Studies on the Interaction of Paraffin Chain Alcohols and Association Colloids

III. The Effect of Decanol-1 on the Conductance of Sodium Alkyl Sulphate Solutions

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The effect of decanol on the conductance of sodium myristyl sulphate and sodium lauryl sulphate solutions has been measured. With respect to the amount of decanol added, three ranges can be distinguished in which the effect on the conductance differs. When small amounts of decanol are added that dissolve completely, the conductance is very little altered. When more decanol is added a new phase is formed and the conductance of the system decreases rapidly at first but then less rapidly. The new phase formed is composed of decanol, alkyl sulphate and water. Finally further additions of decanol no longer alter the conductance; in this range drops of free decanol are observed. The composition of the separated decanol-myristyl sulphate-water phase has been estimated from the courses of the conductance curves. The decanol content of this phase decreases with the myristyl sulphate concentration in the more dilute solutions, but remains constant at higher colloid concentrations. Above the C.M.C., the interaction between decanol and association colloid has a different effect on the conductance in different colloid concentration ranges; with respect to the colloid concentration, three ranges can be distinguished. These data are compared with corresponding data previously obtained for fatty acid soap solutions and are discussed in the light of other properties of association colloid solutions.

In Part II of this series [1] we described the effect of decanol on the conductance of solutions of sodium oleate and sodium laurate. We have now studied the effect of decanol on the conductance of the solutions of sodium myristyl sulphate and sodium lauryl sulphate with the purpose of determining whether this effect varies with the type of association colloid.

MATERIALS AND METHODS

The sample of sodium myristyl sulphate was the same as that used in Part I of this series [2]. The sample of sodium lauryl sulphate was prepared from Duponol P E (E. J. du Pont de Nemours & Co.) by repeated extraction with and recrystallization from absolute ethanol. The sample of p-xylene was a product of the Eastman Kodak Co., Rochester.

The water employed in the preparation of the solutions had a specific conductance of $0.6 - 1.0 \times 10^{-6}$ reciprocal ohms. The solutions were prepared in ampoules as described in Part I and the conductance was measured in the manner described in Part II.

In the following, the concentrations of the association colloid solutions are given in moles of colloid per 1 000 g of solution (M).

SODIUM MYRISTYL SULPHATE SOLUTIONS CONTAINING DECANOL

The properties of sodium myristyl sulphate solutions are modified similarly as those of oleate solutions when decanol is added to them. In myristyl sulphate solutions in the small micelle range, decanol dissolves forming clear solutions until the decanol content rises to 0.41 mole of decanol per mole of myristyl sulphate [2]. When decanol is added in excess of this ratio, the solutions become turbid (curve a, Fig. 1). The degree of turbidity increases with further addition of decanol to a maximum value (this increase in turbidity is considerably greater than in the oleate solutions) and then decreases at the same time as the solutions become more and more viscid; finally an almost transparent gel is produced, the opacity of which remains practically unchanged on further addition of decanol.

The effect of decanol on the conductance has been studied in detail only in the 0.1—0.3 M sodium myristyl sulphate range. In addition, conductances
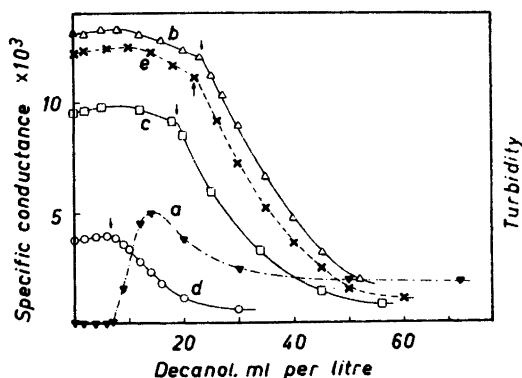

Fig. 1. a) Turbidity curve for a 0.100 M sodium myristyl sulphate solution containing decanol. 40° C.

Specific conductances of sodium myristyl sulphate solutions containing decanol. 40° C.
          b) 0.300 M sodium myristyl sulphate
          c) 0.232 M   »   »   »
          d) 0.100 M   »   »   »
e) Specific conductance of 0.300 M sodium lauryl sulphate solution containing decanol. 40° C.

have been measured for myristyl sulphate solutions (of lower and higher concentration) in a narrow region around the point where the solutions become turbid because of the separation of a new phase on adding decanol. The conductance curves in Fig. 1 (b, c and d) show that small additions of decanol bring about small increases in the conductance of myristyl sulphate solutions, but when the myristyl sulphate concentration exceeds $0.2 M$, further additions effect a reduction in the conductance. Above the point where the systems become heterogeneous, the variation of the conductance is fully analogous to that found for the oleate solutions. With increasing decanol content, the conductance falls rapidly at first, then more slowly until finally a point is attained where further addition of decanol alters the conductance of the solution relatively little. In this region drops of free decanol begin to separate, and if the myristyl sulphate concentration is high, the systems have a gel-like consistency.

As far as one can judge from the relatively meagre experimental data, it seems that there exists an appreciable difference between the decanol-oleate system and this system with respect to the variation of the effect of decanol on the conductance with the concentration of association colloid (Fig. 2, curves a and b). Up to a colloid concentration of about 0.2 M, the conductance of the myristyl sulphate solutions containing decanol at the turbidity point (curve b) is higher than the conductance of the pure solutions (curve a); only for higher colloid concentrations is the reverse true. Curve c shows on a larger scale how these changes of the conductance vary with the initial myristyl sulphate concentration. Curve d in Fig. 2 shows how the conductance varies with the myristyl sulphate concentration in the presence of large amounts
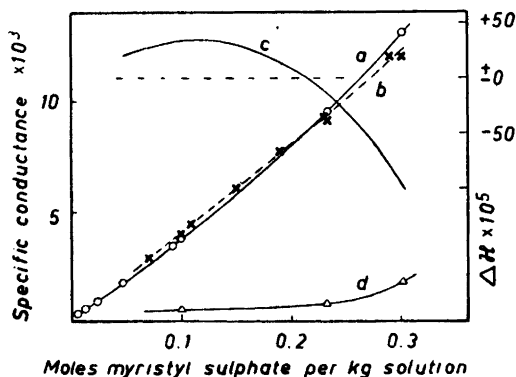

Fig. 2. a) Specific conductances of pure sodium myristyl sulphate solutions.

b) Specific conductances of myristyl sulphate solutions containing decanol at turbidity points.

c) The lowering of the conductance, $\Delta\varkappa$ ($= \varkappa$ at turbidity point minus $\varkappa$ of pure solution).

d) The final conductances of sodium myristyl sulphate solutions containing decanol.
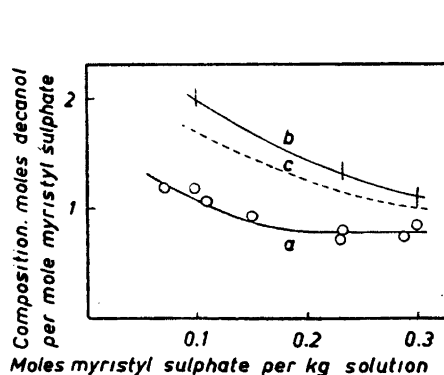
Fig. 3. The composition of the phase separating from sodium myristyl sulphate solutions containing decanol.

a) At the turbidity point.
b) The final composition.
c) The total composition of the whole system in the range where the conductance remains constant.

of decanol, *i. e.* in the range where the conductance is no longer altered by addition of decanol. This curve is similar to the corresponding curve for the decanol-oleate system.

On the basis of the available data, it appears that the composition of the separated phase varies with the myristyl sulphate concentration in a similar manner as in the decanol-oleate system (Fig. 3). In the concentration range 0.18—0.3 *M*, the phase that separates immediately above the turbidity point (curve a) contains 0.8 mole of decanol per mole of myristyl sulphate; with decreasing myristyl sulphate concentration, the ratio increases slowly to approximately 1.2 mole of decanol per moles of myristyl sulphate in the 0.07 *M* solution. The final composition attained by the separating phase when larger amounts of decanol are added (*i. e.* in the range where the conductance is no longer altered by addition of decanol) is about 1 mole of decanol per mole of myristyl sulphate in the 0.3 *M* solution and increases to about 1.5 moles per mole in the 0.2 *M* solution and to about 2 moles per mole in the 0.1 *M* solution (curve b, Fig. 3). Curve c gives the total composition of the whole system in the region where the conductance remains practically constant; it thus gives a lower limit for the final composition of the separated phase at each colloid concentration.

SODIUM LAURYL SULPHATE SOLUTIONS CONTAINING DECANOL

The effect of decanol on the conductance of a 0.3 *M* solution of sodium lauryl sulphate (curve e, Fig. 1) has also been studied. The conductance curve is similar in form to that found for the myristyl sulphate solution of the same concentration. It thus seems that a similar small increase in the conductance occurs in general within certain concentration ranges when small amounts of decanol are added to solutions of long-chain alkyl sulphates.

The maximum amount of decanol that can be incorporated in the micelles before a new phase separates is 0.38 mole per mole of lauryl sulphate (estimated from the conductance curve). Immediately above the turbidity point, the separated phase contains about 0.8 mole of decanol per mole of lauryl sulphate. The final composition of this phase seems to be about 1.0 mole of decanol per mole of lauryl sulphate.

DISCUSSION

The experimental data presented here and in Part II[1] show clearly that the effect of added alcohol on the conductance of association colloids differs greatly if the solution remains homogeneous owing to the complete solubilization of decanol in the micelles or if a new phase composed of decanol, association colloid and water or of free decanol is produced. When considering the properties of solutions containing paraffin-chain alcohols or other polar-nonpolar substances, it is hence necessary to take into account the state of the system and also the type and the degree of the interaction that takes place in the system.

Our experiments show that in the systems studied the conductance changes continuously and relatively slightly up to the point where it can be established

nephelometrically that the system becomes heterogeneous and where an abrupt decrease is noted in the conductance. Neither with the aid of a microscope with a phase contrast nor with a dark field condenser have we been able to observe any particles in the solutions below this point, whereas above it there exist not only larger particles but also a great number of very minute ultra-microscopic particles [3]. It is thus evident that below the point mentioned the system is really composed of only a single phase and that emulsified particles are not present in these solutions but only mixed micelles in thermodynamic equilibrium with the other components of the system. This is of interest as it is believed that in quaternary systems in some cases transparent emulsions are produced as a result of solubilization which are assumed to contain microscopic emulsified particles and which cannot easily be optically distinguished from solutions containing ordinary micelles [4].

As long as the system is homogeneous, the molecules of the long-chain alcohol are incorporated in the palisade layers of the micelles. If the number of the micelles remains constant, the weights and volumes of these mixed micelles must become larger than those of the original micelles; the increase in the volume is, however, to some extent counteracted by a denser packing caused by interaction between the hydroxyl groups of the alcohol molecules and the charged groups of the colloid ions [5,6]. These changes should effect a decrease in the conductance. Experiments have shown that decanol additions produce an increase in the viscosity of the solution [7,8]; this may also decrease the conductance. On the other hand, the charge density on the micelle surface becomes lower when alcohol is incorporated in the palisade layers; both this and possibly also the interaction between the hydroxyl groups and the charged groups, which may lead to the formation of hydrogen bonds, effect a decrease in the number of gegenions bound to the micelle surface. This must lead to an increase in the conductance. Probably even other factors resulting from the solubilization of the alcohol, such as changes in the form of the micelle and in the number of soap ions per micelle, can influence the conductance.

For the present, it is not possible to calculate theoretically to what extent these various factors affect the conductance. Some elementary calculations made on the basis of Stokes' formula show that the lowering of the conductance that can be ascribed to the increase in volume of the micelles due to solubilized decanol must be small if the form and the number of the micelles and the percentage of the gegenions bound to the micelle surface remain the same in colloid solutions containing decanol as in the pure colloid solutions. In the case of oleate solutions this calculated lowering of the conductance seems to be much smaller than the experimentally observed lowering.

In this connection it is of interest to compare the effects of decanol and a hydrocarbon on the conductance. Fig. 4 (curves a, b and c) shows that the conductance of sodium oleate solutions undergoes a slow decrease when p-xylene is solubilized. When the solutions become saturated with xylene further additions of it alter the conductance only very little (the points where saturation occurs are marked by arrows in Fig. 4). This indicates that the separating phase (xylene) contains practically no oleate. The ordinates for the curves d and e in Fig. 4 give the ratio of the conductances of oleate solutions containing xylene and decanol, respectively, to those of pure oleate solutions.
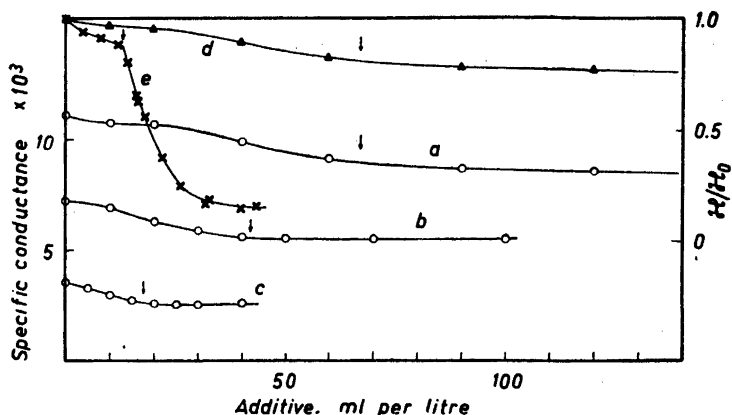
Fig. 4. Specific conductances of sodium oleate solutions containing p-xylene. 40° C.

a) 0.300 M sodium oleate
b) 0.199 M » »
c) 0.100 M » »

The ratio of the specific conductances of sodium oleate solutions containing additive to the specific conductance of the pure oleate solution, $\varkappa/\varkappa_0$.

d) 0.300 M oleate + p-xylene
e) 0.275 M oleate + decanol.

It is immediately seen that decanol has a greater effect on the conductance than the same volume of xylene, even in the range where the additives are solubilized in the micelles. (The same result is obtained if the amount of solubilized substance is expressed in grams per litre, of solution or in moles per mole of oleate.) This seems to show that the increase in the volume of the micelles has only a small effect on the conductance. Calculations made on the basis of Stokes' formula show that as long as only small amounts of xylene are solubilized the calculated and experimental values of conductance are nearly equal, but that when the amount of xylene increases, the calculated values are considerably greater than the observed conductances. It therefore seems probable that the relatively small decrease in the conductance caused by small amounts of solubilized xylene is due to the increase in volume of the micelles, whereas the greater lowering of the conductance effected by decanol and by larger amounts of xylene suggests that changes also occur in the form and number of the micelles.

The effect of the liberation of the gegenions bound to the micelle surface must be considerable. If we suppose that all sodium ions initially bound by the micelles (about 50 %) would be liberated when decanol is solubilized, this would effect a large increase in the conductance. It is evidently this factor that dominates in alkyl sulphate solutions where small additions of decanol effect, as we have seen, a slight increase in conductance. In some cases the increase turns into a decrease before the turbidity point. This is presumably due to the fact that the decanol content of the micelles has become so high

that the effects that reduce the conductance begin to predominate. The recent observations of Heckmann [8], according to which addition of hexanol increases the conductance of sodium hexadecyl sulphate solutions, are evidently due to the same phenomenon. Further discussion of his results is rendered difficult by the fact that Heckmann gives no exact data on the hexanol content of the system when it becomes heterogeneous and on the composition of the separating phase.

The rapid decrease in conductance that we have observed in the case of fatty acid soap and alkyl sulphate solutions as soon as the systems become turbid owing to the separation of the decanol-association colloid-water phase is naturally due to the decrease in the colloid content of the aqueous solution. On the basis of the conductance values we have calculated that the greater part of the colloid in the aqueous solution is gradually transferred to the new phase. When further additions of decanol do not dissolve, the cause of the decrease in the conductance seems to disappear. Within the whole range above the turbidity point, the conductance changes continuously when decanol is added. No break point indicating a phase change in the emulsion is evident in the curve. This shows that even at fairly high decanol-colloid ratios, also in the gel-like systems, we are dealing with a two-phase system in which the aqueous solution is the continuous phase.

Of the four association colloids studied, only sodium laurate has been examined in concentrations below the C.M.C. The data confirm the earlier results [9] that decanol does not alter the conductance below the L.A.C. of the colloid; no interaction occurs between alcohol and soap in this range, and the excess alcohol separates in the free form [9, 10, 3]. Above the L.A.C., however, interaction is observed at all concentrations which leads to a decrease in the conductance. The amounts of decanol that are necessary to bring about the separation of a decanol-soap-water phase are very small between the L.A.C. and C.M.C.; in the vicinity of and above the C.M.C., this amount increases rapidly with increasing colloid concentration.

Above the C.M.C., the interaction between decanol and association colloid has a slightly different effect on the conductance in different concentration ranges. This is shown by the data given in Table 1, the main part of which applies to oleate solutions. Both with respect to the variation of the conductance of oleate solutions and to the composition of the separated phase as computed from the conductance values, two concentration ranges may be distinguished, one below 0.1—0.14 M and the other above the latter limit. The first range corresponds to that where according to our earlier measurements [2] the maximum content of decanol in the mixed micelles as calculated per mole of oleate remains constant; in the upper range this proportion increases, passes through a maximum, and then decreases. This latter range can be divided into two parts, a transition range between approximately 0.1 M and about 0.25 M where larger changes are noted, and a part above the latter limit where the observed changes are less pronounced. We should like to draw attention particularly to the fact that the different concentration ranges become clearly evident in the effect on the conductance due to solubilized decanol. This shows that the differences become evident already when relatively small amounts of decanol are incorporated in the micelles and may

Table 1. Concentration ranges in sodium oleate and sodium myristyl sulphate solutions.

Property	Sodium oleate solutions			Sodium myristyl sulphate solutions		
	Range 1	Range 2	Range 3	Range 1	Range 2	Range 3
Maximum decanol content of mixed micelles [2]	constant 0.01—0.12 M	passes through a maximum 0.12—0.20 M	decreases 0.20 $M \rightarrow$	constant 0.01—0.18 M	passes through a maximum 0.18—0.25 M	decreases 0.25 $M \rightarrow$
Slope of conductance *vs.* decanol content curve below the turbidity point	increases slowly 0.006—0.14 M	increases rapidly 0.14—0.22 M	remains relatively constant 0.22 $M \rightarrow$			
$\Delta\varkappa = \varkappa$ at turbidity point *minus* $\varkappa$ of pure solution	negative, increases slowly 0.006—0.14 M	negative, increases rapidly 0.14—0.27 M	negative, remains relatively constant 0.27 $M \rightarrow$	positive, $\rightarrow 0.22\ M$		negative, 0.22 $M \rightarrow$
Final conductance	increases 0.006—0.10 M	approximately constant 0.10—0.20 M	increases 0.20 $M \rightarrow$		approximately constant 0.1—0.23 M	increases 0.23 $M \rightarrow$
Decanol content of separated phase at turbidity point	decreases $\rightarrow 0.1\ M$	remains constant 0.1—0.4 M		decreases $\rightarrow 0.18\ M$	remains relatively constant 0.18 $M \rightarrow$	
Final decanol content of separated phase	decreases rapidly $\rightarrow 0.1\ M$	decreases slowly 0.1—0.4 M				

hence be attributed to differences in the original micelles in the different concentration ranges. The first concentration range coincides with the so-called small micelle range, where the properties of the micellar substance remain constant. In the upper range many of the properties differ from those in the first range; the new properties of these solutions occur at the so-called second critical concentration which lies in the above-mentioned transition range. Our results support the conception of the occurrence of a new step in micelle formation in the vicinity of this concentration limit.

Similar conclusions may be drawn in the case of myristyl sulphate solutions. In this case the following concentration ranges may be distinguished: the first below the approximately 0.18 M myristyl sulphate concentration and the second above the approximately 0.25 M concentration and a transition range between these two limits (about 0.18—0.25 M). Also in this case the first range coincides with the small micelle range and the transition range with the second critical concentration.

A comparison of the curves showing the effect of decanol on the conductance of solutions of the four association colloids studied reveals that the curves for the two fatty acid soaps, oleate and laurate, have completely similar courses (Part II, Figs. 2, 3, 6 and 7). The curves for the two alkyl sulphates, myristyl and lauryl sulphates, are also similar to each other (Fig. 1). Below the turbidity points, the curves for the fatty acid soaps are different from those for the alkyl sulphates but above the turbidity points the curves for the substances of these two classes have a very similar course.

Marked similarities are observed between the effects of decanol and fatty acids on the conductance of fatty acid soap solutions. This is especially the case when the acids are liquid and the reaction product, the acid soap, is liquid-crystalline. In very dilute soap solutions up to a certain limit, no change is effected by the addition; both the alcohol and the fatty acid are only emulsified. Above the concentration limit mentioned, the conductance decreases in both cases since interaction takes place that leads to the formation of a liquid-crystalline product containing soap, water and alcohol or fatty acid. This concentration limit is approximately the same in both cases; we have called it the limiting association concentration, L.A.C. Above the critical concentration increasing amounts of the polar-nonpolar substance dissolve in both cases in the solution with increasing soap concentration and are incorporated in the micelles until a point is reached where a liquid-crystalline phase begins to separate from the solution. When this separation begins, the conductance decreases abruptly. Addition of greater quantities of the polar-nonpolar substance lowers the conductance to a constant value. When the concentration of the soap solution is in the range between the L.A.C. and the C.M.C., the constant value is the same as that for the pure colloid solution at the L.A.C.; at higher soap concentrations the constant value attained is somewhat higher.

Also in respect of the composition of the separated liquid-crystalline phase, marked similarities are noted. The composition of the acid soaps has been found to vary from 0.5 mole to 2 moles of fatty acid per mole of soap. In the anisotropic decanol-soap phase, the decanol content varies from 0.5 mole to 2—3 moles per mole of soap. In both cases the separating phase also contains water.

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