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SHORT COMMUNICATION

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Effect of pH on the Flocculation of SDS Micelles by Al^{3+}

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Abstract SDS micelles flocculate in the presence of Al^{3+}, creating an aggregate with pollutant-removing properties. The fraction of SDS micelles flocculating depends on the concentrations of SDS and Al^{3+}. This paper describes how this fraction also changes with pH. There are two reasons for this dependence: a change in pH has a strong effect in the solution chemistry of Al^{3+}, converting it into the compound $[Al_{13}O_4(OH)_{24}]^{7+}$, a strong flocculant, or precipitating it as $Al(OH)_3$; and at low pH protons may compete with Al^{3+} as binding counter-ions for micelles. An increase in pH allows flocculation of SDS at high concentrations of Al^{3+}, which under unmodified pH does not occur. Micelle flocculates are reported in this work to exist between pH 5 and pH 8, suggesting the potential use of Adsorptive Micellar Flocculation for the removal of anionic pollutants from waste waters not necessarily limited to acidic solutions.

Key words AMF · Micelle · Adsorption · Flocculation · Dodecyl sulfate

Introduction

The binding of Al^{3+} onto SDS (sodium dodecylsulfate) and AOS (α-olefinsulfonate) micelles [1, 2] is a peculiar case of binding of cations onto surfactant micelles [3–6]. Binding of Al^{3+} neutralizes the electrostatic repulsion between negatively charged micelles [7], which flocculate forming a sub-stoichiometric Al-SDS aggregate easily filterable and with the ability to bind anionic organic pollutants to itself [8, 9]. This allows the removal of water-soluble anionic compounds (pesticides, organic acids) from aqueous solutions by filtration. This separation is named Adsorptive Micellar Flocculation (AMF), as the capture of the pollutant by the flocculate is an adsorption [9]. That the pollutant remains bound after flocculation is a consequence of the coagulation of the aggregate to liquid crystal [9]. AMF may be regarded as an adsorption process combined with a filtration step. A number of factors must be considered to evaluate the possible restrictions of the applicability of AMF, like interference by high enough concentrations of heavy metals [2] or the presence of hydrocarbons [10] in the process of micelle flocculation. Amongst these factors special attention must be paid to the effect of pH, due to the sensitivity of Al^{3+} to it.

The residual [SDS] in the region of minimum solubility (Fig. 1) is in the order of magnitude of the $CMC_{Al(DS)3}$ value given by Talens et al. [2]. Outside this region part or all of the micellar SDS remains in solution. The increase in solubility of SDS at high Al^{3+} concentration may be justified through the existence of aqua-complexes by analogy with other cation-surfactant systems [12–14]. Another possibility is that high ionic strengths will reduce the chemical activity of Al^{3+}, weakening its tendency to bind onto the micelle.

Talens at al. [2] describe a decrease in pH (Fig. 2) with increasing $[Al^{3+}]$ until it stabilizes between pH 3.2 and pH 3.4. The main equilibria governing the aqueous chemistry of Al^{3+} are shown in Table 1 [11].

The values suggest that under unmodified pH Al^{3+} is the predominant species. This paper discusses the effect of changes in the pH of the solution on the process of micellar flocculation. This study is relevant for the general applicability of AMF based on Al^{3+} to the

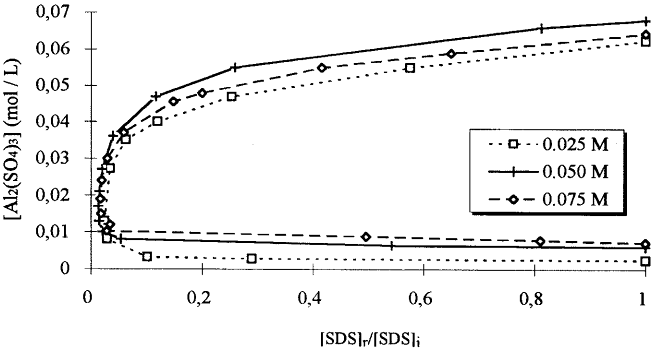

Fig. 1 Total $[Al_2(SO_4)_3]$ in the mixture vs $[SDS]_r/[SDS]_i$, the ratio between [SDS] remaining in solution and initial [SDS]. The parameters are the SDS concentrations for each curve

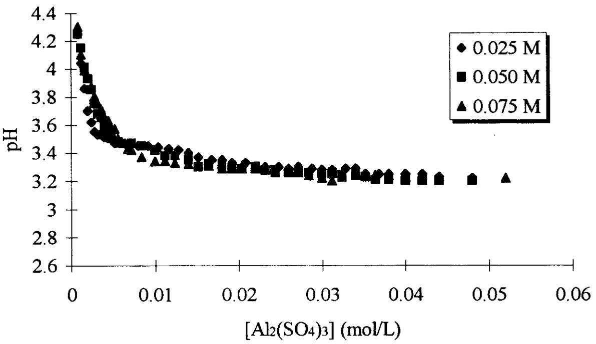

Fig. 2 pH vs total $[Al_2(SO_4)_3]$ in the mixture. There is a sharp decrease from the pH of water to a region corresponding to the onset of flocculation, where the pH stabilizes

Table 1 Main equilibria governing the aqueous chemistry of Al^{3+}

Reaction	log K_a
$Al^{3+} + H_2O\ 1\ Al(OH)^{2+} + H^+$	−4.97
$Al^{3+} + 2H_2O\ 1\ Al(OH)_2{}^+ + 2H^+$	−9.3
$Al^{3+} + 3H_2O\ 1\ Al(OH)_{3(aq)} + 3H^+$	−15
$Al^{3+} + 4H_2O\ 1\ Al(OH)_4{}^- + 4H^+$	−22
$2Al^{3+} + 2H_2O\ 1\ Al_2(OH)_2{}^{4+} + 2H^+$	−7.7
$3Al^{3+} + 4H_2O\ 1\ Al_3(OH)_4{}^{5+} + 4H^+$	−13.9
$13Al^{3+} + 28H_2O\ 1\ Al_{13}O_4(OH)_{24}{}^{7+} + 32H^+$	−98.7

treatment of highly acidic, neutral or alkaline waste waters.

Experimental

The surfactant used was sodium dodecylsulfate (SDS), kindly provided by KAO Corporation (Barber del Vallès, Spain). Its organic matrix had a 98% active matter (surfactant) and 2% unsulfated (fatty alcohol). Salt content (Na_2SO_4) was also about 2% of the active matter. The material was used as received, after analyzing the unsulfated content by extraction with ether (boiling point 40 °C). The reason is that technical grade surfactant is the case of practical interest for the purpose of water-treatment separation processes. The concentration level of saline impurities in the samples has irrelevant impact upon the flocculation ratio [2]. Other reagents were SR grade H_2SO_4 and NaOH from Panreac; AR Hyamine 1622 from Carlo Erba; AR Disulphine Blue V150 from Merck Schuchardt; HP diimidium Bromide, HP $Al_2(SO_4)_3$, and HP $CHCl_3$ from Probus. Water was Milli-Q grade. The pH was measured with a Crison 2001.

Stock solutions of the various reagents (surfactant, aluminum salt, and either acid or alkali) were kept at 25 ± 0.10 °C. These solutions were mixed also at 25 ± 0.10 °C in 100-ml volumetric flasks, thoroughly shaken, and allowed so settle for 1 h before further handling [8]. The last component to be added before bringing the sample to final volume was the acid or base. One point in each series corresponds to the unmodified pH conditions. Experiments in the presence of H_2SO_4 and NaOH covered a range of pH values between 1 and 13. The initial SDS concentration for all the experiments is 0.05 mol/l. The variables investigated were pH, residual SDS in solution, and residual aluminum in solution (denoted by $[Al^{3+}]_{sol}$). Some experiments with unmodified pH have been performed in the presence of NaCl to compare the competition of both H^+ and Na^+ with Al^{3+} as binding counterions. After the solutions had settled and flocculation had been completed, samples were filtered with 45-μm 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. $[Al(H_2O)_6]^{3+}$, $[Al(OH)]^{2+}$ and $[A(OH)_4]^-$ were calculated from the experimental $[Al^{3+}]_{tot}$ and the set of equilibrium reactions described above. For the calculations the activity coefficient of Al^{3+} is arbitrarily taken as 0.15, a value slightly lower than the value of 0.18 predicted by the extended Debye-Hückel theory [11] for an ionic strength of 0.1 (the actual ionic strengths in these experiments was above 0.5).

Results

There are three cases in the variation of $[SDS]_{sol}$ with pH (Fig. 3). For $[Al_2(SO_4)_3] = 0.005$ mol/l (below the onset of flocculation with unmodified pH) at pH 4–6 some amount of SDS becomes insoluble. This is connected with a pronounced drop in $[Al^{3+}]_{sol}$ (Fig. 4). The strong flocculant $[Al_{13}O_4(OH)_{24}]^{7+}$ exists within this range of pH, and either this species is able to flocculate some micellar SDS at lower concentrations than Al^{3+} would, or else adsorption of SDS onto $Al(OH)_3$ occurs. The adsorption of SDS by $Al(OH)_3$ must be weak, because at pH 8 substantial amounts of Al^{3+} remain insoluble

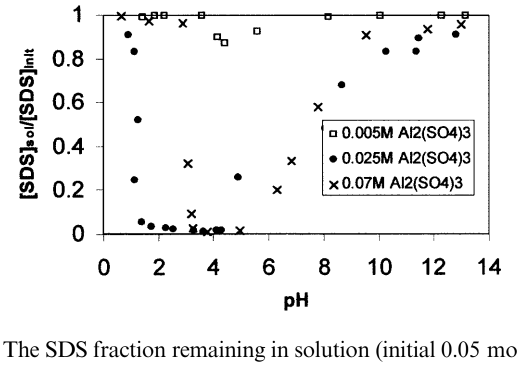

Fig. 3 The SDS fraction remaining in solution (initial 0.05 mol/l SDS solution), plotted against the pH of the samples

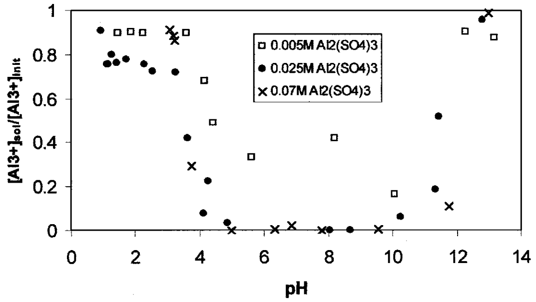

Fig. 4 Ratio of $[Al^{3+}]$ in any soluble form (the experimental value) relative to the total amount of aluminum added to the samples plotted vs the pH of the various samples. Below pH 4 the missing aluminum is captured in the flocculate. Above pH 4 there is a variable combination of Al combined by SDS or forming hydroxide. Under higher pH the proportion of hydroxide is higher

while nearly all the SDS is again dissolved. For $[Al_2(SO_4)_3] = 0.025$ mol/l (in the full flocculation region with unmodified pH) the flocculation ratio remains constant between pH 1.5 and pH 4. The flocculation ratio may remain at its maximum value with a substantial fluctuation in pH. There is a region between pH 5 and pH 8 where SDS is partially soluble, yet Al^{3+} is almost completely insoluble. This indicates that part of the Al^{3+} is in the form of flocculates and the rest as $Al(OH)_3$. The inflection at pH 8 is to some extent observed in series not included in the figure. This inflection suggests a drop in the proportion of flocculate present. $[Al_2(SO_4)_3] = 0.07$ mol/l is in the range of high salt concentrations where flocculation does not take place. However, an increase in pH leads to full flocculation of SDS within the range of pH 3–5. The results suggest that an increase in pH shall reduce the effective $[Al^{3+}]$ to a value suitable to cause flocculation.

The effect of the concentration of monovalent cations on $[Al^{3+}]_{sol}$ is seen in Fig. 5. In the presence of $[Na^+]$ there is a slight increase in the concentration of aluminum remaining in solution $[Al^{3+}]_{sol}$. The trend is more pronounced at $[Al_2(SO_4)_3] = 0.01$ mol/l. The trends are similar although more pronounced when $[H^+]$ varies by addition of acid. The similarity of the behaviors suggests that at low pH the effect of H^+ may be assumed to be competitive, binding onto the micelles and variation of the CMC of SDS. The increase in the concentration of soluble Al^{3+} indicated that the micelles and flocs are replacing some Al^{3+} by monovalent cations. In the points investigated (see Fig. 3) the flocculation of surfactant is complete, and therefore the change in $[Al^{3+}]$ is due to competition between binding of H^+ or (less effectively) Na^+ and binding of Al^{3+} to SDS micelles.

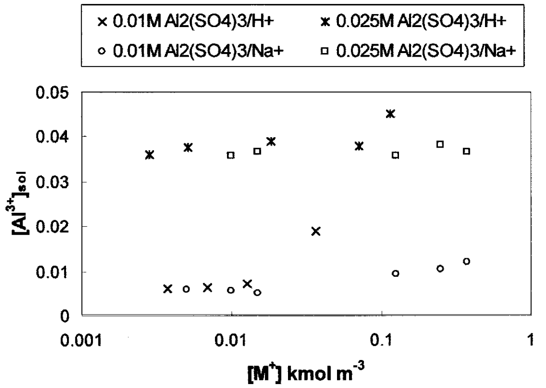

Fig. 5 Soluble aluminum (any form) vs concentration of monovalent ions Na^+ and H^+

In a flocculate obtained without added acid or alkali the ratio SDS/Al^{3+} ranges between approximately 3.5 and 4 [10]. The SDS/Al^{3+} ratios for insoluble aggregates in the pH range 3.5–10 (Fig. 6) varies from values of about 2.5 down to 0.05. The increasing contribution of $Al(OH)_3$ to the composition of the flocculate explains both lower ratios at higher pH and lower ratios at higher overall $[Al_2(SO_4)_3]$. The low ratios are not connected with high residual [SDS] (Fig. 7). For $[Al_2(SO_4)_3] =$

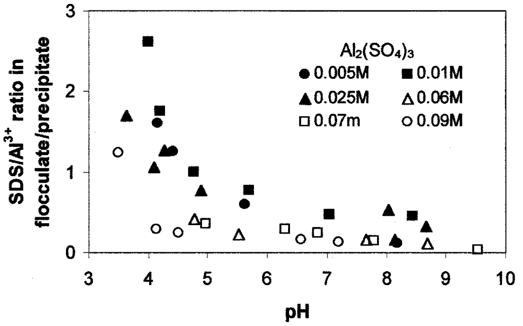

Fig. 6 The ratio SDS/Al^{3+} in the composition of the flocs/precipitates formed over a range of pH with various aluminum concentrations and an [SDS]init = 0.05 mol/l. The amount of insoluble Al^{3+} is constant within each series save 0.005 mol/l $Al_2(SO_4)_3$, and the ratio reflects the decrease in the concentration of micellar SDS flocculated at higher pH

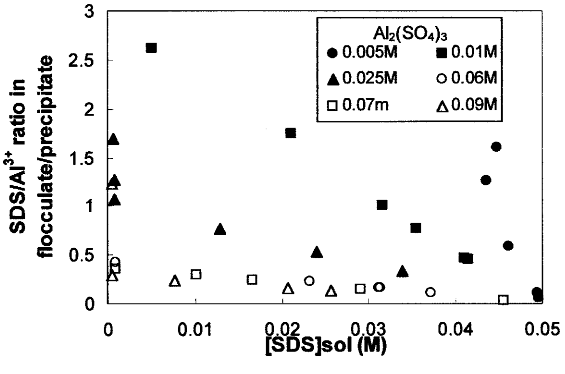

Fig. 7 The residual [SDS] show that significant amounts of flocculate can be achieved under low acidic, neutral and moderately alkaline conditions

0.07 mol/l in Figs 6 and 7, the point at pH about 5 has a residual [SDS] of about 10^{-3} mol/l. A large amount of surfactant is therefore flocculated, and even at higher pH significant amounts of SDS are made insoluble. The weak adsorption capacity of $Al(OH)_3$ suggests that in all cases most of this insoluble SDS is due to micellar flocculation.

The presence of large amounts of $Al(OH)_3$ together with the flocculate might be regarded as troublesome, but it must be taken into account that micellar flocculation under optimal conditions leaves Al^{3+} concentrations in the order of 0.01 mol/l free in the solution, while between pH 5 and pH 8 the residual Al^{3+} concentration is very low (Fig. 5). As the target of AMF is the dissociated form of pollutants, the range of compounds effectively removable is enlarged. For example, removal by AMF (with SDS) of 80 ppm of 2,4-dichlorophenoxyacetic acid (pKa about 2.8) yields the removal of in excess of 90% of the pollutant while preliminary tests showed that the removal of a similar amount of benzoic acid (pKa about 4.2) is about 80% [15]. The pH conditions were about 3–3.5 in all cases. Working under more alkaline conditions will cause higher dissociation degrees and improve the efficacy of the process with compounds with higher pKa.

Conclusions

Micellar flocculation is the mechanism by which SDS is made insoluble by Al^{3+} at neutral or alkaline pH. Adsorption of SDS on $Al(OH)_3$ is irrelevant compared with the amount of SDS which is made insoluble by micellar flocculation even in neutral or alkaline pH. Micellar flocculates may exist and be used over a more extended pH range than originally expected. A potential application of this behavior is to use micellar flocculation to concentrate metals, as other heavy metals like Zn(II) [2] can be incorporated into the flocculate, and then remove these metals by precipitating their hydroxides, releasing the surfactant. At low pH, protons compete with Al^{3+} as binding counterions.

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