactant to the dilute phase also had to be a concern.

The Oily Treatment by Continuous Froth Flotation: Foam Characteristics. Sunisa Watcharasing*[1], Sumaeth Chavadej[1], and John F. Scamehorn[2], [1]*The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand*, [2]*School of Biological, Chemical and Materials Engineering, University of Oklahoma, Oklahoma, USA*.

Froth flotation is one of surfactant-based separation processes which is suitable for treating dilute oily wastewaters. The objective of this study is to investigate the relationship between both the low IFT and foam characteristics to the efficiency of cutting oil removal by continuous froth flotation process. Single surfactant systems (branched alcohol propoxylate sulfate, sodium salt, Alfoterra 145-5PO and sodium dodecyl sulfate, SDS) and a mixed surfactant system (Alfoterra 145-5PO and sodium bis-2-ethylhexylsulfosuccinate, AOT) are used to form microemulsions with cutting oil. In froth flotation experiment, the effects of surfactant concentration, salinity, air flux, foam height, and hydraulic retention time (HRT) on the oil removal will be studied. To obtain a better understand of flotation process, ability of foam formation and foam stability will be studied. In addition, the dynamic surface tension and interfacial tension will be measured.

Toluene Removal from Nonionic Surfactant Coacervate Phase Solution by Vacuum Stripping. Suratsawadee Kungsanant*[1], Boonyarach Kitiyanan[1], Thirasak Rirksomboon[1], Somchai Osuwan[1], and John F. Scamehorn[2], [1]*The Petroleum and Petrochemical College, Chulalongkorn University, Pathumwan, Bangkok, Thailand*, [2]*Institute for Applied Surfactant Research, University of Oklahoma, Norman, OK, USA*.

Cloud point extraction (CPE) is an aqueous-aqueous phase extraction induced by addition of nonionic surfactants above their cloud point to water. It is critical to the economics of the process to recover the surfactant for recycle from the coacervate (concentrated surfactant solution) from the extraction column. This study utilized a continuous bench-scale flash vacuum column to strip out toluene from a coacervate phase containing t-octylphenolpolyethoxylate. The column was a differential stripper packed with glass Raschig rings and operated under rough vacuum. The equilibrium vapor-liquid partition coefficient for the toluene in the coacervate phase was measured and used to evaluate transfer unit properties in the co-current flash vacuum stripping. The apparent Henry's constant in the coacervate phase is lower than that in water due to partitioning of toluene in surfactant micelles. The liquid loading rate increases with decreasing fractional removal of toluene. The value of mass transfer coefficient increases significantly as harder vacuum is used, particularly at pressures lower than 70 torr. Effect of liquid distributor design on the mass transfer coefficient is also discussed.

S&D 2.1: Industrial Applications of Surfactants, Part I

Chairs: M. Rosen, Surfactant Research Institute, Brooklyn College, City University of New York, USA; and T.-C. Jao, Afton Chemical Corporation, USA

Characterizing the Behaviour of Individual Ethylene-Propylene Copolymers in Solution Using Fluorescence. M. Zhang and J. Duhamel*, *University of Waterloo, Waterloo, ON, Canada*.

The behaviour of individual ethylene-propylene (EP) copolymers in solution is investigated. The study focuses on maleated EP copolymers where the succinic anhydride is used to covalently attach a fluorescent probe onto the polymer, typically 1-pyrenemethylamine, which results in the formation of succinimide moieties. Taking advantage of the sensitivity of fluorescence, polymer solutions containing as little as 0.02 g/L of EP copolymer were studied. In apolar solvents, the polar succinimides aggregate and the level of aggregation between the pyrenyl pendants can be determined. Since the polar succinimide linkers drive the associations in an apolar solvent, the fraction of aggregated pyrenes reflects the level of aggregation between succinimides. Interestingly, adding an aromatic compound such as toluene to the apolar solvent melts the associations between the succinimide moieties. This fluorescence-based procedure can also be used to determine the distribution of maleic anhydride distributed along a maleated EP copolymer. Based on the expertise developed with the above systems, the study of the crystallization of individual EP chains was undertaken in toluene. A semi-crystalline and an amorphous EP copolymers were maleated and labelled with pyrene. Fluores-

第５９回
コロイドおよび界面化学討論会
講演要旨集

The 59th Divisional Meeting on Colloid and Surface Chemistry,
the Chemical Society of Japan
13-15 September, 2006, Hokkaido University, Sapporo

会期　２００６年９月１３日（水）～１５日（金）

会場　北海道大学　高等教育機能開発総合センター

主催　日本化学会コロイドおよび界面化学部会
共催　北海道大学21世紀ＣＯＥプログラム「バイオとナノを融合する新生命科学拠点」

協賛
応用物理学会
高分子学会
色材協会
電気化学会
ナノ学会
日本家政学会
日本化粧品技術者会
日本食品科学工学会
日本トライボロジー学会
日本セラミックス協会
日本表面科学会
日本薬学会
光化学協会
表面技術協会
粉体粉末冶金協会
化学工学会（材料・界面部会）
触媒学会
材料技術研究協会
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日本農芸化学会
日本農学会
日本油化学会
日本レオロジー学会
腐食防食協会
錯体化学会

後援　（財）花王芸術・科学財団　（財）札幌国際プラザ

子膜構造(山形大工・埼玉大理)○藤森厚裕・星沢裕子・舛屋諒介・増子徹・中原弘雄

3G13 高分子ナノシートによる自己保持型薄膜の作製について(東北大多元研)三ツ石方也・○遠藤洋史・宮下徳治

H 会場

9 月 13 日(水)

シンポジウム 4 (光ー分子強結合反応場形成を目指して)

座長 武井孝(11:00ー12:10)

1H01 【依頼講演】光ー分子強結合反応場の形成・制御(北大電子研・JST-CREST)○三澤弘明

1H02 感熱応答性高分子のパルスレーザー誘起相分離(北大院理)○坪井泰之・吉田康弘・岡田健作・喜多村昇

1H03 ランダム構造を用いた光反応場への応用(北大電子研)○藤原英樹・笹木敬司

座長 山田淳(13:10ー14:20)

1H04 【依頼講演】金属ナノ粒子の精密構造制御と光物性(筑波大院数理物質科学)○寺西利治

1H05 酸化チタン単結晶表面における銀ナノ粒子の析出と多色フォトクロミズム(東大生研)○立間徹・松原一喜

1H06 球状メソポーラスシリカ粒子/チタニアナノシート複合薄膜の作製と光誘起電子移動(名大院工・豊田中研)○小林由佳・由井樹人・矢野一久・山田有理・岡崎健一・福嶋喜章・高木克彦・鳥本司

座長 三澤弘明(14:20ー15:10)

1H07 【依頼講演】高規則ポーラス構造によるナノ・マイクロ空間の形成と光機能化(首都大都市環境)○益田秀樹・西尾和之

1H08 単分子膜リソグラフィによるナノオブジェクトの自在空間配置(京都大学大学院工学研究科材料工学専攻)○杉村博之

座長 岡崎健一(15:30ー16:40)

1H09 【依頼講演】電場増強金ナノ構造の化学的設計と光エネルギー変換への応用(九大院工)○山田淳

1H10 局所増強電場による少数分子の検出・制御(北大院理)高瀬舞・沢井良尚・○村越敬

1H11 構造敏感な単層カーボンナノチューブの光応答を利用した集積法の開発(科学技術振興機構・北大院理)○武田憲彦・村越敬

I 会場

9 月 13 日(水)

国際シンポジウム

座長 阿部正彦(09:30ー10:50)

1I01 [Invited] Advanced Surfactant Microemulsions: Technology Development/Application (The University of Oklahoma, USA) ○SABATINI,David. A.

1I02 [Invited] Continuous Froth Flotation to Remove Cutting Oil from Wastewater (Chulalongkorn University, Thailand) ○ CHAVADEJ, Sumaeth; LAPEE-A, Alweeya; WATCHARASING, Sunisa; RANGSUNVIGIT, Pramoch; SCAMEHORN, John

1I03 Foaming Properties of Mono and Diglycerol Fatty Acid Esters in Different Nonpolar Oils (Yokohama National University, Japan) ○ SHRESTHA, Lok; KATO, Hiroyuki; TAKASE, Yoshihiko; ARAMAKI, Kenji

座長 Jin Jian(10:50ー11:50)

1I04 Strategies to Control the Properties and Placement of Phosphonate Inhibitor in Oil Reservoir (University of Michigan, Michigan, USA; Chulalongkorn University, Thailand; Tokyo University of Science, Japan) ○ TANTAYAKOM, Veerapat; FOGLER, Scott H.; CHAVADEJ, Sumaeth

1I05 Formation of Wormlike Micelle in a Mixed Amino-Acid Based Anionic Surfactant and Cationic Surfactant Systems (Yokohama National University, Japan) ○ SHRESTHA, Rekha; SHRESTHA, Lok; ARAMAKI, Kenji

1I06 Effects of Additives on the Internal Dynamics and Properties of Reverse Micellar Formulations (Panjab University, India) MEHTA, S.K.; SHWETA, Sharma

座長 高草木達(13:00ー14:40)

1I07 Formation of Viscoelastic Micellar Solution in Nonionic Fluorinated Surfactant Solution (Yokohama National University, Japan) ○ SHARMA, Suraj Chandra; ACHARYA, Durga P.; ARAMAKI, Kenji; KUNIEDA, Hironobu

1I08 Free-Standing Inorganic Thin Films Prepared by Dried Foam Films (National Institute for Materials Science, Japan) ○JIN, Jian; ICHINOSE, Izumi

1I09 Convectional, Sedimentation and Drying Dissipative Structures of Colloidal Dispersions (Yamagata University, Japan) ○OKUBO, Tsuneo

1I10 Dispersion Stability of Colloids in Supercritical Fluids (Japan Agency for Marine-Earth Science and Technology, Japan) ○GHOSH, Swapan; DEGUCHI, Shigeru; TSUJII, Kaoru; HORIKOSHI, Koki

1I11 Fractality controlled porous silica with a designed template method (Hokkaido University, Japan) ○ MAYAMA, Hiroyuki; TSUJII, Kaoru

座長 大塚俊明(14:40ー16:10)

1I12 Spontaneous Formation of Fractal Structures on a Wax Surface and Its Super Water-Repellency (Hokkaido University, Japan; CREST-JST) ○FANG, Wenjun; MAYAMA, Hiroyuki; TSUJII, Kaoru

1I13 [Invited] Plasma Electrolytic Oxidation of Aluminum (Korea Institute of Machinery and Materials, Korea) ○ MOON, Sung-Mo; PARK, Pyung-Youn; JEONG, Yongsoo

1I14 Micropatterning and Area Selective Metallization on Anodic Oxide Film of Aluminum by Laser Irradiation (Hokkaido University, Japan) ○ JHA, Himendra; KIKUCHI, Tatsuya; SAKAIRI, Masatoshi; TAKAHASHI, Hideaki

1I15 Corrosion Prevention of Steel by using Conductive Polypyrrole Coating (Hokkaido University, Japan) ○ KOWALSKI, Damian; UEDA, Mikito; OHTSUKA, Toshiaki

座長 阿部竜(16:10ー17:50)

1I16 [Invited] Hydrogen Storage on Modified Graphite: Effect of Metal Loading and Milling Time (Chulalongkorn University, Thailand) ○ RANGSUNVIGIT, Pramoch; JANNATISIN, Visara; SUTTISAWAT, Yindee; KITIYANAN, Boonyarach; KULPRATHIPANJA, Santi

1I17 Photocatalytic Degradation of Dye Using Nano-TiO_2 Immobilized on Activated Carbon (Burapha University, Thailand) ○NGAOTRAKANWIWAT, Pailin

1I18 Preparation and elastico-luminescence of highly crystalline nanoparticles of europium-doped strontium aluminate (National Institute of Advanced Industrial Science and Technology, Japan) ○LI, Chengzhou; IMAI, Yusuke; ADACHI, Yoshio; NISHIKUBO, Keiko; TERASAKI, Nao; SAKAI, Kazufumi; YAMADA, Hiroshi; XU, Chao-Nan

1I19 [Invited] Preparation and Characterization of Surfactant-modified Polymeric Films for Potential Use in Biomedical Applications (Chulalongkorn University, Thailand) RUJIRAVANIT, Ratana; PORNSUNTHORNTAWEE, Orathai; WONGPANIT, Panya; CHAVADEJ, Sumaeth

9 月 14 日(木)

国際シンポジウム

座長 Olaf KARTHAUS (09:00ー10:20)

2I01 [Invited] Friction and Lubrication of Hydrogels (Hokkaido University, Japan) ○GONG, Jian Ping ; OSADA, Y

2I02 [Invited] In-situ Investigation of Molecular Diffusion in Hydrogels (ICCAS, CAS, China) ○XU, Jian; WENG,

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Continuous Froth Flotation to Remove Cutting Oil from Wastewater

Sumaeth Chavadej*, Alaweeya Lapee-A*, Sunisa Watcharasing*,
Pramoch Rangsunvigit*, and John F. Scamehorn**

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Froth flotation, a surfactant-based separation process, is suitable for treating dilute oily wastewaters. The objective of this study was to investigate the relationship between the ultra-low interfacial tension (IFT) and the efficiency of cutting oil removal from water using continuous froth flotation process. Branched alcohol propoxylate sulfate sodium salt(Alfoterra 145-5PO) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) were used for microemulsion formation with cutting oil. Surfactant concentration, salinity, and oil-to-water ratio were varied in the microemulsion formation experiments in order to determine the compositions required to obtain the ultra-low IFT conditions which were selected for running froth flotation experiments. For the froth flotation experiments, the effects of surfactant concentration, salinity, foam height, air flow rate, hydraulic retention time (HRT), and adding polyelectrolyte on the oil removal were investigated. From the results, the maximum oil removal efficiency of the froth flotation process was found not to correspond to the minimum IFT of the system. Interestingly, foam stability was revealed experimentally to be another crucial factor affecting the performance of forth flotation. Sodium dodecyl sulfate SDS) was added to improve both foamability and foam stability in the continuous froth flotation operation. The system with 0.1 wt.% SDS, 5 %wt.% NaCl, 0.15 L/min air flow rate, 30 cm foam height and 60 min HRT gave a maximum oil removal of 96 %.