

Removal of 2,4-Dichlorophenoxyacetic Acid from Water by Adsorptive Micellar Flocculation

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Adsorption of Al^{3+} cations onto the surface of lauryl sulfate micelles causes their flocculation. The resulting flocs have pollutant-sequestering properties which have never been observed in the precipitates of other Al^{3+} surfactant salts or other metal lauryl sulfate salts. In this paper the removal of the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) is presented as an example of the application of this phenomenon, which will be called thereafter adsorptive micellar flocculation (AMF). The results show that AMF is more effective than expected from the octanol/water partition coefficient of the solute, and the kinetics is very fast (less than 2 min for equilibrium). 2,4-D seems to bind itself to micelle-bound Al^{3+} following a Guoy–Chapman–Stern isotherm. The shape of the isotherm suggests that the surface potential of the micellar flocculate increases at higher surface concentrations of the pollutant on the floc. This is confirmed by a slight disruption of the micellar flocculation by pollutant effect. AMF seems potentially valuable for the development of intensive surfactant-based environmental technologies, as the flocs can be easily filtered and, by a variety of inexpensive methods, redissolved and regenerated providing a fresh adsorption substrate.

Introduction

The binding of solutes onto the surface of surfactant micelles or their solubilization into the micellar cores (1–5) is the basis of micellar-enhanced ultrafiltration (MEUF). The purpose of MEUF is to allow ultrafiltration membranes, with relatively large molecular weight cutoff (1000–10 000) to retain small solutes such as metallic cations. The micelles are retained by the membrane, together with any species bound or solubilized by the micelle. The permeate contains surfactant (at its cmc, critical micelle concentration) and a free solute concentration in equilibrium with the micelle-bound solute. MEUF presents a number of problems: membrane fouling; relatively high volume ratios between retentate and permeate, which may be about 0.2 under conditions of continuous operation (5); and the removal of the surfactant present in the retentate.

The binding of cations to micelles is also a relevant research subject because precipitation of linear alkylbenzenesulfonates, alkanesulfonates, and alkyl sulfates affects

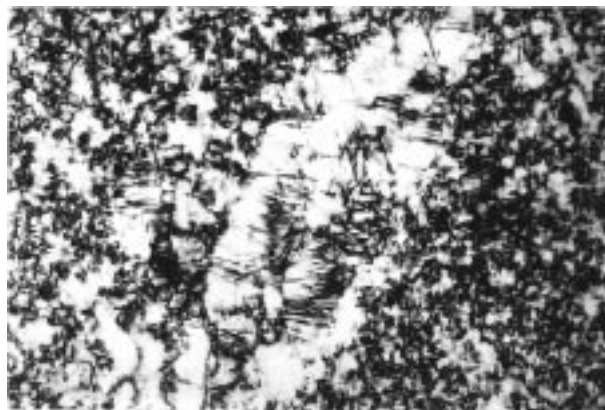


FIGURE 1. Flocculate with large fragments of liquid crystal (40000 \times (reproduced at 65% of original size). These are embedded in an amorphous bulk.

the efficiency of processes such as enhanced oil recovery (EOR) or the efficiency of household washing products. The enhanced resistance of micellar surfactant to precipitation in the presence of polycalent cations (6–8) is explained by assuming that binding of cations onto the surface of micelles takes preference over precipitation with the surfactant monomers. Once the available micellar surface is saturated, any excess cations precipitate with the surfactant (9). A higher surfactant concentration results then in a higher cation concentration being needed to initiate precipitation.

Binding of Al^{3+} onto lauryl sulfate (DS) micelles has been recently described in the literature (10, 11). Unlike other cations, it leads to electroneutralization of the micelles and their subsequent coagulation, leading to an amorphous aggregate (Figure 1) with variable stoichiometry $[\text{Al}_{(1-x)}\text{Na}_{3x}(\text{DS})_{3/2}]_n$. The ζ -potential of the lauryl sulfate micelles is reduced to a value of zero in the zone of minimum surfactant solubility when Al^{3+} is added, while adding Ca^{2+} only reduces the micelle ζ -potential to a value of -40 mV (12) even during precipitation of $\text{Ca}(\text{DS})_2$. This is why in the case of Ca^{2+} –DS solutions a crystalline solid precipitates, while in the case of Al^{3+} –DS solutions flocculation of the micelles takes place first.

The disordered aggregate resulting from flocculation contains fragments of liquid crystal but lacks any macroscopic structure (it appears as a unique amorphous floc, spongy and sometimes buoyant). The floc is formed from all the micellar surfactant in the solution and can be removed from solution by gross filtration. Because of this, and its ability to hold solutes (13) due to its liquid-crystalline microstructure, micellar flocculation might be the basis of a new approach to wastewater and chemical separation techniques.

Experimental Section

Sodium lauryl sulfate (SDS) was kindly supplied by KAO Corp., as an aqueous paste with approximately 70 wt % of surfactant content and a purity of about 98%. Because the performance of purified surfactants is irrelevant, SDS was used as received. The test pollutant was 2,4-dichlorophenoxyacetic acid (2,4-D) AR grade from Merck-Schuchardt. Aluminum sulfate (dodecahydrated) was HP grade. Surfactant content was analyzed by two-phase titration with benzenonium chloride (Hyamine 1622) from Carlo Erba, following the standard test ISO 2271-1972. Indicator reagents were Blue Acid 1 and dimidium bromide AR grade from Merck-Schuchardt. Chlo-

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roform and sulfuric acid were both HP grade from PROBUS. 2,4-D was analyzed by high-performance liquid chromatography (HPLC) using a Waters 481 UV spectrophotometer and a reverse phase C-18 column. The mobile phase was 50/49/1 acetonitrile/water/acetic acid. Acetonitrile HPLC grade and acetic acid HP grade were from PROBUS (Badalona, Spain). Milli-Q grade water was obtained by means of a Millipore Waters filtration equipment. 2,4-D concentration was estimated from the height of its UV absorption signal at 236 nm.

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 filtration. There was an exception with experiments performed to confirm that 1 h was an adequate equilibration time; these were filtered between 2 min and 60 h after mixing. pH was that naturally occurring in each solution. Random measures were made in various samples to confirm that, for the working 2,4-D concentrations, pH was around 3 ± 0.1 , while the values found in previous work (10) in the absence of solutes for micellar flocculation were about $\text{pH } 3.3 \pm 0.1$. After the solutions had settled for 1 h and flocculation had been completed, samples were vacuum-filtered with $0.45 \mu\text{m}$ Whatman cellulose nitrate filters. In all the experiments the filtrate was analyzed to obtain the residual 2,4-D and surfactant content. The amounts in the flocculate were obtained by difference with the initial concentration at the initial volume.

To confirm that the behavior observed in the surfactant flocs was singular, calcium lauryl sulfate was precipitated in the presence of 50 ppm of 2,4-D, by mixing CaCl_2 and NaDS solutions to final concentrations between 0.005 and 0.05 M in Ca^{2+} and 0.05 M in NaDS. No variation was found in the concentration of 2,4-D in the filtrate, in agreement with the fact that precipitation of DS with Ca^{2+} has been proposed (14) as a method for the recovery of the surfactant from its aqueous mixtures with organic pollutants resulting from other surfactant-based separation methods.

The octanol–water partition coefficient of 2,4-D was also measured. This coefficient is used as a reference value for the relative solubility of an organic pollutant between water and the nonpolar micellar core of surfactant micelles and can provide information on the relative efficiency of micellar flocculation and techniques such as admicellar solubilization. The coefficient is defined as

$$K_{\text{OW}} = [2,4 - \text{D}]_{\text{O}} / [2,4 - \text{D}]_{\text{W}} \quad (1)$$

and the micelle–water or admicelle–water partition coefficient is defined as

$$K_{\text{HW}} = \frac{[2,4 - \text{D}]_{\text{Ads}} / [\text{SDS}]_{\text{H}}}{[2,4 - \text{D}]_{\text{W}}} \quad (2)$$

For the case of lauryl sulfate micelles and admicelles, both have been found to be similar for K_{OW} below 1000 (15, 16). Therefore, the comparison of the octanol–water partition coefficient with the flocculate–water partition coefficient defined as

$$K_{\text{FW}} = \frac{[2,4 - \text{D}]_{\text{Ads}} / [\text{SDS}]_{\text{F}}}{[2,4 - \text{D}]_{\text{W}}} \quad (3)$$

will provide a clear idea of the relative effectiveness (defined as amount of pollutant removed per unit mass of surfactant) of admicellar solubilization and AMF. The octanol–water partition coefficient for 2,4-D was obtained by placing in contact equal volumes (50 mL) of an aqueous 2,4-D solution at different concentrations and octanol, vigorously shaking for 20 min and allowing to settle for 1 day. 2,4-D content was

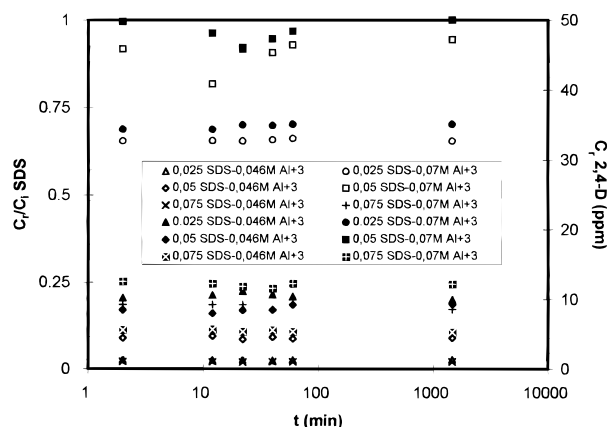


FIGURE 2. Left scale: Evolution of the ratio between residual [SDS] and initial [SDS] with time. Right scale: Evolution of the residual [2,4-D] with time. Initial [2,4-D] = 50 ppm.

analyzed in the aqueous solution. A value of 6.2 was found, and used as a reference to compare the equilibrium reached in AMF with the adsolubilization equilibrium.

Results and Discussion

Kinetics of Flocculation and Solute Removal. Both the flocculation of SDS and the capture of the pollutant are fast (Figure 2). The residual SDS concentration (white symbols and black cross symbols) left in solution reaches a constant value within 2 min of mixing. The Al^{3+} concentrations correspond to the region for fast flocculation of the surfactant micelles (11). The results for solute removal (black symbols and white cross symbols on black field) also show that equilibrium is reached within 2 min. This suggests that micellar flocculation is the limiting step, at least in the case of removal of 2,4-D. For all SDS concentrations a 0.023 M $\text{Al}_2(\text{SO}_4)_3$ concentration (leading to efficient surfactant flocculation) and a 0.035 M $\text{Al}_2(\text{SO}_4)_3$ concentration (leading to incomplete flocculation) were tested, to verify if there is a significant change in the partition coefficient depending on the flocculation conditions. The results show that the 2,4-D/DS molar ratio is unaffected by the Al^{3+} /DS ratio. This suggests that, as far as appropriate conditions for effective micellar flocculation are met, minor changes in the composition of the flocculate do not affect its adsorbing capacity. One aspect which will be discussed below is that the residual Al^{3+} concentration is high, at least 100 ppm. Further treatment or recycling of the effluent should be part of the practical application of this process. Alternatively, a suitable polycation should be found to replace Al^{3+} .

Partition Coefficients. By analogy with adsolubilization, partition coefficients K_{FW} were calculated for SDS as adsorbent of 2,4-D. The units are (L solution)/(kg of flocculated SDS) to be consistent with the data for adsolubilization compiled by Valsaraj (16) for various organic compounds. The partition coefficient is not constant, and it is always higher (at least 50 and in some cases 1500, with values between 200 and 600 in most cases) than the octanol–water coefficient for 2,4-D (found to be 6.2) over the entire range investigated. This means that, on average, some 50 times more pollutant may be removed per unit mass of SDS by AMF than by admicellar solubilization.

Adsorption Mechanism. The data were further elaborated, to produce a pseudoisotherm defined as the 2,4-D/SDS molar ratio in the flocculate vs free $[2,4\text{-D}]_{\text{water}}$. Because of the relatively low $[2,4\text{-D}]$ values, it is not possible to generalize the 2,4-D/SDS molar ratio to give θ , the fraction of the saturation surface concentration. The results allow identification of a region of infinite slope (Figure 3). Dissociation

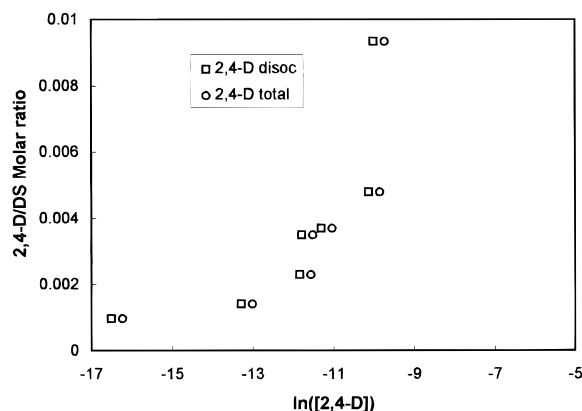


FIGURE 3. Pseudoisotherm: 2,4-D/SDS molar ratio in the floc vs [2,4-D] left in the solution. Considering dissociation or ignoring it is qualitatively unimportant here. Initial [2,4-D] in the range 20–80 ppm.

of 2,4-D does not leads to large differences in the calculations (about 60% of 2,4-D is dissociated), with pH about 3 and a pK_a of 2.8. The ionic nature of the relevant species and the electrolyte concentrations make it reasonable to assume that the adsorption conforms to a Guoy–Chapman–Stern isotherm (17),

$$c = K(T)e^{\frac{zF\phi(0)}{(RT)}} \frac{\theta}{1 + \theta} \quad (4)$$

The equation is very similar to the Temkin (18) equation,

$$c = Ke^{\beta\theta} \frac{\theta}{1 + \theta} \quad (5)$$

which requires that $\beta = 4$ for the critical case of infinite slope. Considering that monovalent 2,4-dichlorophenoxyacetate is the adsorbate, the critical condition to achieve infinite slope would be that $\theta = 10\phi(0)$. This means that when the surface concentration of 2,4-D increases, the surface potential $\phi(0)$ expressed here in volts should also increase. This is consistent with the assumption of adsorption of the dissociated form of 2,4-D to micelle-bound Al^{3+} , as shown in the scheme (Figure 4): the surface potential would increase as part of the charge of micelle-bound Al^{3+} cations would be neutralized by 2,4-D instead of micellar surface charges. This qualitative model predicts that pollutant adsorption should eventually lead to disruption of the flocculation. Figure 5 shows this effect of the presence of 2,4-D, with concentrations of 20 and 80 ppm and with the pollutant present in the solution at the time of flocculation or being incorporated afterward. A concentration of 80 ppm of 2,4-D lead to higher residual SDS concentrations than 20 ppm. It can also be seen that the flocculation ratio tends to be higher if the flocs have formed first, but only at the lower 2,4-D concentration.

Potential Uses of AMF. Continuous adsorption, with the flocs being continuously generated, circulated through a suitable contactor, and removed by filtration, is the most interesting development which could derive from the separation phenomenon here described. There are some weaknesses in the process as described here: it is only useful for anionic pollutants; the effect of pH on Al^{3+} limits the operation conditions to pH 2–3.5, and the residual concentration of Al^{3+} is at least 100 ppm. The most immediate solution for the first problem is to concentrate in the recovery or acidic species (phthalic, maleic acid) from aqueous effluents with pH adjusted to be within the range of pH 2 and 3.5. Regarding the controversial presence of high Al^{3+} concentrations in the effluent, removal from the effluent water (by solvent extraction, ion exchange) or recycling in

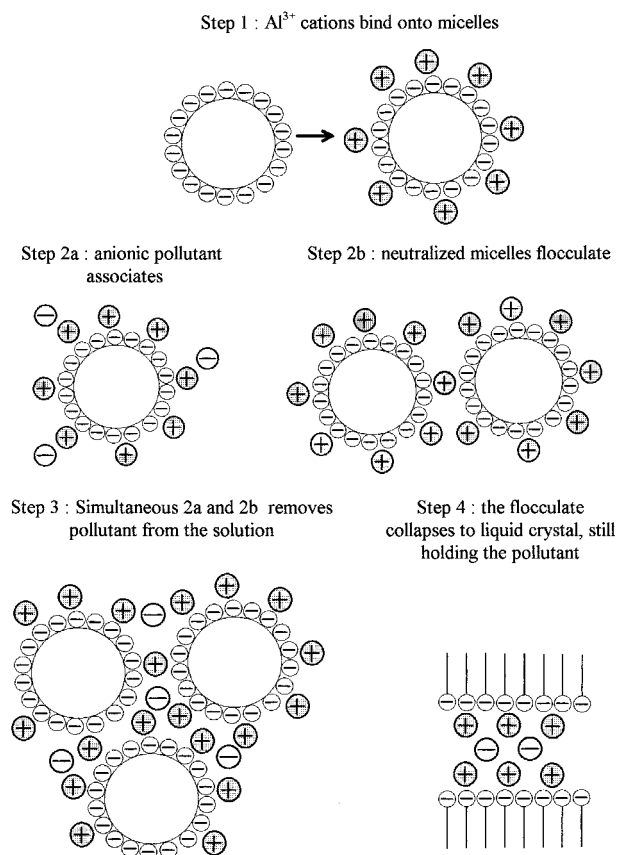


FIGURE 4. Suggested mechanism for adsorptive micellar flocculation.

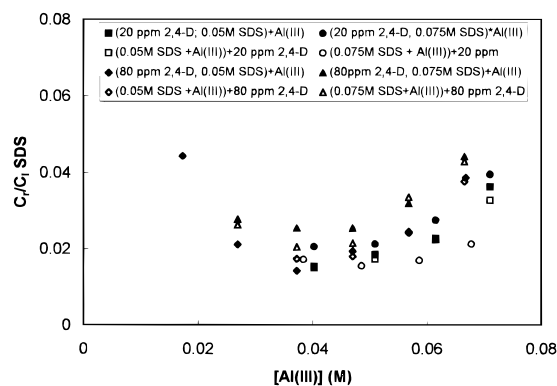


FIGURE 5. Residual [SDS] to total [SDS] molar ratio. Black symbols refer to flocculation of the surfactant in the presence of 2,4-D. White symbols refer to flocculation and subsequent addition of 2,4-D. $[2,4-D]_{initial} = 20$ and 80 ppm.

a closed loop should be considered. Finding a polycationic substitute of Al^{3+} would be the best option, as this would expand the pH range for application and avoid toxicological issues.

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Nomenclature

c	volumetric concentration of the solute in equilibrium with its surface concentration
F	Faraday constant
K	dissociation constant of the adsorption process
T	temperature (K)
z	charge of the adsorbing solute

Greek Letters

β	μ/RT
$\varphi(0)$	surface potential (V)
θ	fraction of the maximum surface concentration of the solute

Subscripts

Ads	volumetric concentration which has been adsorbed
F	volumetric concentration which has been flocculated
FW	floc-water
H	volumetric concentration in hemimicellar

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