Studies on the Interaction of Paraffin Chain Alcohols and Association Colloids

II. The Effect of Decanol-1 on the Conductance of Fatty Acid Soap Solutions *

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The effect of decanol on the conductance of sodium oleate and sodium laurate 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 decreases very little. 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, soap 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-oleate-water phase has been estimated from the courses of the conductance curves. The decanol content of this phase decreases with the oleate concentration in the more dilute solutions, but remains constant at higher oleate concentrations. Below the L.A.C. no interaction occurs between decanol and association colloid and the conductance of the solution is not altered by addition of decanol. 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.

Considerable data has been accumulated on the effect of polar-nonpolar substances on the conductance of solutions of association colloids. Most of these studies have been made with compounds where the polar part of the molecule has been a carboxyl or a hydroxyl group. The great similarity of the effects of these two classes of substances has not always been taken into account.

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The earliest investigations in this field are those of McBain and co-workers [1-4] and Ekwall [5-10], who studied the effect of an excess of fatty acid on the conductance of a soap solution. Their measurements showed that the conductance of the solution first diminishes rapidly with increasing excess of fatty acid up to a certain point above which the conductance remains practically constant. At the time the first of these experiments were conducted, attention was mainly paid to the amount of added fatty acid necessary to decrease the conductance to a minimum value in order to be able to determine the composition of the acid soap formed. Ekwall [5,6] also calculated the composition of the latter from the lowering of the conductance before this minimum value was reached. He established further that the fatty acid lowered the conductance both above and below the critical micelle concentration (C.M.C.) of the soap; the interaction between fatty acid and soap was, however, found to begin only after the soap concentration had attained a certain level which was later called the limiting concentration [5,8] (or limiting association concentration, L.A.C. [11]). Below this concentration no change in the conductance was effected by the fatty acid. The value to which the conductance decreased above the L.A.C. when a sufficient amount of fatty acid was added was approximately equal to the conductance of the pure soap solution at the L.A.C. (when the original soap concentration was not much higher than the C.M.C.). Also conductometric titrations of soap solutions with hydrochloric acid conducted by Ekwall [9,10] revealed an effect of excess fatty acid on the conductance which conforms with the above results.

Recently Flockhart and Graham [12] studied the effect of a fatty acid on a soap solution (oleic acid was added to oleate solutions) in a relatively narrow concentration range below and above the C.M.C. and observed that the fatty acid effected a decrease in the conductance. Similar results were obtained in a study of the effect of propionic acid on the conductance of dodecyl sulphate solutions by Flockhart and Ubbelohde [13].

The first observations on the effect of paraffin chain alcohols on the conductance of soap solutions seem to have been reported in 1947. Ekwall [14] found that a liquid-crystalline product separated from oleate solutions when octanol or hexadecanol was added to them and that this was accompanied by a fall in the conductance. Ralston and Eggenberger [15] measured the conductances of dodecylamine hydrochloride solutions saturated with hexanol, octanol, dodecanol or octadecanol. They established that these alcohols lowered the conductance over the whole colloid concentration range studied (i. e. in solution both above and below the C.M.C.) and further that the C.M.C. seemed to shift simultaneously to lower concentrations. All the systems were apparently heterogeneous, milklike, viscous liquids. Brown, Grieger and Kraus [16], in a study of the influence of dodecanol on the conductance of dodecylamine hydrochloride solutions, found that the curves plotting conductance against colloid concentration for solutions containing various mole ratios of long-chain alcohol to soap had two break points. When the soap concentration was less than that corresponding to the first break point, the conductance was not altered by dodecanol. Above the first break point, the conductance decreased when dodecanol was added. When the mole ratio of dodecanol to association colloid was low (0.044 and 0.111 moles of dodecanol per mole of colloid), the mixtures seem to have been homogeneous. At higher dodecanol concentrations (mole ratio 0.24—0.26), the solutions remained clear as long as the soap concentration was high, but became turbid when the solutions were diluted. At a still higher dodecanol content (0.65 mole of dodecanol per mole of colloid), the solutions were cloudy, yet stable, over the whole range of colloid concentration studied. In these investigations a 25.6 % methanol-water mixture was used as solvent. This fact renders it difficult to compare these results with measurements made on aqueous solutions. Ekwall and co-workers [11,17,18] found that decanol does not influence the conductance of association colloid solutions when the concentration of the latter is below the L.A.C., but lowers the conductance at and above this concentration. A recently published paper by Ekwall, Passinen and Danielsson [19] deals with the effect of decanol on the conductance of oleate solutions and a paper of Heckmann [20] describes the effect of hexanol and other alcohols on the conductance of hexadecyl sulphate solutions.

Many investigations have been carried out on the effect of shorter alcohols (C_1—C_4) on the conductances of various association colloids (Brown, Grieger and Kraus [16], Bose[21-24], Flockhart and Ubbelohde [13] and others) but they are of lesser interest in connection with the present study. Neither shall we consider the studies carried out on systems containing, in addition to association colloid, water and alcohol, also a hydrocarbon or a mixture of hydrocarbons [25-27].

Also the effect of straight-chain glycols has been investigated by Ekwall and co-workers [18],[19] who found that 1,10-decanediol has a negligible effect on the conductance of caprate, laurate, myristate and oleate solutions when the colloid concentration is below the L.A.C., but lowers the conductance when this concentration is exceeded; slightly above the C.M.C., however, the diol causes an appreciable increase in the conductance.

Many other types of polar-nonpolar compounds have also been observed to influence the conductance of association colloid solutions. Already in the 30's, Angelescu and co-workers [29]-[31] studied the effect of various cresols on the properties of soap solutions and found that the conductances of $0.1-0.2$ M solutions first increased to a maximum and then decreased with increasing cresol content. Ekwall and Henriksson [14] followed the change in the conductance of sodium oleate solutions when terpineol was added. As long as terpineol continued to dissolve, the conductance diminished slowly, but when a new phase composed of terpineol and oleate began to separate, the conductance rapidly decreased. When still more terpineol was added, the conductance began to increase and finally attained a constant value when pure terpineol began to separate. Ralston and coworkers [32],[15] found that the conductances of dodecylamine hydrochloride solutions containing methyl lauramide or lauronitrile are lower than those of solutions of the pure colloid both below and above the C.M.C. When solutions of dodecylamine hydrochloride are saturated with stearyl amine, stearonitrile or undecyl chloride, the conductance is lowered if the colloid concentration exceeds the C.M.C., but is unaffected when the colloid concentration is below this limit. McBain and McHan [33] found that dimethyl phthalate lowers the conductance of laurate solutions when the concentration of laurate is less than 0.5 M, but effects an increase when the concentration of the colloid is higher.

In this and in a following study we shall deal with the effect of the long-chain paraffin alcohols on the conductance of solutions of association colloids. In many of the above-mentioned investigations on the effect of these polar-nonpolar substances on the conductance, very little attention appears to have been paid to the physical state of the system involved, whether it has been homogeneous or not and how much of the alcohol has been added in excess of that sufficient to effect a separation of the system into two phases. These phenomena are, however, of pronounced significance for the correct interpretation of the results. Earlier studies [34],[19] have shown that when the association colloid concentration is above the C.M.C., (a) relatively small amounts of decanol dissolve completely forming mixed alcohol-association colloid micelles; (b) when decanol is added in larger amounts, a new phase composed of decanol, association colloid and water separates; (c) addition of still larger amounts of decanol leads to the separation of free decanol. We have now studied the effect of decanol on the conductance of the solutions in these three ranges. We want also to elucidate how this effect changes with the concentration of the association colloid solution. In addition, we have attempted to determine the composition of the separated phase from the observed variation of the conductance. We also wish to draw attention to the great similarity between the effects of decanol and fatty acids on the conductance of association colloid solutions.

In the present paper data will be reported on the effect of decanol on the conductance of sodium oleate and sodium laurate solutions. In the following paper corresponding data relating to solutions of sodium alkyl sulphates will be presented.

MATERIALS AND METHODS

The samples of sodium oleate and decanol-1 used in this study were those used in Part I of this series [34]. The sample of sodium laurate was prepared by neutralizing purest lauric acid (Eastman Kodak Co., Rochester) with sodium ethylate in absolute ethanol.

The water employed in the preparation of the solutions had a specific conductance of 0.6 — 1.0 × 10⁻⁶ reciprocal ohms. The solutions were prepared in ampoules as described in Part I, and shaken in a thermostat at 40° C during 2 — 4 days. Some of the solution was withdrawn into a cylindrical conductance cell and after flushing the latter several times with the solution, the conductance was measured in the usual manner; the accuracy of the conductance values was approximately ± 0.5 %. In the case of dilute oleate solutions below 0.006 M, it was difficult to obtain reproducible values, probably owing to the adsorption of decanol on the electrodes, and it was found necessary to clean the electrodes thoroughly with warm water and ethanol before introducing a new solution. The current was turned on immediately before each measurement.

In the following, the concentrations of the association colloid solutions are given in moles of soap per 1 000 g of solution and are denoted by M.

SODIUM OLEATE SOLUTIONS CONTAINING DECANOL

The effect of increasing amounts of decanol. As was shown in Part I of this series, sodium oleate solutions in the 0.01—0.12 M range solubilize a constant amount of decanol per mole of oleate before the solutions become turbid. At higher oleate concentrations, this maximum amount of decanol dissolved increases, attains a maximum in the 0.15 M solution and then begins to decrease.

To illustrate how the appearance of the oleate solutions changes when decanol is added, several turbidity curves are reproduced in Fig. 1. When the above-mentioned maximum amounts of decanol are exceeded and the system becomes heterogeneous, the turbidity increases very rapidly to a maximal value; when more decanol is added, the turbidity begins to decrease. The sharpness of the turbidity maximum gives the impression that a new factor begins to influence the turbidity of the solution above the maximum with the result that the turbidity decreases rapidly. The heterogeneous systems are very stable. At higher oleate concentrations they become viscous when larger amounts of decanol are introduced and gradually become gel-like. When the amount of added decanol is increased further, the turbidity again increases.
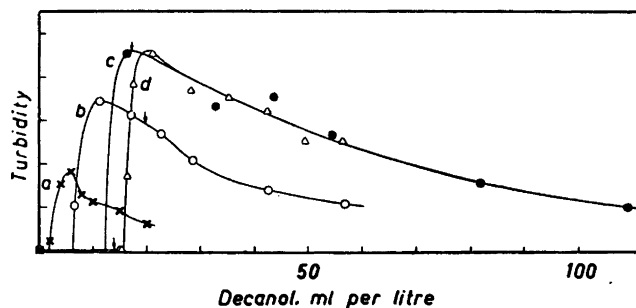

Fig. 1. Turbidity curves for sodium oleate solutions containing decanol (Pulfrich Step Photometer). 40° C.

a) 0.0500 M sodium oleate
b) 0.143 M » »
c) 0.275 M » »
d) 0.357 M » »

The solutions become highly viscous near the points marked with arrows.

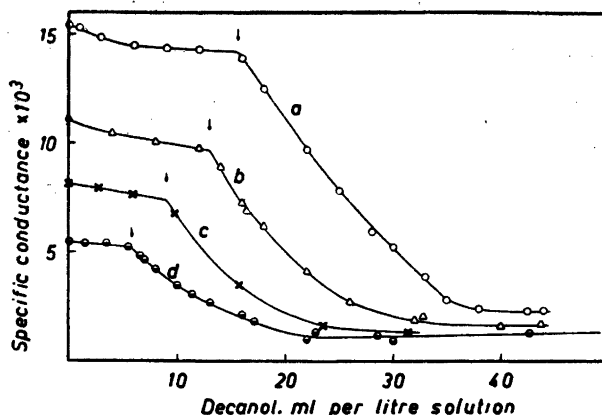*Fig. 2. Specific conductances of sodium oleate solutions containing decanol. 40° C.*

    a) 0.385 M sodium oleate
    b) 0.275 M   »   »
    c) 0.207 M   »   »
    d) 0.143 M   »   »

The effect of decanol on the conductance was studied in the oleate concentration range from *ca.* 0.006 to 0.4 M. It could be established with certainty that decanol lowers the conductance even at the lowest oleate concentration studied (0.006 M).

The change of the conductance of an oleate solution varies with the amount of decanol added (Figs. 2 and 3). When small amounts are added that dissolve completely and do not give rise to turbidity, the conductance decreases gradually. When enough decanol has been added to effect the formation of a new phase (the points where turbidity is first observed are marked by arrows in Figs. 2 and 3), the conductance of the solution decreases rapidly at first but then less rapidly; finally further additions of decanol no longer alter the conductance. The gel-like nature which solutions containing large amounts of decanol often assume renders difficult the measurement of the conductance. When the oleate concentration is high, *e. g.* 0.2 M, this type of solution was produced already after 1 mole of decanol had been added per mole of oleate; when the oleate concentration was lower, the conductance could be measured even when the solution contained 4 moles or more decanol per mole of oleate. Observations made with the microscope revealed that drops of free alcohol were present in the systems in the range where the added decanol no longer altered the conductance.

With respect to the amount of decanol added, three different ranges can thus be distinguished in which the effect on the conductance differs. The limits of these ranges coincide with those where changes occur in the nature of the interaction between decanol and oleate.

The effect of decanol at different oleate concentrations. The curves in Figs. 2 and 3 show that as long as the added decanol does not give rise to turbidity,
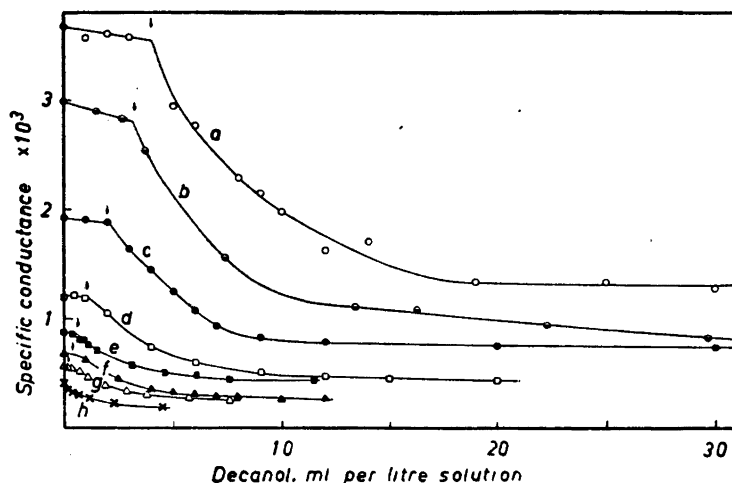
Fig. 3. *Specific conductances of sodium oleate solutions containing decanol. 40° C.*

a) 0.0971 **M** *sodium oleate*
b) 0.0782 **M**   »   »
c) 0.0500 **M**   »   »
d) 0.0300 **M**   »   »
e) 0.0199 **M**   »   »
f) 0.0150 **M**   »   »
g) 0.00998 **M**   »   »
h) 0.00592 **M**   »   »

the conductance curves have small negative slopes and are in most cases practi-
cally linear. The slope of the straight part of the curve is a measure of the
effect of solubilized decanol on the conductance. From the slope we have
calculated the lowering of the conductance due to solubilized decanol, when the
latter is expressed in moles of decanol per mole of oleate. The slope is plotted
as a function of initial oleate concentration in the upper part of Fig. 4 (curve a).
Up to an oleate concentration of about 0.14 M, the absolute value of the slope
is seen to increase slowly with the soap concentration; at higher oleate concen-
trations the slope increases more rapidly but appears to attain a maximum value
in the approximately 0.3 M solution. Thus, when decanol is incorporated in
the oleate micelles, it does not effect the same changes in all concentration
ranges; the lowering of the conductance due to solubilized decanol is much grea-
ter for oleate concentrations above 0.2 M than for those below 0.1 M.

Curve b in the lower part of Fig. 4 gives the specific conductances of pure
sodium oleate solutions (containing no decanol) and curve c the conductances
of solutions containing decanol when turbidity is first observed. The difference
between the conductance values of these two curves is seen to increase when
the oleate concentration increases. Curve d shows on a larger scale how this
difference (Δx = the conductance of the solution containing decanol at the
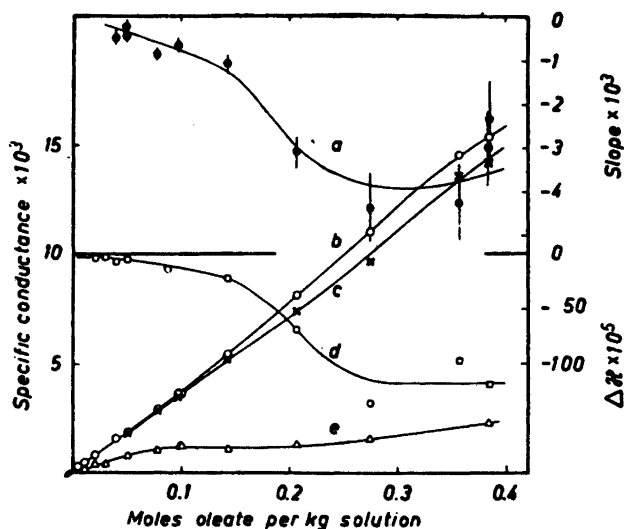turbidity point *minus* the conductance of the pure solution) varies with the

Fig. 4. *a)* *Slopes of the conductance vs. decanol content curves below the turbidity point*
($\Delta\varkappa$/mole of decanol per mole of oleate).

    b) *Specific conductances of pure sodium oleate solutions.*
    c) *Specific conductances of sodium oleate solutions containing decanol at the turbidity*
       points.
    d) *The lowering of the conductance, $\Delta\varkappa$ (= $\varkappa$ at turbidity point minus $\varkappa$ of pure*
       solution).
    e) *The final conductances of sodium oleate solutions containing large amounts of decanol.*

oleate concentration; because this difference is negative the curve has been
drawn with negative values increasing downwards. The absolute value of the
difference remains relatively small until the oleate concentration rises to about
0.10—0.14 M, above which it increases rapidly to about six times its value in
the 0.14 M solution and then remains relatively constant when the oleate
concentration exceeds 0.27 M. This rapid increase of the lowering of the con-
ductance occurs in the same oleate concentration range where the proportion
of decanol in the mixed micelles increases to a maximum. As shown in Part
I [34], the increase in the latter is only about 30 %, whereas we see here that the
difference in the conductance increases about 500 %. It seems therefore that
the change in the composition of the micelles cannot alone explain this change
in the effect of decanol on the conductance.

The final values to which the conductances fall when large amounts of
decanol are added are given by curve e in Fig. 4. As already seen in Figs. 2
and 3, these values are appreciably lower than those for the pure soap solu-
tions; in magnitude they correspond to the specific conductances of 0.001—
0.05 M oleate solutions containing no added decanol. It is of interest to note
that this final conductance increases with the initial oleate concentration up
to the 0.08—0.15 M solutions, then remains practically constant until the
oleate concentration becomes approximately 0.2 M, after which it again in-
creases slowly.

In respect of the oleate concentration, there thus exist three ranges in which the effect of decanol on the conductance varies in a different manner: one up to about 0.08—0.15 M oleate, a second from about 0.08—0.15 M to 0.2—0.27 M, and a third above the latter limit.

Estimation of the Composition of the Separated Phase. Our previous studies (Part I) have shown that interaction between decanol and oleate solutions in the small micelle range up to an oleate concentration of approximately 0.12 M leads primarily to the formation of mixed micelles that contain at most 0.23 mole of decanol per mole of oleate. At somewhat higher oleate concentrations, the maximum decanol content of the mixed micelles increases to about 0.30 mole of decanol per mole of oleate and then decreases to 0.14 mole of decanol per mole of oleate.

The rapid decrease of the conductance that occurs when the system becomes heterogeneous gives evidence that the phase separating contains also oleate in addition to decanol and water. By making certain assumptions, it is possible to calculate the approximate composition of the separated phase from the courses of the conductance curves. We assume that the part played by the separated phase in the transport of current can be disregarded and that the formation of this phase alters only the colloid concentration of the aqueous phase, but does not alter its micellar structure. We assume further that the volume of the aqueous phase remains unaltered. As long as the separated phase is small in amount, these assumptions may be considered valid; when larger amounts have separated, at least the last assumption is no longer true since the decanol-oleate phase that separates also contains water. The separated phase also surely participates to a certain extent in the transport of the current.

The composition of the substance causing the turbidity has been computed from the slope of the conductance curve in the region immediately above the turbidity point. The results obtained are shown by curve a in Fig. 5. It will be seen that the phase separating from the 0.1—0.4 M oleate solutions contains 0.5 mole decanol per mole of oleate, but that the decanol content becomes somewhat higher with decreasing oleate concentration, *e. g.* the separated phase formed from a 0.02 M oleate solution contains about 1.2 mole decanol per mole of oleate.

With the purpose of illustrating the calculation of the composition of the separated phase, we will take one case. From the conductance curve for the 0.0971 M oleate solution, it can be seen that the slope of the curve just above the turbidity point is such that an addition of 1.0 ml decanol per litre of solution decreases the conductance by $\Delta \varkappa = 0.68 \times 10^{-3}$ rec. ohms. With the aid of the conductance curve for solutions containing decanol at their turbidity points (curve c in Fig. 4), it can be estimated that this decrease in the conductance corresponds to a decrease in the oleate concentration of the aqueous phase of about 0.019 mole oleate per litre of solution. Thus an addition of 1.0 ml of decanol per litre or 0.00524 mole of decanol per litre diminishes the oleate concentration of the aqueous phase by 0.019 mole per litre. The ratio of these values is 0.28 mole of decanol per mole of oleate. To this value must be added the decanol content of the mixed micelles (0.23 mole of decanol per mole of oleate) and so we finally find that the separated phase contains 0.51 mole of decanol per mole of oleate.
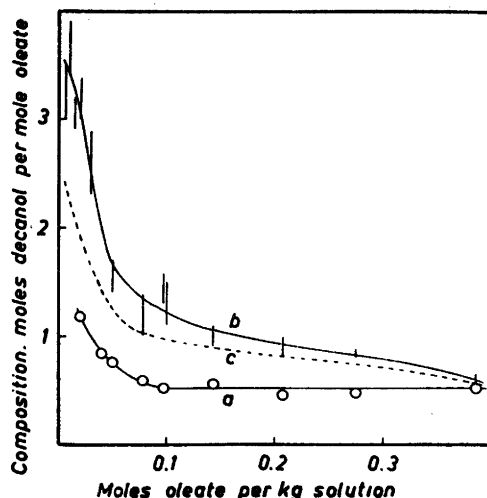
Fig. 5. The composition of the phase separating from sodium oleate solutions containing decanol.

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.

Analogously, it is possible to calculate the composition of the separated phase with the aid of the latter parts of the conductance-decanol content curves. It is found that the larger the amount of decanol added to the soap solution the higher the decanol content of the separated phase. However, this increase in the proportion of decanol takes place more slowly when the concentration of oleate is high. The final composition which the separated phase tends to assume, that is, the composition when the conductance becomes constant on adding decanol, is given by curve b in Fig. 5; the conductance curves do not, however, exhibit any sharp break points, and hence it is only possible to give two limits for the final composition. Owing to the fact that the assumptions made in the calculation can no longer be considered valid (especially the assumption that the volume of the aqueous phase remains unchanged), the calculated decanol content of the separated phase is too high.

A lower limit for the final composition of the separated phase is obtained by computing the total composition of the whole system in the range where the conductance remains practically constant (curve c, dotted line, Fig. 5). The final composition of the separated phase lies somewhere between curves b and c in Fig. 5. In the most concentrated solutions, this phase hence contains 0.5—0.6 mole of decanol per mole of oleate, in the 0.05—0.1 M solutions, the ratio seems to be 1—1.4 moles of decanol per mole of oleate, and in the most dilute range 2—3 moles of decanol per mole of oleate.
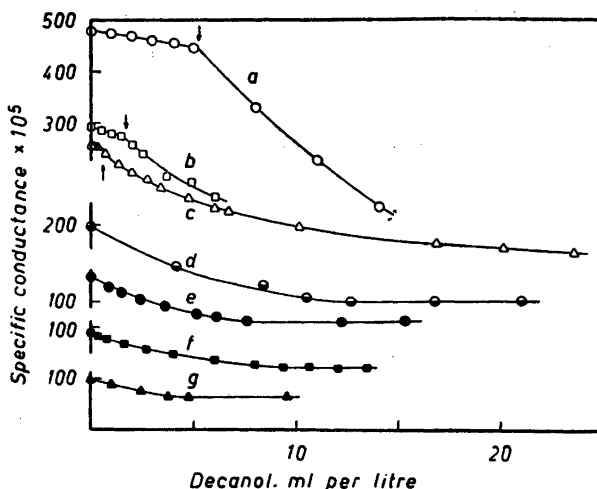
Fig. 6. Specific conductances of sodium laurate solutions containing decanol.

a) 0.100 M sodium laurate 40° C
b) 0.050 M » » 40° C
c) 0.035 M » » 40° C
d) 0.022 M » » 40° C
e) 0.016 M » » 40° C
f) 0.014 M » » 20° C
g) 0.010 M » » 40° C

The present study thus shows that the phase that separates immediately above the turbidity point is appreciably richer in decanol than the mixed micelles produced by the solubilization of decanol below this point and that the decanol content of the separated phase increases further when more decanol is added to the system. Moreover it is seen that the composition of the separated phase varies with the concentration of oleate in the solution in which it is formed. Its final composition rapidly changes with oleate concentration in dilute oleate solutions, but is almost independent of the oleate concentration when the latter is high.

SODIUM LAURATE SOLUTIONS CONTAINING DECANOL

Some measurements have been made on the effect of decanol on the conductance of sodium laurate solutions in the 0.002—0.10 M concentration range. Small amounts of sodium hydroxide were added to most of these solutions to suppress the hydrolysis and hence the conductance values are not fully comparable.

Curves a, b and c in Fig. 6 apply to laurate solutions above the C.M.C., 0.027 M. Owing to the relatively high value of the C.M.C. for sodium laurate, it was possible to study the effect of decanol also in laurate solutions below the C.M.C. (curves d—g). The curves in Fig. 6 are seen to resemble those for
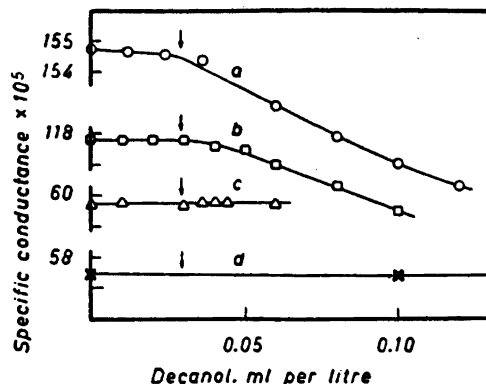
Fig. 7. *Specific conductances of sodium laurate solutions containing decanol.* 40° C.
  a) 0.014 M sodium laurate
  b) 0.012 M   »   »
  c) 0.006 M   »   »
  d) 0.005 M   »   »

the decanol-oleate system. As long as the solutions remain clear (the points where turbidity is observed are marked by arrows), the conductance decreases slowly with increasing decanol content, but falls rapidly when the solution becomes turbid owing to the separation of a new phase consisting of decanol, laurate and water; when greater amounts of decanol are added, the conductance approaches a constant value. Microscope observations showed that in this latter region drops of free decanol are present in the system.

A more detailed study was made both above and below the turbidity points in laurate solutions below the C.M.C. (Fig. 7). The effect of decanol is similar here as in solutions above the C.M.C., but the first part of the conductance curve is relatively short since the solution becomes turbid when very small amounts of decanol have been added (curves a and b). The lowering of the conductance is observed down to the 0.007 M laurate concentration. Below the limiting concentration (L.A.C., about 0.006 M), addition of decanol does not alter the conductance, although the system becomes heterogeneous (curves c and d, Fig. 7). In this range the separating phase is not composed of decanol, laurate and water but consists of free decanol.

We prefer to discuss the above results in the next paper of this series together with the results of similar measurements on sodium alkyl sulphate solutions.

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