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SOLUBILIZATION OF CALCIUM DODECYL SULFATE IN A MICELLAR SOLUTION AND IN LAMELLAR LIQUID CRYSTAL

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ABSTRACT

Calcium dodecyl sulfate (CDS) was solubilized in the aqueous micellar solution of sodium dodecyl sulfate and in the lamellar liquid crystal obtained from water, sodium dodecyl sulfate and decanol.

The solubilization of CDS in the micellar solution was strongly increased with the concentration of sodium dodecyl sulfate while the maximum amount of CDS solubilized in the liquid crystal remained similar. The solubilization in the micellar solution was gradually increased with the alcohol content with a sudden reduction to zero at the decanol/sodium-dodecyl-sulfate ratio marking the end of the micellar region with no calcium soap being present. The dependence of the solubilization on the decanol/sodium-dodecyl-sulfate ratio was the opposite in the lamellar liquid-crystalline phase. It suddenly rose to a maximum at the lowest values of the alcohol/sodium-dodecyl-sulfate ratio and the interlayer spacing in the lamellar liquid crystal showed a pronounced reduction for initial addition of the calcium soap.

INTRODUCTION

The phase equilibria and structures encountered in systems containing ionic surfactants with monovalent counter ions have been extensively investigated over the years [1—3].

On the other hand, surfactant systems with multivalent counter ions have not been investigated to a similar degree. Goddard has described the early contributions in his review of 1975 [4], Shinoda and co-workers have published a series of articles on different means to alleviate the problem of the high Krafft point of surfactants with multivalent counter ions [5—7] and Robb and co-workers have focussed on solubilization in aqueous systems [8—10]. Somasundaran and co-workers have made extensive investigations on the solubilization of calcium dodecyl benzenesulfonate [11—13] against their interest in mineral dressing problems. Corkill and Goodman [14] interpreted their results as double micellization.

Peacock and Matijević [15] have studied the precipitation mechanisms of alkyl benzenesulfonates revealing the reactions using precipitation curves and Kahn et al. [16] have recently published the first complete phase diagram of the calcium-octyl-sulfate/decanol/water system. This calcium-octyl surfactant has a sufficiently short chain to be soluble in water and the interesting comparison with the corresponding sodium-surfactant system showed the only significant difference to be a drastic reduction of the region of the lamellar liquid-crystalline phase. The authors explained the lack of stability of the liquid crystal at high water content as due to a strong compression of the electric double layer from the calcium ion being more closely attached to the negative counter ions.

With the background of these investigations, we found the question of solubilization of an insoluble calcium surfactant in a lamellar liquid-crystalline phase of the corresponding sodium surfactant to be an interesting scientific problem. We decided a comparison of the solubilization in the micellar area and in a lamellar liquid-crystalline phase to be a most useful exercise giving an opportunity to compare the behavior of a soluble calcium soap [16] with that of an insoluble one [11—13].

The investigations used the partial phase diagram of the system water/sodium-dodecyl-sulfate/decanol published by Ekwall [1] as a basis (Fig. 1).

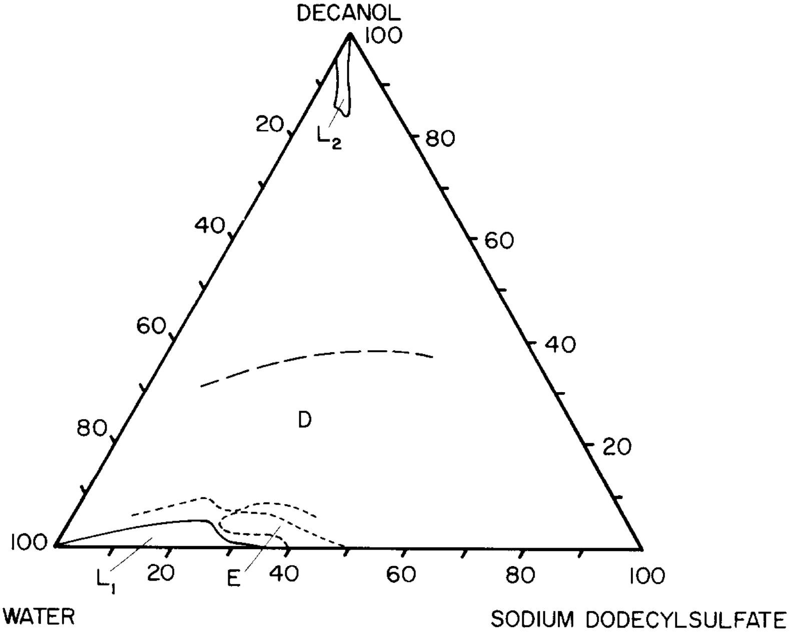

Fig. 1. Normal micellar (L_1), inverse micellar (L_2), lamellar liquid-crystalline (D), and hexagonal liquid-crystalline (E) phase regions in the system water—sodium-dodecyl-sulfate—decanol according to Ekwall [1] (Courtesy Academic Press).

EXPERIMENTAL

Materials

The sodium dodecyl sulfate was BDH, specially pure, recrystallized twice from ethanol. The calcium soap of the dodecyl-sulfate ion was prepared by precipitation of the recrystallized SDS with calcium chloride dihydrate (Fisher reagent). The calcium soap was then filtered and dried over Fisher reagent phosphorus pentoxide. The decanol (Aldrich, 99%), was used as received.

Solubility regions

Both the normal micelle and liquid-crystal regions were determined by mixing three of the components and addition of either decanol or calcium dodecyl sulfate. Solutions were mixed with a vibromix prior to being thermostated at 30 ± 0.2°C. Special care was required in determining the liquid-crystal solubility boundary due to the initially lower phase rising to the top in the high alcohol content two-phase region. Hence, centrifuging the sample in this two-phase region mixed the two phases rather than separating them.

Low-angle X-ray diffraction

Samples for X-ray measurements were prepared by adding calcium soap to aliquots of the appropriate liquid-crystal formulation. The samples were then sealed and allowed to equilibrate for approximately two weeks. Measurements were completed by use of a Kiessig low-angle camera from Richard Seifert. Ni filtered Cu radiation was used and the reflection determined by a Tennelec position-sensitive-detection system (Model PSD-1100).

RESULTS

The area of aqueous micellar solution was not changed to a significant degree by replacing part of the sodium dodecyl sulfate with calcium dodecyl sulfate. Figure 2 shows the alcohol solubilization to be virtually unchanged

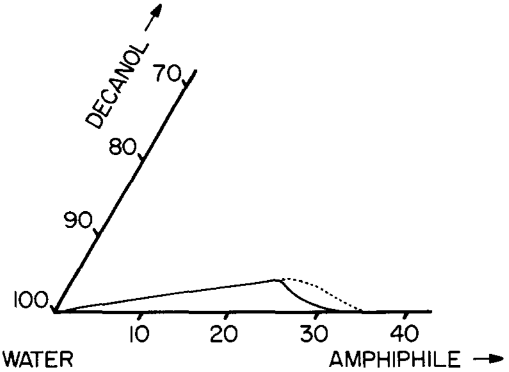

Fig. 2. Comparison of the aqueous micellar area when the amphiphile consists of pure SDS (——) or a CDS/SDS ratio of 0.225 (- - -) showed no difference at water content values greater than 75%.

while the transition to the liquid-crystalline phase at the limit of high surfactant content was delayed by approximately 2 percent.

An overview of the solubilization of the calcium dodecyl sulfate in the micellar solution and in the lamellar liquid crystalline phase is presented in Fig. 3. The water/sodium-dodecyl-sulfate ratio was held constant for each set of curves for both the micellar solution and the liquid crystalline phase. The trend of solubilization was the same for each of the three water/surfactant ratios investigated.

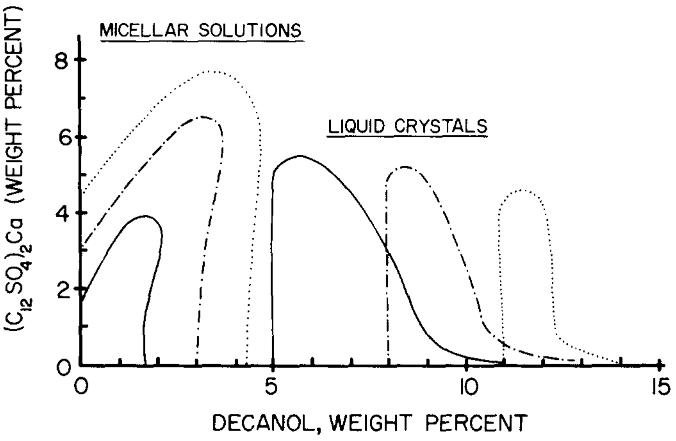

Fig. 3. The n-micelle and lamellar liquid-crystal region for SDS/water ratio of 0.083 (——), 0.183 (— · —) and 0.305 (- - -) shows that addition of CDS causes little change of the micelle region. However, addition of less than 0.5% of CDS drastically reduces the lamellar liquid-crystal region producing the "tailing off" effect.

The solubilization of the calcium surfactant in the micellar solution monotonically increased with the alcohol content almost to the solubility limit of the alcohol. Hence, in a small range at this solubility limit, the solubilization of the calcium compound was suddenly reduced to zero. The solubilization in the lamellar phase showed the opposite trend. It rose extremely fast to a maximum close to the lower limit of alcohol solubility but was reduced to zero at an alcohol content far below the stability limit of the liquid-crystalline phase without the calcium soap. The mode of reduction depended on the sodium-surfactant/water ratio. The higher this ratio, the more sudden was the reduction and the more narrow the range of stability of the lamellar structure. Hence, the solubilization of the calcium compound was limited to the part of the liquid crystal with low alcohol content. The solubilization was found only at modest soap concentrations. At the lower limit of surfactant concentration for the liquid-crystalline phase with the hexagonal structure (Fig. 1) to form no significant solubilization was found in the lamellar phase.

A change of pH to higher values by adding NaOH give only insignificant changes, Fig. 4.

The interlayer spacings were determined in detail for the sodium-dodecyl-sulfate/water ratio of 0.183 (Fig. 5) and for one alcohol content for the higher sodium-dodecyl-sulfate content, Fig. 6. All the spacings are characterized by an initially steep reduction of the values. Approximately constant numbers were found for calcium-dodecyl-sulfate content in excess of one percent. For the higher soap content, an increase was actually found (Fig. 6).

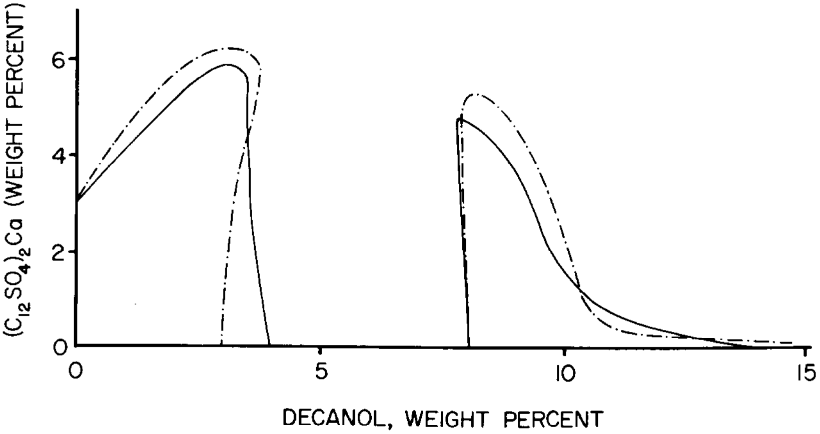

Fig. 4. Example of the effect of pH on the n-micelle and lamellar liquid-crystal region. The SDS/water ratio of 0.183 with pH 6.8 (— · —) compared to SDS/water ratio of 0.200 with pH 10.5 (——).

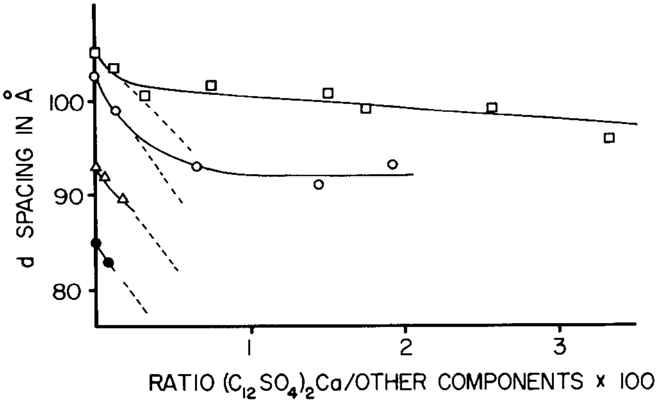

Fig. 5. Low-angle X-ray diffraction results for the ratio SDS/water = 0.183 containing varying percentages of decanol. The 12 and 14% decanol concentrations represent samples in the "tailing off" portion of the lamellar liquid-crystal region (Fig. 3). (□) 8.5% decanol; (○) 9.5% decanol; (△) 12.0% decanol; (●) 14.0% decanol.

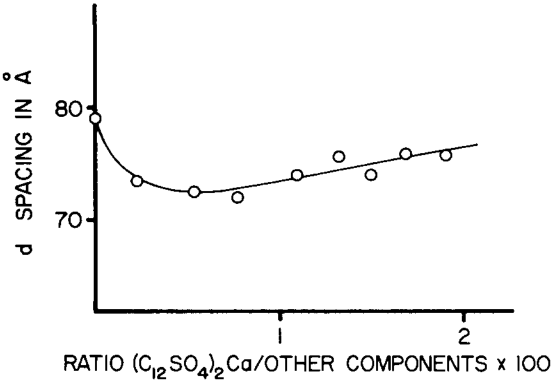

Fig. 6. Low-angle X-ray diffraction results for the ratio SDS/water = 0.305 with 12% decanol content demonstrates the sudden decrease in *d* spacing with the addition of CDS, followed by a gradual increase in the interlayer spacing.

DISCUSSION

The present results should be compared mainly with those by Kahn et al. [16], and Somasundaran and co-workers [11—13]. Kahn et al. could explain the difference from the behavior of sodium soaps as resulting mainly from a compression of the electric double layer. Such a compression well explained the insufficient stability at high water content; the large interlayer spacings would leave the repulsion potential from overlapping electric double layers inoperable.

Kahn's octyl compounds enjoyed a sufficiently low value of the Krafft point to be water soluble at room temperature while Somasundaran's dodecyl compounds were virtually water insoluble and subject to common solubilization in normal micelles in an aqueous solution.

Our present results are with the dodecyl compounds and the results in the aqueous solution are similar to Somasundaran's. In addition, our results of the micellar solubilization show several features that merit a closer examination.

The first feature is the increase of solubilization with the alcohol content (Fig. 3). The increase was approximately proportional to the amount of alcohol. This enhanced tolerance for the calcium soap with the alcohol content may be ascribed to electric double-layer effects or primarily to geometric-packing conditions according to Mitchell and Ninham [17]. A firm decision about the cause cannot be made without complementary information but the latter factor appears more probable against the form of the solubility curves (Fig. 3). The phase transition from the aqueous micellar solution to the lamellar liquid-crystalline phase was to a first approximation independent of the calcium-soap content indicating the influence of the latter on the interfacial properties to be without significance.

The solubilization in liquid-crystalline phase revealed two distinct features which rule out changes in the electric double layer as the sole factor for the stability. In contrast to the results of Kahn et al. [16] who found stability for the calcium-soap/alcohol lamellar liquid crystal at low water content only, the stability of the liquid crystal containing calcium dodecyl sulfate was found at high water content only. Figure 7 shows the solubilization from the present investigation contrasted to the solubility area of Kahn et al. [16]. Significant solubilization of the insoluble calcium soap took place only at low alcohol content and at high amounts of water as demonstrated by the black areas. A decisive influence by the electric double layer on the stability would require the opposite pattern as found in contribution of Kahn et al. [16]. In their system, the liquid-crystalline phase was found in the low-water-content area of the liquid-crystalline phase as expected.

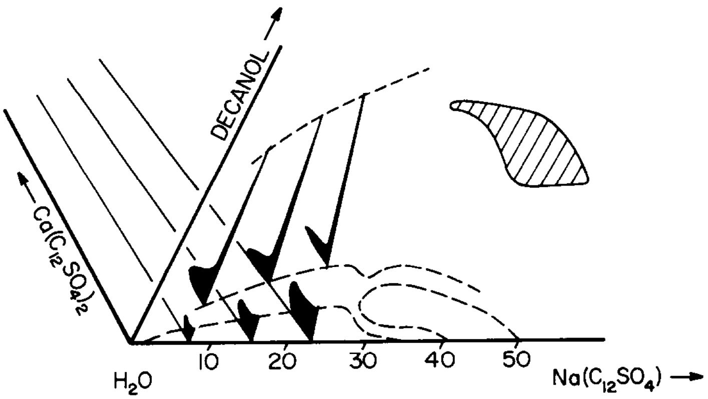

Fig. 7. Three dimensional representation of the four component system SDS/CDS/decanol/water. The blackened areas correspond to the regions diagramed in Fig. 3, while the dashed lines represent the base diagram determined by Ekwall (Fig. 1). The shaded region is the low water content lamellar phase discussed by Kahn et al. [16] for the calcium-octyl-sulfate/decanol/water system.

The solubilization also critically depended on the alcohol/soap ratio; and this pronounced dependence on the alcohol content of the solubilization in the lamellar phase does not appear to lend itself to a correspondingly direct explanation based on the extension of the electric double layer. Studies of counter-ion binding in similar systems [18] have shown no pronounced dependence on the alcohol content.

The X-ray determinations display a strong reduction of the interlayer spacing with the initial addition of the calcium dodecyl sulfate according to Figs 5 and 6. This would conveniently be interpreted as a consequence of a reduction in the repulsion potential from the electric double layer due to its compression caused by the presence of the calcium ions.

This explanation, however tempting, is obviously not sufficient to explain the drastic dependence of the solubilization on the alcohol content according to Figs 3 and 4. The initial reduction of the distance with increased calcium-dodecyl-sulfate content (Fig. 5) was identical in the high alcohol range of extremely limited solubilization and in the low alcohol range with pronounced solubilization. These results appear difficult to conform with a pure electric double-layer compression effect on the stability.

An alternate, but related, explanation focussing on the zeroth order geometrical structure determining ratio by Mitchell and Ninham [17] is also accompanied by serious reservations. The cross-sectional area of the calcium surfactant cannot be expected to be much different from the corresponding values for the sodium soap. Kahn et al. [16] found only insignificant differences between calcium- and sodium-octyl compounds and the cross-sectional area of calcium-dodecyl-sulfate in the present investigation was similar to the value for the sodium soap.

The reduction of interlayer spacing in Fig. 6 reached a maximum value of 10% which would mean a corresponding increase of the cross-sectional area. This increase is obviously accepted by the system while a less than 5% change for the system with 12% decanol (Fig. 5) and even less change for the compositions with 14% decanol initially led to destabilization (Fig. 5). Since alcohol has a smaller cross-sectional area than the soap, purely geometrical considerations should lead to the opposite result; addition of calcium soap should stabilize the structure against addition of alcohol.

The explanation of the stability reduction must be tentative in lieu of further experimental evidence. A possible basis for the instability with high alcohol content may be found in a difference in hydration of the calcium surfactant from the sodium one. The addition of alcohol to a lamellar phase leads to a one-dimensional swelling, e.g., reduced penetration of water between the molecules of the layer. Hence, the presence of a calcium surfactant with its water of hydration may prevent the alcohol from being solubilized. Another possibility is the precipitation of an alcohol/calcium-surfactant mixture, which in principle, corresponds to an increase in the Krafft point of the soap. The acid soaps and alcohol soap crystalline compounds are well known [19,20] as are the corresponding cationic compounds [21]. However, the excess phase, when the calcium soap was added to more than the limit of stability was the pure alcohol. This fact obviously invalidates the latter mechanism as an explanation. In lieu of further results, we would suggest the former mechanism as an explanation being well aware of its tentative nature.

REFERENCES

1 P. Ekwall, Adv. Liq. Cryst., 1 (1975) 1.
2 H. Wernerstrom and B. Lindman, Phys. Rep., 52 (1979) 1.

3 G.J.T. Tiddy, Phys. Rep., 57 (1980) 1.
4 E.D. Goddard, Adv. Chem. Ser., 144 (1975) 67.
5 M. Hato and K. Shinoda, J. Phys. Chem., 77 (1973) 378.
6 M. Hato and K. Shinoda, Bull. Chem. Soc. Jpn., 46 (1973) 3889.
7 K. Shinoda and T. Hirai, J. Phys. Chem., 81 (1977) 1842.
8 D.E. Clarke, R.S. Lee and I.D. Robb, Faraday Discuss. Chem. Soc., 61 (1976) 165.
9 R.S. Lee and I.D. Robb, J. Chem. Soc. Faraday Trans. 1, 75 (1979) 2116.
10 R.S. Lee and I.D. Robb, J. Chem. Soc. Faraday Trans. 1, 75 (1979) 2126.
11 P. Somasundaran, P. Celik and A. Goyal, in D.O. Shah (Ed.), Surface Phenomena in Enhanced Oil Recovery, Plenum, New York, NY, 1981.
12 M.S. Celik, E.D. Manev and P. Somasundaran, AIChE Symp. Ser. 79 (1982) 86.
13 E.D. Manev, M.S. Celik, K.P. Ananthapadmanabhan and P. Somasundaran, Soc. Pet. Eng., Reprint 10598.
14 J.M. Corkill and J.F. Goodman, Trans. Faraday Soc., 56 (1962) 206.
15 J.M. Peacock and E. Matijević, J. Colloid Interface Sci., 77 (1980) 548.
16 A. Kahn, K. Fontell, G. Lindblom and B. Lindman, J. Phys. Chem., 86 (1982) 4266.
17 D.J. Mitchell and B.W. Ninham, J. Chem. Soc. Faraday Trans. 2, 77 (1981) 601.
18 G. Lindblom, B. Lindman and G.J.T. Tiddy, J. Am. Chem. Soc., 100 (1978) 2299.
19 P. Ekwall, Z. Anorg. Allg. Chem., 210 (1933) 337.
20 P. Ekwall, Kolloid Z., 80 (1937) 77.
21 H.C. Kung and E.D. Goddard, in Th. Overbeek (Ed.), Proc. 14th Int. Congr. Surf. Act., Brussel, 1964, Elsevier, Amsterdam, p. 751.