Studies on the Interaction of Paraffin Chain Alcohols and Association Colloids. I. The Solubility of Decanol-1 in Sodium Oleate and Sodium Myristyl Sulphate Solutions above the Critical Micelle Concentration

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In 1947 Harkins [1,2] suggested the term "penetration" to define the process by which polar-nonpolar compounds such as paraffin chain alcohols and amines are brought into aqueous solution by association colloids. The term was introduced to differentiate this process from the process of hydrocarbon solubilization. From X-ray studies Harkins concluded that the molecules of polar-nonpolar compounds are built into the micelles in a different way than nonpolar hydrocarbon molecules; whereas the latter enter into the lipophilic inner region of the micelles between the palisade layers, the former penetrate between the ions in the palisade layer and with their polar groups in direction of the surface of the micelle. The studies later conducted by Klevens [3,4] have confirmed that different regions of the micelle are involved in the hydrocarbon solubilization and in the penetration of polar-nonpolar compounds and hence these are two different processes. Ekwall and co-workers [5-7] have further pointed out that the solubilization of hydrocarbons and polar-nonpolar substances differ from each other in many respects.

The different behaviour of polar-nonpolar compounds is due to the operation of a new factor not involved in the solubilization of hydrocarbons, namely the interaction between the hydrophilic dipole end groups of the polar-nonpolar molecules and the water dipoles on one hand and between former and the ionic groups of the colloid on the other. As Ekwall and Danielsson have shown [6,7] this interaction occurs at very low association colloid concentrations, at the so-called limiting association concentration of the colloid, L.A.C., which is much below the critical micelle concentration, C.M.C. Owing to this interaction the properties of the colloid solutions are altered in many respects. Frequently it happens that the interaction leads to the precipitation of a complex substance composed of polar-nonpolar compound, association colloid and water.

The penetration process has been the subject of numerous studies during the last six years, but despite this it is still incompletely understood in several respects.

We have therefore considered it desirable to undertake a detailed study of the penetration process in its most typical form, as it appears when long paraffin chain alcohols are dissolved in aqueous solutions of ionic association colloids of the paraffin chain type. The experiments were conducted mainly with decanol-1 and the association colloids used were fatty acid soaps and monoalkyl sulphates. In the following we will describe the results of quantitative determinations of the solubility of decanol-1 in sodium oleate and sodium myristyl sulphate solutions above their critical micelle concentrations.

EXPERIMENTAL

The decanol-1 (Light & Co) used was purified by repeated recrystallization.

Sodium oleate was prepared in the usual manner by neutralizing purest oleic acid (British Drug Houses Ltd.) with sodium ethylate in absolute ethanol.

Sodium myristyl sulphate was prepared from Duponol M E (E. J. du Pont de Nemours & Co, Inc.) by repeated extraction with and recrystallization from absolute ethanol. Analyses and molecular weight determinations indicated that the substance contained small amounts of homologous compounds.

The aqueous colloid solutions were prepared by weighing both the colloid and the water (specific conductance $\varkappa = 1.0 \cdot 10^{-6}$ mho).

The solubility of decanol in the soap solutions was determined by the turbidity method. Equal amounts of the same soap solution were transferred to ampoules, and different amounts of decanol were introduced into the ampoules with an Agla micrometer syringe. The ampoules were then sealed and shaken $2-4$ days at 40° C. During this period the solutions either dissolved the decanol or became saturated with the alcohol or its complex with soap. When the alcohol added was in excess of the amount required for saturation, the solutions remained turbid. The turbidities were measured with a Pulfrich Step Photometer.

Comparative experiments were conducted to determine whether the shaking time and the method of preparation of the solutions affected the solubility values. Oleate solutions of different concentrations containing decanol were prepared in three different ways: method 1, as described above; method 2, by warming several minutes at 90° C on a water bath and then shaking at 40° C; method 3, by warming to 90° C, allowing to stand two days at 20° C, and then shaking at 40° C. In some cases the period of shaking at 40° C was prolonged to 30 days during which the turbidity was measured several times. The length of shaking period was not found to be of any significance with method 1. In the case of the other two methods, somewhat greater deviations were observed in some cases and the character of the turbidity underwent slight changes with time; however the turbidity values agreed fairly well with those obtained using method 1. It was established that the solubility values determined by the turbidity method used in this study did not deviate more than $\pm$ 0.2 ml decanol per liter.

RESULTS

There is a limit to the amount of decanol-1 that is dissolved by association colloid solutions. When the alcohol is added in excess of this amount, the solution becomes turbid. The substance causing the turbidity is composed of decanol, association colloid and water [8]. The amount of decanol dissolving in the solution before turbidity appears is dependent on the soap concentration of the solution. Tables 1 and 2 give the maximum amounts of decanol that

Table 1. *The maximum amounts of decanol dissolved by sodium oleate before the solutions become turbid.*

Moles oleate per 1 000 g solution	Millilitres decanol per 1 000 g solution
0.00500	0.1
0.00997	0.2
0.0200	0.5
0.0300	1.2
0.0395	1.5
0.0500	1.9
0.0638	2.4
0.0782	3.3
0.101	4.2
0.111	4.5
0.125	5.2
0.144	6.3
0.171	7.8
0.198	9.0
0.215	9.9
0.224	10.3
0.233	10.9
0.241	11.2
0.250	11.6
0.267	12.2
0.275	12.4
0.279	13.0
0.300	13.5
0.304	13.7
0.308	13.7
0.329	14.9
0.357	15.7
0.387	16.8
0.412	17.5
0.434	17.9

Table 2. *The maximum amounts of decanol dissolved by sodium myristyl sulphate before the solutions become turbid.*

Moles myristyl sulphate per 1 000 g solution	Millilitres decanol per 1 000 g solution
0.00999	0 65
0.0300	2.5
0.0700	5.7
0.0902	7.1
0.109	8.2
0.130	10.4
0.150	11.8
0.170	13.6
0.190	15.0
0.210	17.2
0.230	18.6
0.260	21.3
0.288	23.7
0.310	25.3
0.347	28.1
0.401	31.8
0.495	37.7
0.593	43.5

are dissolved by sodium oleate and sodium myristyl sulphate solutions before the solutions become turbid (referred to as the solubility in the following).

Fig. 1 illustrates the concentration dependence of the solubility of decanol in the oleate and myristyl sulphate solutions. Up to oleate concentrations of about 0.12 M, the solubility of decanol increases linearly with the oleate concentration. Above this concentration the increase appears to be somewhat more rapid but above 0.25 M it diminishes perceptibly. The points marked with a cross refer to experiments in which the solutions were prepared in a different manner than usual (warmed, cooled, longer shaking period). It is seen that these values have not been greatly affected by the difference in treatment. In the myristyl sulphate solutions the solubility increases linearly up to a myristyl sulphate concentration of about 0.18 M after which the slope of the curves increases at first and then clearly begins to decrease when the concentration exceeds 0.3 M.

The dotted lines for both substances indicate, how the solubility should increase with the association colloid concentration if the relation continued to
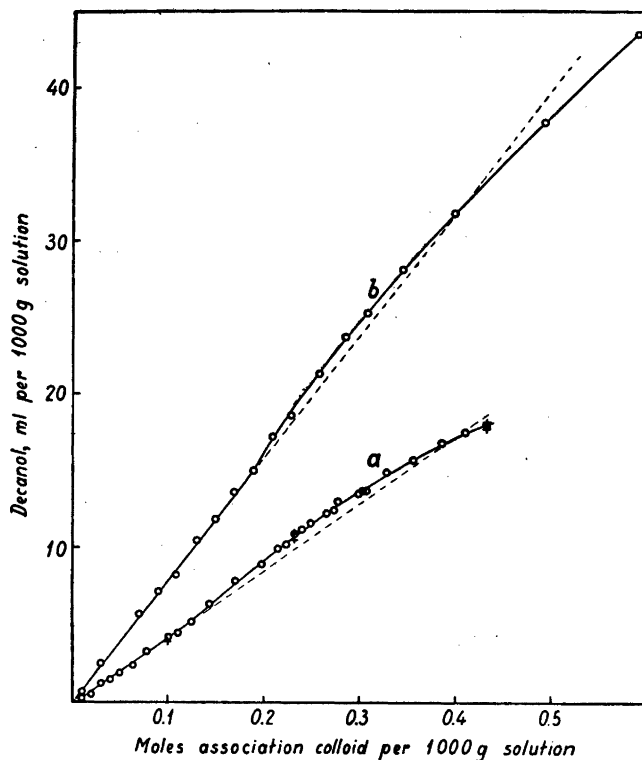
Fig. 1. The maximum amounts of decanol dissolved before the solutions become turbid.
  a) Sodium oleate solutions
  b) Sodium myristyl sulphate solutions

be linear as at the low concentrations. The deviations from linearity are greater than the relatively wide error limits of the method, ± 0.2 ml decanol per liter, and must hence be considered significant.

<div style="text-align:center">DISCUSSION</div>

According to the measurements of Harkins and his co-workers [2] the curves representing the solubility of heptanol-1 in potassium dodecanoate and potassium tetradecanoate solutions are concave toward the colloid concentration axis, whereas the corresponding solubility curves for decanol-1 and dodecanol-1 are slightly convex towards the same axis. Klevens [4] is also of the opinion that the solubility curve for heptanol-1 is concave, but he states that the curves for alcohols with ten or more carbon atoms appear to be linear.

As was shown above, our measurements have given a somewhat different result; the solubility curves for decanol are linear above the C.M.C. up to relatively high concentrations of the association colloid, after which it tends to rise slightly and then curves downwards at still higher concentrations.

Table 3. Composition of the mixed micelles when the solutions become turbid; the proportion of decanol in moles per mole micellar soap.

Association Colloid.	Concentration range	Maximum proportion of decanol in moles decanol per mole micellar soap
Sodium oleate	0.005 — 0.12 M 0.15 M 0.4 M	0.23 0.30 0.14
Sodium myristyl sulphate	0.005 — 0.18 M 0.22 M 0.5 M	0.41 0.50 0.30

It may be mentioned in this connection that the solubility of decanol in solutions of several other paraffin chain soaps also increases linearly with the soap concentration above their C.M.C., *i.e.* within the small micelle range.[8]

When hydrocarbons and many other substances are solubilized, the excess separates in the pure state. From the slopes of the solubility curves it is in such cases possible to calculate the saturation capacity of the micellar substance for the solubilized substance. The turbidity which is observed in oleate and myristyl sulphate solutions when decanol is added in excess is not, however, due to pure decanol, but is due to a mixture of decanol, association colloid and water [5,7,8]; with increasing excess of decanol, a part of the colloid is precipitated.

The solubility curves shown in Fig. 1 are hence not directly comparable with those obtained in the study of hydrocarbon solubilization. Owing to the penetration there are formed mixed micelles; the surfaces of the micelles become less hydrophilic when more decanol molecules are built into the micelles, and the solubility of the micelles decreases. It seems most probable that the solutions become turbid, when these mixed micelles begin to separate. Our solubility determinations thus give the maximum amount of decanol which the micelles are able to take up before this separation begins. From the slopes of the curves the composition of this mixed micelle substance can be estimated. In Fig. 2 it is shown how the decanol content of the mixed micelles, expressed in moles of decanol per mole of micellar oleate and micellar myristyl sulphate, varies with the association colloid concentration. Their decanol content remains constant up to a association colloid concentration of 0.12—0.18 M, after which it tends to increase to a slightly higher value, but falls off rapidly with further increase in the colloid concentration. Data taken from these curves are given in Table 3.

It is known that the solubilization power for hydrocarbons increases with the chain length of the association colloid [4,5]. One of us has previously shown that the saturation capacity of sodium oleate for *p*-xylene is 40 per cent higher than the saturation capacity of myristyl sulphate for the same hydrocarbon [5].

The opinion prevailing in the literature seems to be that the ability to dissolve alcohols increases with the chain length of the colloid [4,9]. This is not
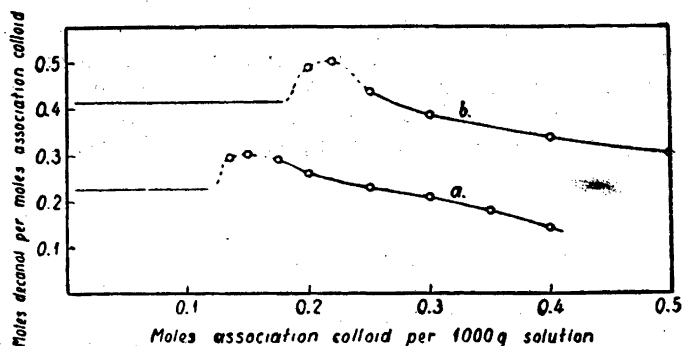
Fig. 2. The decanol content per mole association colloid of the mixed micelles.

a) Sodium oleate solutions
b) Sodium myristyl sulphate solutions

correct, at least not in all cases, as shown by the results of the present study. The ability of myristyl sulphate to dissolve decanol is about 80 % higher than that of oleate although the latter has the longer chain length. This must be attributed primarily to the different ionic end groups in the two colloids. The sulphate group is more hydrophilic than a carboxyl group, and the incorporation of decanol in the palisade layer has evidently a greater influence on the hydrophilic properties of the micelle surface in the case of the latter end group. This is confirmed by the fact that the solubilization power of sodium myristate for decanol is less than that of sodium myristyl sulphate [8].

In this connection it may be mentioned that unpublished measurements carried out in this laboratory [8] show that the "solubilization" of decanol by sodium myristate, sodium laurate and sodium caprinate solutions above their C.M.C. (in the small micelle range) increases in the order mentioned and is greater for all three soaps than the "solubilization" by oleate. This proves that the solubility of decanol increases with decreasing chain length when the ionic group is the same and indicates that the solubility of the alcohol-containing mixed micelles increases when the ratio of the total number of hydrophobic CH_2-groups to the number of hydrophilic groups in the micelle decreases.

The fact that the upper limit for the composition of the soluble decanol-association colloid micelles expressed in moles of decanol per mole of soap is constant over an extended concentration range above the C.M.C. shows that the micellar substance has constant properties in this concentration range. This latter range is the region where the small micelles occur. It is interesting to note that deviations first become evident in oleate solutions above 0.12 —0.25 M and in myristyl sulphate solutions above 0.18—0.3 M. (See Figs. 1 and 2.) At these points the ability of the micelles to incorporate decanol without precipitions begins to decrease. It may be noted that also other properties of the micellar substance undergo change at the same concentrations; the saturation capacity for hydrocarbons (p-xylene), which remains constant over the small micelle range, begins to increase when the corresponding oleate and myristyl sulphate concentrations, about 0.2 M, are exceeded [6,10,11].

Our studies on the solubilization of decanol indicate that the properties of oleate and myristyl sulphate solutions undergo pronounced alterations in the concentration ranges referred to. Whether these concentration limits, which undoubtely are real, indicate the occurrence of a new step in micelle formation or requires another explanation, will be considered in a later paper.

SUMMARY

The maximum amounts of decanol-1 that are solubilized by sodium oleate and sodium myristyl sulphate solutions of various concentrations before turbidity occurs have been determined. In the small micelle range of both association colloids the decanol solubility increases linearly with the soap concentration, but in the concentration range 0.12—0.18 M the solubility curves reveal a tendency to rise more rapidly. At still higher concentrations the curves become concave toward the soap concentration axis. The deviations from linearity occur at approximately the same concentration regions at which earlier studies have shown the properties of oleate and myristyl sulphate solutions to undergo marked changes.

The solubilities of decanol and other paraffin chain alcohols in aqueous solutions of association colloids of the paraffin chain type can not be directly compared with the solubilities of hydrocarbons in these solutions. In the latter case the excess substance separates from the solution in the pure state, whereas when the alcohol is solubilized, a substance composed of alcohol, association colloid and water separates. It seems probable that the latter substance is a mixed micelle substance which is formed by the incorporation of alcohol in the palisade layer of the micelle as a result of which the surface of the micelle becomes less hydrophilic. The measurements show that the solubility of decanol is greater when the ionic end group is a sulphate group than when it is a carboxyl group and increases with decreasing length of the paraffin chain of the association colloid.

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