

Articles

Effect of Ionic Strength and Competitive Adsorption of Na^+ on the Flocculation of Lauryl Sulfate Micelles with Al^{3+}

P. Paton-Morales and F. I. Talens-Alesson*

TALENCO Consulting, P.O. Box 1035, Hospitalet de Llobregat 08902, Spain

Received March 5, 2001. In Final Form: July 19, 2001

The binding of Al^{3+} to SDS micelles is best described by means of Guoy–Chapman–Stern isotherms. A method is described to estimate parameters for a Guoy–Chapman–Stern competitive adsorption isotherm for the system $\text{Na}^+/\text{Al}^{3+}/\text{SDS}$ from data of the composition of micellar flocculates obtained in conditions of optimum flocculation. The dissociation coefficient $K_{\text{Al}^{3+}}$ is found to be equal to 17.67 if the bound fraction is defined as the ratio of bound Al^{3+} to SDS ions in the micelle. Experiments performed in the presence of a range of NaCl concentrations between 0 and 0.5 M show that the absence of flocculates in micellar solutions of lauryl sulfate in the presence of high $[\text{Al}^{3+}]$ cannot be explained by a drop in the chemical activity of Al^{3+} at high ionic strengths, although the chemical activity of Al^{3+} strongly influences the binding of Al^{3+} to SDS micelles. One effect of increasing $[\text{Na}^+]$ is to increase the critical micelle concentration of the surfactant in solution, from a value close to that of $\text{Al}(\text{DS})_3$ to another close to that of SDS. This reduces the proportion of surfactant in micellar form and susceptible therefore of being flocculated.

Introduction

Research on cation binding has involved a wide range of surfactants, and cations investigated have ranged from monovalent to trivalent cations,^{1–5} including Cr^{3+} , La^{3+} , and Al^{3+} . The significance of the particular system $\text{Al}^{3+}/\text{SDS}$ (lauryl sulfate)⁶ is that together with α -olefin-sulfonate– Al^{3+} , those are the two systems described with some detail^{7,8} which show adsorptive micellar flocculation (AMF). In this process (Figure 1), the surfactant micelles flocculate and capture anionic compounds such as benzoic acid or 2,4-dichlorophenoxyacetic acid (2,4-D) if these are present in the solution. This allows their separation from the solution by filtration. This provides the grounds for a potentially valuable separation process with advantages over other micelle-enhanced separations such as MEUF (micelle-enhanced ultrafiltration). The advantages are those of a filtration or sedimentation against an ultrafiltration (no fouling, no need for high overpressures), plus consideration of the aggravated problems presented by MEUF: worse fouling problems,^{9,10} permeation of micellar surfactant when using anionic surfactants (above 0.1 M

for SDS, with permeating concentrations above 0.03 M, 5 times the cmc_{SDS} ¹¹), and the fact that the process leads to the existence of a retentate which represents a significant fraction of the initial wastewater and which also now contains a high surfactant concentration. In the case of cationic surfactants, where the micellar permeation is not observed, this means a high concentration of a biocide in the retentate. This is why a surfactant-based separation technique without any of these inconveniences is an interesting alternative.

The flocculation has a number of characteristics described in previous work:

(i) The adsorption of Al^{3+} reduces strongly the superficial charge of the micelles, which reflects on zero or near-zero ζ -potentials within the full flocculation range.¹² Precipitation of SDS in the presence of Ca^{2+} only causes a reduction in ζ -potential from about -70 mV (normal ζ -potential for SDS micelles) to about -40 mV¹³ (associated to an ion binding ratio Ca/SDS around 0.1 according to the literature^{5,14}).

(ii) The ζ -potentials closest to zero (most unstable particles) are found with $[\text{Al}^{3+}]$ between 0.02 and 0.06 M, which corresponds with the minimum solubility of the surfactant.¹² Afterward, the ζ -potentials become more negative. Beyond $[\text{Al}^{3+}] = 0.11$ M, no readings are obtained.¹² The size of suspended particles (micelles and small micelle aggregates sizing up to 400 nm) above the minimum solubility region decreases again to a size of about 10 nm before readings are not possible.⁶ This strongly suggests that micelles actually disappear by some

* Corresponding author. Current address: School of Chemical, Environmental & Mining Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom.

(1) Hafiane, A.; Issid, I.; Lemordant, D. *J. Colloid Interface Sci.* **1991**, *142*, 167–178.

(2) Rathman, J. F.; Scamehorn, J. F. *J. Phys. Chem.* **1984**, *88*, 5807–5816.

(3) Bozic, J.; Krznaric, I.; Kallay, N. *Colloid Polym. Sci.* **1979**, *257*, 201–205.

(4) Somasundaran, P.; Ananthapadmanabhan, K. P.; Celik, M. S. *Langmuir* **1988**, *4*, 1061–1063.

(5) Stellner, K. L.; Scamehorn, J. F. *Langmuir* **1989**, *5*, 70–77.

(6) Talens, F. I.; Paton, P.; Gaya, S. *Langmuir* **1998**, *14*, 5046–5050.

(7) Porras, M.; Talens, F. I. *Sep. Sci. Technol.* **1999**, *34* (13), 2679–2684.

(8) Porras, M.; Talens, F. I. *Sep. Sci. Technol.* **2000**, *35* (12), 1973–1978.

(9) Akay, G.; Wakeman, R. J. *J. Membr. Sci.* **1994**, *88*, 177–195.

(10) Talens-Alesson, F. I.; Urbanski, R.; Szymanowski, J. *Colloids Surf.* **2001**, *178*, 71–77.

(11) Azoug, C.; Steinchen, A.; Charbit, F.; Charbit, G. *J. Membr. Sci.* **1998**, *145*, 185–197.

(12) Paton, P.; Talens, F. I. *J. Surfactants Deterg.* **1998**, *1* (3), 399–402.

(13) Talens-Alesson, F. I. *J. Dispersion Sci. Technol.* **1999**, *20* (7), 1861–1871.

(14) Kallay, N.; Pastuovic, M.; Matijevic, E. *J. Colloid Interface Sci.* **1985**, *106*, 452–458.

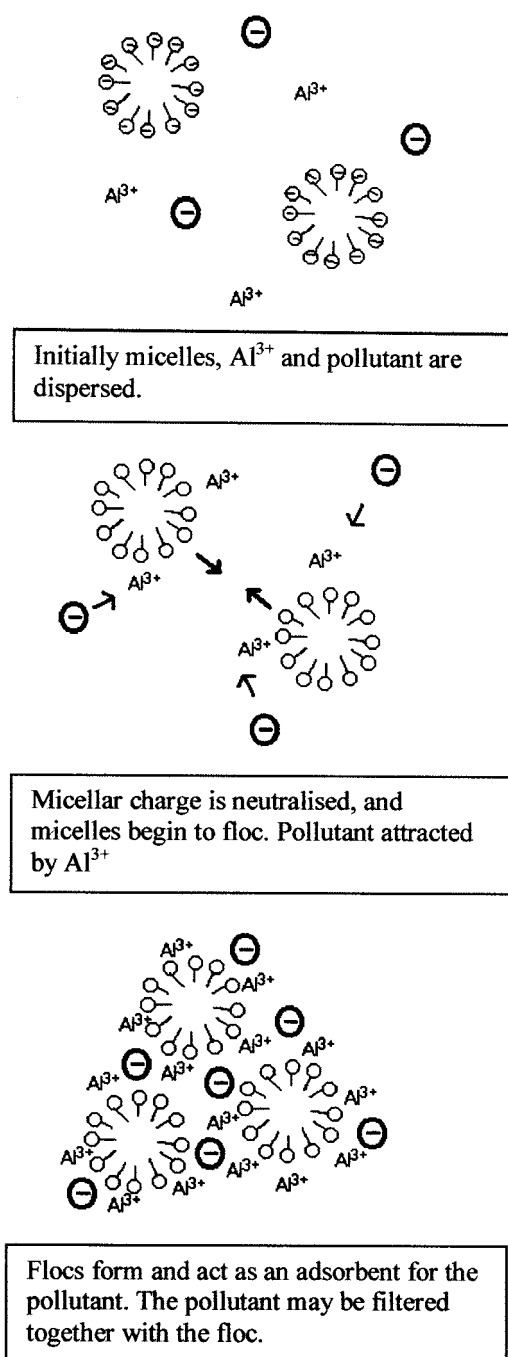


Figure 1. A three-step view of adsorptive micellar flocculation.

cation–surfactant complexation as proposed for other surfactant systems.

(iii) High concentrations of NaCl and heavy metals such as Zn^{2+} reduce the extent of flocculation.⁶ These effects are opposite to the ones expected from research in precipitation of insoluble lauryl sulfates from micellar solutions. Additional amounts of salts of polyvalent cations should cause further precipitation due to either an earlier saturation of the binding capacity of the micelles or an increase in the critical micelle concentration (cmc) (concentration of monomer which may precipitate). High NaCl concentrations, which reduce precipitation by reducing the cmc, should cause more micellar surfactant to flocculate. Hydrocarbons¹⁵ also cause a reduction in the range

of Al^{3+} concentrations causing flocculation and an increase in the residual surfactant concentration.

(iv) The ratio $\text{Al}^{3+}/\text{SDS}$ in the flocculate is substoichiometric,⁶ and the flocculate shows under microscopic inspection that it is composed of disordered fragments of liquid crystal.¹⁶

As these characteristics define the process of micellar flocculation, it is important to fully identify their causes in order to optimize the technique for its application in water treatment. As the technique requires the maximum feasible ratio of surfactant flocculation to be achieved, the limiting factors should be fully understood. High saline concentrations are present in several effluents containing organic acids (e.g., spinning effluents in the paper industry which contain high concentrations of heavy metal and sodium ions).

The binding of cations onto the surface of anionic micelles may be described in terms of an adsorption controlled by electrostatic forces. Defining the adsorption as the confinement of cations within the Stern layer limited by but excluding the polar heads of the surfactant (localized adsorption model)² gives results with good agreement with experimental observations. Such a model was tested against binding of Na^+ and Cl^- onto micelles of anionic and cationic surfactants, respectively. It has been confirmed,¹ using micelle-enhanced ultrafiltration as a direct, nonintrusive technique for ascertaining cation/micelle binding ratios, that the binding is best described in terms of an adsorption isotherm rather than as a complexation reaction. This was successfully done by mathematically expressing the problem as a Langmuir adsorption within the Stern layer and a entropic distribution outside of it. If multivalent cations were involved, a Frumkin (or Temkin) isotherm was found to be more appropriate. The estimation of the variation in the surface potential between micelles purely of $\text{Cu}(\text{DS})_2$ and micelles purely of SDS was 45.7 mV. The estimated value of 45.7 mV for the variation of surface potential is consistent with experimental values of the ζ -potential reported for $\text{Ca}^{2+}/\text{Na}^+/\text{DS}^-$ systems.¹³ In that work, micelles of commercial SDS (from KAO Corp., Barbera del Valles, Spain) showed a ζ -potential of about 70 mV, while on mixtures containing total $\text{Ca}(\text{NO}_3)_2$ and SDS concentrations of 0.025 and 0.05 M (including precipitated $\text{Ca}(\text{DS})_2$) micelles exhibited a ζ -potential of about 38 mV. The difference of about 32 mV between purely Na-bound micelles and micelles bound to a mixture of Na and Ca ions is consistent with the estimation of Hafiane et al.¹ for Cu^{2+} , another divalent cation.

Talens¹⁷ reported that binding of pollutants to micellar flocculates of NaDS or AOS can be described in terms of a Guoy–Chapman–Stern adsorption isotherm,¹⁸ with an apparent surface potential dependent on the pollutant/floc binding ratio. The present work shows that a Guoy–Chapman–Stern is also adequate to describe $\text{Al}^{3+}/\text{DS}^-$ binding.

Experimental Procedures

The surfactant employed was sodium lauryl sulfate (NaDS) kindly provided by KAO Corp. For some comparative experiments, both dodecylbenzenesulfonic acid (DBBS) and α -olefin-sulfonate (AOS) also from KAO Corp. were employed. The NaDS organic matrix had 98% active matter (surfactant) and 2%

(16) Porras-Rodriguez, M.; Talens-Alession, F. I. *Environ. Sci. Technol.* **1999**, 33 (18), 3206–3209.

(17) Talens-Alession, F. I. *Colloids Surf., A* **2001**, 180, 199–203.

(18) Kohler, H.-H. In *Coagulation and Flocculation, Theory and Applications*; Dobias, B., Ed.; Marcel Dekker: New York, 1993; pp 14–23.

(15) Paton-Morales, P.; Talens-Alession, F. I. *Colloid Polym. Sci.* **2000**, 278, 697–700.

insulfonated. Salt content (Na_2SO_4) was also about 2% of the active matter. The material was used as received, after analyzing the insulfated content by extraction with ether. This was done because the behavior of this surfactant quality is the case of practical interest for the purpose of water-treatment separation processes. It will be shown later that these impurities have little impact on the results. The cmc was estimated on this material as well. Other reagents were ZnSO_4 , NaCl , and *n*-decane from Panreac, all HP grade; AR Hyamine 1622 from Carlo Erba; AR Disulfine Blue V150 from Merck Schuchardt; and HP Diimidium Bromide, $\text{HP Al}_2(\text{SO}_4)_3$, HP CaCl_2 , and HP CHCl_3 from Probus. Water was Milli-Q grade.

Stock solutions of the various reagents were kept at 25 ± 0.1 °C. These were mixed also at 25 ± 0.1 °C in 100 mL volumetric flasks, and the solutions were allowed to settle for 1 h before further handling. pH was that naturally occurring in each solution. After the solutions had settled and flocculation had been completed, samples were filtered with $45\mu\text{m}$ cellulose nitrate filters. Surfactant content in the filtrates was analyzed by two-phase titration, with Hyamine 1622 as standard and Blue 1 acid and diimidium bromide as mixed indicator. Aluminum was determined by ICP, with a Jovyn-Ivon JI-38 apparatus. The wavelength was set to 308.215 nm. The detection limit was 45 ppb. ζ -Potentials of NaDS solutions and filtrates of solutions with varying $[\text{Al}^{3+}]$ and $[\text{Ca}^{2+}]$ were also measured. The measurements were performed in a Malvern ZetaMasterS.

Equations of the Model

Mass Balance in the Flocculate and the Solution.

The total concentration of aluminum may be divided among micelle- or floc-bound aluminum, free aluminum in the form of Al^{3+} , and other aqua-complexes combining Al^{3+} , H_2O , and OH^- :

$$[\text{Al}]_{\text{total}} = [\text{Al}^{3+}]_{\text{free}} + [\text{Al}^{3+}]_{\text{bound}} + [\text{Al}]_{\text{other}} \quad (1)$$

The amount of $[\text{Al}^{3+}]_{\text{free}}$ is calculated from adequate equilibria equations and the pH of the solution.

The total amount of Na^+ is provided by SDS (sodium lauryl sulfate) and NaCl and is equal to the amounts present free in the solution and bound to the micelles:

$$[\text{Na}^+]_{\text{total}} = [\text{SDS}]_{\text{total}} + [\text{NaCl}]_{\text{total}} = [\text{Na}^+]_{\text{free}} + [\text{Na}^+]_{\text{bound}} \quad (2)$$

The total lauryl sulfate concentration is equal to the sum of the surfactant concentration which has flocculated, the surfactant concentration present in micellar form, and the surfactant concentration present as monomer, which is the cmc in the case of micellar systems in which flocculation can occur.

$$[\text{SDS}]_{\text{total}} = [\text{SDS}]_{\text{floc}} + [\text{SDS}]_{\text{mic}} + [\text{SDS}]_{\text{mon}} \quad (3)$$

If β_{Al} is taken as the ratio between Al and SDS ions in both micelles and flocs (assuming the value to be the same in case a significantly high $[\text{SDS}]_{\text{mic}}$ coexists with flocculate) and β_{Na} is similarly defined, then

$$[\text{Al}]_{\text{total}} = [\text{Al}^{3+}] + \beta_{\text{Al}}([\text{SDS}]_{\text{total}} - [\text{SDS}]_{\text{mon}}) + [\text{Al}]_{\text{other}} \quad (4)$$

$[\text{SDS}]_{\text{mon}}$ is derived from experimental data at the minimum solubility conditions, where it is assumed that the $[\text{SDS}] = \text{cmc}$ under the particular conditions of that experiment.

Electrostatic Binding Ratio. The binding ratio of Al^{3+} on lauryl sulfate micelles, according to the definition of the cation binding factor given by Rathman and

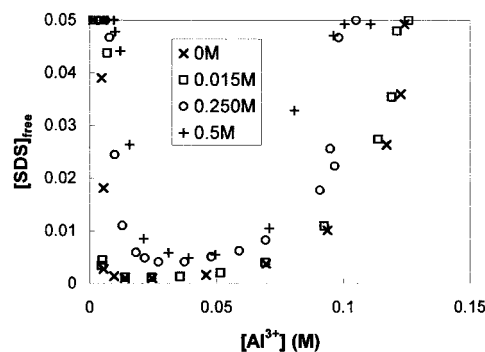


Figure 2. SDS remaining in solution in the presence of a given free Al^{3+} concentration for different overall NaCl concentrations.

Scamehorn⁵ for their localized adsorption model, has the form

$$\beta_{\text{Al}} = \frac{K_{\text{Al}} C_{\text{Al}} e^{(-ze\psi/kT)}}{1 + K_{\text{Al}} C_{\text{Al}} e^{(-ze\psi/kT)}} \quad (5)$$

This equation is similar to a Guoy–Chapman–Stern adsorption isotherm, which is one of the forms of isotherm where the adsorption process causes a change in the adsorbing properties of the substrate. This isotherm is very similar to the Temkin–Frumkin¹⁹ isotherm used by Hafiane et al.¹ for binding of Cu^{2+} . By analogy, we can expand eq 5 to

$$\beta_{\text{Al}} = \frac{K_{\text{Al}} C_{\text{Al}} e^{(-z_{\text{Al}}e\psi/kT)}}{1 + K_{\text{Na}} C_{\text{Na}} e^{(-z_{\text{Na}}e\psi/kT)} + K_{\text{Al}} C_{\text{Al}} e^{(-z_{\text{Al}}e\psi/kT)}} \quad (6)$$

which would include the effect of the binding of Na^+ . These equations consider that β refers to counterion binding (ratio between bound cations and surfactant monomers in the binding micelle). For eqs 5 and 6, we can make $C_{\text{M}^{n+}} = f[\text{M}^{n+}]$ and calculate the activity coefficient as $\log f = -0.5z^2(I^{0.5}/(1 + I^{0.5}) - 0.2I)$, where the ionic strength $I = 0.5\sum_i [X]_i z_i^2$. This equation proposed by Davies for the activity coefficient is valid only up to ionic strength 0.5, and the effect of this restriction on the results will be shown later.

Results and Discussion

Figure 2 shows the effect of changing NaCl on the flocculation curves. At low $[\text{NaCl}]$ (0.015 M), there is no difference with a solution without added NaCl . An increase in $[\text{NaCl}]$ results in an increase in the residual surfactant concentration and a narrowing of the region of minimum flocculation. Except for the highest $[\text{NaCl}]$ of 0.5 M, significant amounts of surfactant remain flocculated up to $[\text{Al}^{3+}] = 0.09$ M.

Figure 3 shows that the binding factor (calculated as the ratio of the differences between total $[\text{Al}^{3+}]$ and $[\text{SDS}]$ in samples and the final concentrations present in the filtered solution) decreases significantly after reaching the maximum flocculation ratio. This is consistent with the fact that the ζ -potential becomes more negative at higher Al^{3+} concentrations after the maximum flocculation point.¹² If the binding fraction of Al^{3+} is lower, the electroneutralization is less effective. This, combined with

(19) Kohler, H.-H. In *Coagulation and Flocculation, Theory and Applications*; Dobias, B., Ed.; Marcel Dekker: New York, 1993; pp 29–32.

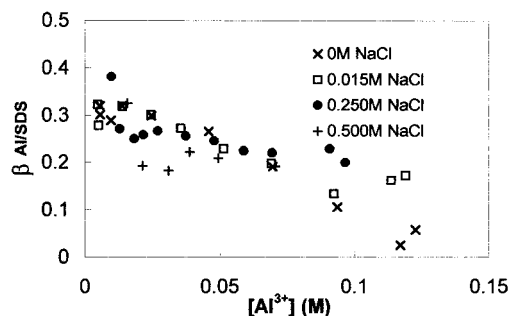


Figure 3. Binding factor (defined as the ratio of Al to SDS ions in the flocculate) vs free Al^{3+} concentration.

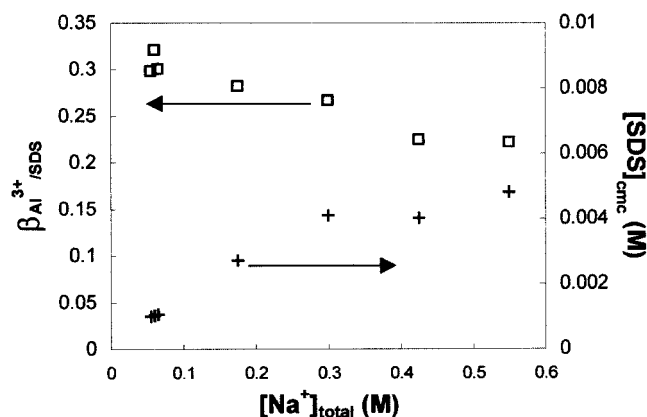


Figure 4. Binding fraction at the minimum solubility conditions for each NaCl concentration (left) and residual SDS concentrations in the same conditions (right) plotted against total Na^+ concentration.

the absence of observable particles above $[Al^{3+}] = 0.11$ M, is in favor of the theory that Al–DS aqua-complexes are predominant by analogy to what is proposed for other systems:^{20,21} some flocculated surfactant would coexist with metal–surfactant aqua-complexes, with the fraction of small colloidal particles being even lower than in the minimum solubility region. At higher overall $[Al^{3+}]$, more surfactant would be incorporated into the complexes.

Figure 4 shows the variation of the free surfactant concentration (right-hand axis), which is labeled $[SDS]_{cmc}$ for the reasons given below, and of the ratio bound Al^{3+}/SDS in the floc (left-hand axis) with the total concentration of $[Na^+]$, including the contribution of the surfactant itself. The values correspond to the condition of minimum solubility of a 0.05 M SDS solution. The concentrations of Al^{3+} in solution are similar but not exactly the same in each case. The residual concentration of the surfactant increases from a value of about 10^{-3} M, which is similar to the $cmc_{Al(DS)_3}$ reported by Paton et al.⁶ to a value of about 5×10^{-3} M, which is consistent with the values of cmc_{SDS} reported most commonly in the literature.²² The concentration of surfactant in solution after micellar flocculation should increase if the cmc increases. A higher Na^+ concentration will make the cmc of the solution closer to that of SDS. The curve may be fitted to the equation

$$\ln[SDS]_{free} = 0.7253 \ln[Na^+] - 2.083 \quad (7)$$

(20) Fisher, L. R.; Oakenfull, D. G. *Chem. Soc. Rev.* **1977**, 6, 25–42.

(21) Tezak, D.; Strajnjar, F.; Milat, O.; Stubicar, M. *Prog. Colloid Polym. Sci.* **1984**, 69, 100–105.

(22) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems* (NSRDS-NBS 36); U.S. Government Printing Office: Washington, DC, 1971.

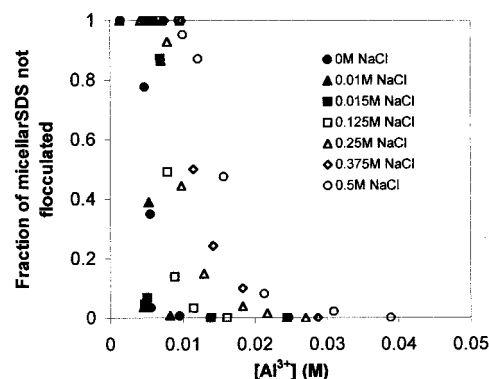


Figure 5. Fraction of micellar surfactant vs free Al^{3+} concentration for the various NaCl concentrations investigated.

with a regression coefficient $r = 0.950$ and valid in the range $0.05 < [Na^+]_{total} < 0.55$. The functional dependence of the residual surfactant concentration is consistent with the logarithmic function dependence with the counterion concentration reported classically.²³ This suggests the residual surfactant concentration to be the cmc plus a small amount of colloidal surfactant in particles of sizes not much larger than micelles (ranging from 10 to around 100 nm⁶).

If we accept this interpretation and recalculate the values in Figure 2, by subtracting $[SDS]_{cmc}$ calculated from eq 7, and represent the fraction of micellar surfactant in solution, we obtain Figure 5. There it can be seen that higher $[NaCl]$ leads to an onset of flocculation at higher $[Al^{3+}]$ and to the minimum solubility being reached at even higher $[Al^{3+}]$. The deflocculation region is not shown as the complexation process cannot yet be incorporated into the calculations.

As the binding factors displayed in Figure 4 are from the region of minimum solubility due to minimum stability of the micelles, we may assume the Stern potential ψ_0 there to be zero. If we accept that the micelles have collapsed and been replaced by an experimental artifact (the floc) in which cations and surfactant are more closely connected, we can assume that the ratio of Al/SDS in the flocculate corresponds to the ratio between Al in the Stern layer and micellar surfactant when the micelles became unstable. Full flocculation (and the incorporation of all the flocculating surfactant into a single large floc) is achieved within 2 min of mixing a sample, and in the time allowed for equilibration (1 h) there is not a substantial amount of time for changes of composition due to molecular diffusion between the bulk of the floc and the surrounding solution (no further stirring is provided after the initial mixing). So we can imagine that the micelles become unstable, diffusing to collide among themselves and forming ever larger aggregates with a composition not substantially different from that of the initial Al^{3+} -bound micelles.

Table 1 shows that there is a difference of less than 5% between experimental $[Al^{3+}]_{sol}$ and the value calculated as a function of pH considering that the only species significantly present within the experimental pH range (3.1–4.2) are Al^{3+} and $Al(OH)^{2+}$. Log K is taken as -4.97 for the equilibrium $Al^{3+} + H_2O = Al(OH)^{2+} + H^+$. The ionic strength is calculated by means of the Davies equation.

(23) Shinoda, K. In *Colloid Surfactants*; Shinoda, K., Tamamushi, T., Nakagawa, T., Isemura, T., Eds.; Academic Press: New York, 1963; Chapter 1.

(24) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*; John Wiley and Sons: New York, 1981.

Table 1

[NaCl] = 0 M				[NaCl] = 0.125 M				[NaCl] = 0.5 M			
[Al ³⁺] _{tot}	pH	[Al ³⁺] _{sol}	[Al ³⁺] _{free}	[Al ³⁺] _{tot}	pH	[Al ³⁺] _{sol}	[Al ³⁺] _{free}	[Al ³⁺] _{tot}	pH	[Al ³⁺] _{sol}	[Al ³⁺] _{free}
0.016	3.71	0.0058	0.0055	0.016	3.64	0.0083	0.0079	0.017	3.64	0.0105	0.01
0.020	3.59	0.0058	0.0056	0.02	3.58	0.0093	0.0089	0.02	3.58	0.0126	0.0122
0.024	3.54	0.0099	0.0096	0.024	3.51	0.0119	0.0115	0.024	3.51	0.0163	0.0158
0.03	3.53	0.0143	0.0138	0.03	3.48	0.0167	0.0161	0.03	3.48	0.022	0.0213
0.04	3.44	0.0254	0.0246	0.05	3.46	0.0357	0.0346	0.04	3.46	0.0318	0.031
0.06	3.39	0.0472	0.0459	0.07	3.42	0.0542	0.0528	0.06	3.38	0.0507	0.0494
0.08	3.33	0.0712	0.0696	0.08	3.38	0.0632	0.0617	0.08	3.36	0.0724	0.0707
0.10	3.32	0.0976	0.0937	0.1	3.36	0.0827	0.0807	0.1	3.33	0.0982	0.0961

Table 2

[NaCl] (M)	$\beta_{\text{Al}^{3+}}^{\text{exp}}$	$\beta_{\text{Al}^{3+}}^{\text{calc}}$	$(\beta_{\text{exp}} - \beta_{\text{calc}})/\beta_{\text{exp}}$	$\beta_{\text{Na}^{+}}^{\text{calc}}$	$\gamma_{\text{Na}^{+}}$	$\gamma_{\text{Al}^{3+}}$	ionic strength <i>I</i>	$\beta_{\text{Na}^{+}}^{\text{calc}} + \beta_{\text{Al}^{3+}}^{\text{calc}}$	electroneutralization fraction
0.000	0.299	0.299	0.000	0.025	0.037	0.025	0.200	0.32	0.92
0.010	0.321	0.298	0.023	0.029	0.042	0.025	0.208	0.33	0.92
0.015	0.301	0.298	0.003	0.029	0.043	0.025	0.214	0.33	0.92
0.125	0.282	0.281	0.023	0.078	0.117	0.022	0.380	0.36	0.92
0.250	0.267	0.255	0.045	0.132	0.204	0.019	0.460	0.38	0.90
0.375	0.225	0.173	0.085	0.192	0.287	0.012	0.640	0.37	0.71
0.500	0.222	0.110	0.139	0.250	0.374	0.007	0.800	0.36	0.58

[NaCl] (M)	$\beta_{\text{Al}^{3+}}^{\text{exp}}$	$\beta_{\text{Al}^{3+}}^{\text{calc}}$	$(\beta_{\text{exp}} - \beta_{\text{calc}})/\beta_{\text{exp}}$	$\beta_{\text{Na}^{+}}^{\text{calc}}$	$\gamma_{\text{Na}^{+}}$	$\gamma_{\text{Al}^{3+}}$	ionic strength <i>I</i>	$\beta_{\text{Na}^{+}}^{\text{calc}} + \beta_{\text{Al}^{3+}}^{\text{calc}}$	electroneutralization fraction
0.000	0.299	0.299	0.000	0.025	0.037	0.025	0.200	0.35	0.92
0.010	0.321	0.298	0.073	0.029	0.042	0.025	0.208	0.33	0.92
0.015	0.301	0.298	0.010	0.029	0.043	0.025	0.214	0.35	0.92
0.125	0.282	0.259	0.082	0.078	0.117	0.022	0.380	0.37	0.85
0.250	0.267	0.245	0.081	0.128	0.204	0.022(*)	0.460	0.38	0.86
0.375	0.225	0.233	-0.036	0.171	0.287	0.022(*)	0.640	0.43	0.87
0.500	0.222	0.221	0.002	0.212	0.374	0.022(*)	0.800	0.43	0.88

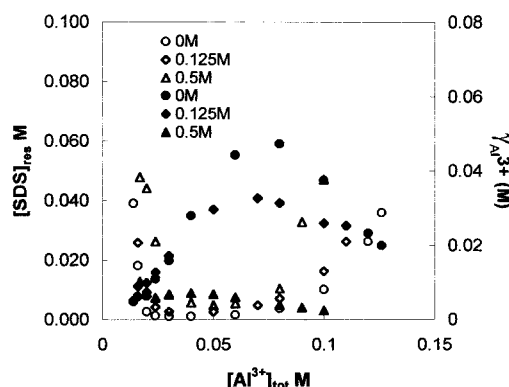


Figure 6. Residual SDS concentration remaining in solution (white symbols) and activities of Al³⁺ (black symbols) against Al³⁺ concentrations.

Table 2 shows the results from iterations to calculate $K_{\text{Al}^{3+}}$ from the experimental $\beta_{\text{Al}^{3+}}$, assuming² $K_{\text{Na}^{+}} = 1$ and $\psi_0 = 0$, with $[\text{Al}^{3+}]_{\text{free}}$ calculated from the experimental pH and the equilibria equations. The appropriateness of the latter assumption has been shown in Table 1. A fit cannot be obtained for all the data, and the best result is obtained for a value of $K_{\text{Al}^{3+}}$ of 17.67. However, it is to be observed that the deviations are significant for the two NaCl concentrations which are connected with ionic strengths above 0.5. Arbitrarily assuming the chemical activity constant above $I = 0.38$ shows that the inability of the Davies equation to give a good estimate of the activity coefficient is to be considered the cause of the deviation observed. With the manipulated activities, the binding ratios for both Al³⁺ and Na⁺ change strongly, and in the second case for all the [NaCl] the electroneutralization fraction is high and consistent with the fact that surface charge on the micelle is shielded. While the electroneutralization is lower at high [NaCl], it must be taken into account that the high charge concentration in the

bulk solution between micelles further suppresses the electrostatic repulsion between micelles.

Figure 6 shows the residual surfactant concentration in solution (left-hand axis) and the activities calculated for Al³⁺ (right-hand axis) at different [Al³⁺]. The effect of any eventual complexes cannot be accounted for. The minimum solubility region loosely corresponds to the higher activities within each series, but the actual values of the activities corresponding to optimum flocculation or full solubility regions are quite different between series. This indicates that a decrease in the ratio of flocculation is not a matter of the activity of Al³⁺ dropping below a given critical value to achieve the adequate binding of Al³⁺ on the micelles.

Conclusions

The ratio of flocculated surfactant in micellar flocculation depends on a number of factors: the value of the critical micelle flocculation, competitive adsorption of cations onto the micellar surfactant, and the effect of ionic strength on the chemical activity of the flocculating cation.

In the case of flocculation of SDS with aluminum sulfate, the effect of NaCl can be accounted for as a change in the surfactant cmc with [Na⁺] and a decrease in the chemical activity due to higher ionic strength of the solution. This effect is observed in the narrowing of the full flocculation region: competition of Na⁺ delays effective shielding of the micelles by Al³⁺ until higher Al³⁺ is present; the deflocculation of the surfactant begins at lower Al³⁺ (as the chemical activity is reduced by the additional concentrations of NaCl); the minimum surfactant concentration remaining in solution is higher. However, while the effects on the activity of Al³⁺ play a role in the ratio of binding to micelles, it is not possible to associate the actual activity value to the occurrence or not of flocculation.

From experiments in the minimum flocculation region, it is possible to estimate a dissociation constant for the adsorption of Al³⁺.

Acknowledgment. This research was funded by the Bureau of Clean Technologies, Regional Ministry of the Environment of Catalonia (Spain), between the years 1993 and 1996. The authors are indebted to the former head of this Bureau, Mr. Jacint Corderas, and want to dedicate this paper to his memory.

Nomenclature

C	chemical activity of subscript species, kmol m^{-3}
e	$1.6 \times 10^{-19} \text{ C}$
f	activity coefficient
I	ionic strength, kmol m^{-3}
K	dissociation constant, $\text{m}^3 \text{kmol}^{-1}$
k	Boltzmann constant, $1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$
T	temperature, K

X	chemical species
z	ionic charge

Greek Symbols

β	cation/surfactant binding ratio (ion/ion)
γ	chemical activity
ψ_0	Stern potential, V
ζ	zeta-potential, V

Subindexes

bound	concentration which is actually bound to micelles
free	concentration existing in solution as the form indicated within brackets
other	concentration of the ion in other forms (complexes)
total	total concentration of the species added to the sample
	LA0103362