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ORIGINAL CONTRIBUTION

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Electrophoretic behaviour and viscosities of metal oxides in mixed surfactant systems

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Abstract The electrokinetic behavior and viscosity of anatase and alumina in mixed-surfactant solutions were investigated. Sodium dodecylsulfate and nonionic polyoxyethylene ethers were investigated as model surfactants. Pure nonionic surfactants adsorbed on anatase and coated the particles, so that the zeta potential was nearly zero near the critical micelle concentration of surfactant. At higher surfactant concentrations, an increase in the zeta potentials was observed, suggesting a change in the microstructure of the adsorbed layer. Addition of nonionic surfactant to positively charged anatase and alumina with some preadsorbed sodium dodecylsulfate reversed the surface charge of the oxide to negative, indicating enhanced coadsorption of the anionic surfactant. At higher concentrations of the nonionic surfactant, the charge reversed back to positive. Nonionic surfactants did not reverse the surface charge of these oxides in the absence of the anionic surfactant. Coenhanced adsorption of nonionic and anionic surfactants was used to stabilize alumina at the isoelectric point, where neither surfactant adsorbed appreciably on its own. These results suggest a dramatic change in conformation of the surfactant chains in mixed systems. Further explanation and justification of the proposed changes in adsorbed surfactant conformation require spectroscopic evidence.

Key words Electrokinetics – mixed surfactant adsorption – viscosity – anatase – alumina

Introduction

The adsorption of surfactants at the solid/liquid interface is important in many processes such as flotation, enhanced oil recovery, powder dispersion, thin-film deposition, detergency and waste-water treatment. In most of these applications, surfactants are present as complex mixtures. The use of mixed-surfactant solutions often results in enhanced performance with the possibility of using lower amounts of both components. This has resulted in a significant increase in studies on the behavior of mixed-surfactant solutions, including their adsorption [1–9]. Surfactants adsorb as monomers at low surfactant concentrations [10], but as the surfactant concentration is increased, the adsorbed molecules form two-dimensional aggregates (hemimicelles) which enhance surfactant adsorption at such concentrations. A further increase in surfactant concentration causes some of the molecules to adsorb in a second layer with their head pointing towards the solution (reverse hemimicelles [11]). Other models for surfactant adsorption mechanisms exist [12–15], but none is so well supported with spectroscopic, bulk and thermodynamic studies as the reverse-hemimicelles model.

When mixed surfactants exist in solution, mixed aggregates will form above the critical micelle concentration

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(CMC). As in the case of pure-surfactant adsorption, above the critical hemimicelle concentration surfactants form hemimicelles on the surface (in this case termed mixed hemimicelles). The more surface-active surfactant, such as dodecanol or the TX-100 used in the present study, will accumulate at the interface [5]. As the concentration of one or another surfactant is significantly increased, the other component can be displaced from the surface. Little is known concerning the microstructure of the adsorbed mixed-surfactant layer [5–8].

While adsorption of mixed surfactants was a rather popular subject in recent years [1–9], little work was performed on the electrokinetic, colloidal stability and rheological behavior of such systems. In this paper we present the results of such studies on sodium dodecylsulfate–TRITON mixed-surfactant systems with anatase or alumina powders as substrates. Electrokinetic behavior and viscosities of suspensions were correlated.

Experimental

Salts, acids, bases and surfactants were purchased from Aldrich Chemicals, Milwaukee, WI. The TRITON surfactants were manufactured by Rohm and Haas for Aldrich Chemicals and are described in more detail in Table 1. All salts used in this work were of the highest purity available. Nitric acid and sodium hydroxide were used to adjust pH.

The alumina powder used in this study, AKP-50, 99.9% pure (α-Al_2O_3) was used as received from Sumimoto Chemical Company, New York, NY. The specific surface area of this sample was 10 $m^2 g^{-1}$ and its isoelectric point (iep) was found to be at pH 9. The mean particle size was 300 nm, as determined by photon correlation spectroscopy (PCS). High-purity anatase powder with a mean particle size of 300 nm and surface area of 20 $m^2 g^{-1}$ was used as received from Sakai Chemical Company, Osaka, Japan.

Electrokinetics measurements

In the electrophoretic mobility studies, 0.01 g of oxide was added to 100 ml of triply distilled water. After a short conditioning period in an ultrasonic bath, the suspensions were equilibrated for an additional 15 h at pH 4 under argon atmosphere. Before the initial pH adjustment, the appropriate amount of salt was added and the suspensions were titrated with NaOH or HNO_3 and agitated for 20 min on a gyratory mixer. Then, the pH was measured again, and if necessary, adjusted to the desired value. After pH equilibration, the appropriate amount of surfactant was added. The systems were then agitated for an additional 20 min before final pH adjustment.

Electrophoretic mobility measurements were conducted with a Zeta Meter 3.0 system manufactured by Zeta Meter Inc., and with a PEN KEM 501 manufactured by PEN KEM Inc. In addition, some electrophoretic mobilities were also measured with a Malvern Zeta Sizer 3 electrophoretic light-scattering system. Excellent correlation was observed with measurements performed with different instruments. Electrophoretic mobilities measured with three different techniques were reproducible within ±2 mV.

Surfactant adsorption measurements

A known weight of alumina (1–5 g) was equilibrated at the desired pH and ionic strength with 50 ml of surfactant solution. The pH of the suspension was adjusted with 0.1 M HNO_3 at the start of the experiment and again 1 h before the end of the equilibration period. The suspension was agitated in a Environ-Shaker at 200 rpm and the temperature was maintained at 20 °C.

Thirty milliliters of the final suspension was centrifuged in a refrigerated centrifuge at 20 °C and 1–10 ml of the resulting supernatant was used for analysis. Dodecylsulfate was analyzed colorimetrically [16] after two-phase

Table 1 (after ref. [17]) Oxyethylenic octylphenol series: $C_8H_{17}C_6H_4$–$(OCH_2CH_2)_nOH$

	Surfactant				
	TX-100	TX-102	TX-165	TX-305	TX-405
$(OCH_2CH_2)_n$ n:	9–10	12–13	16	30	40
CMC (M)	2.7×10^{-4}	4×10^{-4}	7×10^{-4}	1×10^{-3}	1.2×10^{-3}
HLB*	13.5	14.6	15.8	17.3	17.9
Surface area (air/water) σ (A^2)	50	—	131	—	88

* Hydrophile–lipophile balance

extraction (water–toluene). The following standard procedure was followed: An aliquot of the supernatant solution was diluted to a final volume of 100 ml and concentration between 1×10^{-7} and 5×10^{-7} M in a 125 ml Erlenmeyer flask with a ground stopper. Five milliliters of acetate buffer (pH 5) and 5 m of 0.001 M ethyl violet (cationic dye) solution were added to the resulting dodecylsulfate solution. After shaking the Erlenmeyer flask for 30 s, 5 ml of toluene was added and the flask was shaken for another 10 min in a Environ shaker at 200 strokes per minute. Afterwards, the flask was left standing for 60 min in order to achieve phase separation. Finally, the toluene phase was carefully removed and the absorbance was measured at 615 nm. The calibration curve was linear in the range 0–5×10^{-7} M of dodecylsulfate in the aqueous solution. The TRITONs were analyzed spectrophotometrically in the UV range.

ESA measurements

Electrokinetic sonic amplitude (ESA), which is a complex quantity that represents the magnitude and phase of the macroscopic pressure-wave induced in a suspension of charged colloidal particles when subjected to an oscillatory electric field, is a new technique for evaluating the electrokinetic behavior of concentrated suspensions. This technique was used to measure the zeta potentials of the concentrated slurries (5 wt%). The ESA device used in this research is a MATEC electroacoustophoresis model MBS 8000.

Viscosity measurements

Viscosity measurements were made with a dynamic stress rheometer (Rheometrics DSR) using a couette-type measuring cell (29.5 mm diameter, 44 mm long). Slurries were subjected to a high shear rate which was decreased until the measured torque was below the sensitivity of the instrument (≈ 0.1 g cm^{-1}). Alumina slurries were prepared by sonication with an ultrasonic horn for 5 min. The slurries were initially dispersed at pH 4 and the surfactants were then added and the pH readjusted to 9 (the isoelectric point) with 1 M KOH.

Results

In this work, the electrokinetic properties and viscosities of anatase and alumina powders in mixed-surfactant systems were studied in order to improve the dispersion of these oxides in aqueous solutions.

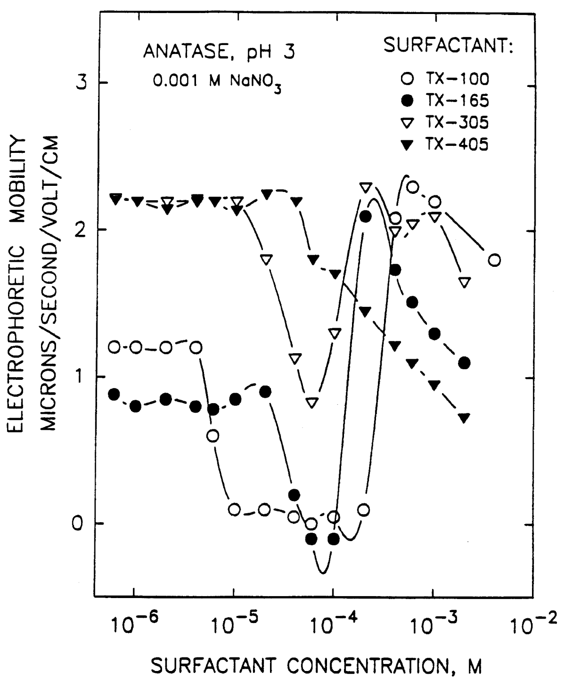
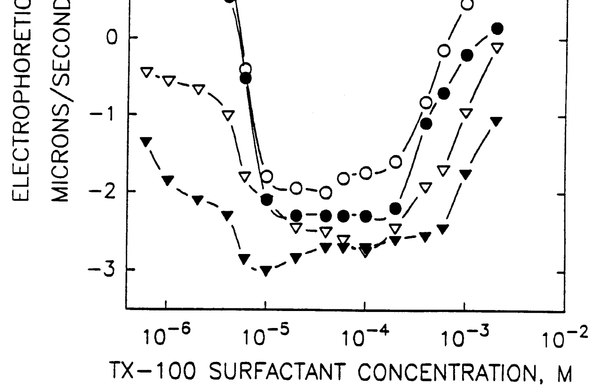


Fig. 1 The electrophoretic mobility of anatase particles at pH 3 in 0.001 M $NaNO_3$ versus the concentration of nonionic surfactants: TX-100; TX-165; TX-305; TX-405

Figure 1 presents the electrophoretic mobilities of anatase particles at pH 3 in 0.001 M sodium nitrate as a function of nonionic surfactant concentration. The surfactants studied are the octylphenol polyoxyethylenes, the so-called TRITON, family of surfactants, and differ only in the length of their oxyethylene unit (n). TX-100 has an average n of 9–10 (TRITONs are polydisperse). At TX-100 concentrations between 6×10^{-7} and 5×10^{-6} M, the electrophoretic mobility of anatase is constant but lower than that in the absence of the surfactant. At TX-100 concentrations between 5×10^{-6} and 1×10^{-5} M the mobility of anatase decreases and becomes zero, but charge reversal never occurs. At TX-100 concentrations between 1×10^{-5} and 2×10^{-4} M, the mobility remains constant (around zero). Further addition of TX-100 increases the mobility of anatase to the values characteristic for pure anatase under the same conditions. At concentrations above 5×10^{-4} M, further addition of TX-100 causes the mobility to decrease slightly. The addition of TX-165 (with an average value of n being 20) to the same anatase influences the mobility in a manner similar to that of TX-100, but more surfactant is needed to decrease the mobility to zero (6×10^{-5} M). On the other hand, less TX-165 is needed to increase the mobility back to the values characteristic for the pure oxide under the same conditions (1×10^{-4} M as compared with 2×10^{-4} M for TX-100). Further addition of TX-165 again caused the mobility of the anatase to decrease. The same trend was observed with TX-305, which has an *n* of 30 and consequently is more hydrophilic than both TX-100 and TX-165. More TX-305 is needed to decrease the electrophoretic mobility of anatase and it never decreases it to zero. At 6×10^{-5} M TX-305, the electrophoretic mobility decreases to 0.95 μm s^{-1} V^{-1} cm and further addition of TX-305 increases the electrophoretic mobility of anatase, similar to the effect with the other two TRITONs. TX-405 has *n* of 40 oxyethylene units and behaves differently in solution [17]. At a concentration between 6×10^{-7} M and 4×10^{-5} M TX-405 does not influence the mobility, but further addition of TX-405 causes the mobility to decrease. Up to 2×10^{-3} M of this surfactant did not cause an increase in the mobility of the anatase particles. Experiments at higher surfactant concentrations were not performed.

A detailed study was undertaken to delineate the behavior of mixed-surfactant systems. Figure 2 presents the electrophoretic mobility of anatase particles at pH 3 in 0.001 M sodium nitrate that had been pretreated with different concentrations of sodium dodecylsulfate. After 1 h of equilibration with the SDS, different concentrations of TX-100 were added to the system. The results are presented in terms of electrophoretic mobilities as a function of the concentration of TX-100. Different symbols present the results of experiments conducted at different dodecylsulfate concentrations. The systems behave similar to the pure TX-100/water/anatase system under same conditions. At low TX-100 concentrations, TX-100 does not cause a change in the oxide mobility, but higher additions of TX-100 decrease the mobility of the anatase particles. After a certain TX-100 concentration, a plateau is reached and further surfactant addition does not change the anatase mobility. Finally, at TX-100 concentrations above the cmc (2×10^{-4} M), further TX-100 addition increases the anatase mobility. The difference in the adsorption behavior of nonionic and mixed nonionic/anionic surfactants is evidenced by the reversal in anatase charge from + to − with the addition of nonionic surfactant in a mixed system. That can be achieved only by coadsorption of nonionic and anionic surfactants. The more anionic surfactant is preadsorbed on the anatase particles the more negative is their mobility and the broader is the plateau region where the mobility of the anatase does not change with an increase in the concentration of TX-100.

Fig. 2 Influence of TX-100 nonionic surfactant on the electrophoretic mobilities of anatase particles with preadsorbed sodium dodecylsulfate (mixed-surfactant system) at pH 3 in 0·001 M $NaNO_3$



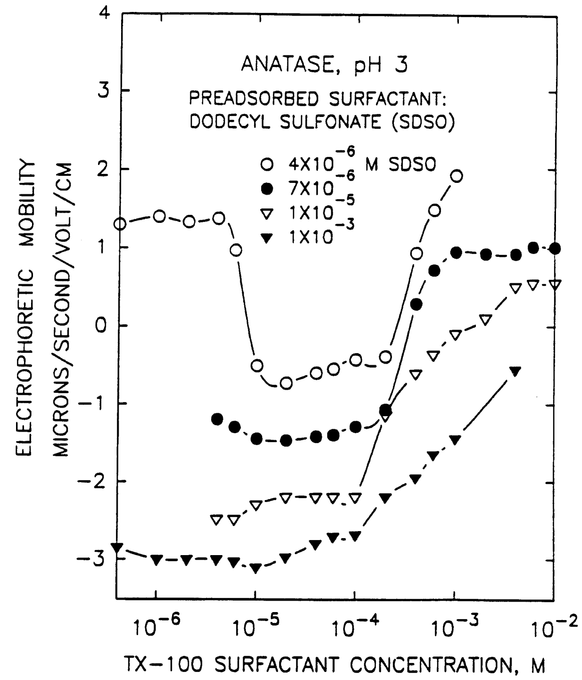


Fig. 3 Influence of TX-100 nonionic surfactant on the electrophoretic mobility of anatase particles with preadsorbed anionic sodium dodecylsulfate surfactant (mixed-surfactant system) at pH 3 in 0.001 M $NaNO_3$

Figure 3 presents the behavior of the system when the preadsorbed surfactant is dodecylsulfonate, showing a behavior similar to that shown in Fig. 2. Figure 4 presents the results for a similar system (as in Fig. 3) except that the preadsorbed surfactants are octyl and hexadecyl sulfonate, respectively. The electrophoretic mobility of anatase in the octyl sulfonate/TX-100/anatase system is more negative than in the case of hexadecylsulfonate/TX-100/anatase system.

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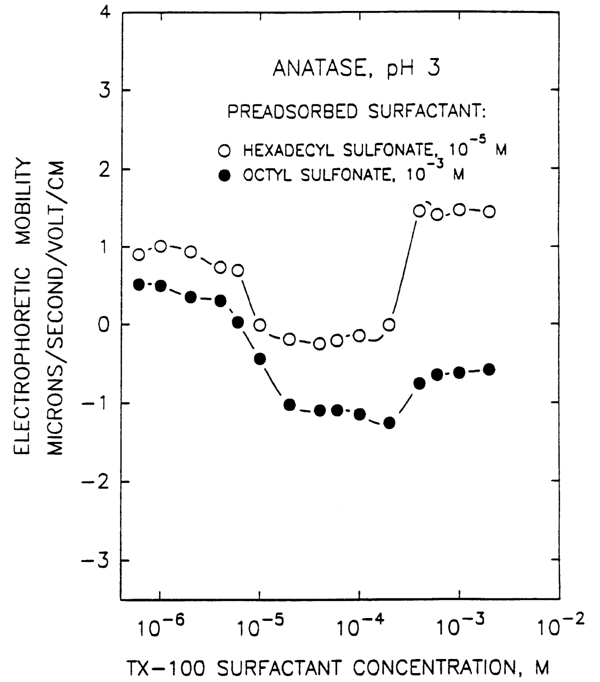


Fig. 4 Influence of nonionic surfactant on electrophoretic mobility of anatase particles with preadsorbed anionic octyl and hexadecylsulfonate surfactant (mixed-surfactant system) at pH 3 in 0.001 M $NaNO_3$

Electrokinetic behavior of alumina in mixed-surfactant systems with the preadsorbed sodium dodecylsulfate was influenced by addition of TRITON surfactants in the same way as anatase (data not shown). Pure TRITON surfactants do not adsorb on alumina in appreciable amounts.

The effect of mixing the anionic and nonionic surfactants on the adsorption behavior of individual components is shown in Figs. 5 and 6. In these experiments, the alumina was first precoated with 10^{-4} M sodium dodecylsulfate for 1 h and then the TRITON TX-100 was added and equilibrated for 24 h. Conditioning also included controlling the ionic strength with 0.001 M $NaNO_3$ at pH 3. Adsorption densities of both sodium dodecylsulfate and TX-100 on the pretreated alumina are presented in Fig. 5. Alumina does not adsorb pure TX-100. In the presence of sodium dodecylsulfate, TX-100 adsorbs on alumina at pH 3. The TX-100 adsorption density increases with increasing concentration of TX-100 in the bulk and reaches a plateau at 3×10^{-4} M of TX-100. The adsorption density of sodium dodecylsulfate also increased in the presence of TX-100, but this cannot be seen from the plot in Fig. 5 because 99% of the initial dodecylsulfate was already adsorbed without the addition of TX-100. Figure 6 presents the results for a similar system (as in Fig. 5) except that the initial concentration of sodium dodecylsulfate was higher, 5.5×10^{-4} M. It is apparent from the results given

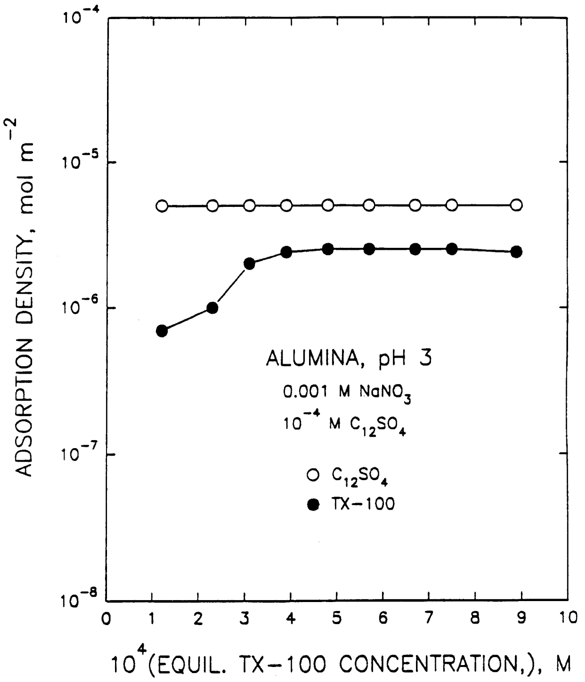
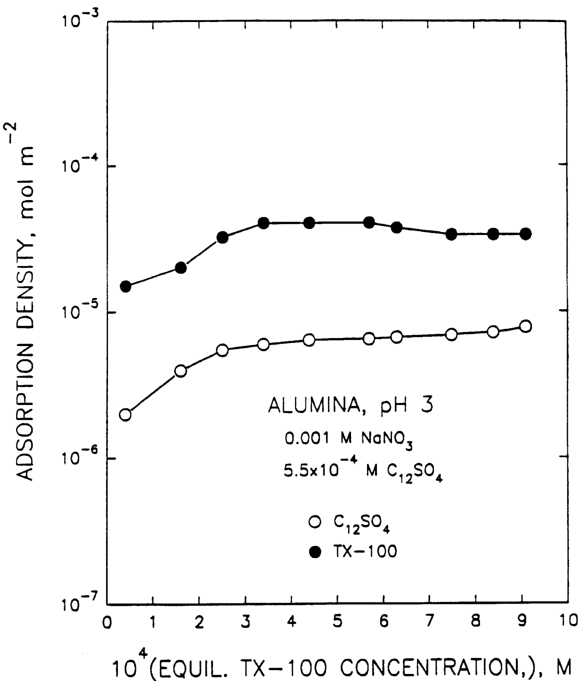


Fig. 5 Adsorption density of dodecylsulfate and TX-100 nonionic surfactant as a function of the equilibrium concentration of TX-100 at pH 3 in 0.001 M $NaNO_3$ with preadsorbed anionic sodium dodecylsulfate surfactant (mixed-surfactant system). Initial concentration of sodium dodecylsulfate: 10^{-4} M

Fig. 6 Adsorption density of dodecylsulfate and TX-100 nonionic surfactant as a function of the equilibrium concentration of TX-100 at pH 3 in 0.001 M $NaNO_3$ with preadsorbed anionic sodium dodecylsulfate surfactant (mixed-surfactant system). Initial concentration of sodium dodecylsulfate: 5.5×10^{-4} M



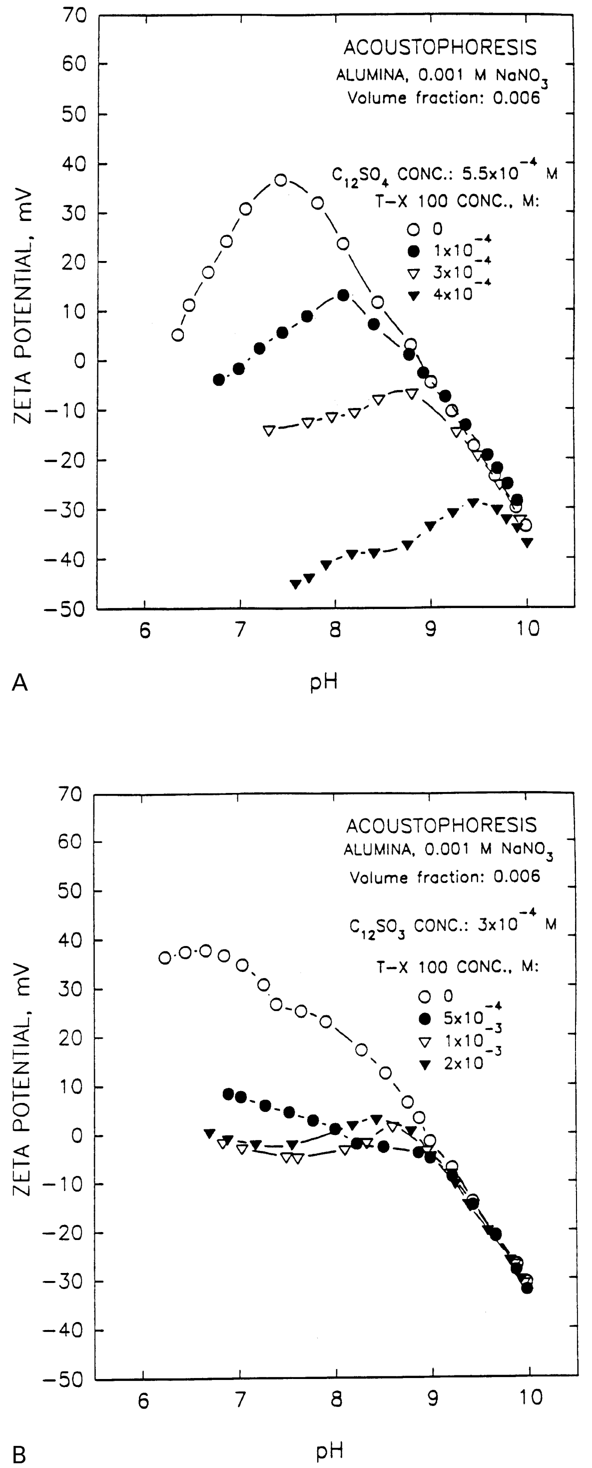


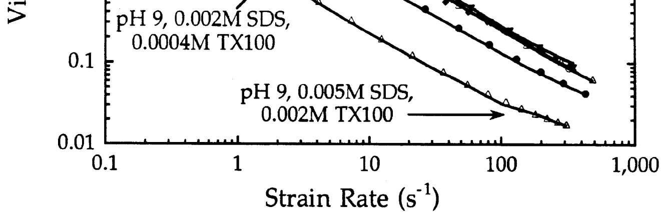
Fig. 7 (A) Acoustophoresis measurements in mixed-surfactant systems (5.5×10^{-4} M dodecylsulfate preadsorbed; TX-100 adsorbed), giving the zeta potential as a function of pH for alumina in 0.001 M NaNO$_3$ at different TX-100 concentrations. (B) Acoustophoresis measurements in mixed-surfactant systems (3.0×10^{-4} M dodecylsulfonate preadsorbed; TX-100 adsorbed), giving the zeta potential as a function of pH for alumina in 0.001 M NaNO$_3$ at different TX-100 concentrations

in Fig. 6 that adsorption density of the TX-100 is substantially increased in the presence of the higher concentration of sodium dodecylsulfate.

Acoustophoretic measurements were also used to investigate mixed-surfactant systems. Figure 7a presents the zeta potential as a function of pH for alumina particles (0.6% vol) in mixed-surfactant systems (dodecylsulfate preadsorbed, then TX-100 adsorbed). The nonionic TX-100 does not adsorb on alumina in the absence of the anionic surfactant. Moreover, the addition of TX-100 to aqueous alumina/SDS suspensions decreases the zeta potential and even reverses the net oxide charge. At TX-100 concentrations above 0.0001 M and dodecylsulfate concentration of 0.0005 M, the zeta potential of anatase is negative at all pHs. In another series of experiments the anionic surfactant was changed to sodium dodecylsulfonate and the results are given in Fig. 7b. The same kind of behavior was observed as in the case of dodecylsulfate/TX-100. The difference between the behaviors of the systems with the two different surfactants is that much more TX-100 was necessary to keep oxide particles negative at all pHs (>0.001 M TX-100 for dodecylsulfonate systems as compared with 0.0001 M TX-100 for sulfate systems).

The results of the viscosity measurements are presented in Fig. 8. Viscosity of 10 vol% alumina slurries at the isoelectric point (pH 9) was measured as a function of the shear rate. The addition of sodium dodecylsulfate or TX-100 as individual surfactants did not change the viscosity of alumina. On the other hand, simultaneous addition of both surfactants did decrease the viscosity. When more

Fig. 8 Viscosity versus shear rate of the alumina slurries at pH 9 (iep) in the presence of various amounts of sodium dodecylsulfate and TX-100. Surfactant concentrations indicated on the plot



sodium dodecylsulfate was added viscosity became even lower. The addition of more TX-100 increased the viscosity to where it was in the absence of surfactants.

Discussion

Surfactant impurities and/or additives are often surface active themselves and influence the behavior of oxides in surfactant/water/oxide systems. In this work systems containing one oxide and two surfactants were studied, particularly anionic/nonionic surfactant mixtures. The percentages of both surfactants in solution were varied and the electrokinetic behavior and viscosity of the suspended oxides were studied.

First, the influence of nonionic surfactants on the electrophoretic mobility of oxides was investigated in order to interpret the behavior of anionic/nonionic surfactant mixtures. As Fig. 1 indicates, the addition of nonionic surfactants from the TRITON series [TX-(number)] at first does not influence the electrophoretic mobility of anatase, but at higher surfactant concentrations, the mobility was found to decrease. Further surfactant addition causes the mobility again to increase (after surfactant cmc is reached) and then decrease with an increase in surfactant adsorption. According to Mathai and Ottewill [18], polyoxyethylene glycols monoalkyl ether nonionic surfactants first adsorb on AgI parallel to the particle surface and remain so until a complete monolayer is reached. We speculate that this probably happens in oxide/nonionic surfactant systems, as well. Monomeric surfactant molecules coat oxide particles and screen the surface charge. Since nonionic surfactants carry no charge, this coating decreases the net charge on the oxide but never reverses it. Mathai and Ottewill [18] suggested that after a monolayer of surfactant molecules adsorbed parallel to the AgI surface is completed (as expected from the plateau in surfactant adsorption), further nonionic surfactant addition increases the angle between the adsorbed molecules and the oxide surface. This change in conformation of the adsorbed molecules happens somewhere around the surfactant's cmc. Subsequent surfactant addition stabilized AgI and produced a hydrophilic surface, suggesting the possibility of forming reverse hemimicelles, bilayers or surface micelles. This highly idealized and *speculative* mechanism might also be used to explain the behavior of oxide/nonionic surfactant systems, too. Moreover, the TRITONs with long polar chains (TX-305: 30 oxyethylene units: TX-405: 40 oxyethylene units) cannot coat the oxide particles completely with the lowest observed oxide mobility being approximately 1 μm s^{-1} V^{-1} cm as compared with 0 μm s^{-1} V^{-1} cm with TX-100 (9–10 oxyethylene units) or TX-165 (16 oxyethylene units)). This is probably due to the difference in configuration of the hydrophilic chains. The enthalpy of micelle formation [17] depends on the length of the polar oxyethylenic chain. The enthalpy of micelle formation is endothermic for all four TRITONs studied. The values of enthalpies of micelle formation suggest a significant change in the micelle and monomer conformation for TRITON molecules having more than 16 oxyethylene groups in the polar head. Calorimetric data for the adsorption of TX-305 and TX-405 on silica [17] suggest adsorption with a part of their oxyethylene head on the solid, and the other part in the bulk. This conformation of the adsorbed molecules would leave the oxide particles only partially coated even at high adsorption densities. Consequently, some oxide charge would not be "screened" and the electrophoretic mobility would not be zero (as was indeed observed).

Spectroscopic evidence exists for hydrogen bonding between polyethylene oxide groups from nonionic surfactants and hydroxyl groups at the silica surface (both FTIR [19] and NMR shift and relaxation time measurements [20]). The presence of two plateaus in the adsorption isotherm of nonionic surfactants on silver iodide and silica also indicates the possible change in orientation of the adsorbed molecules from horizontal to more vertical. The presence of either bilayers or surface micelles on the silica surface at higher nonionic surfactant concentrations was indicated with neutron reflectivity [21] and fluorescence probe studies [22]. Wettability and contact-angle studies [23] also indicated an inclined vertical orientation of the surfactant molecules (hydrophobic chains) at sub-cmc surfactant concentrations. Such orientation of the adsorbed nonionic surfactant molecules yielded a hydrophobic surface. At higher surfactant concentrations, the silica surface became hydrophilic again, which also indicated the formation of either a bilayer or surface micelles. Adsorption measurements confirmed the presence of at least two layers at the maximum surfactant adsorption. Similar spectroscopic measurements should be performed with nonionic surfactants adsorbed on anatase and alumina surfaces to confirm the validity of the proposed mechanism.

The addition of anionic/nonionic surfactant mixtures to oxides produced similar behavior to that observed for nonionic surfactants alone. Figures 2 and 3 present the electrophoretic mobility versus the TX-100 concentration for anatase particles at pH 3. Different amounts of sodium dodecylsulfate were preadsorbed on the anatase. The addition of TX-100 first decreased the electrophoretic mobility. Further additions of TX-100 only changed the electrophoretic mobility slightly, until a certain concentration was reached, at which further addition increased the anatase mobility. Despite the fact that the electrophoretic mobility versus TX-100 concentration plots have a similar shape in the presence and absence of the anionic surfactants some significant differences were observed. For instance, the addition of nonionic surfactant in the presence of anionic surfactant reversed the oxide-particle charge. This can be explained only by coadsorption of anionic and nonionic surfactants. TRITONs only weakly interact with anatase and the presence of dodecylsulfate enhances their adsorption strongly. The same behavior was observed with alumina even though TRITON surfactants by themselves barely adsorb on the alumina surface.

Somasundaran and coworkers [4] explained the enhanced coadsorption of nonionic and anionic surfactants on kaolinite in terms of chain–chain interaction between the tails of anionic and nonionic surfactant molecules adsorbed on adjacent sites. It was suggested that the free energy gain from such chain–chain interactions decreases the residual SDS concentration (or the chemical potential) required to achieve a certain level of adsorption. It was also claimed that chain–chain interactions in mixed-surfactant systems will favor the formation of mixed-surfactant clusters on the surface. Such mixed-surfactant clusters could serve as hydrophobic pools and enhance the adsorption of the nonionic surfactant by abstracting the hydrocarbon chains of the highly surface-active nonionic surfactant into the clusters leaving the oxyethylene segments protruding into the bulk solution.

Figure 4 shows that some chain–chain interactions indeed are important in mixed-surfactant adsorption. Anatase particles were precoated with octyl and hexadecylsulfonate, and electrophoretic mobility was then measured as a function of the TX-100 concentration (TX-100 has an octyl hydrophobic chain). As expected, TX-100 interacted more strongly with octylsulfonate. The anatase particles precoated with hexadecylsulfonate never reversed their charge. On the other hand, a charge reversal occurred in the TX-100/octylsulfonate system, suggesting stronger coadsorption, probably due to more favorable chain–chain interactions.

The current results also correlate nicely to the recent studies on adsorption of mixed cationic/nonionic surfactants on alumina [8]. Somasundaran et al. [8] clearly showed that at low concentrations of nonionic surfactant a decrease in the adsorption of cationic surfactant occurred with the addition of nonionic surfactant. On the other hand, at intermediate surfactant concentrations where individual molecules of the adsorbed surfactants start to form hemimicelles, the addition of nonionic surfactant results in an increase in the adsorption of cationic surfactants. As mentioned earlier, Somasundaran proposed that this happens due to the formation of mixed hemimicelles and enhanced abstraction of the hydrophobic chains from solution. As the concentration of nonionic surfactant and the ratio of the nonionic/cationic surfactant increases, the nonionic surfactant molecules displace the adsorbed cationic surfactant at most concentrations studied.

In the present study, similar results were obtained in electrokinetic measurements. The addition of low concentrations of nonionic surfactant decreased the zeta potential due to the enhanced adsorption of anionic surfactant (Figs. 2 and 3). Further addition of nonionic surfactant displaced the adsorbed anionic surfactant, resulting in coating of the oxide particles with the nonionic surfactant. The electrokinetic behavior was then similar to that of the pure nonionic surfactant system with a subsequent increase in the zeta potential. Since experiments are performed with initially positive oxides, charge reversal occurred due to enhanced coadsorption of the anionic surfactant. As the amount of preadsorbed anionic surfactant was increased, charge reversal at high amounts of nonionic surfactant did not occur because some anionic surfactant molecules were not replaced with the nonionic surfactant.

The results of the electrokinetic measurements were applied to improve the dispersion of alumina and anatase powders, particularly around the isoelectric point. Metal oxides carry no surface charge at the isoelectric point and are strongly flocculated. Most dispersants do not adsorb at such pHs due to lack of particle charge. Acoustophoresis experiments showed the adsorption of anionic surfactant at and around the isoelectric point of alumina in the presence of TRITON-X100. Viscosity experiments showed that simultaneous addition of anionic and nonionic surfactants could be used to lower the viscosity of powders at the isoelectric point where both surfactants adsorb very poorly when studied separately. Similar experiments were performed with mixtures of sodium dodecylsulfate and monodisperse polyethyelene oxide dodecyl ethers with no aromatic ring and no change in viscosity was observed. On the other hand, when mixtures of sodium dodecylsulfate and fairly polydisperse sorbitan nonionic surfactants were used, dramatic changes in viscosity and zeta potentials were observed. We speculate that polydisperse chains might have some role in the coenhanced mixed-surfactant adsorption but more work remains to be done before any conclusions can be drawn.

Conclusions

Electrophoretic and viscosity studies of anatase and alumina in mixed-surfactant solutions were performed. The anionic surfactant sodium dodecylsulfate and nonionic surfactants from the TRITON series (polyoxyethylene alkyl ethers) were investigated. Adsorption of nonionic surfactants reduces the zeta potential of these oxides to zero due to a screening effect but never causes a reversal of the sign of the surface charge. However, when coadsorbed with anionic surfactants, nonionic surfactants suppress the anionic surfactant adsorption at low and high ratios, but mutually enhanced coadsorption is observed at near 1 : 1 molar ratios. An enhancement of anionic surfactant adsorption occurs in the concentration range where the surfactants appear to form surface aggregates. It seems that mixed-surfactant hemimicelles are thermodynamically more stable than pure surfactant hemimicelles. Enhanced coadsorption of anionic and nonionic surfactant was used to improve oxide dispersion near the isoelectric point where both surfactants adsorb poorly when considered alone. Chain–chain interactions and conformational changes might contribute to this adsorption phenomena, but molecular mechanisms of mixed-surfactant adsorption are still largely unknown. Further spectroscopic studies should be performed to understand the mechanisms of adsorption in nonionic and mixed-surfactant systems.

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