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SHORT COMMUNICATION

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Flocculation of anionic surfactant micelles in the presence of hydrocarbons

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Abstract Adsorptive micellar flocculation (AMF) is a surfactant-based separation process based on the flocculation of micelles of suitable anionic surfactants by Al^{3+}. The micelles form large amorphous flocs which can be removed by filtration, which is attractive because soluble pollutants are captured by the floc, thus providing a simple separation method. As the primary aim of AMF is the removal of anionic pollutants from aqueous streams, it is important to investigate the influence of the various substances which may affect it. This article discusses the influence of the presence of insoluble hydrocarbons on the flocculation of micelles of the anionic surfactant dodecyl sulfate by Al^{3+}. The ratio between surfactant remaining in solution and total surfactant and the ratio between Al^{3+} and surfactant in the flocculate are determined in systems composed of an aqueous solution containing a constant dodecyl sulfate concentration of 0.05 M and a variable Al^{3+} concentration and an organic phase (decane) with phase volume ratios of decane/water ranging from 0 (no decane) to 0.15. The flocculation is only slightly affected by the presence of decane for decane/solution ratios below 0.05, while the effect (lower flocculated fraction) is more marked above this ratio.

Key words Dodecyl sulfate · Hydrocarbon · ζ potential · Adsorption · Micellar flocculation

Introduction

Adsorptive micellar flocculation (AMF) is a two-step process, by which Al^{3+} adsorbs on the surface of micelles of some anionic surfactants and then anionic solutes, such as the pesticide 2,4-D-(dichlorophenoxyacetic acid) [3, 4] or benzoic acid [5], bind themselves to the micelle-bound Al^{3+}. The adsorption of Al^{3+} leads to the flocculation of micelles due to the reduction of their effective surface charge. The anionic surfactants dodecyl sulfate (DS) and α-olefin sulphonate have been reported to exhibit this behavior [1, 2]. The process is represented schematically in Fig. 1. The resulting pollutant-holding floc can be removed by coarse filtration, this being an interesting alternative to membrane-based surfactant-enhanced separations. It has been confirmed that binding of the pollutant slightly affects the flocculation of the surfactant micelles [3], which can be explained by a weak alteration of the surface charge shielding which is achieved in the absence of anionic species susceptible to association with the forming floc. The effect of Al^{3+} on the surface charge of micelles (with reduction of the ζ potential to zero or near zero) has been compared with the effect of Ca^{2+} [6]: an increase in the Ca^{2+} concentration from 0 to 0.025 M, well into the precipitation region of $Ca(DS)_2$, leads to a change in the ζ potential from an initial value of −80 mV (corresponding to NaDS alone) to approximately −30 mV, a value which remains constant throughout the precipitation region. This marks the difference between precipitation of $Ca(DS)_2$ and flocculation of $[Al_{(1-x)}Na_{3x}(DS)_3]_n$: precipitation occurs in the presence of the micelles, which are not directly involved and will eventually prevent or reduce the extent of precipitation acting as

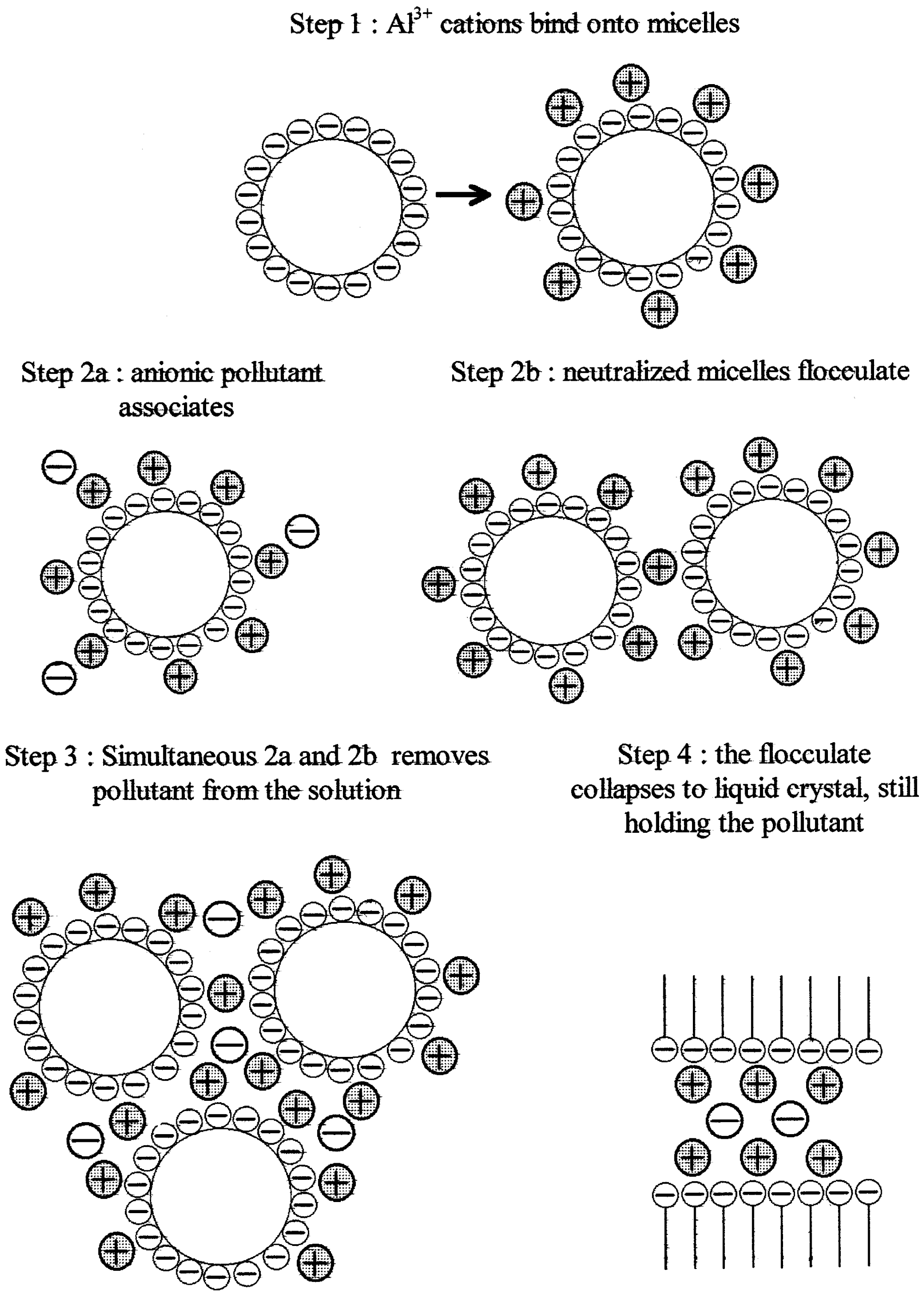

Fig. 1 Schematic view of the mechanism of adsorptive micellar flocculation

Ca^{2+} sequesters [7–10], while flocculation involves the micelles themselves, and it is their loss of colloidal stability which causes the phenomenon.

Because of its potential interest for the treatment of waste waters, the influence of a number of factors which may affect AMF, such as overall salinity, the presence of heavy metals, pH, and the presence of dispersed or insoluble substances, should be investigated. In this article we describe the effect caused on the surfactant flocculation by the presence of hydrocarbons (using decane as a test substance) in the effluent to be treated.

Experimental

NaDS kindly provided by KAO Corporation (technical grade with 1% dodecyl alcohol in weight relative to the surfactant content) was used as received. As the potential application is that of a large-scale separation, the performance of an expensive purified chemical is not relevant. Previous work [1] showed that, for the NaDS concentration used, sodium salt (as NaCl) contents below 0.015 M have no effect on the interaction between DS and Al^{3+} and, therefore, the reagents were not desalted. Chemically pure aluminum sulfate from Probus was used as the flocculant. *n*-Decane was grade from Panreac, with a purity of 98%. Analytical grade reagents hyamine 1622 from Carlo Erba and disulphine blue V150 from Merck Schuchardt and high-performance grade reagents diimidium bromide, $Al_2(SO_4)_3$, $CaCl_2$, and $CHCl_3$ from Probus were used. Water was Milli-Q grade.

The samples were prepared in the following way. Samples (25 ml) were taken from a stock solution with a NaDS concentration of 0.2 M. Additional volumes of Al^{3+} solutions (corresponding to the amounts required to reach the desired final Al^{3+} and DS concentrations in a 100 ml solution) as well as decane were added in a proportion ranging from 1 to 15% in volume of decane relative to the final volume of the aqueous solution. The aqueous phase was then brought to 100 ml. The mixture was shaken vigorously. As the hydrocarbon is not investigated as a pollutant to be removed, but as an interfering substance, it was considered enough to know the overall amount present. In addition, as the large-scale water treatment procedure would include the injection of a concentrated mixture of Al^{3+} and DS (flocculation does not takes place at high concentrations) with varying concentrations of both species and the phase volume ratio of decane during the addition and homogenization, the sequence was considered reasonably representative for a workbench experiment. All the chemicals were kept at 25 °C. The samples were allowed to reach equilibrium at 25 °C for 1 h. Previous work on micellar flocculation (in the absence of hydrocarbons) indicates that within 2 min both flocculation [2] and AMF [4] equilibrium are reached with the DS/Al^{3+} system. After equilibrium the samples were decanted and filtered with 0.45-μm pore size Whatman cellulose nitrate filters.

The surfactant content in the clarified water was analyzed by two-phase titration, with hyamine 1622 as a standard and blue 1 acid and diimidium bromide as a mixed indicator. The aluminum content was determined by inductively coupled plasma studies with a Jovyn-Ivon JI-38 apparatus. The wavelength was set to 308.215 nm; the detection limit was 45 ppb.

Results and discussion

The effect of the presence of decane on the variation in the flocculated/total surfactant ratio with free Al^{3+} concentration is shown in Fig. 2. Within the optimum flocculation region (Al^{3+} concentration between 0.02 and 0.05 M) the differences in the extent of flocculation are small for up to 5% of decane by volume. Outside this region, there is a strong increase in surfactant solubility associated with the increase in the overall decane fraction (from 0 to 2.5%) while higher amounts of decane do not cause any noticeable effect. A possible cause could be micellar swelling, due to the fact that there would be a maximum value for the amount of decane solubilized inside the micelles and therefore an upper limit to any alteration. The decrease in the flocculation ratio at Al^{3+} concentrations above 0.07 M is assumed to be a consequence of the existence of aqua complexes of Al^{3+}–DS. These compounds have been proposed by several authors [11–13] to explain the solution behavior of various surfactants in the presence of high metallic cation concentrations.

The ratio Al^{3+}/DS in the floc is plotted versus free Al^{3+} concentration in Fig. 3. The data correspond to the region for high flocculation, where data-scatter due to experimental error can be considered small. The results show some dispersion and in some series a monotonous trend (0 and 1% decane) or an inflection (10 and 15%). The dispersion of the Al^{3+}/DS values is higher at higher Al^{3+} concentrations.

The connection between the Al^{3+}/DS ratio and the flocculation ratio of the surfactant is shown in Fig. 4.

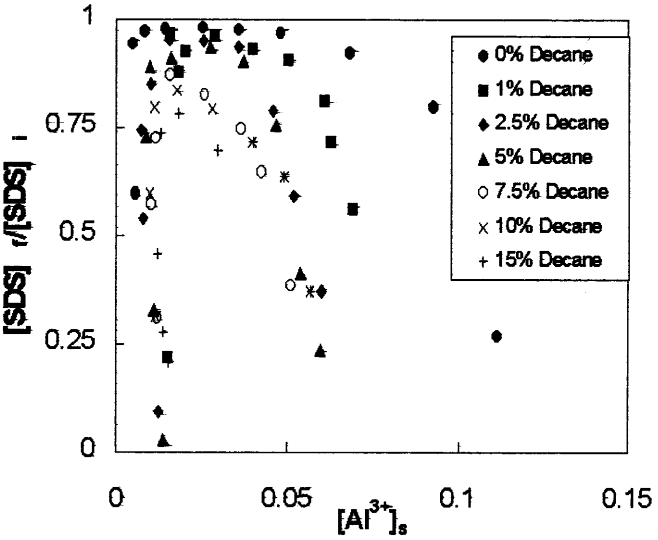

Fig. 2 Flocculated surfactant ratio versus free Al^{3+} concentration

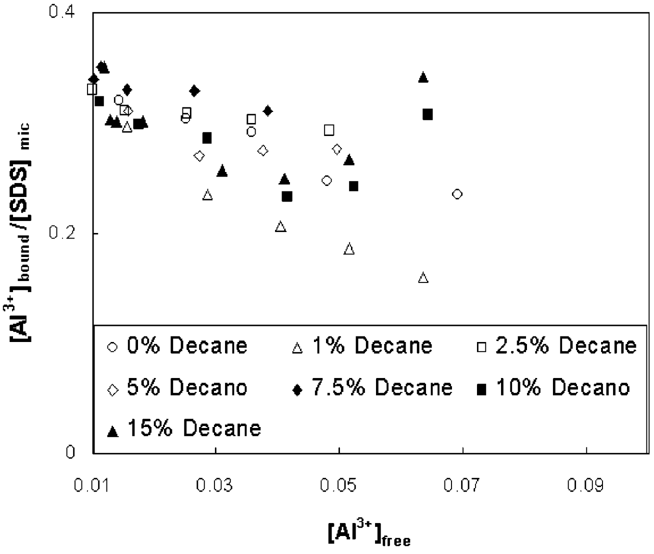

Fig. 3 $[Al^{3+}]$/[dodecyl sulfate (*DS*)] ratio in the flocculated versus $[Al^{3+}]$ in the solution at equilibrium

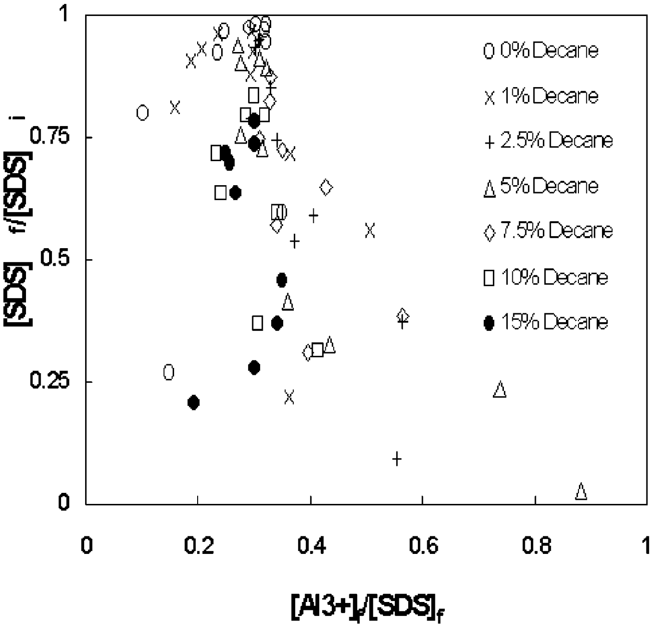

Fig. 4 Flocculated surfactant ratio versus Al^{3+}/DS ratio in the floc

The optimum flocculation ratios are connected with a range of Al^{3+}/DS ratios between 0.2 and 0.33, which is consistent with the fact that flocculation may occur with a sufficiently low surface potential. As the decane proportion increases, the maximum achievable flocculation ratio decreases. For 0 and 1% decane high flocculation ratios (above 0.8) can be reached with Al^{3+}/DS ratios of 0.2 or even less. For higher decane proportions, the Al^{3+}/DS ratio cannot be that low if a substantial degree of flocculation is to be achieved. The scatter below a flocculation ratio of 0.6, which includes values of the Al^{3+}/DS ratio well above 0.33, suggests that these results are affected by large experimental error; however, some measurements of the ζ potential in Al^{3+}/DS systems have produced Gaussian potential distributions with positive values [6], which means that inversion of surface charge may occur.

Conclusions

The presence of hydrocarbons in an aqueous medium where micellar flocculation takes place has two main effects:

1. Within the Al^{3+} range where flocculation achieves its maximum, the value of the maximum is significantly reduced if the amount of decane exceeds 5% of the volume of the aqueous phase.
2. Outside the maximum flocculation region, the fraction of flocculated surfactant drops dramatically for decane amounts up to 5%, and afterwards no additional effect is observed.

As a consequence, relatively small amounts of hydrocarbons would not significantly affect micellar flocculation, as the conditions sought must be those leading to maximum flocculation and effect 2 would thus be avoided. Larger amounts of hydrocarbons would cause a strong increase in the amount of surfactant remaining in solution, with a loss of efficiency in the adsorption process (less substrate would be available) and loss of reagent (more DS and Al^{3+} would be lost through the membrane).

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References

1. Talens F, Paton P, Gaya S (1998) Langmuir 14:5046
2. Paton P, Talens F (1998) J Surfact Deterg 1:399
3. Porras P, Talens-Alesson FI (1999) Environ Sci Technol 33:3206
4. Porras M, Talens-Alesson FI (1999) Sep Sci Technol 34:2679
5. Talens FI, Patón P, Porras M (1997) J Com Esp Deterg 495
6. Talens FI (1999) J Disp Sci Technol 20:1871
7. Peacock JM, Matijevic E (1980) J Colloid Interface Sci 77:548
8. Chou SI, Bae JI (1983) J Colloid Interface Sci 96:192
9. Somasundaran P, Ananthapadmanabhan KP, Celik MS (1988) Langmuir 4:1061
10. Stellner KL, Scamehorn JF (1989) Langmuir 5:70
11. Bozic J, Krznaric I, Kallay N (1979) Colloid Polym Sci 257:201
12. Tezak D, Strajnar F, Milat O, Stubicar M (1984) Prog Colloid Polym Sci 69:100
13. Fisher L, Oakenfull DG (1977) Chem Soc Rev 6:25
14. Porter MR (1994) Handbook of surfactants. Blackie, Bury St. Edmunds, p 57