

## Precipitation-Redissolution Phenomena in Sulfonate- $\text{AlCl}_3$ Solutions

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In this paper, the precipitation-redissolution behavior of  $\text{AlCl}_3$  and the dependence of it on pH in sodium dodecyl benzenesulfonate and sodium dodecanesulfonate solutions are discussed. As in the case of bivalent metal ion-sulfonate systems, the redissolution is found to be caused by micelles. In contrast to the bivalent metal ion systems, precipitation in  $\text{AlCl}_3$ -sulfonate solutions is influenced markedly by pH. The results indicate that the competition among sulfonate monomers, micelles, and hydroxyl ions for Al species controls the system behavior. The thermodynamic solubility product for the precipitation of aluminum trisulfonates and the dependence of onset of redissolution on  $\text{AlCl}_3$  concentration have been determined.

### Introduction

The interaction of surfactants with multivalent ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$  can lead to their precipitation and consequently to surfactant loss in micellar flooding systems. Past studies on interactions of sulfonate with various ions have shown that the sulfonates precipitated by multivalent ions can be redissolved by adding excess sulfonate<sup>1-10</sup> or monovalent salts.<sup>1-5</sup> Further addition of the sulfonate or the salt resulted in reprecipitation. Some of the proposed mechanisms to account for the above phenomenon are briefly examined below.

The proposed mechanisms for the precipitation-redissolution process in surfactant-multivalent ions systems include micellar solubilization,<sup>1-9</sup> complexation,<sup>6,10</sup> and redispersion of coagulated micelles/sols.<sup>1,7</sup> In the case of  $\text{CaCl}_2$ -NaDDS (sodium dodecanesulfonate)/NaDBS (sodium dodecyl benzenesulfonate) systems, our detailed study involving precipitation tests, chemical analysis, conductivity, counterion activity, dye solubilization, and surface tension measurements clearly showed that redissolution occurred only in the presence of micelles. Peacock et al.<sup>7</sup> also have demonstrated that the redissolution occurring in sulfonate-multivalent ion systems is governed by micellar solubilization. Bozic et al.<sup>9</sup> have shown that the phase behavior in dodecyl sulfate-lanthanum system is governed by the above type of interactions. Some of the recent work by Hirasaki et al.<sup>11</sup> and Chou et al.<sup>12</sup> also clearly reveal the important role of micelles in the redissolution process. Both these studies have used simple electrostatic models to account for the interaction between the cations and the anionic micelles. Tezak et al.<sup>10</sup> have shown that in addition to the above type of monomer-precipitate and monomer-micelle-precipitate equilibria, under conditions of excess metal ion concentration, aqua

complexes also form in the system. The mechanism involving the redispersion of sols has been observed by Matijevic et al.<sup>13</sup> in calcium nitrate-potassium oleate systems.

In addition to calcium, the reservoir fluid may contain other multivalent cations such as magnesium and aluminum. Peacock et al.<sup>7</sup> have shown that the precipitation characteristics of the *p*-(1-methylnonyl)benzenesulfonate- $\text{Al}^{3+}$  system under low pH conditions are similar to those of bivalent cation-sulfonate systems in the sense that the redissolution is caused by micellar solubilization. Tezak et al.<sup>10</sup> have examined the precipitation behavior of the dodecyl benzenesulfonate system but stated that their work on  $\text{Al}^{3+}$  was done in a "non-reliable pH region". In this paper, the precipitation behavior of linear dodecyl benzenesulfonate and dodecanesulfonate in  $\text{AlCl}_3$  solutions

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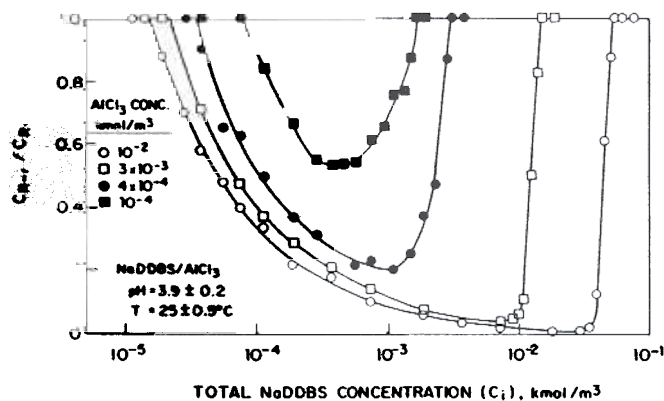


Figure 1. Ratio of residual to initial sulfonate as a function of NaDDBS.

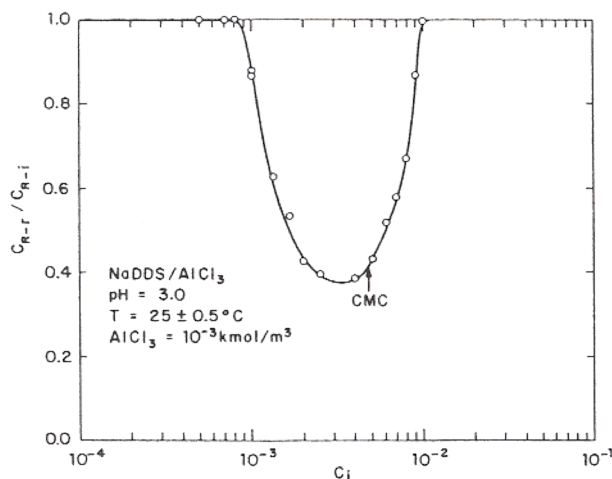


Figure 2. Ratio of residual to initial sulfonate as a function of NaDDBS.

is discussed. Since aluminum can undergo a number of hydrolysis reactions, the pH dependence of precipitation is also discussed.

### Experimental Section

NaDDBS specified to be 90% pure by Lachat Chemicals was purified by deoiling, recrystallization, and desalting techniques.<sup>1</sup> NaDDS (99% purity according to manufacturer's chromatographic analysis) was purchased from Aldrich Chemicals and used without further purification.  $\text{AlCl}_3$ , NaCl, NaOH, and HCl were also of A.R. grade.

The procedure for conducting the precipitation tests is described elsewhere.<sup>4,5</sup> The dye solubilization test<sup>14</sup> with pinacyanol chloride as the probe was used to determine the cmc of the surfactant-mono/multivalent ion systems.

### Results and Discussions

**Precipitation of DDBS and DDS in  $\text{AlCl}_3$  Solutions.** The precipitation behavior of NaDDBS- $\text{AlCl}_3$  and NaDDS- $\text{AlCl}_3$  systems is illustrated in Figures 1 and 2 in the form of  $C_{R-r}/C_{R-i}$  where  $C_{R-r}$  and  $C_{R-i}$  refer to the residual and initial (same as total) concentrations of surfactant. It is evident from these figures that (a) the precipitation of sulfonate occurs above a certain concentration and (b) precipitation continues to increase up to a certain concentration above which the redissolution of the precipitate occurs in the system. With further increase in sulfonate concentration in the tested range, reprecipitation of the sulfonate did not occur. Importantly, the sulfonate

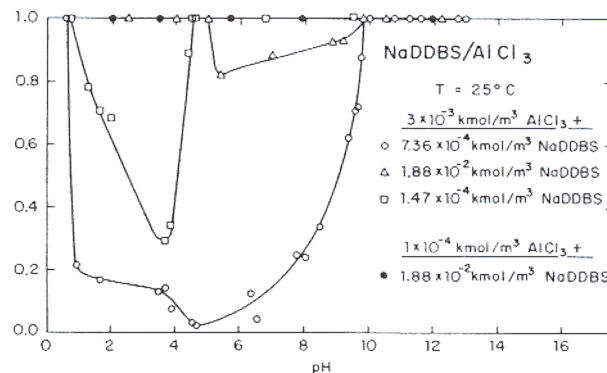


Figure 3. pH dependence of precipitation of DDBS in  $\text{AlCl}_3$  solutions.

concentration at the onset of redissolution is found to coincide with the cmc of the system, indicating that the precipitate redissolution is caused by micelles. Several features of this system are similar to those reported earlier for the  $\text{CaCl}_2$ -sulfonate system.<sup>1-5,7</sup>

**Solubility Product.** The solubility product of both the aluminum sulfonates was calculated by using the equation  $K_{sp} = a_{\text{Al}^{3+}} (a_{\text{R}})^3$ , where  $a_i$  is the activity of the species  $i$ . The concentration of  $\text{Al}^{3+}$  for a given  $\text{AlCl}_3$  was calculated by using the equilibria, taking into account the formation of  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3$ , and  $\text{Al}(\text{OH})_4^-$ . The constants for the equilibria were obtained from ref 15. The activity coefficients were estimated by using the Guntelberg equation.<sup>15</sup>

The solubility product of  $\text{Al}(\text{DDBS})_3$  calculated with the data for the onset of precipitation is found to vary over 1 order of magnitude ( $2.5 \times 10^{-17}$  for  $10^{-4}$  kmol/m<sup>3</sup>  $\text{AlCl}_3$ ,  $2 \times 10^{-18}$  for  $10^{-2}$  kmol/m<sup>3</sup>  $\text{AlCl}_3$ ). The multicomponent nature of the recrystallized sulfonate<sup>1</sup> may account for the observed differences. In contrast to this, the concentration product  $K_{sp}^* = C_{\text{Al}^{3+}}/(C_{\text{R}})^3$  is found to be fairly constant for this system (range =  $(1.3-3.4) \times 10^{-17}$ , average =  $2.5 \times 10^{-17}$ ).

In the case of  $\text{Al}(\text{DDS})_3$ , where the sulfonate is isomerically pure, the solubility product (range =  $(1.35-1.78) \times 10^{-13}$ , average =  $1.6 \times 10^{-13}$ ) was found to be fairly constant along the entire precipitation curve, and this, in turn, confirms that the precipitate is  $\text{Al}(\text{DDS})_3$ .

**Onset of Redissolution.** The increase in the onset of redissolution (which also coincides with the system cmc) with increase in  $\text{AlCl}_3$  concentration in the NaDDBS- $\text{AlCl}_3$  system can be represented by the equation  $\log C_{\text{rediss}} = \log \text{cmc} = -0.16 \log C - 4.13$ , where  $C$  is the total counterion concentration.

### Effect of pH on Precipitation-Redissolution

The results for the pH dependence of precipitation in the NaDDBS- $\text{AlCl}_3$  system are given in Figure 3. The three sulfonate levels used in these tests with  $3 \times 10^{-3}$  kmol/m<sup>3</sup>  $\text{AlCl}_3$  are selected from the precipitation (see Figure 1) region ( $1.47 \times 10^{-4}$  kmol/m<sup>3</sup>), the region of maximum precipitation ( $7.36 \times 10^{-4}$  kmol/m<sup>3</sup>), and the region of total redissolution (micellar region,  $1.88 \times 10^{-2}$  kmol/m<sup>3</sup>). In all of these cases, it is evident that precipitation does not occur at pH values below 0.6 and above 10. The absence of precipitation above pH 10 is due to the hydrolysis of aluminum to form  $\text{Al}(\text{OH})_4^-$  species in solution. The absence of precipitation below pH 0.6, on the other hand, is attributed to the competition between

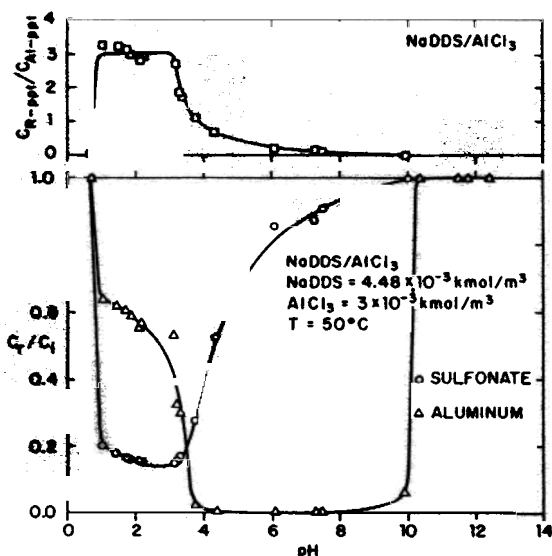


Figure 4. pH dependence of precipitation of DDS in  $\text{AlCl}_3$  solutions.

$\text{H}^+$  and  $\text{Al}^{3+}$ , which turns in favor of the former under those conditions. Both the reduction in the activity of  $\text{Al}^{3+}$  and the enhanced micelle formation favored by the increase in the ionic strength at such low pH values can also contribute to the observed absence of precipitation under very low pH conditions.

An increase in pH above 0.6 increased precipitation of sulfonate at  $1.47 \times 10^{-4}$  and  $7.36 \times 10^{-4}$   $\text{kmol/m}^3$  NaDDBS. In both cases, precipitation increased up to a certain pH and decreased above it. At  $1.88 \times 10^{-2}$   $\text{kmol/m}^3$  sulfonate, on the other hand, precipitation occurred only at pH values above 5. Thus the pH dependence of sulfonate precipitation appears to be a complex phenomenon. In addition to the aluminum sulfonate precipitate, formation of such soluble complexes as  $\text{Al}(\text{DDBS})_2^{2+}$  and  $\text{Al}(\text{DDBS})_2^+$  and even charged hydroxy sulfonate complexes can be expected. In micellar solutions, interaction of various charged species with the micelle surface also needs to be taken into account.

At  $1.47 \times 10^{-4}$   $\text{kmol/m}^3$  sulfonate ( $[\text{AlCl}_3] = 3 \times 10^{-3}$   $\text{kmol/m}^3$ ), the pH above which the concentration of  $\text{Al}^{3+}$  is not enough to cause precipitation of aluminum sulfonate is estimated by using the earlier estimated solubility product to be 5.3. This is in reasonable agreement with the experimental results.

At  $7.36 \times 10^{-4}$   $\text{kmol/m}^3$  sulfonate ( $[\text{AlCl}_3] = 3 \times 10^{-3}$   $\text{kmol/m}^3$ ), surfactant depletion is observed in the pH region 0.6–9.8. In this case, precipitation of  $\text{Al}(\text{DDBS})_3$  is expected only at pH values below 6. The reasons for the depletion of sulfonate in the region 6–9.8 are not clear at present. Similarly, the reasons for the sulfonate depletion in the pH region 5–9.8 at  $1.88 \times 10^{-2}$   $\text{kmol/m}^3$  are also not clear at present. In both these cases, the precipitate in the

above range may be Al hydroxy sulfonate or sulfonate adsorbed on precipitated colloidal  $\text{Al}(\text{OH})_3$ . Additional experiments are required to test this hypothesis. The observation made during the experimentation that the texture and the settling characteristics of the precipitate formed in this region were distinctly different from those formed at pH values below 5 supports some of the above considerations.

It is interesting that at  $1.88 \times 10^{-2}$   $\text{kmol/m}^3$  sulfonate and  $10^{-4}$   $\text{kmol/m}^3$   $\text{AlCl}_3$  precipitation of sulfonate did not occur in the entire pH range. Note that the sulfonate level in this case is well above the cmc of the system (total sulfonate at the onset of micellization =  $5 \times 10^{-4}$   $\text{kmol/m}^3$ , cmc =  $2.6 \times 10^{-4}$   $\text{kmol/m}^3$ , both at pH 3.9). Because of Al hydrolysis, the precipitation of  $\text{Al}(\text{DDBS})_3$  in this case can be expected only at pH values below 5.5. Even below this pH, the concentration of free  $\text{Al}^{3+}$  will be significantly lower than  $10^{-4}$   $\text{kmol/m}^3$  since a major part of it will be bound to the micelle. An estimate of the amount of  $\text{Al}^{3+}$  bound to the micelle surface can be obtained from the excess sulfonate required for the redissolution of the precipitate. Calculations indicate that micelles can bind as much as  $1.1 \times 10^{-3}$   $\text{kmol/m}^3$   $\text{Al}^{3+}$  on its surface.<sup>1</sup> Since the concentration of Al in the system is 1 order of magnitude lower than the micelle capacity, the absence of precipitation in this case can be explained.

**pH Dependence in the NaDDS- $\text{AlCl}_3$  System.** The pH dependence of precipitation in the NaDDS- $\text{AlCl}_3$  system at 50 °C is given in Figure 4. In this case, concentrations of both the Al and sulfonate in equilibrium with the precipitate have been determined. The ratio of sulfonate to aluminum depleted from solution is also given in the same figure. Evidently, the DDS/Al ratio is fairly constant and equal to 3 in the pH range 1–3. This finding confirms that the precipitate in this region is  $\text{Al}(\text{DDS})_3$ . A marked decrease in this ratio observed at pH values above 3 indicates the absence of formation of hydroxy sulfonate precipitates such as  $\text{AlOHR}_2$  or  $\text{Al}(\text{OH})_2\text{R}$  over a wide pH range. Precipitation of  $\text{Al}(\text{OH})_3$  can be expected only at pH values above 4.6. It is speculated again that the depletion of sulfonate above 4.6 is possibly due to the adsorption of sulfonate on precipitated colloidal aluminum hydroxide.

The reasons for the absence of precipitation below pH 0.7 and above 10.3 in this system can also be considered to be the same as those discussed earlier for the NaDDBS- $\text{AlCl}_3$  system.

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