for 3 minutes and maintained in a shaker bath at 25 ± 0.2°C for 24 h for adsorption equilibrium to be established. The solid particles were separated from the polymer solution by centrifugation, and the concentration of polyelectrolyte in solution was determined using a Dohrmann total organic carbon analyzer (Rosemount Analytical, Santa Clara CA). The quantity of QUAT adsorbed on the particles was calculated as the difference between the initial concentration and the final equilibrium concentration,

$$q_e = \frac{(C_i - C_e)V}{W}$$

where C_i and C_e are the initial and final (equilibrium) QUAT concentrations in solution (mg/L), q_e is the QUAT concentration retained in the adsorbent phase (mg/g); V is the solution volume (L); and W is the mass of adsorbent (g).

Crystal Morphology Characterization

The morphology of precipitate particles formed with and without QUAT were observed by scanning electron microscopy and the presence of elements with molecular weight higher than were continue by energy dispersive x-ray spectrometry (JSM 6400, Jeol, Japan/Link ISIS Oxford Instruments, UK). Fourier transform infrared spectrophotometer (Bio-Rad CA) was used to confirm presence or absence of watwe where indicated. Powder x-ray diffraction spectra (Bruker/Siemens, D5005, Germany) were used to identify the crystalline phases present.

Results

Precipitation of arsenate by barium(II) with different molar ratios of Ba:As and at different pH values leads to a variety of precipitated solids; $BaHAsO_4 \cdot H_2O$, $Ba_3(AsO_4)_2$, $Ba_5Cl(AsO_4)_3$, and $NaBaAsO_4 \cdot 9H_2O$.[23] In this work the white solids formed on mixing barium chloride and sodium arsenate solutions were characterized by using x-ray diffraction, energy dispersive x-ray fluorescence analysis, and Fourier transform infrared spectrophotometry. The energy dispersive x-ray fluorescence analysis on the solids reported herein shows that the particles contain only barium and arsenic, and the only crystalline phase observed in the x-ray diffraction patterns is barium hydrogen arsenate monohydrate, $BaHAsO_4 \cdot H_2O$.[5]

Sedimentation Rate

The settling of barium arsenate suspensions as a function of the percentage of solid volume fraction and time are shown in Figures 1-4. The average particle size at the stoichiometric ratio is relatively large (46 μm at 25°C), so the sedimentation occurs rapidly, and there is no distinct interface between the settling solids in the overlying suspension and an observable layer of sediment at the base of the vessel.

For sedimentation in the presence of QUAT, the sediment volume increased and a cloudy liquid containing finer particles in the suspension formed. The finer particles settle over a long period of time. Bell and Crowl[22] described this type of sedimentation as typical of a deflocculated dispersion. Settling times and the average particle diameters for the precipitates formed are given in Table 1.

Figure 1 presents the sedimentation of barium arsenate in the absence of QUAT and in the presence of 0.2 M QUAT at 10°C, 25°C, and 50°C for a barium to arsenate concentration ratio of 1.0. The solid volume fraction of sediment increases with increasing temperature. In the presence of QUAT the residence time required for suspended solids to settle to the base of the vessel decreases with increasing temperature (Table 1). The influence of QUAT concentration on the sedimentation properties was investigated at a constant barium to arsenate concentration ratio of 1.0 as shown in Figure 2 at 25°C. The sedimentation volume increases with increasing QUAT concentration. The solid volume sediment fraction at the completion of settling, without added QUAT gives a nearly constant value which is much smaller than when QUAT is added. The residence time required for all suspended solids to settle to the base of the vessel increases with increasing QUAT concentration.

The sedimentation of the crystals at barium to arsenate concentration ratios of 0.50, 1.0, 1.5, and 3.0 in the absence of QUAT and in the presence of 0.2 M QUAT at 25°C are shown in Figure 3. Without QUAT, an increase in barium to arsenate concentration ratio from 0.5 to 3.0 results in increases in the sedimentation volume and sedimentation time, while in the presence of polymer the sedimentation time decreases with increasing barium to arsenate ratio. Figure 4 shows the effect of ionic strength on sedimentation volume in the absence and presence of QUAT. Salt concentration does not significantly affect the rate of solid sedimentation. The sedimentation in the presence of QUAT at various salt concentrations is slower than in the absence of QUAT.

Viscosity

Table 2 shows the viscosity of QUAT at barium to arsenate concentration ratios of 0.0, 0.50, 1.0, 1.5, and 3.0, at several salt concentrations, and at different temperatures. The viscosities presented in this work are the relative kinematic viscosities of the polymer solutions in the absence of solid particles. Figure 5 shows the viscosity of QUAT solution as a function of QUAT concentration at 10°C, 25°C, and 50°C. The viscosity increases with increasing polymer concentration, decreasing temperature, decreasing barium to arsenate concentration ratio from 3.0 to 0.50, and decreasing salt concentration.

Zeta Potential

The zeta potential and electrophoretic mobility of the particles as a function of barium to arsenate concentration ratio is shown in Figure 6. At the stoichiometric ratio of 1.0, the zeta potential is zero, which represents no net charge on the surface of the particles. A negative charge is observed at barium to arsenate concentration ratio < 1.0, and a positive charge at barium to arsenate concentration ratio > 1.0. This is consistent with earlier studies, which have found that the point of zero charge (PZC) of barium arsenate occurs at the barium to arsenate concentration ratio of 1.0. At lower barium to arsenate concentration ratio values (< 1.0), the particles are negatively charged with zeta potential reaching –19.5 mV (electrophoretic mobility about -1.42×10^{-8} $m^2v^{-1}s^{-1}$) at a barium to arsenate concentration ratio of 0.25, while the zeta potential increases with increasing barium to arsenate concentration ratio, reaching +40.2 mV (electrophoretic mobility about $+3.02 \times 10^{-8}$ $m^2v^{-1}s^{-1}$) at a barium to arsenate concentration ratio of 10.

Due to high viscosity, the zeta potential of the solid could not be accurately calculated in the presence of QUAT, but electrophoretic mobility could be measured. Figure 6 shows the measured electrophoretic mobility of barium arsenate in the presence of 0.2 M QUAT, and the termed electrophoretic mobility in the absence of QUAT, in contrast to the behavior in the absence of QUAT, as a function of barium to arsenate concentration ratio. It can be seen that the electrophoretic mobility values in the presence of QUAT are positive and nearly constant when the barium to arsenate concentration ratio is increased from 0.25 to 5.0, with a slight decrease at a barium to arsenate concentration ratio of 10.0.

Particle Size Distribution

Particle size distributions of barium arsenate as a percentage of volume as a function of the logarithm of average particle diameter, are shown in Figures 7-10. Table 1 includes the average particle diameter (the particle size exceeded by 50% by volume of the distribution, $d_{0.5}$) of the solid particles under different conditions.

The particle size distributions in the absence of QUAT and in the presence of 0.2 M QUAT at 10°C, 25°C, and 50°C are shown in Figure 7. The average particle diameter in the presence of 0.2 M QUAT is larger than the average particle diameter in the absence of QUAT.

Figure 8 presents the effect of barium to arsenate concentration ratios of 0.50, 1.0, 1.5, and 3.0 on the particle size distribution in the absence and in the presence of 0.2 M QUAT at 25°C. The average particle diameter increases with decreasing barium to arsenate concentration ratios, while particle size distribution increases with increasing barium to arsenate concentration ratio. The average particle size at barium

to arsenate concentration ratios of 1.0 in the presence of 0.2 M QUAT at 25°C is higher than at other ratios, while particle size distribution is narrower than at other ratios as shown in Figure 8.

Figure 9 illustrates the effect of added NaCl concentration on the particle size distribution in the absence of QUAT and in the presence of 0.2 M QUAT at 25°C. The average particle diameter increases with increasing salt concentration from 0.01 to 0.1 M and increases more in the presence of QUAT.

Figure 10 shows the effect of QUAT concentration on particle size at low and high concentration ranges from 0.005 to 0.05 M and 0.1 to 0.3 M, respectively. An increase in QUAT concentration results in an increase in average particle size and generated a broader particle size distribution. Adding of 0.2 M QUAT increased the average particle size to approximately 88 μm (compared to approximately 46 μm without QUAT).

QUAT Adsorption on Particles

The equilibrium adsorption isotherms of QUAT on barium arsenate particles at various barium to arsenate concentration ratios in water at 25°C are shown in Figure 11. The results of polymer adsorption are given as adsorption isotherms in mg of QUAT adsorbed per g of solid versus final polyelectrolyte concentration. Adsorption of polyelectrolyte increases with increasing polyelectrolyte concentration. Figure 11 shows that the amount of QUAT adsorbed is higher for lower barium to arsenate concentration ratios. However, the adsorption of QUAT in 0.1 M NaCl at a

barium to arsenate concentration ratio of 1.0 is lower than the adsorption of QUAT in water.

In a summary plot, the effect of QUAT concentration on sedimentation of the particles, average particle size, relative viscosity, and polymer adsorption at barium to arsenate concentration ratio 1.0 at 25°C are shown in Figure 12. The average particle diameter increases, adsorption of polymer on the particles increases, and the relative viscosity of QUAT increases, while the sedimentation rate decreases with increasing polymer concentration.

Structure Morphology

Scanning electron micrographs of barium arsenate particles in the absence of QUAT and in the presence of 0.2 M QUAT are shown in Figure 13. Primary particle seems to be plates in both cases, but the plates in the presence of QUAT (Figure 13 D-F) are much larger on their faces than the ones in the absence of QUAT (Figure 13 A-C). Maybe QUAT selectively adsorbs on the faces decreasing the growth rate of the faces and thus increasing the growth length in solution resulting in larger faces and thinner crystals.

Discussion

Dispersion Stability

The effect of polymer on the dispersion stability of the suspension of barium arsenate particles as quantified by the sedimentation rate was probed by measurement of viscosity, particle size, adsorption, and electrokinetic behavior.

In the absence of polyelectrolyte, the particles form aggregates and their size is polydisperse (contains many different sizes of particles), with average particle size increasing from 14 to 67 μm with decreasing barium to arsenate concentration ratios from 3.0 to 0.50. These particles settle rapidly because gravitational force acting on the particles easily overcomes the weak net force from solvent water opposing sedimentation[24] or the increasing absolute value of the zeta potential when the barium to arsenate concentration ratio becomes less than unity (and the particles became negatively charged). The sedimentation rate and average particle size increase with increasing temperature, and decreasing barium to arsenate concentration ratio. Sedimentation rate also increases with increasing salt concentration.

Comparison of zeta potential values between barium arsenate and barium chromate show the same qualitative trend. Zeta potential value of barium arsenate at a barium to arsenate ratio of 0.5 is –7 mV (compare to barium chromate = -15 mV) whereas that for a barium to arsenate ratio of 10 is +40 mV (compare to barium chromate = +35 mV). In comparative study of electrophoretic mobility obtained from particles in the presence and in the absence of QUAT, the electrophoretic mobility of particles at barium to arsenate concentration ratio of 0.25 increases from -1.42×10^{-8} $m^2v^{-1}s^{-1}$ (in the absence of QUAT) to $+3.6\times10^{-8}$ $m^2v^{-1}s^{-1}$ with adding of 0.2 M QUAT (Figure 6).

With the addition of QUAT, barium arsenate particles are also more polydisperse in size, form larger or more aggregates, and exhibit significant average particle size increase with average diameter ranging from 78 to 94 μm. This phenomenon was observed in aggregate size distributions of nonionic and anionic polymer with alumina at pH 5.[25] The average particle diameter of alumina was 0.43 μm without polymer and increased above 55 μm and 200 μm in the presence of

nonionic polymer (*ca.* 7 mg/L) and anionic polymer (> 12 mg/L), respectively. As QUAT concentration increases, polymer adsorption on the barium arsenate particles increases, average particle size increases, viscosity increases, the particle size distribution broadens, electrophoretic mobilities increases, and sedimentation rate decreases. The sedimentation rate probably decreases because the very fine particles are stabilized as a dispersion by QUAT absorption and the increased viscosity leading to longer settling times for the total particulate material. Polymer adsorption increases with decreasing barium to arsenate concentration ratios. This phenomenon was found in adsorption of QUAT on barium chromate; adsorption increases with decreasing barium to chromate concentration ratio.[8] At barium to arsenate concentration ratio of 1.0 (the point of zero charge, PZC, of the solid in the absence of QUAT) polymer can adsorb on the particles presumably because of attractive interactions between the polymer and local charged sites on the neutral barium arsenate particles. At low barium to arsenate concentration ratios the negative surface charge on the particles will enhance electrostatic attraction between the anionic solid and the cationic polymer, causing adsorption to increase. At high barium to arsenate concentration ratio, similar charge on the particles and polyelectrolyte result in repulsive interaction forces and reduced adsorption and increased dispersion stability.[26] The solid volume is decreased by the presence of the QUAT, an effect accentuated at higher barium to arsenate concentration ratios. At high ratios, this is probably due to reduction of zeta potentials or electrophoretic mobilities due to QUAT adsorption, these values being greater with increasing barium to arsenate concentration ratios in the absence of QUAT (Figure 6), but not highly dependent on the ratio in the presence of 0.2 M QUAT (Figure 6). The electrophoretic mobility increases with increasing QUAT concentration. At low barium to arsenate concentration ratio of 0.25, the

electrophoretic mobility is -1.42×10^{-8} $m^2v^{-1}s^{-1}$ (in the absence of QUAT) and $+3.6 \times 10^{-8}$ $m^2v^{-1}s^{-1}$ (in the presence of 0.2 M QUAT) while, the electrophoretic mobility is $+2.9 \times 10^{-8}$ $m^2v^{-1}s^{-1}$ (in the absence of QUAT) and $+2.7 \times 10^{-8}$ $m^2v^{-1}s^{-1}$ (in the presence of 0.2 M QUAT) at barium to arsenate concentration ratio of 10 (Figure 6).

At PZC, there is no net charge on particles-there can still be charges depending heterogeneity of surface. It is interesting that addition of cationic polymer (positively charged particles) to the stoichiometric barium arsenate system (uncharged particles) favors the growth of larger particles. Polymer adsorption on the neutral particles must occur through hydrogen bonding. Adsorption of polyacrylamides can occur through hydrogen bonding.[25, 27]

An important result observed in Figure 6 is the higher mobility values for the nominally neutral stoichiometric barium arsenate particles in the presence of QUAT. The high mobility must result from the particles acquiring positive charge due to adsorption of polyelectrolyte to the surface. Attachment of polyelectrolyte to a particle endows the formerly neutral particle with several hundred positive charges per polyelectrolyte molecule adsorbed, leading to high mobility particle-polyelectrolyte complexes. Only on datum at the highest barium to arsenate concentration ratio shows a decrease in electrophpretic mobility. The other data are essentially constant. The particle becomes more positively charged in absence of QUAT as ratio increases, so adsorption should decrease (as shown in Figure 11).

An increase in electrolyte concentration results in an increase in particle size, an increase in sedimentation rate, and a decrease in viscosity. Adsorption of polymer on the particles also decreases with increasing electrolyte concentration. This

phenomenon were also observed in adsorption of low molecular weight poly(styrene sulphonate), PSS, on $CaCO_3$ and adsorption of quaternized poly(vinylpyridine), PVP^+, at pH 8 on TiO_2; adsorption decreases with increasing ionic strength.[28-29] At the same time the polymer molecules change from the coiled form to the extended conformation, and are then able to form bridges between neutral particles.[30] Larger particle formation in the presence of polyelectrolyte has also been observed in polyacrylamides adsorbed on alumina.[25] Addition of salt screens the electrostatic repulsion of neighboring adsorbed QUAT molecules, which tends to increase adsorption. The electrostatic attraction between polymer and surface, however, is also weakened, because the salt ions (Na^+) compete with the polymer for surface sites, tending to decrease the adsorption[29, 31], as observed in Figure11. In pure water, highly charged polyelectrolytes adopt an extended (more rodlike) conformation because of repulsive interactions between charged segments. As salinity or ionic strength increases, the interactions are screened so the polyelectrolyte tends to adopt a coiled structure. A more coiled molecule with fewer sites attached to the barium arsenate is consistent with the lower adsorption as salinity increases.[32] The coiled polymer is rougher than the flattened polymer, and the coiled polymer can cause increased steric and electrostatic repulsion between particles as the charged polymer chain extends into solution. When the salt concentration is increased, the average particle size increases in both the absence and in the presence of polymer. Larger particles in the absence of polymer are rapid coagulated by addition of sodium chloride. At 25°C. as NaCl concentration increases from 0 to 0.01 M to 0.1 M, average particle diameters increase from 46 μm to 60 μm to 75 μm. The coagulation effect of salts of have been observed in other systems.[25, 33-34]

From Figure 12 the average particle diameter increases and adsorption of polymer on barium arsenate particles increases with increasing QUAT concentration. The sedimentation rate of barium arsenate decreases because of the increase in solution viscosity and as the particle size distribution shifts to smaller particle, and increased dispersion stability.

The morphology of barium arsenate formed plate-like crystal in both of in the presence and in the absence of QUAT. The Figure 13 shows that polymer increases growth rate of surface crystal. The average particle size of barium arsenate in the presence of QUAT is about 94 μm, larger than in the absence of QUAT (size about 67 μm).

Implications for PEUF Process

In the presence of QUAT, barium arsenate forms larger crystals (average particle size about 94 μm) than in the absence of QUAT (average particle size about 67 μm). In contrast, the particle size diameter of barium chromate in the presence of QUAT (about 0.9 μm) is smaller than in the absence of QUAT (about 2 μm).[8] In the chromate case a difficult separation was made worse by the addition of QUAT, requiring the investigators to resort to batch settling to remove the barium chromate precipitate[35]. The arsenate case is highly favorable, not only because the average particles formed during the precipitation are initially quite large, but also because they become much larger when formed in the presence of the QUAT. Furthermore, the particles become larger still when formed in the presence of added electrolyte. Thus, the large particle size and high sedimentation rate of barium arsenate augments

regeneration of polyelectrolyte from the PEUF process in a steady-state crystallization process with gravity settling. The time required for complete settling of the particles increased when QUAT was added due to the enhanced dispersion stability for the smallest particles. One potential solution to this technological problem is to take advantage of the high positive electrophoretic mobility of the particles on the presence of QUAT; adding an electric field across the solution could cause the dispersed particles to settle rapidly.

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Figure 8 Particle size distribution at various barium to arsenate concentration ratios at 25°C. in the absence of QUAT, [barium]/[arsenate]: (◊) 0.50, (□) 1.0 M, (Δ) 1.5, (○) 3.0; in the presence of 0.2 M QUAT, [barium]/[arsenate]: (♦) 0.50, (■) 1.0, (▲) 1.5, (●) 3.0.

Figure 9 Particle size distribution at barium to arsenate concentration ratio of 1.0 at various NaCl concentrations at 25°C. in the absence of QUAT, [NaCl]: (◊) 0 M, (□) 0.01 M, (Δ) 0.05 M, (○) 0.1 M; in the presence of 0.2 M QUAT (♦) 0 M, (■) 0.01 M, (▲) 0.05 M, (●) 0.1 M.

Figure 10 Particle size distribution at barium to arsenate concentration ratio of 1.0 at 25°C in the presence of low QUA Γ concentration [QUAT]: (◊) 0 M, (□) 0.005 M, (Δ) 0.01, (○) 0.05 M; in the presence of high QUAT concentration [QUAT]: (♦) 0.1 M, (■) 0.2 M, (▲) 0.3 M.

Figure 11 Adsorption isotherms of QUAT on particles in water and in 0.1 M NaCl at various barium to arsenate concentration ratios at 25°C. [barium]/[arsenate]: (♦) 0.5 in water, (■) 1 in water, (▲) 1.5 in water, (○) 3 in water, (□) 1 in 0.1 M NaCl.

Figure 12 Effect of QUAT concentration on barium arsenate sedimentation rate (cm/min, ○) and kinematic viscosity (mm^2/sec, ♦) (in the right scale); average particle size (μm, ▲) and QUAT adsorption(mg /g of solid, ■) (in the left scale) at barium to arsenate concentration ratio of 1.0 at 25°C.

Figure 13 SEM micrographs of barium arsenate particles formed in the absence QUAT (A-C), and in the presence of 0.2 M QUAT (D-F).

Table 1. Settling times and average particle diameters under various conditions.

Temperature (°C)	[QUAT] (M)	[barium]/[arsenate] (M/M)	[NaCl] (M)	Settling time[a]	Average particle diameter (μm)
10	0	0.50	0	25min	60.2
	0	1.0	0	25min	59.1
	0	1.5	0	25min	58.9
	0	3.0	0	25min	45.9
	0	1.0	0.005	20min	65.1
	0	1.0	0.01	20min	71.7
	0	1.0	0.1	20min	88.2
	0.005	1.0	0	30min	68.5
	0.01	1.0	0	10h	81.0
	0.05	1.0	0	15h	109.2
	0.1	1.0	0	24h	123.2
	0.2	1.0	0	48h	111.8
	0.3	1.0	0	48h	116.5
	0.2	0.50	0	48h	85.4
	0.2	1.0	0	48h	105.1
	0.2	3.0	0	48h	63.7
	0.2	1.5	0.005	48h	130.3
	0.2	1.0	0.01	48h	102.6
	0.2	1.0	0.1	48h	110.2
25	0	0.50	0	17min	67.4
	0	1.0	0	17min	46.2
	0	1.5	0	20min	39.5
	0	3.0	0	20min	14.4
	0	1.0	0.005	15min	39.0
	0	1.0	0.01	15min	59.9
	0	1.0	0.1	15min	74.9
	0.005	1.0	0	35min	82.9
	0.01	1.0	0	45min	78.3
	0.05	1.0	0	2h	89.9
	0.1	1.0	0	8h	80.1
	0.2	1.0	0	35h	88.6
	0.3	1.0	0	40h	94.7
	0.2	0.50	0	35h	67.5
	0.2	1.5	0	35h	76.9
	0.2	3.0	0	35h	60.7
	0.2	1.0	0.005	35h	95.1
	0.2	1.0	0.01	35h	106.5
	0.2	1.0	0.1	35h	111.7
50	0	0.50	0	12min	66.7
	0	1.0	0	12min	59.8
	0	1.5	0	15min	53.6
	0	3.0	0	15min	44.1
	0	1.0	0.005	8min	52.9
	0	1.0	0.01	8min	51.6
	0	1.0	0.1	8min	49.0
	0.005	1.0	0	20min	68.5
	0.01	1.0	0	40min	67.5
	0.05	1.0	0	90min	56.7
	0.1	1.0	0	10h	77.7
	0.2	1.0	0	20h	97.2
	0.3	1.0	0	30h	67.1
	0.2	0.50	0	20h	93.1
	0.2	1.5	0	20h	75.1
	0.2	3.0	0	20h	44.1
	0.2	1.0	0.005	20h	63.3
	0.2	1.0	0.01	20h	67.3
	0.2	1.0	0.1	20h	79.9

a. The required time for suspended solids (fine particle) to settle to the base of vessel; (±2 min for 0 M QUAT, ±5 min for 0.005-0.1 M QUAT, and ±3 h for 0.2-0.3 M QUAT)

Table 2. Relative kinematic viscosity of particle free QUAT solutions.

[QUAT] (M)	[barium]/[arsenate] (M/M)	[NaCl] (M)	Relative kinematic viscosity (mm^2/sec)		
			10℃	25℃	50℃
0.0005	0	0	1.3	1.4	1.4
0.001	0	0	1.7	1.7	1.7
0.005	0	0	2.9	3.0	2.9
0.01	0	0	3.8	3.7	3.6
0.05	0	0	7.1	7.1	6.9
0.1	0	0	10.2	10.3	9.8
0.2	0	0	15.7	15.7	15.6
0.005	1.0	0	1.1	1.1	1.1
0.01	1.0	0	1.1	1.1	1.1
0.05	1.0	0	1.8	1.8	1.7
0.1	1.0	0	2.7	2.7	2.6
0.2	0.50	0	5.0	5.0	4.5
0.2	1.0	0	4.8	4.9	4.5
0.2	1.5	0	4.7	4.7	4.5
0.2	3.0	0	4.1	4.2	3.7
0.2	1.0	0.005	4.8	4.9	4.4
0.2	1.0	0.01	4.4	4.9	4.1
0.2	1.0	0.1	4.2	4.3	3.9

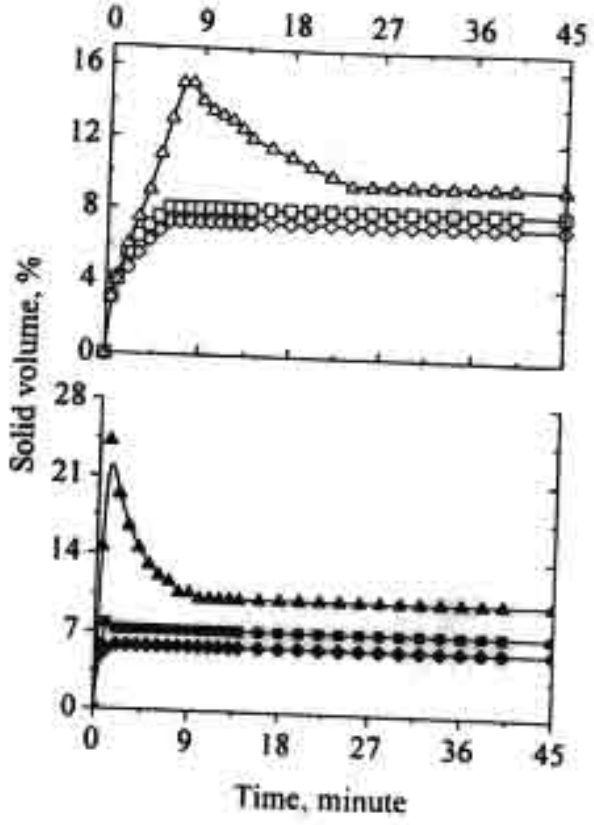

Figure 1. Sedimentation of particles at barium to arsenate concentration ratio of 1.0 at different temperatures. in the absence of QUAT: (♦) 10°C, (■) 25°C, (▲) 50°C; in the presence of 0.2 M QUAT: (◊) 10°C, (□) 25°C, (Δ) 50°C.

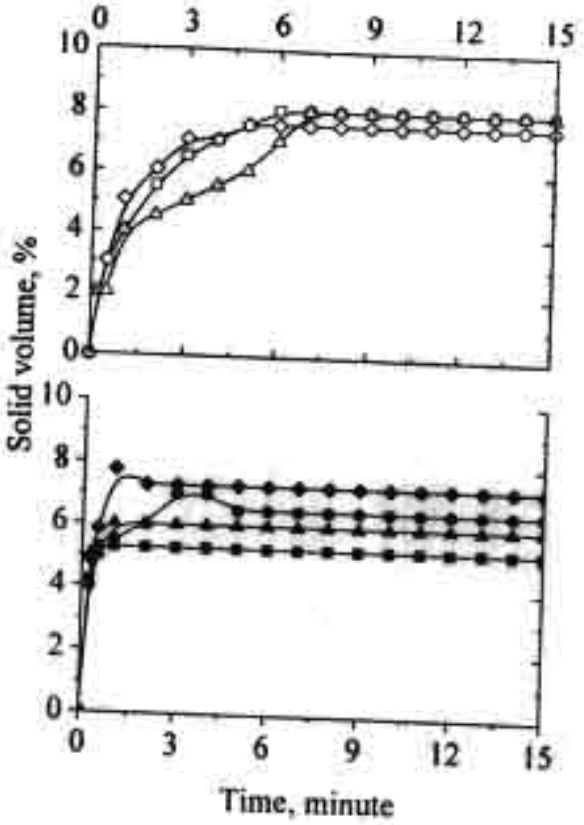

Figure 2. Sedimentation of particles at barium to arsenate concentration ratio of 1.0 in the presence of QUAT at 25°C. [QUAT]: (◊) 0 M, (□) 0.005 M, (Δ) 0.01, (○) 0.05 M, (♦) 0.1 M, (■) 0.2 M, (▲) 0.3 M.

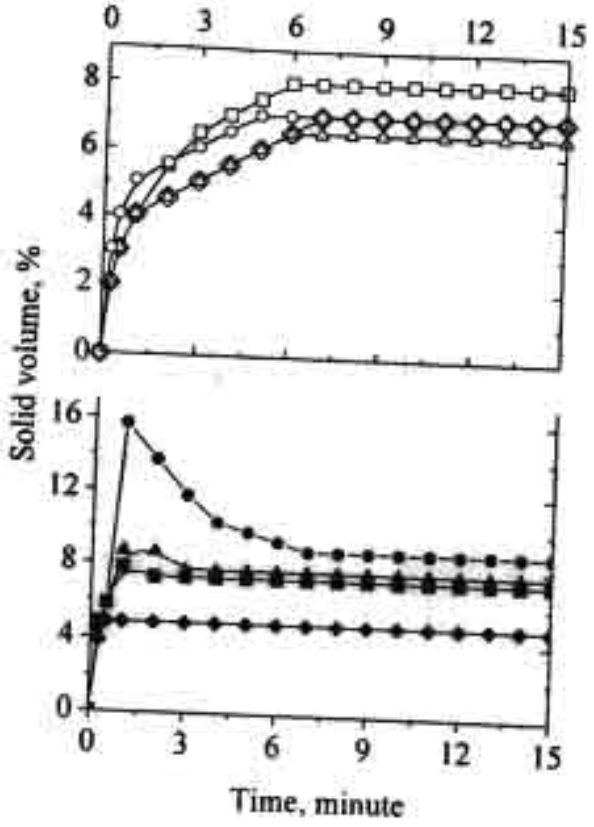

Figure 3. Sedimentation of particles at various barium to arsenate concentration ratios at 25°C. in the absence of QUAT, [barium]/[arsenate]: (♦) 0.5, (■) 1, (▲) 1.5, (●) 3; in the presence of 0.2 M QUAT, [barium]/[arsenate]: (◊) 0.5, (□) 1 M, (Δ) 1.5, (○) 3.

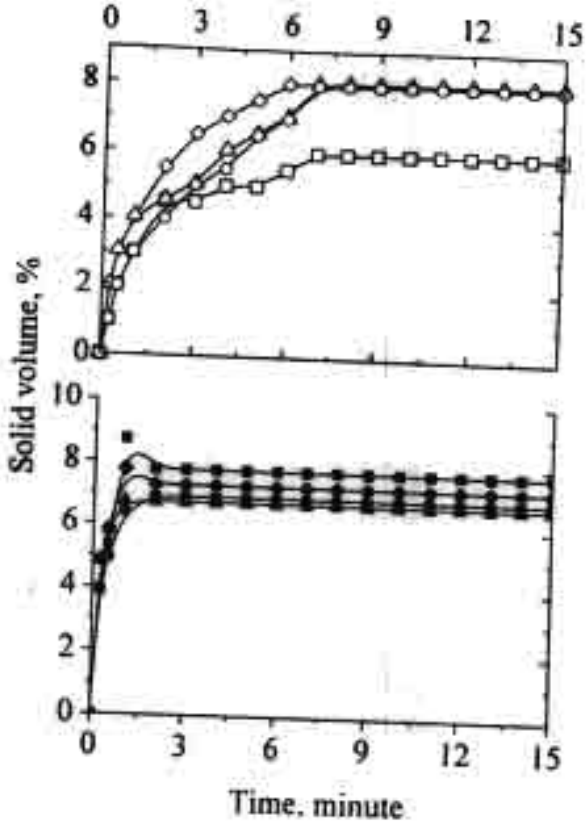

Figure 4. Sedimentation of particles at barium to arsenate concentration ratio of 1.0 at various NaCl concentrations at 25°C in the absence of QUAT, [NaCl]: (♦) 0 M, (■) 0.01 M, (▲) 0.05 M, (●) 0.1 M; in the presence of 0.2 M QUAT, [NaCl]: (◊) 0 M, (□) 0.01 M, (Δ) 0.05 M, (○) 0.1M.

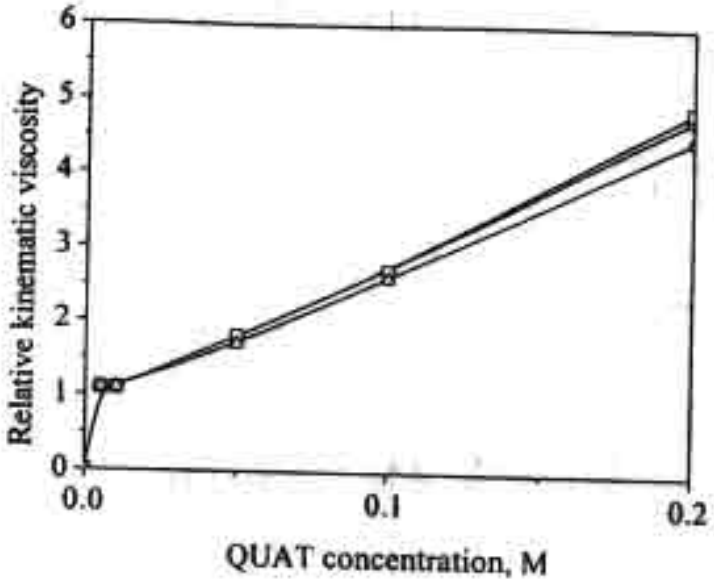

Figure 5. Relative kinematic viscosity of QUAT at barium to arsenate concentration ratio of 1.0 for different temperatures, (◊) 10°C, (□) 25°C, (Δ) 50°C.

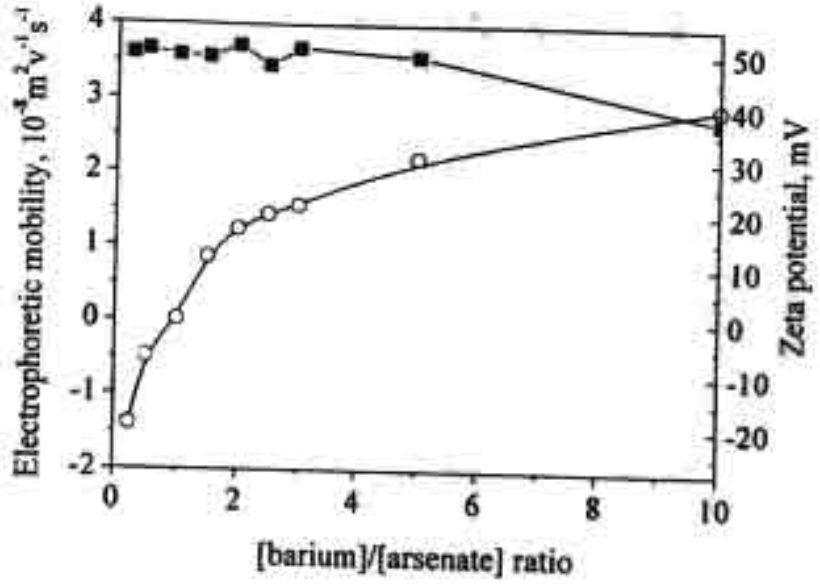

Figure 6. The effect of barium to arsenate concentration ratio on (○) zeta potential in the absence of QUAT, (●) electrophoretic mobility in the absence of QUAT, and (■) electrophoretic mobility in the presence of 0.2 M QUAT.

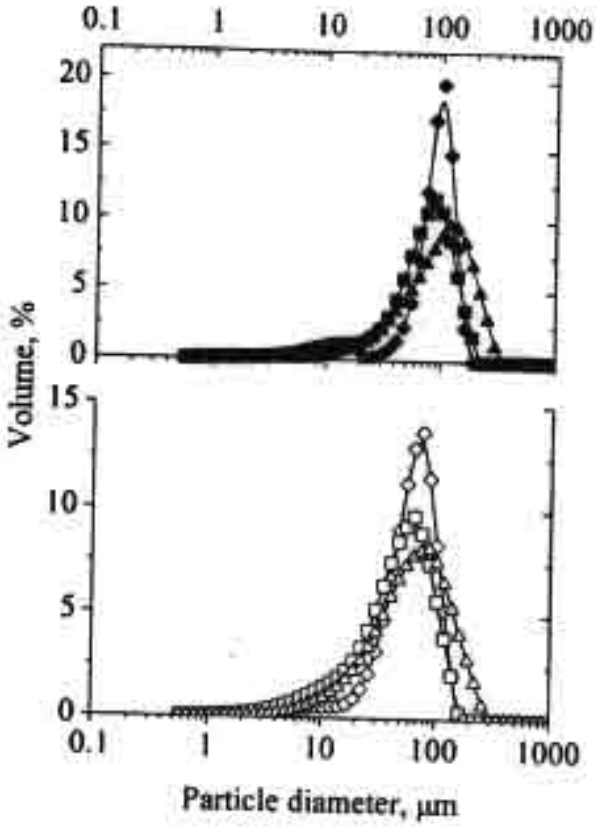

Figure 7. Particle size distribution at barium to arsenate concentration ratio of 1.0 at different temperatures. in the absence of QUAT: (◊) 10°C, (□) 25°C, (Δ) 50°C; in the presence of 0.2 M QUAT: (♦) 10°C, (■) 25°C, (▲) 50°C.

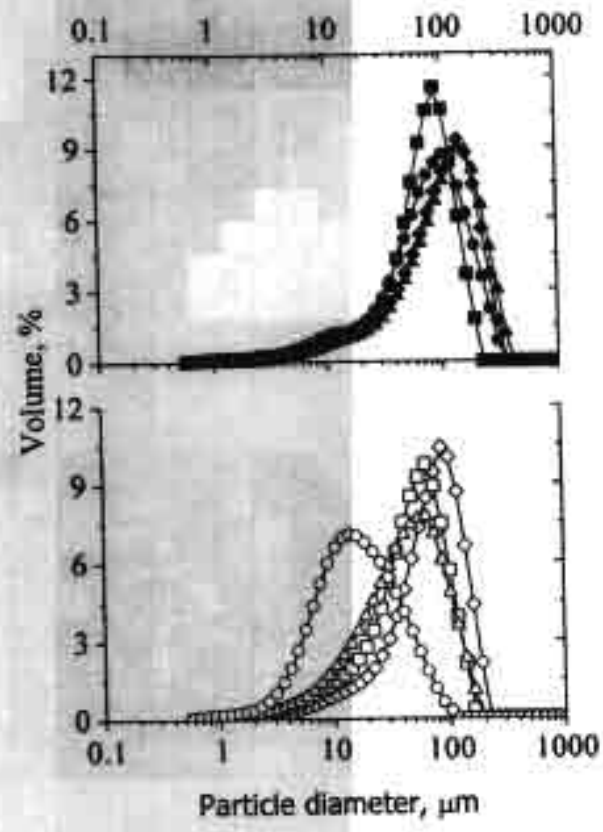

Figure 8. Particle size distribution at various barium to arsenate concentration ratios at 25°C. in the absence of QUAT, [barium]/[arsenate]: (◊) 0.50, (□) 1.0 M, (Δ) 1.5, (○) 3.0; in the presence of 0.2 M QUAT, [barium]/[arsenate]: (♦) 0.50, (■) 1.0,(▲) 1.5, (●) 3.0.

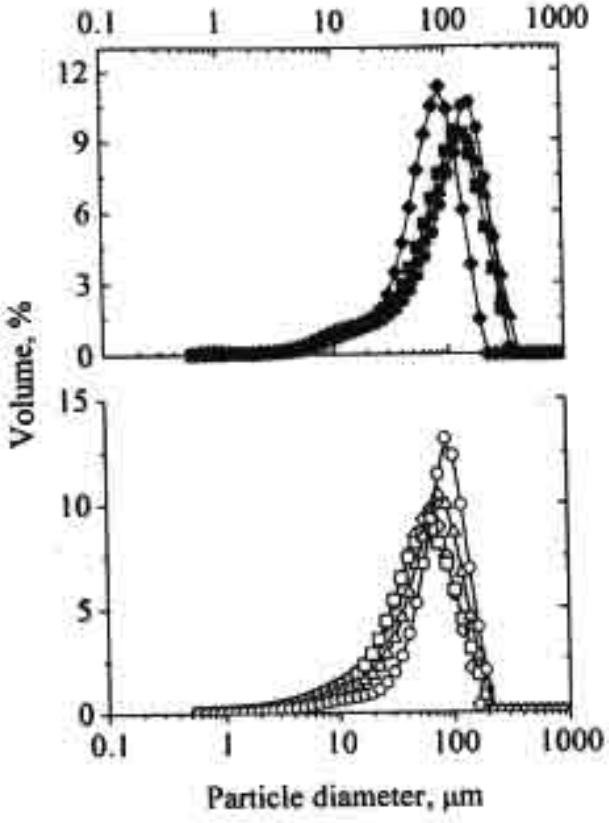

Figure 9. Particle size distribution at barium to arsenate concentration ratio of 1.0 at various NaCl concentrations at 25°C. in the absence of QUAT, [NaCl]: (◊) 0 M, (□) 0.01 M, (Δ) 0.05 M, (○) 0.1 M; in the presence of 0.2 M QUAT (♦) 0 M, (■) 0.01 M, (▲) 0.05 M, (●) 0.1 M.

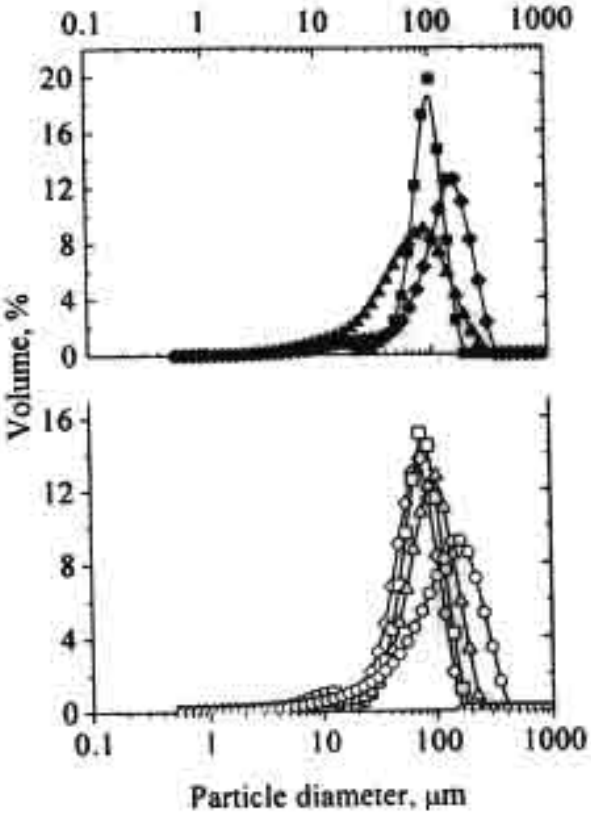

Figure 10. Particle size distribution at barium to arsenate concentration ratio of 1.0 at 25°C in the presence of low QUAT concentration [QUAT]: (◊) 0 M, (□) 0.005 M, (Δ) 0.01, (○) 0.05 M; in the presence of high QUAT concentration [QUAT]: (♦) 0.1 M, (■) 0.2 M, (▲) 0.3 M.

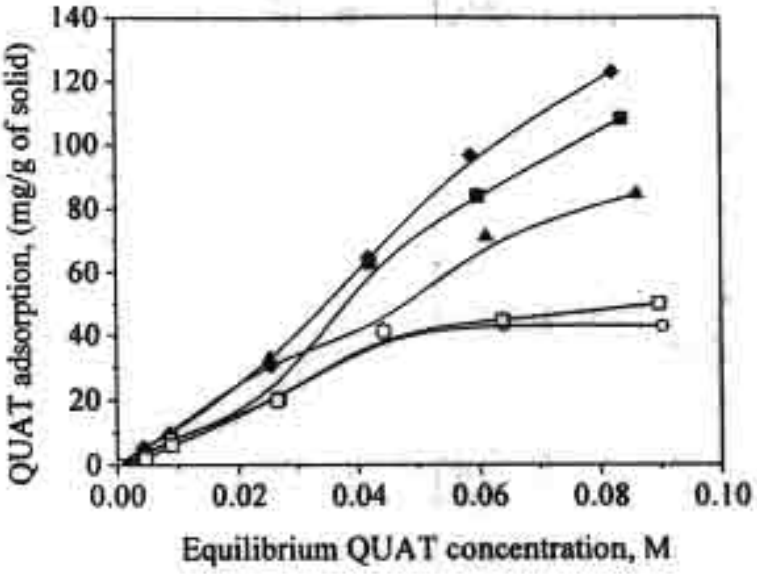

Figure 11. Adsorption isotherms of QUAT on particles in water and in 0.1 M NaCl at various barium to arsenate concentration ratios at 25°C.

[barium]/[arsenate]: (♦) 0.50 in water, (■) 1.0 in water, (▲) 1.5 in water, (○) 3.0 in water, (□) 1.0 in 0.1 M NaCl.

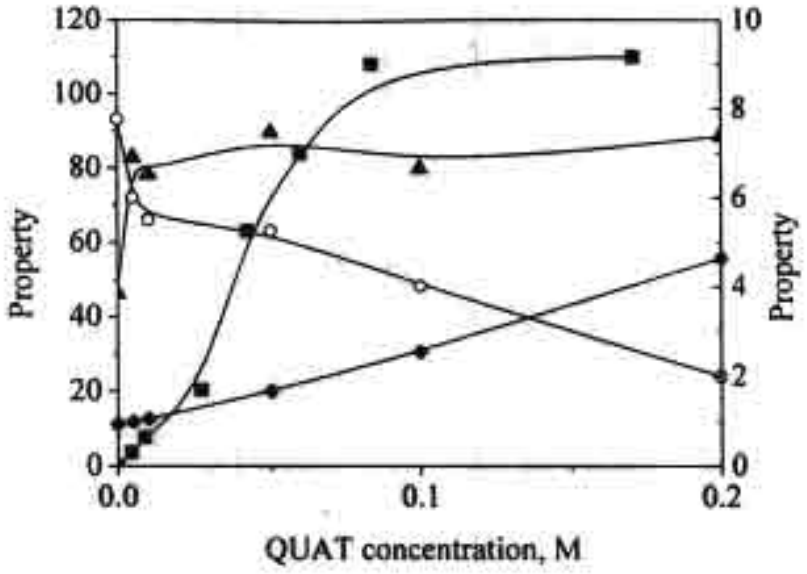

Figure 12. Effect of QUAT concentration on barium arsenate sedimentation rate (cm/min, ○) and kinematic viscosity (mm^2/sec, ♦) (in the right scale); average particle size (μm, ▲) and QUAT adsorption(mg /g of solid, ■) (in the left scale) at barium to arsenate concentration ratio of 1.0 at 25°C.

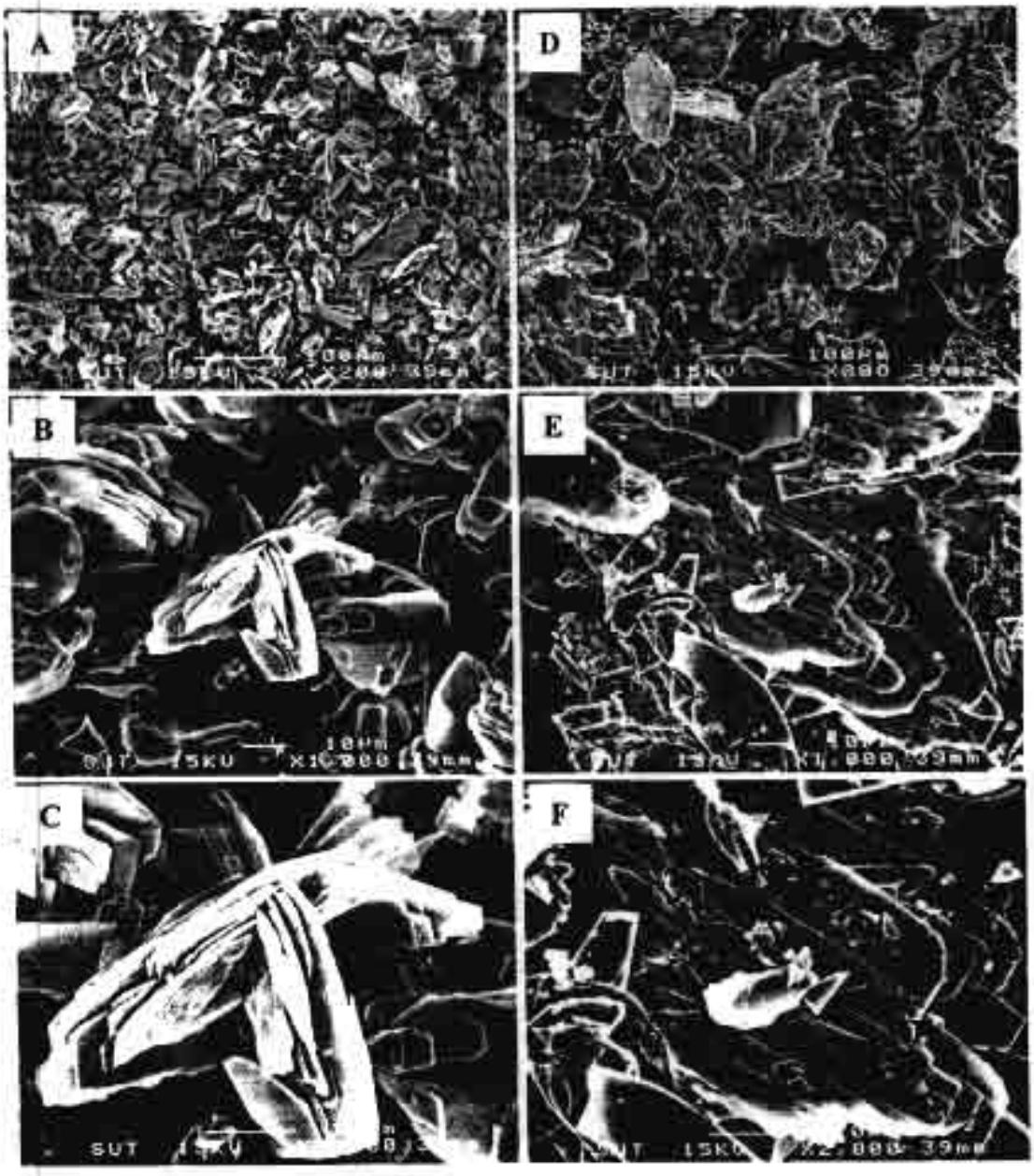

Figure 13. SEM micrographs of barium arsenate particles formed in the absence QUAT (A-C), and in the presence of 0.2 M QUAT (D-F).

Manuscript 3

Precipitation of Arsenate with Copper(II) in the Presence of Cationic Polyelectrolyte

Precipitation of Arsenate with Copper(II) in the Presence of Cationic Polyelectrolyte

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Abstract

The adsorption of polyelectrolyte onto copper arsenate particles and the consequent influence on the dispersion stability was studied. The adsorption of QUAT on copper arsenate particles increases with increasing polymer concentration, decreasing ionic strength, and decreasing copper to arsenate ratio. The copper arsenate gives spherical crystal agglomerates. Copper arsenate in the absence of QUAT shows bimodal particle size distributions with a major peak at larger particle size and a minor peak at smaller size, while particles in the presence of QUAT show multimodal distributions with small peaks at both smaller and larger sizes. The average particle size decreases with increasing polymer concentration, increasing salt concentration, decreasing temperature, and decreasing copper to arsenate concentration ratio. The smaller size in the absence of QUAT leads to slow sedimentation while the larger size in the presence of QUAT gives higher

sedimentation rates. The sedimentation rate of the crystals increases with increasing polymer concentration, increasing electrolyte concentration, and increasing temperature. The viscosity of the supernatant solution increases with increasing polymer concentration, decreasing ionic strength, decreasing temperature, and decreasing copper to arsenate concentration ratio.

Introduction

Polyelectrolytes find application in the industrial areas of paper making, the mining industry, and in numerous products used in daily life[1] for example in water and wastewater treatment processes.[2] We are particularly interested in the polyelectrolyte-enhanced ultrafiltration (PEUF) process, which can remove ionic species from aqueous solution by using a water-soluble polyelectrolyte of opposite charge to that of the target ion to be removed. The polyelectrolyte binds the target ion, and the solution is then treated by ultrafiltration with membrane pore sizes small enough to block the polymer and polymer/ion complexes. PEUF is particularly effective for multivalent ions. PEUF, with cationic poly(diallyldimethyl ammonium chloride) polyelectrolyte was used to investigate the removal of arsenic(V) naturally present as anionic oxide complexes, like arsenate, in many water supplies from dilute aqueous solutions[3]. Only the unbound arsenate at the concentration in the retentate (solution not passing through the membrane) is present in the permeate solution passing through the membrane. Arsenic rejections as high as 99.95% were observed in PEUF.

For this process of arsenate removal by PEUF to be economically competitive the QUAT must be recovered from the retentate for reuse.[4] The method of recovery

studied was addition of divalent metal ion to precipitate the arsenate.[5] After removal of the metal arsenate crystals from solution, the concentrated QUAT solution is reused by recycling to the PEUF feed. While filtration or centrifugation can recover the solid, gravity settling is the most economical separation technique. This study of the effect of the polyelectrolyte on the sedimentation rate of metal arsenate aids in the design of this solid/liquid separation. In this paper the underlying physical chemistry of the effect of the QUAT on copper arsenate particle formation and dispersion stability is probed.

An important property of polyelectrolytes is their tendency to adsorb on solid surfaces of dispersed particles.[6] Calcium phosphate precipitation significantly inhibited by addition of low concentrations (few parts per million, ppm) of low molecular weight poly(acrylic acid) in aqueous solution, while the cationic polymer, QUAT, does not inhibit amorphous calcium phosphate precipitation. High QUAT concentration (0.2 M QUAT) has been shown to inhibit barium chromate crystallization.[8] The adsorption of polyphosphinoacrylates, polyacrylate, and copolymer of maleic acid, and vinyl sulfonic acid on barium sulfate was investigated.[9-10] Showing that polyelectrolytes retard barium sulfate crystal growth. The effect of polymer on the dispersion stability and settling of barium sulfate has also been studied.[11-12] Barium sulfate dispersions were relatively stable to high electrolyte In the presence of excess sodium (carboxymethyl)cellulose, and in the presence of polystyrene sulphonate and polyacrylic acid are well dispersed and no aggregation occurs. The adsorption of an amphoteric polymer or dual polymer combination of QUAT and acrylic acid on barium sulfate crystals was shown to enhance to colloid stability of barium sulfate dispersions. The adsorption capacity of

barium sulfate under the condition increases with increasing ionic strength.[13] Schwarz *et al.*[14] described the adsorption of QUAT onto silica, mica, and acidic polymer latex and have related the adsorption characteristics to the stability of the QUAT dispersions. The results show that the adsorption of QUAT increases with increasing surface charge density of the particles and increasing electrolyte concentration. The influence of the adsorption of cationic polyelectrolytes of different charge density, QUAT, and copolymers of QUAT with N-methyl-N-vinylacetamide on the stability of precipitated silica, sikron, and latex suspensions has been studied.[15-19] The adsorbed amount and the layer thicknesses of polymer on silica and latex increases with ionic strength and pH, with decreasing chain charge density of the polycations, and at high electrolyte concentration with the molar mass of the polymers. The dispersion stability of polymer and surfactant on the drug particles of 5-(3-ethoxy-4-penty-loxyphenyl)-2,4-thiazolidinedione (CT112), was estimated by measuring the particle size, zeta potential, adsorption isotherm, and sedimentation rate.[20] The addition of celluloses rather than sodium dodecyl sulfate (SDS) provided a high stable suspension of CT112. In addition, mixed systems of celluloses and SDS enhanced CT112 dispersion more effectively. The behavior of QUAT on barium hydrogen arsenate monohydrate particle has been studied in our group.[21] Average particle size of particles increases with increasing polymer concentration.

In the present study we have investigated the formation of copper arsenate. The effect of the copper to arsenate concentration ratio, QUAT concentration, temperature, and added electrolyte on particle size distribution, sedimentation rate, and zeta potential of copper arsenate particles was measured. In addition, scanning electron microscopy has been used to study the morphology of the copper arsenate crystals formed in the absence and in the presence of polymer.

Experimental Section

Materials

Disodium hydrogen arsenate heptahydrate, $Na_2HAsO_4 \cdot 7H_2O$, (98.5%) was from Fluka (Buchs, Switzerland). Sodium chloride, NaCl, (99.5%) and cupric chloride dihydrate, $CuCl_2 \cdot 2H_2O$, (97%), were from Carlo Erba (Milan, Italy). All chemicals except the QUAT were analytical reagent grade and used as received. Deionized and distilled water were used to prepare solutions.

Commercial grade poly(diallydimethyl ammonium chloride) or QUAT, a quaternary ammonium polymer, with a number average molecular weight of 2.4×10^5 Da produced by Calgon Corporation (Pittsburgh PA) as a 40% solution in water was the cationic polyelectrolyte. Dilute solutions of the polymer were purified prior to precipitation experiments using a spiral wound ultrafiltration unit with a 10 kDa molecular weight cutoff (MWCO) membrane to remove lower molecular weight fractions. A stirred cell equipped with a 10 kDa molecular weight cut-off regenerated cellulose acetate membrane (Millipore, Bedford MA) was used to concentrate the purified polymer solution up to the desired polymer concentrations for preparing stock solutions. The repeating unit of the polymer is $(H_2CCHCH_2)_2N(CH_3)_2Cl$; the QUAT concentrations are based on moles per liter of the repeating unit and not on the total molecular weight.

Methods

Sedimentation Rate Measurement

This method involves the visual observation of the sedimentation of copper arsenate particles in the absence and in the presence of polyelectrolyte. Batch settling experiments[22-23] were conducted in screw cap test tubes and the copper arsenate precipitate was left undisturbed to settle throughout the period of study. The sedimentation was observed as the height of suspended solutions and the interface between clear liquid and suspended solids as a function of time, measured until the height was constant.

Viscosity Measurement

The viscosity of supernatant QUAT solutions was determined using a capillary viscometer. The liquid samples of the polymer solutions were obtained from the sedimentation experiments by separating the dispersed solid by centrifugation at 4500 rpm for 10 min. Flow time measurements were conducted in a thermostated bath at 10, 25, and 50 ± 0.10°C. The viscosity measurements were carried out automatically with an AVS360 viscometer from SCHOTT (Germany) which uses optical sensors to measure the time taken for the solution to flow between fixed marks in a capillary tube during gravity drainage. The kinematic viscosity, in m^2/s ($x10^{-6}$), was calculated from the viscometer constant, C, and the measured flow time, t, according to the equation

$$\eta = Ct$$

Relative kinematic viscosity is defined as the kinematic viscosity of a polymer solution divided by the kinematic viscosity of water.

$$\eta_r = \eta/\eta_s$$

Particle Size Measurement

The particle size distributions of copper arsenate dispersions in the absence and in the presence of QUAT were estimated with a Mastersizer S (Malvern Instrument Ltd, UK) using a small volume sample cell employing an internally mounted overhead stirrer to keep the sample suspended. Copper arsenate dispersions were shaken to ensure complete suspension before adding a few drops to the sample cell. Particle size distributions used average particle size parameter $d_{0.5}$, the particle size exceeded by 50% by volume of the particles.

Zeta Potential Measurement

A Zeta Meter 3.0+ (Zeta Meter Inc., Staunton, VA) was used to measure the zeta potential of copper arsenate particles in deionized water. Calculated zeta potentials from measured electrophoretic mobilities in high viscosity suspensions are unreliable, so electrophoretic mobilities are reported for the particles in the presence of 0.2 M QUAT.

Polyelectrolyte Adsorption Measurement

Adsorption isotherms of polymer on copper arsenate particles were determined from depletion[15] of QUAT from the solution after equilibrium with copper arsenate (0.3g) dispersed in 30 mL of polyelectrolyte solution at various initial QUAT concentrations from 0.005 to 0.1 M. The solutions were mixed with a vortex stirrer (Barnstead/Thermolyne, Dubuque IA) for 3 min and maintained in a shaker bath at 25 ± 0.2°C for 24 h for adsorption equilibrium to be established. The solid particles were

separated from the polymer solution by centrifugation, and the concentration of polyelectrolyte in solution was determined using a Dohrmann total organic carbon analyzer (Rosemount Analytical, Santa Clara CA). The quantity of QUAT adsorbed on copper arsenate was calculated as the difference between the initial concentration and the final equilibrium concentration,

$$q_e = \frac{(C_i - C_e)V}{W}$$

where C_i and C_e are the initial and final (equilibrium) QUAT concentrations in solution (mg/L), respectively; q_e is the QUAT concentration retained in the adsorbent phase (mg/g); V is the solution volume (L); and W is the mass of adsorbent (g)

Crystal Morphology Characterization

The copper arsenate precipitate particles formed with and without QUAT were observed by scanning electron microscopy/energy dispersive x-ray spectrometry (JSM 6400, Jeol, Japan/ Link ISIS Oxford Instruments, UK), Fourier Transform Infrared Spectrophotometer (Bio-Rad CA), and Powder x-ray diffraction spectra (Bruker/Siemens D5005, Delft, The Netherlands).

Results

Aqueous suspensions initially containing arsenate and copper in various proportions were allowed to react under ambient conditions. The precipitate was characterized by x-ray diffraction, energy dispersive x-ray fluorescence analysis, and Fourier transform infrared spectrophotometry. The results of the XRD analysis indicated that most of the blue copper arsenate precipitate was sodium copper arsenate

chloride hydrate, $NaCu_6(AsO_4)_4Cl{\cdot}4H_2O$.[5] The energy dispersive x-ray fluorescence analysis shows that the particles contain only copper, sodium, chlorine, and arsenic consistent with the XRD results.

Sedimentation

Figures 1-4 show the sedimentation of copper arsenate precipitates as the percentage of solid volume as a function of time. Table 1 summarizes the average of required settling time to obtain solid volume below 50% of copper arsenate for different conditions.

At the stoichiometric ratio the sedimentation of copper arsenate in the absence of QUAT and in the presence of 0.2 M QUAT at 10°C, 25°C, and 50°C are shown in Figure 1 Sedimentation rate and sedimentation volume increase with increasing temperature. and also sedimentation rate increases with increases . The sedimentation in the presence of QUAT is slower than in the absence of QUAT. The sedimentation of copper arsenate in the presence of QUAT at 25°C is shown in Figure 2. The sedimentation rate increases with increasing polymer concentration. This behavior also occurs in other copper to arsenate concentration ratio.

Figure 3 shows the sedimentation of copper arsenate at copper to arsenate concentration ratios of 0.50, 1.0, 1.5, and 3.0 in the absence of QUAT and in the presence of 0.2 M QUAT at 25°C. An increase in the copper to arsenate concentration ratio results in an increase in the rate of sedimentation. Comparison of sedimentation rate results at the same copper to arsenate concentration ratios show higher sedimentation in the absence of QUAT where the settling time for solid volume below

50% are 80, 235, 205, and 80 min. The settling time for solid volume below 50% of copper to arsenate concentration ratios at 1.0, 1.5, and 3.0 in the presence of 0.2 M QUAT are 160, 100, and 70 min. At copper to arsenate concentration ratio of 0.50 in absence of QUAT, settling time is as at copper to arsenate concentration of 3.0, whereas in the presence of 0.2 M QUAT, the particle can not settle to bottom of vessel at the consideration time. It caused turbidity dispersion in the solution.

The effect of ionic strength on sedimentation rate of copper arsenate in the absence and presence of QUAT is presented in Figure4. As salt concentration increases, the sedimentation rate increases.

Viscosity

Figure 5 shows the relative viscosity of QUAT in aqueous solution as a function of QUAT concentration at 10°C, 25°C, and 50°C. The relative viscosity increases with increasing polymer concentration. The viscosities presented in this work are the relative kinematic viscosities of the supernatant polymer solutions from the sedimentation measurements in the absence of the dispersed solid copper arsenate particles measured with a capillary viscometer. Table 2 shows the kinematic viscosity of QUAT at copper to arsenate concentration ratios of 0.0, 0.50, 1.0, 1.5, and 3.0, and several salt concentrations and different temperatures. The viscosity increases with increasing polymer concentrations, decreasing temperatures, decreasing ionic strengths, and decreasing copper to arsenate concentration ratios.

Zeta potential

The zeta potential of copper arsenate particles as a function of copper to arsenate concentration ratio is shown in Figure 6. At the stoichiometric ratio the zeta potential is zero, which represents no net charge on the surface of particles, whereas a negative charge is observed at copper to arsenate concentration ratio < 1.5, and a positive charge at copper to arsenate concentration ratio > 1.5. The point of zero charge (PZC) of copper arsenate chloride hydrate occurs at a copper to arsenate concentration ratio of 1.5; a standard deviation of the zeta potential and electrophoretic mobility values are around ±0.97 to ±2.5 mV and ±0.05 to ±0.3x10^{-8} $m^2v^{-1}s^{-1}$. At lower copper to arsenate concentration ratio values (< 1.5), the copper arsenate particles are negatively charged with zeta potential reaching –27.7 mV (electrophoretic mobility about -2.09 $10^{-8}m^2v^{-1}s^{-1}$) at a copper to arsenate concentration ratio of 0.25. The zeta potential increases with increasing copper to arsenate concentration ratio and becomes positive +30.7 mV (electrophoretic mobility about +2.31 $10^{-8}m^2v^{-1}s^{-1}$).

Due to high viscosity, the zeta potential of the solid could not be accurately calculated in the presence of QUAT, but electrophoretic mobility could be measured. The electrophoretic mobility of copper arsenate particles in the presence of 0.2 M QUAT as a function of copper to arsenate concentration ratios is shown in Figure 6. It can be seen that the electrophoretic mobility values were constant and positive when the copper to arsenate concentration ratio increased from 0.25 to 5.0, with a slight decrease at the copper to arsenate concentration ratio of 10.0.

Particle size distribution

The particle size distribution of copper arsenate as a percentage of volume as a function of the logarithm of average particle diameter is shown in Figures 7-10. Table 1 summarizes the average particle diameter (the particle size exceeded by 50% by volume of the distribution, $d_{0.5}$) of copper arsenate particles under different conditions.

Figure 7 shows the particle size distribution of copper arsenate with and without 0.2 M of QUAT at 10°C, 25°C, and 50°C. The average particle diameter of copper arsenate particles increases with increasing temperature, however, the average particle diameter of copper arsenate particles in the presence of 0.2 M of QUAT is smaller than in the absence of QUAT. The particle size distribution of copper arsenate in the absence of QUAT shows bimodal distribution, while in the presence of 0.2 M QUAT shows trimodal distribution at low temperature (10 and 25°C). The effect of QUAT concentration on copper arsenate particle in low and high ranges from 0.005 to 0.05 M and 0.10 to 0.40 M at 25°C is shown in Figure 8, respectively. An increase in QUAT concentration decreases the average particle size of copper arsenate particles and gives broader particle size distributions at high QUAT concentration. By adding 0.2 M QUAT, the average particle size of copper arsenate was around 7 μm (compared to 11 μm without of QUAT). The particle size distribution of copper arsenate in the presence of QUAT exhibited multimodal with the smaller, main, and larger particle size (approximately 0.7 to 1.2 μm, 4.6 to 7.5 μm, and 65 to 163 μm).

Figure 9 presents the effect of copper to arsenate concentration ratios of 0.50, 1.0, 1.5, and 3.0 on the particle size distribution of copper arsenate in the absence of QUAT and in the presence of 0.2 M QUAT at 25°C. Average particle diameter increases with decreasing copper to arsenate concentration ratios. Copper to arsenate concentration ratios of 0.50, 1.0, and 1.5 in the presence of 0.2 M QUAT has an insignificant effect on particle size, but generated a broader particle size distribution at copper to arsenate concentration ratio of 3.0. Figure 9 shows multimodal size distributions in the presence of QUAT (approximately 1.06 μm, 7.7 to 8.9 μm, and 65 to76 μm).

Figure 10 illustrates the effect of adding NaCl on the particle size distribution of copper arsenate in the absence of QUAT and in the presence of 0.2 M QUAT at 25° C. The average particle size decreases with increasing salt concentration. Figure 18 also shows multimodal size distribution (approximately 1.06 μm, 6 to 8 μm, and 65 to 76 μm).

QUAT Adsorption on Particles

Figure 11 shows adsorption isotherms for QUAT onto copper arsenate particles at various copper to arsenate concentration ratios in water at 25°C. The results of polymer adsorption are given as adsorption isotherms in mg QUAT adsorbed per g of copper arsenate solid versus equilibrium QUAT concentration. Adsorption of polyelectrolyte increases with increasing polyelectrolyte concentration. Figure 11 shows that the amount of QUAT adsorbed is higher for lower copper to arsenate concentration ratios. The adsorption of QUAT in 0.1 M NaCl at a copper to

arsenate concentration ratio of 1.0 is shown in Figure 11, demonstrating lower adsorption of polymer in electrolyte solution than water.

Figure 12 summarizes plot of the effect of QUAT concentration on sedimentation of copper arsenate particles, copper arsenate average particle size, relative viscosity, and polymer adsorption at copper to arsenate concentration ratio of 1.5 at 25°C. The sedimentation rate of copper arsenate increases with increasing QUAT concentration. The average particle diameter of copper arsenate decreases and adsorption of polymer on copper arsenate particles increases with increasing QUAT concentration, and the relative viscosity of the supernatant solution QUAT increases.

Structure Morphology

Scanning electron micrographs of copper arsenate particles in the absence of QUAT and in the presence of 0.2 M QUAT are shown in Figure 13. The roughly spherical particles, which appear to be made up of thin plate, formed in the presence of QUAT are smaller, but more densely packed due to more face-to-face contact of adjacent plates as compared to those formed in the absence of QUAT. In the absence of QUAT agglomerates of copper arsenate have the particles touching edges or corners, forming looser, more open structures.

Discussion

Dispersion Stability

In the without polyelectrolyte, the average particle size of main peak of copper arsenate increases from 8.6 to 18.5 μm with decreasing copper to arsenate concentration ratios from 3.0 to 0.50. Copper arsenate in the absence of QUAT shows bimodal particle size distributions with a major and a minor at smaller particle sizes peak. In the small particle, Brownian motion is caused by random variations of in the incessant diffusion of particles and due to the velocity difference under gravity and centrifugal force (Okuyama, 1997). The small size of particle leads to slow sedimentation. While resulting from agglomeration by Brownian motion and collision between particles lead to growth of the particle. The sedimentation rate increases with increasing temperature, increasing salt concentration, and increasing copper to arsenate concentration ratio. The copper arsenate particles form soft and loosely packed sediments with large sedimentation volume. The sedimentation rate of copper arsenate is slower than barium hydrogen arsenate monohydrate due to the average particle size of copper arsenate is smaller than the average particle size of barium hydrogen arsenate monohydrate (Pookrod, Haller & Scamehorn, 2003) under the same condition. The average particles increase from 14 to 67 μm with decreasing barium to arsenate concentration ratios.

In this results show that the morphology of copper arsenate in addition of QUAT gives more densely packed due to more face-to-face contact of adjacent plates as compared to copper arsenate formed in the absence of QUAT (Figure 6.13). In the presence of QUAT, the average particle size of copper arsenate particles decreases with average diameter ranging from 7.5 to 4.6 μm at the main peak (compared to 11 μ

m in the absence of QUAT). This phenomenon was observed in QUAT dispersion behavior of barium chromate (Soponvuttikul, Scamehorn & Saiwan, 2003). The average particle diameter of barium chromate was 2 μm without polymer and decreased to 0.9 μm in the presence of QUAT (0.2 M). Another sample, the adsorption of SDS or cellulose on CT112 (Terayama, Okumura, Sakai, Torigoe & Esumi, 2001). The particle diameter of CT112 in the presence of 1 mM SDS or 0.2 g/L cellulose was 10 μm (compared to 47 μm in the absence of additive). As QUAT concentration increases, polymer adsorption on the copper arsenate particles increases, sedimentation rate increases, electrophoretic mobility increases, average particle size decreases, viscosity increases, and the particle size distribution broadens. The copper arsenate in the presence of QUAT leads to development of multimodal size distribution. The distributions consisted of a smaller peak (approximately 0.8-2 μ m) remains close to the primary particle (approximately 11 μm) while the coarse shifts progressively to larger sizes with increasing polymer concentration (approximately 65-163 μm) This behavior has been observed in barium chromate in the added of QUAT (Soponvuttikul, Scamehorn & Saiwan, 2003) and in the addition of nonionic and anionic polymer on alumina (Rattanakawin & Hogg, 2001). In practice, the phenomenon is often noted as a combination of high settling rates and very high supernatant turbidity (Hogg, 1999).

QUAT adsorption increases with decreasing copper to arsenate concentration ratios. This phenomenon was also found in adsorption of QUAT on barium hydrogen arsenate monohydrate (Pookrod, Haller & Scamehorn, 2003) due to attractive and repulsive interactions between the polymer and local charged sites of particles. Copper arsenate solid surface consists of polar groups lead to produce an electric field that induces dipoles in the adsorbed molecules. The electrophoretic mobilities of

copper arsenate particle with and without adsorbed QUAT are given as a function of copper to arsenate concentration ratio in Figure 6.6. The particles alone remain negatively charged at low stoichiometric ratio of copper arsenate, whereas with 0.2 M QUAT adsorbed they become positively charged.

When the salt concentration is increased, the average particle size at the main peak decreases in both the absence and in the presence of polymer. The dispersion is more stable to the addition of polyelectrolyte in the presence of NaCl compared to in the absence of polyelectrolyte. An increase in sedimentation of copper arsenate with increasing electrolyte concentration and decrease in viscosity is observed. Adsorption of polymer on copper arsenate also decreases with increasing electrolyte concentration. A similar result is found in the adsorption of QUAT on barium arsenate (Pookrod, Haller & Scamehorn, 2003) and also in adsorption of low molecular weight anionic poly(styrene sulphonate) on $CaCO_3$ and adsorption of cationic quaternized poly(vinylpyridine), at pH 8 on TiO_2 (Adam & Rodd, 1983; Esumi, 1999). Addition of salt screens the electrostatic repulsion of neighboring adsorbed QUAT molecules which tends to increase adsorption. The electrostatic attraction between polymer and surface, however, is also weakened, because the salt ions (Na^+) compete with the polymer for surface sites, tending to decrease the adsorption (Figure 6.11) (Esumi, 1999; Hoogeveen, Stuart & Fleer, 1996). An explanation for this has been proposed (Liu, Min & Ducker, 2001).

From Figure 6.12 the average particle diameter decreases and adsorption of polyelectrolyte on copper arsenate particles increases with increasing QUAT concentration. The sedimentation rate of copper arsenate and viscosity of QUAT in water increases with increasing QUAT concentration.

Implications for PEUF Process

In the presence of QUAT, copper arsenate forms smaller crystals (approximately 7 μm) than in the absence of added polymer (approximately 11 μm) Comparison to barium hydrogen arsenate monohydrate, particle size diameter of barium hydrogen arsenate monohydrate in the presence of polyelectrolyte (about 94 μ m) is larger than in the absence of polyelectrolyte (about 67 μm). Average particle size of copper arsenate is smaller than barium hydrogen arsenate monohydrate, but still larger than barium chromate. In the presence of QUAT, copper arsenate is more stable dispersion than barium hydrogen arsenate monohydrate. Sedimentation of copper arsenate is slower than barium hydrogen arsenate monohydrate, but no fine particles in the suspension, so settling requirement time of copper arsenate is more quickly than barium hydrogen arsenate monohydrate. In copper arsenate, increasing temperature and/or increasing added electrolyte decreases dispersion stability. Thus, copper arsenate is still useful for regeneration of polyelectrolyte from the PEUF process. By adding polymer slowly and continuously with vigorous agitation would be give larger size of copper arsenate.

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List of Tables and Figures

(◊) 10°C, (□) 25°C, (Δ) 50°C; in the presence of 0.2 M QUAT: (♦) 10°C, (■) 25°C,(▲) 50°C.

Figure 8 Particle size distribution of copper arsenate at copper to arsenate concentration ratio of 1.5 at 25°C in the presence of low QUAT concentration [QUAT]: (◊) 0 M, (□) 0.005 M, (Δ) 0.01, (○) 0.05 M; in the presence of high QUAT concentration [QUAT]: (♦) 0.1 M, (■) 0.2 M, (▲) 0.3 M, (●) 0.4 M.

Figure 9 Particle size distribution of copper arsenate at various copper to arsenate concentration ratios at 25°C in the absence of QUAT, [copper]/[arsenate]: (◊) 0.5, (□) 1 M, (Δ) 1.5, (○) 3; in the presence of 0.2 M QUAT, [copper]/[arsenate]: (♦) 0.5, (■) 1, (▲) 1.5, (●) 3.

Figure 10 Particle size distribution of copper arsenate at copper to arsenate concentration ratio of 1.5 at various NaCl concentrations at 25°C in the absence of QUAT, [NaCl]: (◊) 0 M, (□) 0.01 M, (Δ) 0.05 M, (○) 0.1 M; in the presence of 0.2 M QUAT, [NaCl]: (♦) 0 M, (■) 0.01 M, (▲) 0.05 M, (●) 0.1 M.

Figure 11 Adsorption isotherms of QUAT on copper arsenate particles in water and in 0.1 M NaCl at various copper to arsenate concentration ratios at 25°C. [copper]/[arsenate]: (♦) 0.5 in water, (■) 1 in water, (▲) 1.5 in water, (○) 3 in water, (□) 1 in 0.1 M NaCl.

Figure 12 Effect of QUAT concentration on copper arsenate sedimentation rate (cm/h, ○), average particle size (μm, ▲), and relative kinematic viscosity (mm^2/sec, ♦) (in the left scale); and QUAT adsorption(mg /g of solid, ■) (in the right scale) at barium to arsenate concentration ratio of 1.5 at 25°C.

Figure 13 SEM micrographs of copper arsenate particles formed in the absence QUAT (A-C), and in the presence of 0.2 M QUAT (D-F).

Table 1 Settling times and average particle diameters under various conditions.

Temperature (°C)	[QUAT] (M)	[copper]/[arsenate] (M/M)	[NaCl] (M)	Settling time (min)[a]	Average particle diameter (μm)
10	0	0.50	0	125	13.5
	0	1.0	0	220	9.5
	0	1.5	0	165	7.0
	0	3.0	0	125	7.6
	0	1.5	0.01	70	8.0
	0	1.5	0.05	80	7.2
	0	1.5	0.1	70	7.1
	0.005	1.5	0	-	4.7
	0.01	1.5	0	-	4.8
	0.05	1.5	0	-	5.6
	0.1	1.5	0	550	5.7
	0.2	1.5	0	385	4.9
	0.3	1.5	0	-	2.9
	0.2	0.50	0	-	5.9
	0.2	1.0	0	525	5.1
	0.2	3.0	0	220	4.3
	0.2	1.5	0.01	308	3.9
	0.2	1.5	0.05	160	4.1
	0.2	1.5	0.1	100	6.2
25	0	0.50	0	80	18.5
	0	1.0	0	235	13.0
	0	1.5	0	205	11.2
	0	3.0	0	80	8.6
	0	1.5	0.01	80	10.7
	0	1.5	0.05	35	9.5
	0	1.5	0.1	15	8.2
	0.005	1.5	0	-	6.2
	0.01	1.5	0	-	7.5
	0.05	1.5	0	-	7.1
	0.1	1.5	0	160	6.4
	0.2	1.5	0	100	7.1
	0.3	1.5	0	-	4.6
	0.2	0.50	0	-	6.5
	0.2	1.0	0	160	7.7
	0.2	3.0	0	70	5.7
	0.2	1.5	0.05	90	6.7
	0.2	1.5	0.05	40	6.4
	0.2	1.5	0.1	20	5.7
50	0	0.5	0	30	29.5
	0	1.0	0	20	15.1
	0	1.5	0	15	31.8
	0	3.0	0	10	22.9
	0	1.5	0.01	10	22.8
	0	1.5	0.05	10	10.3
	0	1.5	0.1	5	9.9
	0.005	1.5	0	-	35.1
	0.01	1.5	0	-	14.4
	0.05	1.5	0	-	18.6
	0.1	1.5	0	30	15.2
	0.2	1.5	0	60	15.3
	0.3	1.5	0	-	16.4
	0.2	0.50	0	-	7.8
	0.2	1.0	0	60	21.8
	0.2	3.0	0	10	28.9
	0.2	1.5	0.01	30	11.3
	0.2	1.5	0.05	10	14.1
	0.2	1.5	0.1	10	6.0

a. Required settling time to obtain a solid volume below 50%.

Table 2. Relative kinematic viscosity of particle free QUAT solutions.

[QUAT] (M)	[copper]/[arsenate] (M/M)	[NaCl] (M)	Relative kinematic viscosity		
			10°C	25°C	50°C
0.0005	0	0	1.3	1.4	1.4
0.001	0	0	1.7	1.7	1.7
0.005	0	0	2.9	3.0	2.9
0.01	0	0	3.8	3.7	3.6
0.05	0	0	7.1	7.1	6.9
0.1	0	0	10.2	10.3	9.8
0.2	0	0	15.7	15.7	15.6
0.1	0.50	0	5.4	5.6	4.8
0.1	1.0	0	5.2	4.9	4.3
0.1	1.5	0	4.6	4.5	4.2
0.1	3.0	0	3.8	3.7	3.5
0.2	0.50	0	10.8	9.7	9.7
0.2	1.0	0	10.7	9.4	9.0
0.2	1.5	0	9.6	9.1	8.2
0.2	3.0	0	7.8	7.8	7.3
0.2	0.50	0.01	10.1	10.6	10.0
0.2	1.0	0.01	10.1	9.3	9.3
0.2	1.5	0.01	9.3	8.9	8.7
0.2	3.0	0.01	7.9	7.4	7.3
0.2	0.50	0.05	8.8	8.6	8.3
0.2	1.0	0.05	9.0	8.5	8.2
0.2	1.5	0.05	8.4	8.2	8.0
0.2	3.0	0.05	7.4	7.1	7.8
0.2	0.50	0.1	8.2	7.9	7.5
0.2	1.0	0.1	8.0	7.6	7.3
0.2	1.5	0.1	7.7	7.4	7.2
0.2	3.0	0.1	6.9	7.1	6.5

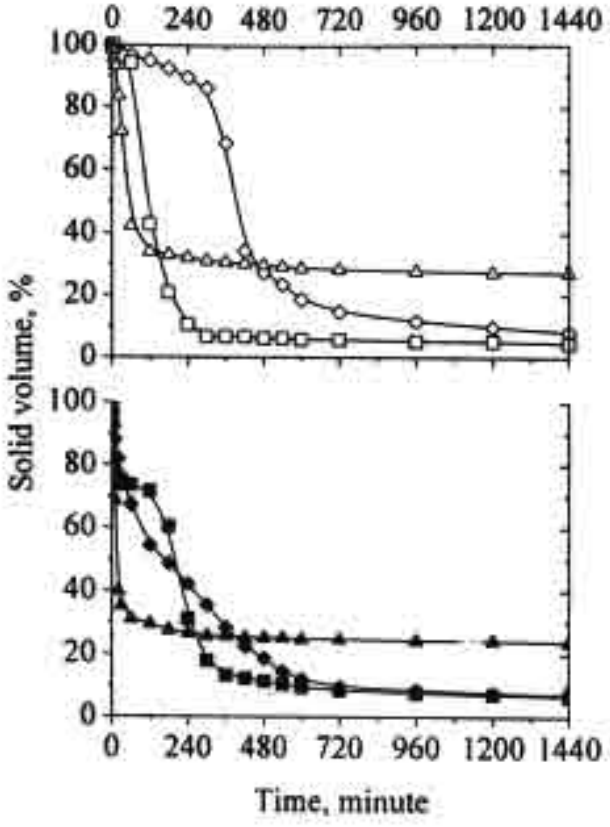


Figure 1. Sedimentation of copper arsenate at copper to arsenate concentration ratio of 1.5 at different temperatures. in the absence of QUAT: (♦) 10°C, (■) 25°C, (▲) 50°C; in the presence of 0.2 M QUAT: (◊) 10°C, (□) 25°C, (△) 50°C.

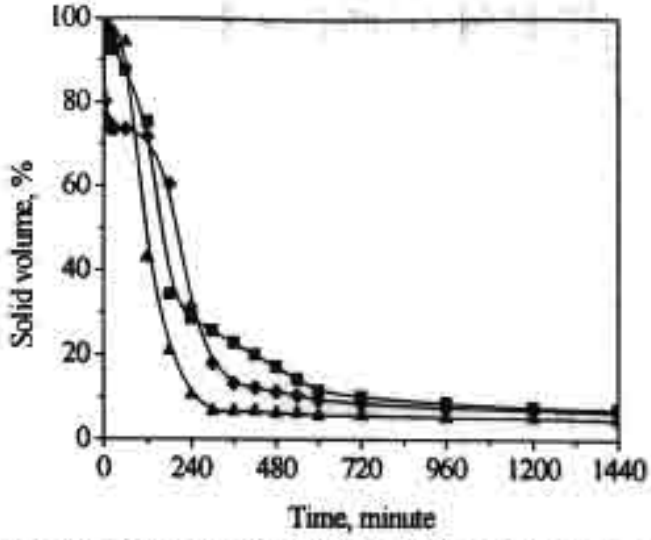


Figure 2. Sedimentation of copper arsenate at copper to arsenate concentration ratio of 1.5 in the presence of QUAT at 25°C. [QUAT]: (♦) 0 M, (■) 0.1 M, (▲) 0.2 M.

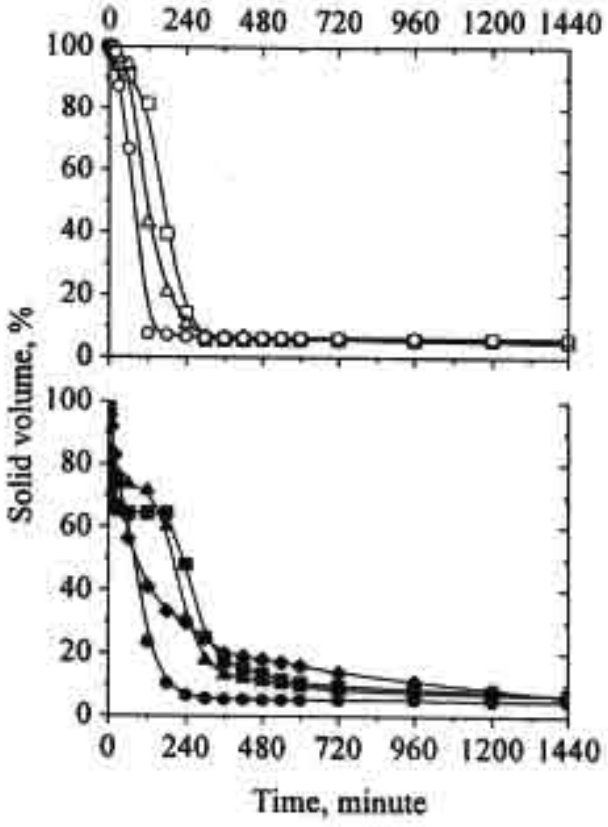


Figure 3. Sedimentation of copper arsenate at various copper to arsenate concentration ratios at 25°C. in the absence of QUAT, [copper]/[arsenate]: (♦) 0.50, (■) 1.0, (▲) 1.5, (●) 3.0; in the presence of 0.2 M QUAT, [copper]/[arsenate]: (□) 1.0 M, (Δ) 1.5, (○) 3.0.

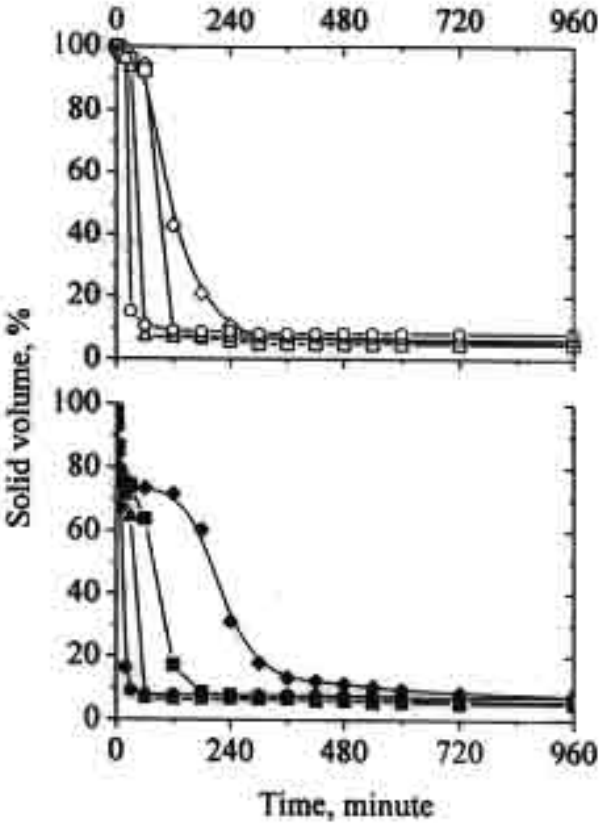


Figure 4. Sedimentation of copper arsenate at copper to arsenate concentration ratio of 1.5 at various NaCl concentrations at 25°C. in the absence of QUAT, [NaCl]: (♦) 0 M, (■) 0.01 M, (▲) 0.05 M, (●) 0.1 M; in the presence of 0.2 M QUAT, [NaCl] (◊) 0 M, (□) 0.01 M, (Δ) 0.05 M, (○) 0.1M.

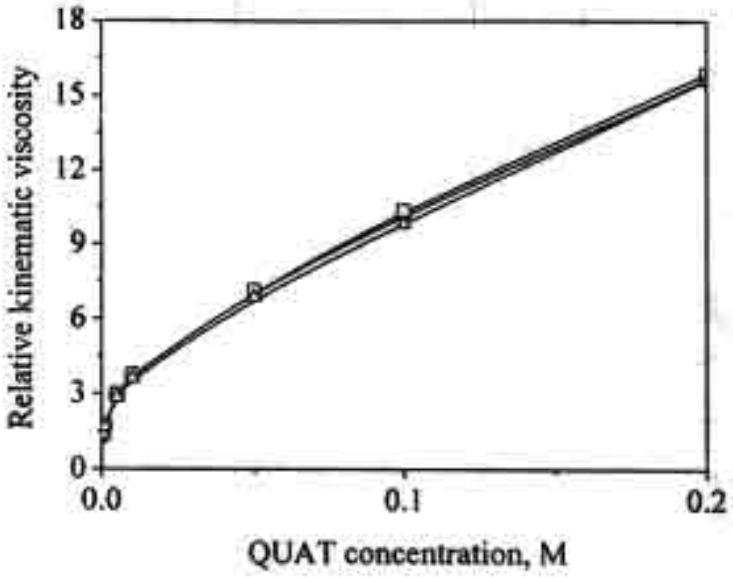


Figure 5. Relative kinematic viscosity of QUAT in water solution for different temperatures; (◊) 10°C, (□) 25°C, (Δ) 50°C.

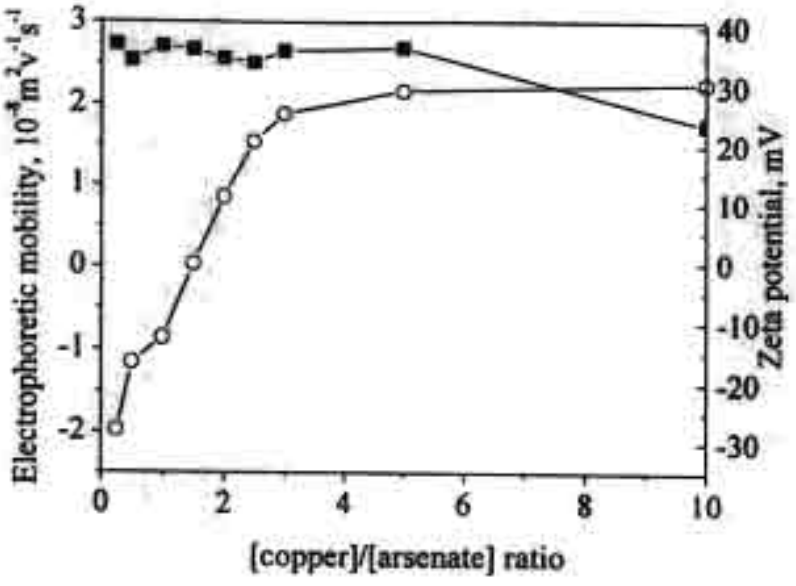


Figure 6. The effect of copper to arsenate concentration ratio on (○) zeta potential in the absence of QUAT (right scale), and (■) electrophoretic mobility in the presence of 0.2 M QUAT, and (○) electrophoretic mobility of particle in the absence of QUAT (left scale).

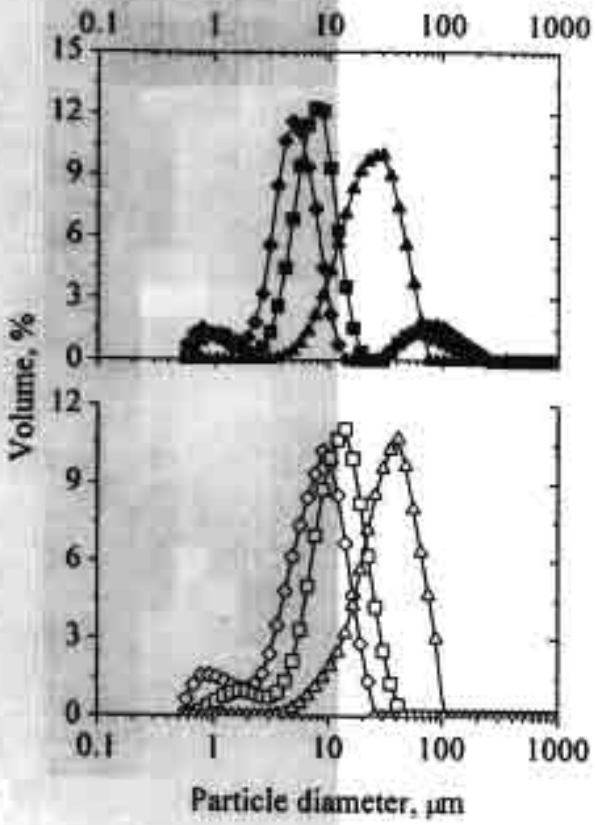
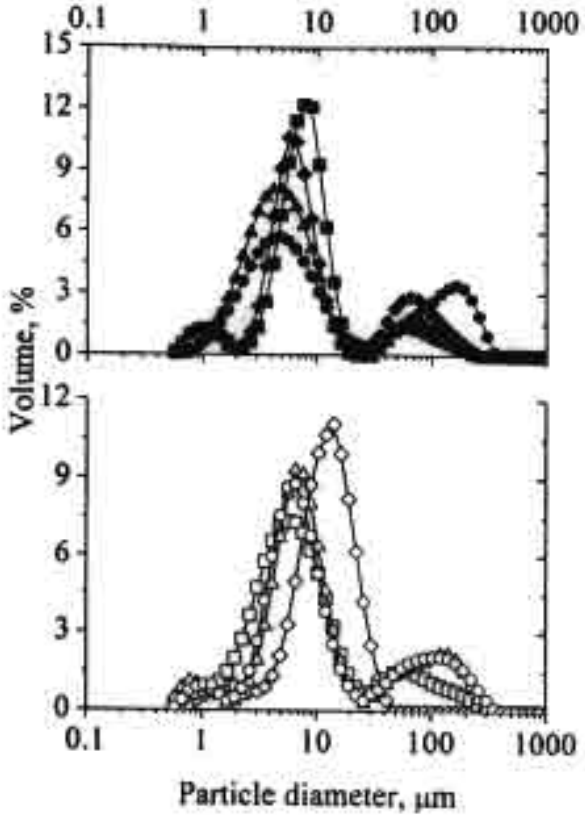


Figure 7. Particle size distribution of copper arsenate at copper to arsenate concentration ratio of 1.5 at different temperatures. in the absence of QUAT: (◊) 10°C, (□) 25°C, (Δ) 50°C; in the presence of 0.2 M QUAT: (♦) 10°C, (■) 25°C,(▲) 50°C.



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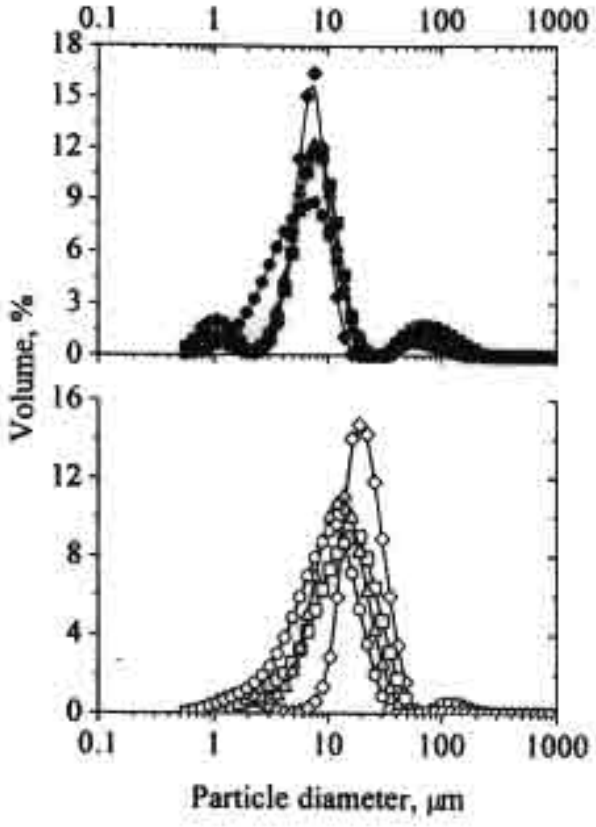

Figure 9. Particle size distribution of copper arsenate at various copper to arsenate concentration ratios at 25°C in the absence of QUAT, [copper]/[arsenate]: (◊) 0.50, (□) 1.0 M, (Δ) 1.5, (○) 3.0; in the presence of 0.2 M QUAT, [copper]/[arsenate]: (♦) 0.50, (■) 1.0, (▲) 1.5, (●) 3.0.

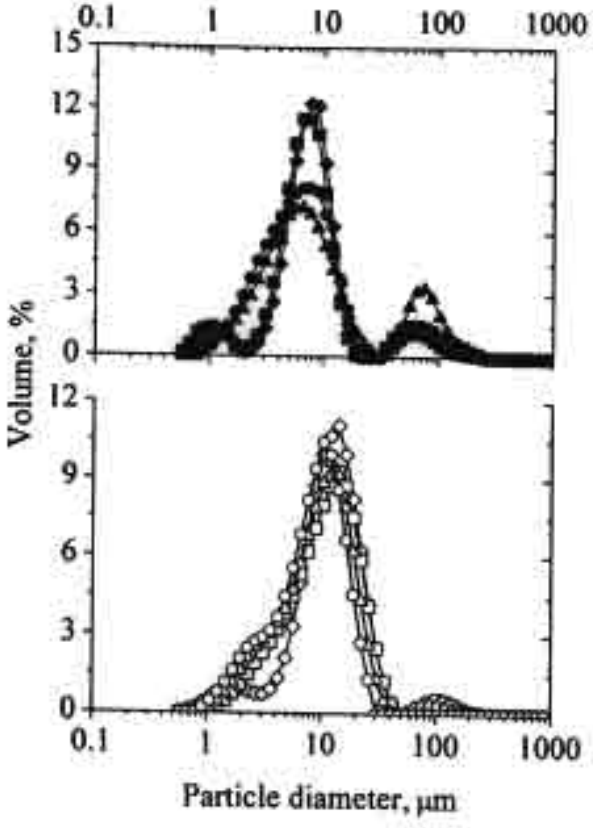

Figure 10. Particle size distribution of copper arsenate at copper to arsenate concentration ratio of 1.5 at various NaCl concentrations at 25°C in the absence of QUAT, [NaCl]: (◊) 0 M, (□) 0.01 M, (Δ) 0.05 M, (○) 0.1 M; in the presence of 0.2 M QUAT, [NaCl]: (♦) 0 M, (■) 0.01 M, (▲) 0.05 M, (●) 0.1 M.

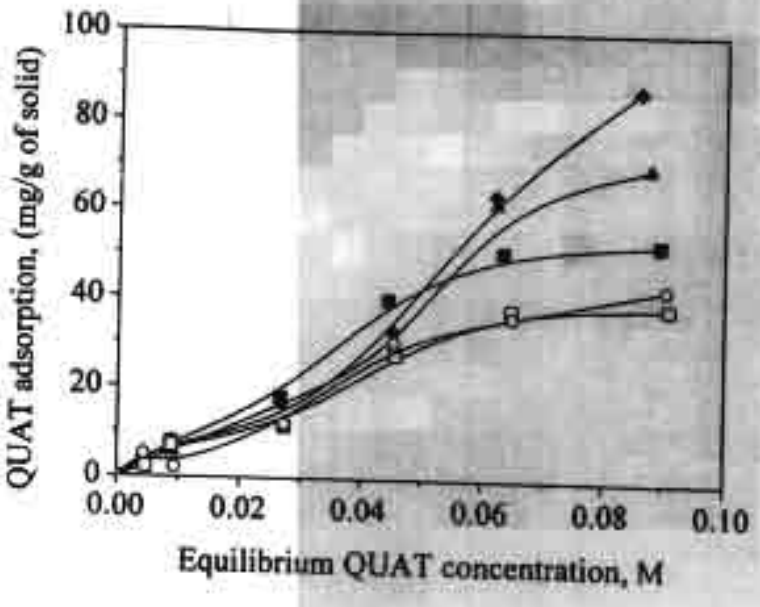

Figure 11. Adsorption isotherms of QUAT on copper arsenate particles in water and in 0.1 M NaCl at various copper to arsenate concentration ratios at 25°C. [copper]/[arsenate]: (♦) 0.50 in water, (■) 1.0 in water, (▲) 1.5 in water, (○) 3.0 in water, (□) 1.0 in 0.1 M NaCl.

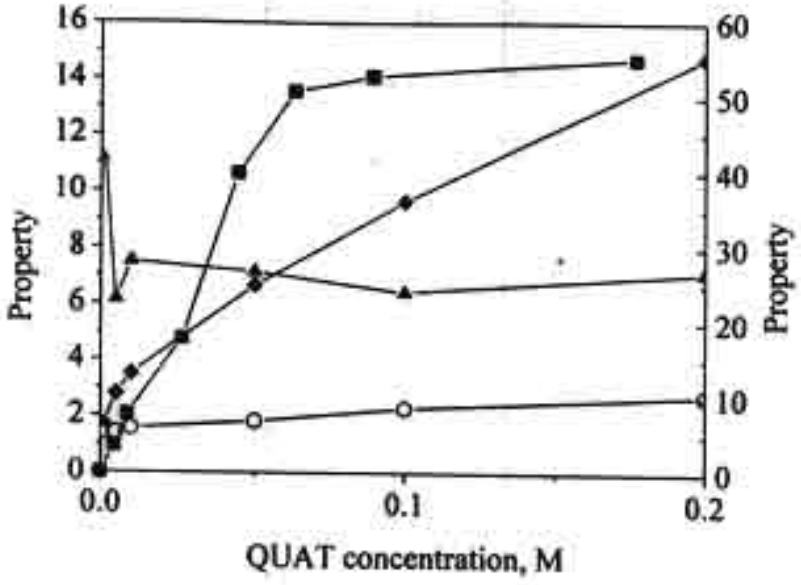

Figure 12. Effect of QUAT concentration on copper arsenate sedimentation rate (cm/h, ○), average particle size (μm, ▲), and relative kinematic viscosity (♦) (in the left scale); and QUAT adsorption(mg /g of solid, ■) (in the right scale) at barium to arsenate concentration ratio of 1.5 at 25°C.

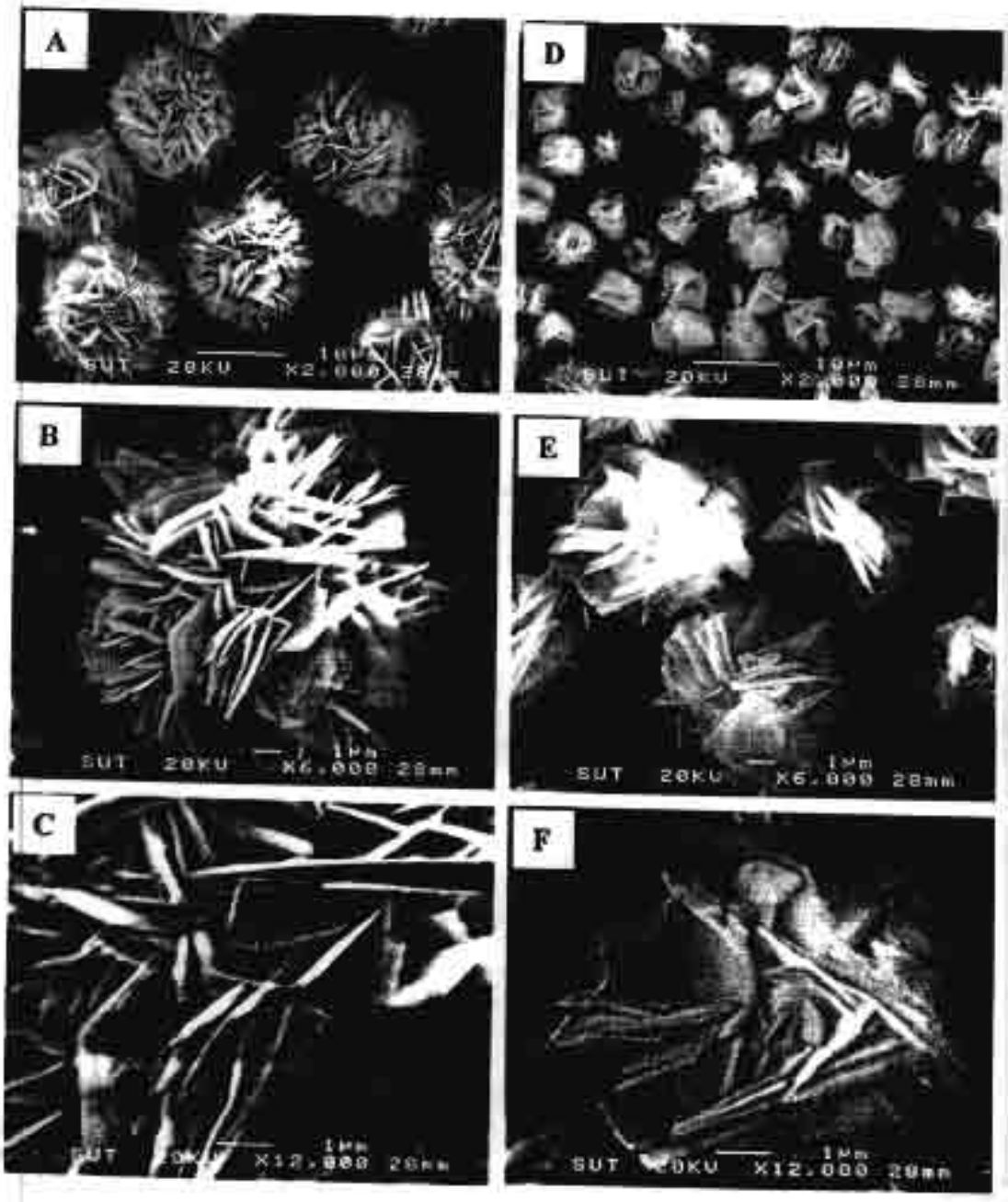

Figure 13. SEM micrographs of copper arsenate particles formed in the absence QUAT (A-C), and in the presence of 0.2 M QUAT (D-F).