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The change in structure of surfactant aggregates during
adsorption/desorption processes and its effect on the stability
of alumina suspension

Lei Huang, P. Somasundaran *

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The change in structure of surfactant aggregates during adsorption/desorption processes and its effect on the stability of alumina suspension

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Abstract

The adsorption/desorption behavior of the cationic surfactant tetradecyl trimethyl ammonium chloride (TTAC) at the alumina–water interface and the change in the structure of surfactant aggregates at the interface were studied using the fluorescence spectroscopic technique along with electrophoresis. As expected, the cationic TTAC adsorbed significantly on the negatively charged alumina particles. It was observed that adsorption was reversible in the high concentration range, but in the low concentration range some hysteresis was observed. This can be attributed to the different operative mechanisms for hemimicelle formation and breakup. An energy barrier is proposed for the formation of the TTAC aggregates at the solid–liquid interface with the result that the hemimicelle concentration for the adsorption process is higher than that for the desorption process. This conclusion was further confirmed by the fluorescence spectroscopic test. This adsorption hysteresis affected dispersion properties of alumina suspension with the maximum settling rate shifting to the lower concentrations.

Keywords: Adsorption/desorption; Alumina interface; Cationic surfactant; Settling rate; Surfactant aggregates

1. Introduction

Adsorption of ionic surfactants on charged mineral oxides has been studied extensively in the literature [1–3]. It is generally accepted that ionic surfactant adsorbs readily due to electrostatic interactions on oppositely charged surfaces in the low surfactant concentration range. We have modeled this adsorption behavior using the Stern–Graham equation in our previous work [4]. With an increase in surfactant concentration, the adsorption

increases sharply above a given concentration, which has been interpreted as being due to the formation of surfactant aggregates on the surface. The concentration at which these aggregates form is referred to as the hemimicelle concentration (HMC) [1]. With a further increase in surfactant concentration, a gradual change from monolayer aggregates (hemimicelle) to aggregates with reverse orientation is postulated, based on a variety of spectroscopic studies and flotation performance, and the aggregate at the solid–liquid interface (hemimicelle, bilayer, etc.) has been called solloid [5].

Harwell and co-workers have suggested formation of bilayer surfactant aggregates called “admicelles” [2,6,7]. Recently Gao et al. [8], Zhu and

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Gu [9] and Leimbach et al. [10] postulated a model of ionic surfactant adsorption on a polar charged surface. In this model, surfactant ions serve as anchors which are bound to the oppositely charged surface. Then isolated surface aggregates, called surface micelles, form at the interface. This model explains the low saturation for adsorption of ionic surfactants on the hydrophilic adsorbents with low surface charge density. However, it cannot explain the flotation and other hydrophobic properties of the surfactant-modified surfaces.

Considering the heterogeneity of an oxide surface, the adsorption isotherm can be considered to consist of a series of step changes in coverage corresponding to a surface with discrete patches or areas of different energy [11]. It is possible then for different types of aggregates to exist on the surface simultaneously, since such association between adsorbed surfactants is a dynamic process, and any one region of the surface can possess a time-averaged aggregate. Despite the importance of the structure of surfactant aggregates at the solid–liquid interface, information on this aspect is still scant. In the present work, possible changes in the structure of surfactant aggregates at the alumina–water interface during adsorption and desorption are examined along with the effect of each structural change on the stability of the alumina suspensions.

2. Materials and Experimental Procedure

2.1. Alumina

Linde A alumina purchased from Union Carbide Corp. was specified to be 90% α -Al₂O₃ and 10% γ -Al₂O₃ and to have a mean diameter of 0.3 μ m. The specific surface area was measured to be 15 m² g⁻¹ by N₂ BET adsorption using a Quantasorb system.

2.2. Surfactant

The cationic surfactant, *n*-tetradecyltrimethylammonium chloride, [CH₃(CH₂)₁₃N(CH₃)₃]Cl (TTAC), from American Tokyo Kasei, Inc., was used as received.

2.3. Reagents

NaCl, used for controlling the ionic strength, was purchased from Fisher Scientific Co. and was certified as A.C.S. grade (purity > 99.9%). NaOH, used for adjusting the pH, was purchased from Fisher Scientific Co. and was certified as the volumetric standard solution (0.1 M). Water used in all experiments was triple distilled water. Conductivity of triple distilled water was measured to be in the range $(1-2) \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$.

2.4. Adsorption

Adsorption experiments were conducted in capped 20 ml vials. First, a 2 g sample of alumina was mixed in 10 ml of 0.03 M NaCl solution for 1 h and then the pH was adjusted to 10 and the solution was allowed to further equilibrate at room temperature ($22 \pm 2^\circ\text{C}$) for 1 h. 10 ml of 0.03 M NaCl solution containing the surfactant was then added, and the samples were allowed to equilibrate for 15 h. pH measurements were then made and, if necessary, the pH was adjusted using 0.1 M NaOH. The samples were allowed to equilibrate for about 3 h after the final pH adjustment, and then centrifuged for 25 min at 5000 rev. min⁻¹. About 20 ml of the supernatant was pipetted out for analysis. The concentration of TTAC was measured by a two-phase titration technique [12].

2.5. Desorption

After adsorption, desorption tests were conducted by adding the same volume of diluent adjusted to the system ionic strength and pH (0.03 M NaCl and pH 10) to make up for the volume of the supernatant removed. The total volume and thus solid to liquid ratio remain constant as the dilution step is repeated many times, with the surfactant concentration monitored at each step. Adsorption density at each step is calculated from the change in concentrations of the surfactant.

2.6. Fluorescence Spectroscopy

A Photon Technology International PTI LS-100 instrument was used for fluorescence experiments.

These experiments were designed to probe *in situ* the micro-properties of the adsorbed surfactant layers in terms of micropolarity [13,14]. The samples—containing pyrene dissolved to its maximum solubility in water (about 2×10^{-7} kmol m^{-3})—were excited at 335 nm and emissions between 365 and 500 nm were recorded. The detail principle and procedure for this technique have been described in our previous study [15].

2.7. Electrokinetic measurements

Zeta potential measurements were made using a Laser zee meter model 501 system.

3. Results & Discussion

The adsorption isotherm of TTAC on alumina at pH 10 is shown in Fig. 1. At this pH the alumina surface is negatively charged and the electrostatic attraction with the cationic TTAC will be domi-

nant. There is a sharp increase in the adsorption density at around 5×10^{-4} kmol m^{-3} which can be attributed to the formation of surfactant aggregates (solloids) at the solid–liquid interface. Comparing the zeta potential to the adsorption at the same residual concentrations, it can be seen that the charge of alumina is neutralized at a very low adsorption density of TTAC (see Fig. 2). The fact that adsorption of the cationic TTAC continues to take place leading to aggregate formation even after the particles have become similarly charged suggests the predominant role of hydrophobic interactions between the hydrocarbon tails in causing the adsorption.

The maximum adsorption density of TTAC on alumina at pH 10 is about 2.5×10^{-6} mol m^{-2} . This translates to roughly 66 \AA^2 molecule which is similar to the reported cross-sectional area of tetradecyltrimethylammonium bromide (TTAB) at the air–solution interface (61 \AA^2) without salt in the system [16]. The calculated molecular area of the TTAC polar group is about 37 \AA^2 . This

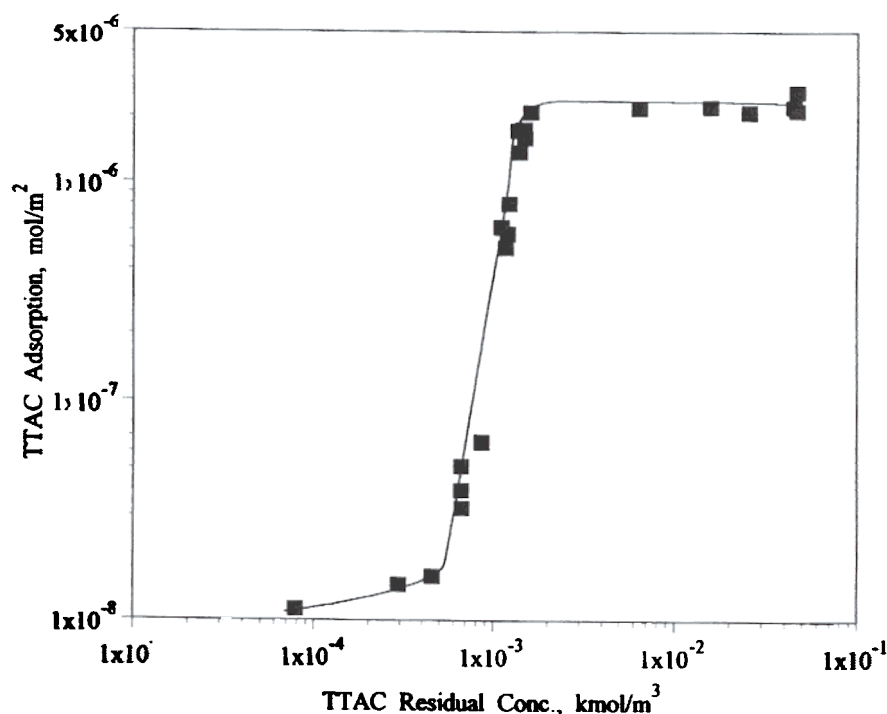


Fig. 1. Adsorption isotherm of TTAC at alumina–water interface pH 10, ionic strength 0.03 M NaCl.

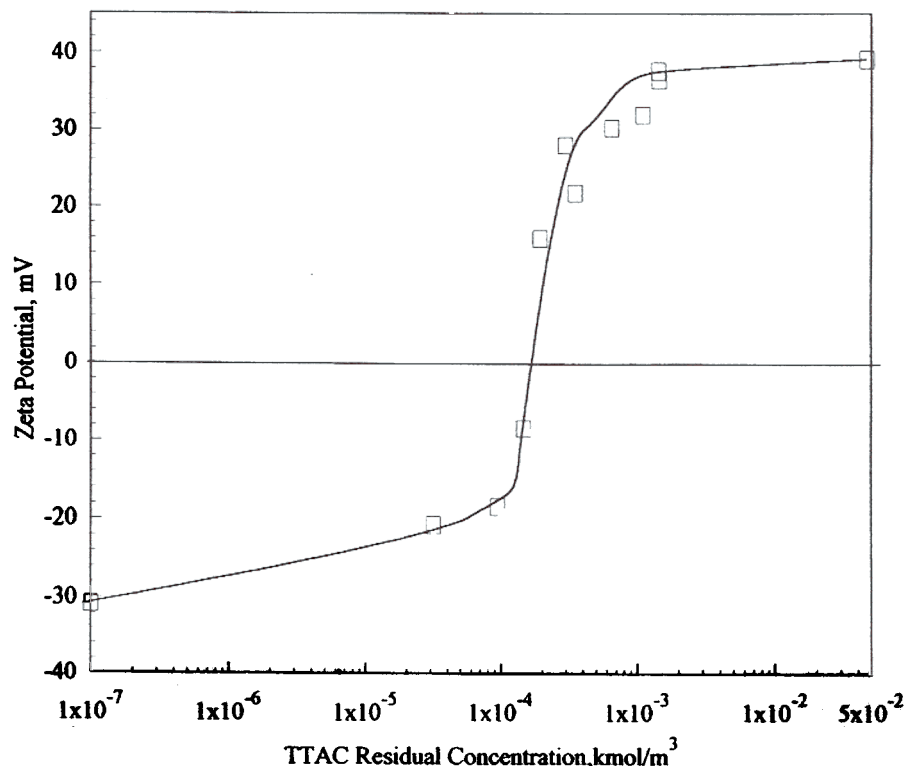


Fig. 2. Zeta potential of alumina after adsorption of TTAC at pH 10, ionic strength 0.03 M NaCl.

molecular area is estimated from the bond length between N–C (about 1.47 Å) and the van der Waals radii of the methyl group (about 2.0 Å), and these data can be found in a CRC or other related handbook. This molecular area indicates that the adsorption layer of TTAC in this system is made up of a loosely packed monolayer or patch aggregates.

To better understand the structure of the adsorption layer in this system, changes in the microstructure of the adsorbed layer were probed using fluorescence spectroscopy. Pyrene monomer fluorescence is sensitive to the medium in which pyrene resides. In hydrophobic environments, the ratio of the intensities of the first and third peaks (I_3/I_1) on a pyrene emission spectrum is higher than that when the pyrene is in a hydrophilic environment. The value for I_3/I_1 is 0.5–0.6 in water, 0.8–0.9 in surfactant micelles, and >1 in nonpolar solvents. Since this ratio can be used to characterize the

polarity of environments, it is termed the polarity parameter [17,18].

The adsorption isotherm of TTAC on alumina is plotted in Fig. 3, along with changes in the polarity parameter of pyrene at the alumina–water interface and in the supernatant. It is observed that pyrene goes to the alumina–water interface completely in a narrow TTAC concentration range which corresponds to the sharp increase in the adsorption isotherm. From this, it is evident that pyrene is solubilized in TTAC aggregates at the alumina–water interface. However, once TTAC micelles form in the supernatant, pyrene is preferentially solubilized into the micelles and does not go to the alumina–water interface in spite of the presence of TTAC colloids. This result is interesting considering that in the alumina–sodium dodecyl sulfate (SDS) system, pyrene is preferentially solubilized in colloids at the alumina–water interface, rather than in SDS micelles in the supernatant

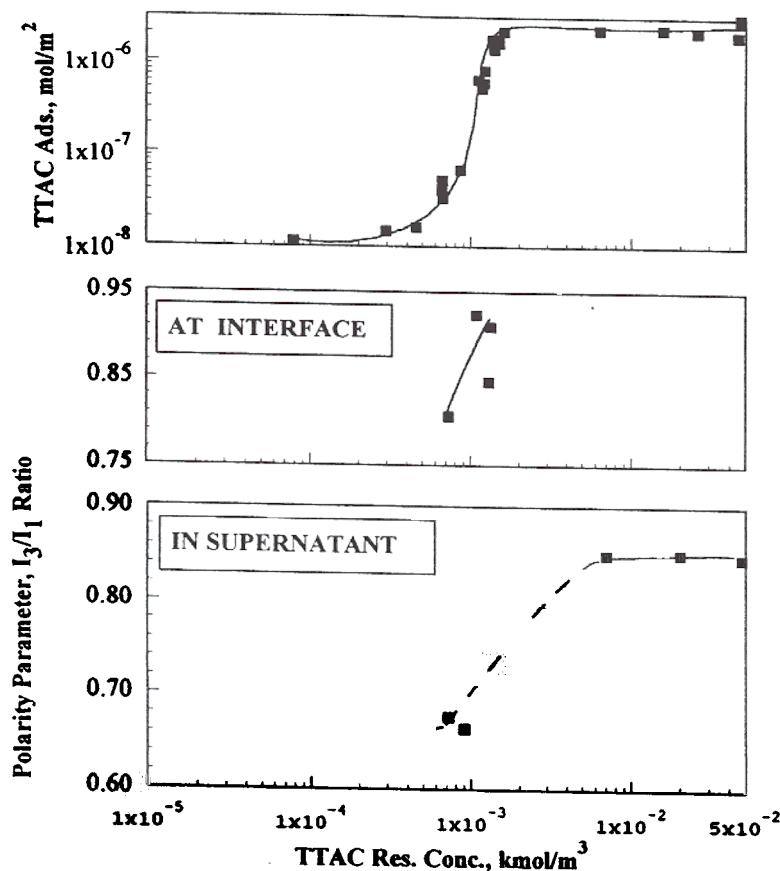


Fig. 3. Adsorption isotherm of TTAC on alumina and corresponding changes in pyrene fluorescence from the alumina-water interface and the supernatant.

[15]. It is generally accepted that SDS will form bilayer aggregates at the alumina–water interface in the high concentration range. A comparison of these results suggests that aggregates of TTAC at the alumina–water interface are not as tightly packed. The solubilizing power of the TTAC solids at the alumina–water interface is not very high.

The settling rate of the alumina suspensions after TTAC adsorption at pH 10 is shown in Fig. 4. In the absence of surfactant, and at low surfactant adsorption densities, the alumina suspension in water is dispersed and the settling rate is low. Once the surfactant forms aggregates at the interface, the alumina surface becomes hydrophobic and the settling rate is markedly increased, which upon correlation with Figs. 1 and 2 can be attributed to

hydrophobic bridging between particles [19]. From these results, it can be concluded that the structure of the adsorption layer in this system is mainly monolayer patches with a hydrophobic tail orientated into the solution. With a further increase in the TTAC concentration, the settling rate decreases. This can be attributed to the formation of TTAC micelles in the solution. The positively charged micelles can cause an increase in the distance between particles and hinder the hydrophobic bridging, with the electrical repulsion force becoming dominant and the settling rate decreasing.

To further understand the structure of the adsorption layer in this system, desorption tests were conducted. The results obtained are shown in Fig. 5. The solid line represents the initial

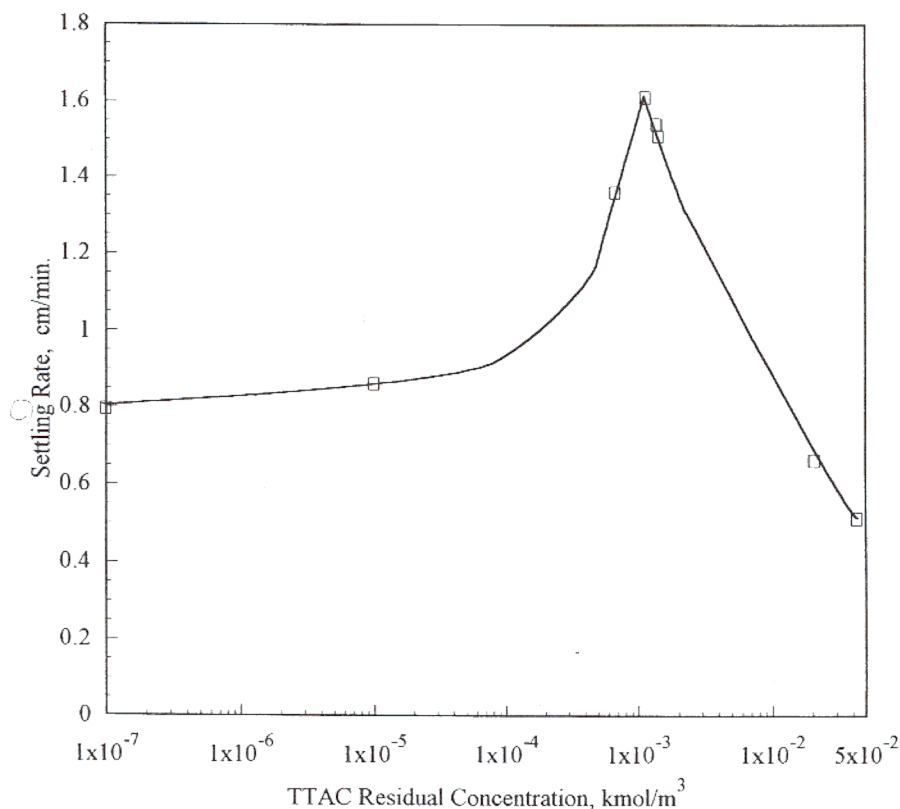


Fig. 4. Settling rate of alumina suspension after TTAC adsorption at pH 10, ionic strength 0.03 M NaCl.

adsorption isotherm. It is observed that adsorption is reversible in most cases, but irreversible in the low concentration range, where significant changes in wettability normally occur. At low concentrations, there is some hysteresis with measurable differences in adsorption and desorption amounts.

Fluorescence spectroscopy was used to probe changes in the aggregation of surfactants at the solid-liquid interface upon dilution. Supernatant solutions of different residual concentrations along the isotherm were diluted with pyrene solutions at the desired ionic strength and the slurry conditioned for 15 h. The procedure was repeated several times. Pyrene emission spectra from the alumina-water interface were then obtained and polarity parameters of the adsorbed layer calculated to gain an insight into the microstructural changes of the adsorbed layer upon dilution. The results are plotted in Fig. 6, along with the polarity parameter for

pyrene dissolved in TTAC solutions of similar concentrations. The presence of pyrene indicates hydrophobic aggregates at the alumina-water interface. It can be found that the value of the $I_3:I_1$ ratio decreased with the decrease in TTAC concentration during desorption. It is to be noted that hydrophobic aggregates are detected at the solid-liquid interface at concentrations lower than that at which they were first detected during adsorption (see Fig. 3). For the residual concentrations discussed here there are no aggregates in solution, as is clear from the results in Fig. 6. Aggregates form in solution only above a concentration of $1.2 \times 10^{-3} \text{ kmol m}^{-3}$ and hence the hydrophobic environment probed by pyrene is considered to be that of the interface. Thus surfactant aggregates are detected at the interface in a concentration range below the critical micelle concentration on the adsorption isotherm. These results indicate that

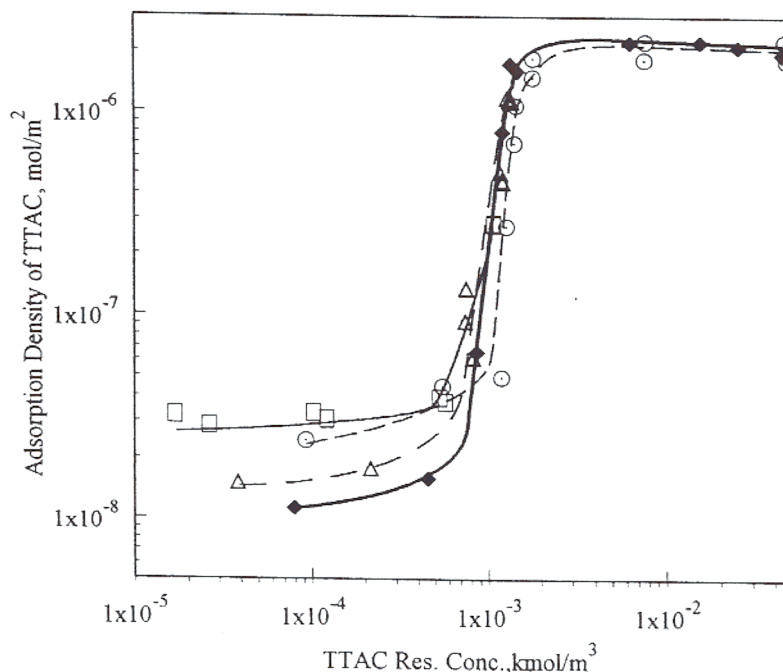


Fig. 5. Desorption of TTAC from alumina upon dilution from different residual concentrations at pH 10, ionic strength 0.03 M NaCl. ◆ Adsorption isotherm, ○ Desorption from $C_R=0.0472$ M, △ Desorption from $C_R=0.0129$ M, □ Desorption from $C_R=0.00108$ M.

the mechanisms involved in the formation of surface aggregates and the breakup of the surface aggregates differ.

This can be attributed to the activation energy needed for the formation of surfactant aggregates at the interface. It is generally accepted that the formation of micelles, hemimicelles and solloids is a pseudophase transition phenomenon. Similar to the mechanism of the nucleation process, the change in Gibbs energy accompanying the formation of surfactant aggregates at the interface can be given by the following equation:

$$\Delta G_{agg} = -N\phi + A_s \xi^s \quad (1)$$

where N is the aggregation number of the surface aggregate, ϕ is the hydrophobic interaction affinity, A_s is the area of solloid at the interface and ξ^s is a constant related to the surface energy at the interface, involving mainly electrical repulsive energy. The first term on the right-hand side of Eq. (1) is always negative, whereas the second term is always positive. Since for small N the magnitude

of the latter term exceeds that of the former, the resulting ΔG_{agg} at first increases. Eventually, the first term becomes larger than the second and ΔG_{agg} starts to decrease, and the formation of surfactant aggregates becomes significant. This maximum ΔG_{agg} is called the energy barrier to the formation of surfactant aggregate. Due to the activation energy needed, the critical solloid concentration (CSC) is at a higher concentration during adsorption than otherwise. In other words, the formation of surfactant aggregates at the interface starts at a higher concentration than that at which thermodynamically favorable conditions exist. In the current solid-surfactant system, the surface charge of alumina was neutralized at a very low concentration (see Fig. 2), and further adsorption of cationic TTAC at the interface to form aggregates must overcome the electrical repulsion forces between adsorbed TTAC species. In other words, ξ^s in Eq. (1) for the TTAC-alumina system is large, and high supersaturation is warranted for the formation of aggregates on the particles.

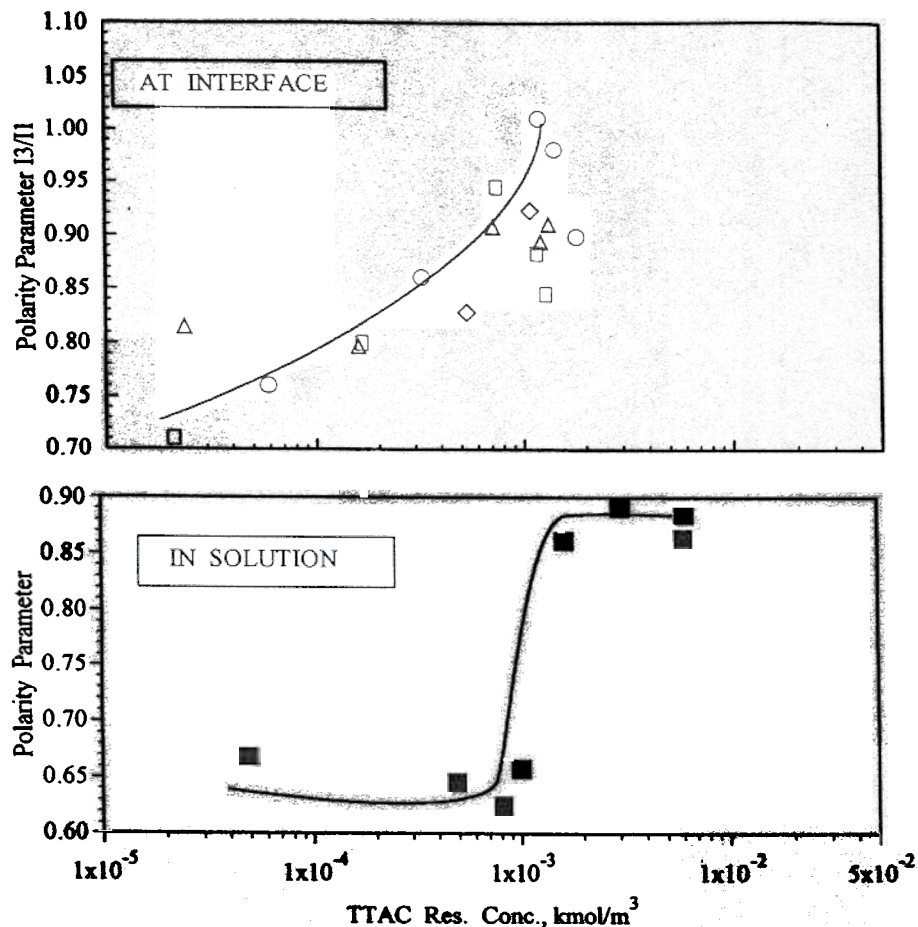


Fig. 6. Changes in pyrene polarity parameter from the TTAC adsorbed layer on alumina upon dilution from different residual concentrations C_R s and also in bulk solution. ■ From bulk solution, ○ From $C_R=0.0472$ M, □ From $C_R=0.00129$ M, △ From $C_R=0.00133$ M, ◇ From $C_R=0.00108$ M.

However, during the desorption process there is no energy barrier needed for the decomposition of the surfactant aggregates at the interface, and the existence of surfactant aggregates will depend only on the chemical potential of the TTAC monomer in the system, so the concentration range over which aggregate can exist on the particles during the desorption process is narrower than that involved in the adsorption process.

Due to the different mechanisms involved in the adsorption and desorption processes, the properties of alumina suspension are also different during these processes. In our current work, the settling rate of alumina suspensions was measured after

adsorption and desorption. The results are shown in Fig. 7. The solid line represents the settling rate immediately after adsorption, and broken lines represent the settling rate for samples starting from different residual concentrations C_R during desorption. The maximum settling rate has shifted markedly to a lower concentration range during desorption. This is attributed to the hysteresis involved in the breakup of surfactant aggregates at the interface. In this system the stability of the alumina suspension below the CMC of TTAC will depend mainly on the relative magnitude of the electrical repulsive force and the hydrophobic attractive force among the particles. As mentioned

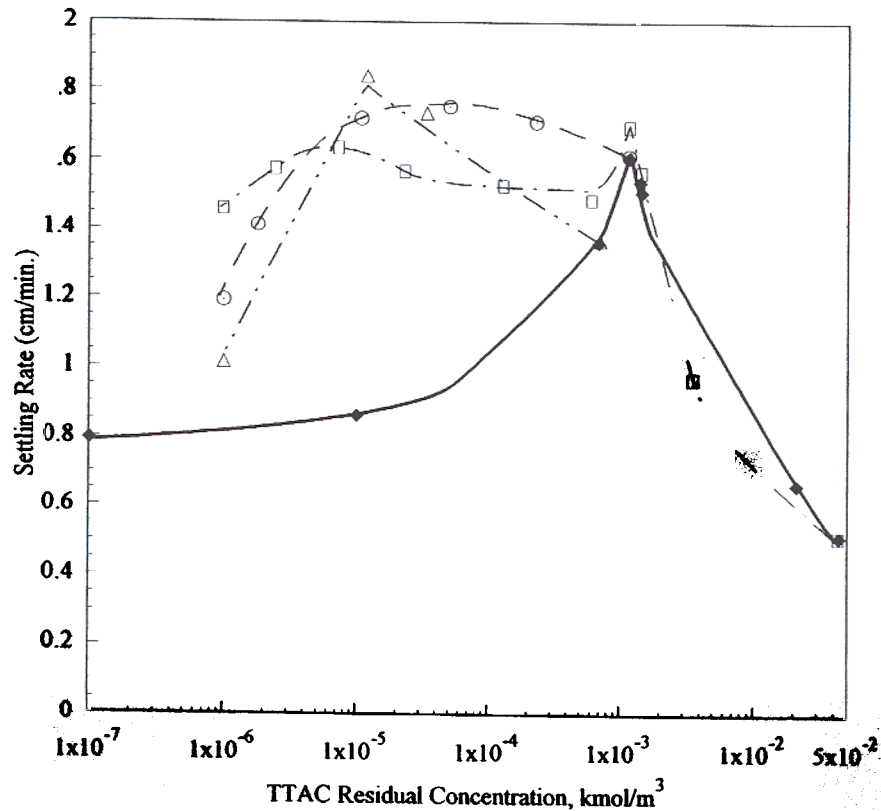


Fig. 7. Settling rate of alumina suspension during adsorption and desorption processes, at pH 10, ionic strength 0.03 M NaCl, ◆ After adsorption, □ Desorption from $C_R=0.043$ M, ⊙ Desorption from $C_R=0.00115$ M, △ Desorption from $C_R=0.000698$ M.

previously in the paper, the surfactant aggregates can exist in a lower concentration range during desorption, providing hydrophobic attractive forces between particles that are nearly constant, but with the electrostatic repulsive force decreasing. This is proposed as the reason for the observed flocculation and good settling of alumina suspension in a low concentration range.

4. Concluding remarks

The adsorption/desorption behavior of cationic surfactant TTAC, particularly the formation and decomposition of its aggregates, at the alumina-water interface has been studied. An energy barrier for the formation of surfactant aggregates at the alumina-water interface is proposed in this system.

Due to this, the adsorption and desorption are not reversible, and the desorption shows some positive hysteresis in the low concentration range. This conclusion was further confirmed by fluorescence spectroscopic tests. The polarity parameter obtained during the desorption suggests that hydrophobic aggregates exist at concentrations lower than that at which they were detected during adsorption. Since the stability of the alumina suspension in this system depends mainly on the relative balance between the electrostatic repulsive force and the hydrophobic attractive force, the hysteresis involved with the breakup of TTAC aggregates from the interface can make the hydrophobic attractive force higher during desorption. This will make it easier for the alumina suspension to flocculate, and the maximum settling rates to shift to a lower concentration range during desorp-

tion. Considering the hydrophobic behavior of the particles and the adsorption density at alumina interfaces, it is proposed that surfactant TTAC forms patchwise monolayer aggregates with carbon chain tails mainly orientated towards the bulk solution.

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