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Studies on the Interaction of Paraffin Chain Alcohols and Association Colloids

IX. The Solubility of Decanol-1 in Solutions of Sodium Caprate, Laurate and Myristate above the C.M.C.

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The maximum amounts of decanol that are solubilized by sodium caprate, laurate and myristate solutions before they become turbid have been determined at concentrations above the C.M.C. The solubility curves are linear over a wide concentration range above the C.M.C., slope upwards in a narrow range (A) and continue again as straight lines. Two concentration ranges can hence be distinguished above the C.M.C. with respect to the solubility of decanol, one from the C.M.C. to the break point A and another above this latter point. The break point A in the solubility curve shifts to lower soap concentrations as the number of carbon atoms in the soap increases in the homologous series, but also other factors operate here. The ratios of decanol to soap in the mixed micelles at the turbidity points in the different soap concentration ranges have been calculated from the slopes of the solubility curves. The maximum decanol content of the mixed micelle decreases with increasing number of carbon atoms in the hydrocarbon chain of the soap both in the range between the C.M.C. and the break point A and in the range above the latter point. The maximum decanol content of the mixed micelles depends also on the nature of the ionic group in the association colloid and on the gegenions. It is shown that in the concentration ranges where the break points A are located in the solubility curves also other changes typical of the *2nd* C.M.C. occur in the properties of the solutions. The meaning of the *2nd* C.M.C. and the factors responsible for the separation of the mesomorphic phase that causes the turbidity are discussed.

In Part VIII[1] of this series it was shown how the solubility of decanol varies with the soap concentration in dilute sodium caprate, laurate and myristate solutions. It was found that the first slight increase in solubility occurs already above the limiting association concentration, L.A.C., but that the solubility then passes through a maximum. After a minimum at a concentration about one-third of the critical micelle concentration (C.M.C.) of the pure soap, the solubility of decanol begins to increase again, the increase being now appreciable. The C.M.C.'s of the decanol-containing soap solutions, *i.e.*, the concentrations where mixed micelles begin to form to a greater extent, are located at these points.

In the present paper data are reported on the solubility of decanol in solutions of the soaps mentioned in the concentration range above the C.M.C. The solubility discussed here is, as in Parts I [2] and VIII [1] of this series, the maximum solubility in the aqueous solution before it becomes turbid owing to the separation of a mesomorphic phase composed of decanol, soap and water. The heterogeneous system as a whole can, as we have shown previously [3-6], bring further, large amounts of decanol into solution, but the decanol is incorporated within the new phase. The solubility relationships when decanol is added in excess of the amount required to produce the turbidity are not considered in this paper.

Previous studies have shown that the micellar substance in solutions of association colloids has constant properties in a relatively wide concentration range above the C.M.C. (in the so-called small micelle range) [7,8]. The saturation capacity of the micellar substance (the solubilizing power expressed as the amount of solubilized substance per mole of micellar soap) has been found to be constant for *p*-xylene, benzene and other hydrocarbons [7,9]. In Part I [2] of this series it was shown that also the maximum amount of decanol that is incorporated in sodium oleate and sodium myristyl sulphate micelles at the turbidity point remains constant over practically the whole small micelle range. We have pointed out earlier that this is the case also for sodium caprate, laurate and myristate solutions [2,3]. The experimental evidence is presented here.

Our earlier studies [2] showed, however, that the linear course of the solubility curve of decanol in solutions of sodium oleate and sodium myristyl sulphate ends at a higher concentration; the curve bends upwards at first and then downwards. The break point is situated in approximately the same concentration range in which the solubilizing power for *p*-xylene and benzene begins to increase more rapidly than at lower concentrations [7,8] and where also many other properties of the solutions undergo a change (see Part IV [6]). Similar results have later been obtained by Markina, Posspelova and Rebinder [10] who studied the solubility of the hydrocarbons benzene, cyclohexane, octane and dodecane and of the polar-nonpolar compounds octanol and acrylonitrile in solutions of sodium oleate. These observations support the view that important changes occur in the properties of oleate (and myristyl sulphate) solutions in the concentration range in question so that one has to assume that changes also occur in the micellar structure. We have investigated whether a corresponding change can also be established in the power of concentrated caprate, laurate and myristate solutions to solubilize decanol.

MATERIALS AND METHODS

The fatty acids were products of Eastman Kodak Co., Rochester. They were recrystallized twice from absolute ethanol. The melting points of the fatty acids were 31.0–31.5°C for capric acid, 42–43°C for lauric acid and 56–57°C for myristic acid. The soaps were prepared in the usual manner by neutralizing the fatty acid with sodium ethylate in absolute ethanol. The decanol-1 was that used in previous investigations of this series [2].

The solutions were prepared and the solubility was measured as described in Part I [2]. The temperature was 40°C. The solubility values are estimated to be accurate to about ±0.1 ml of decanol per litre of solution in most cases but are perhaps slightly less accurate for the most concentrated myristate solutions owing to the fact that these solutions are gel-like at 40°C and hence very difficult to work with.

The concentrations of the soap solutions are given in moles of soap per 1 000 g of soap solution and denoted by *M*.

EXPERIMENTAL RESULTS

The solubility of decanol has been studied in the following concentration ranges: sodium caprate 0.08—0.5 *M*, sodium laurate 0.02—0.6 *M*, sodium myristate 0.006—0.2 *M* and potassium myristate 0.01—0.06 *M*.

Figs. 1, 2 and 3 show how the solubility of decanol varies with the soap concentration. The solubility values reported in Part VIII have been marked with crosses in these figures; the curves joining the new solubility values (marked with circles) are seen to be continuations of the previously drawn curves. In the case of all soaps the solubility begins to increase definitely a little below the C.M.C. of the pure soap. The solubility curves rise steeply and exhibit a constant slope. The linear course is maintained over a comparatively wide concentration range. In the case of all three soaps there then follows a narrow range (A) where the curves bend upwards and continue as straight lines. (In the solubility curve of myristate (Fig. 3) a weak suggestion of a downward trend can be noted at still higher concentrations. The determination of the course of the curve in this region was a little uncertain owing to the

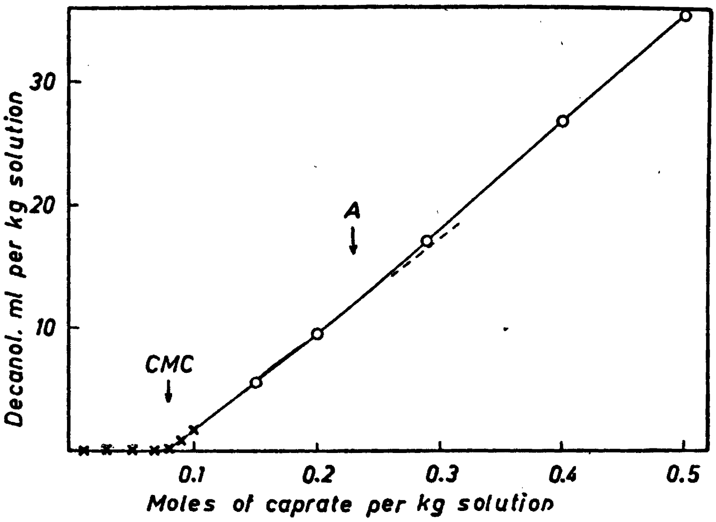

Fig. 1. The maximum amounts of decanol dissolved at the turbidity point in solutions of sodium caprate. 40°C.

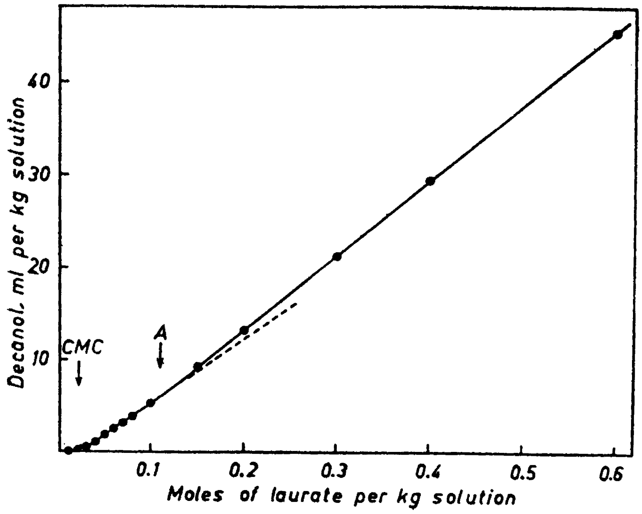

Fig. 2. The maximum amounts of decanol dissolved at the turbidity point in solutions of sodium laurate. 40°C.

difficulty of determining the solubility of decanol in sodium myristate solutions of higher concentrations than about 0.2 *M*; both the pure and the decanol-containing solutions are very viscous in this concentration range.) Above the C.M.C. two concentration ranges can hence be distinguished with respect to the solubility of decanol: one from the C.M.C. to the break point A and another above this latter point.

It should be emphasized that the solubility of sodium myristate in water is so low at 40°C that separated sodium myristate appears in pure myristate

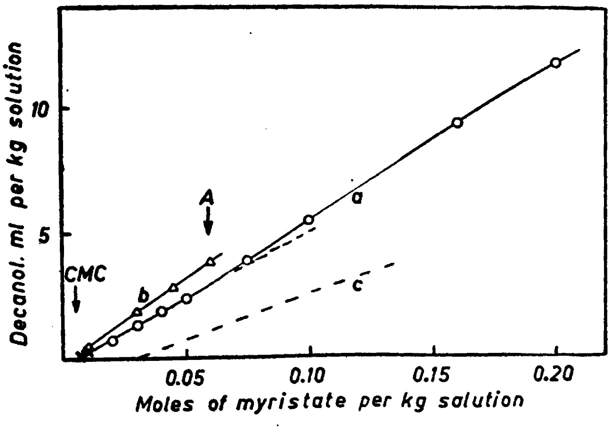

Fig. 3. The maximum amounts of decanol dissolved at the turbidity point. 40°C. a) Sodium myristate solutions, b) Potassium myristate solutions, c) Boundary line separating clear and turbid (lower right) solutions, the turbidity being caused by separated myristate.

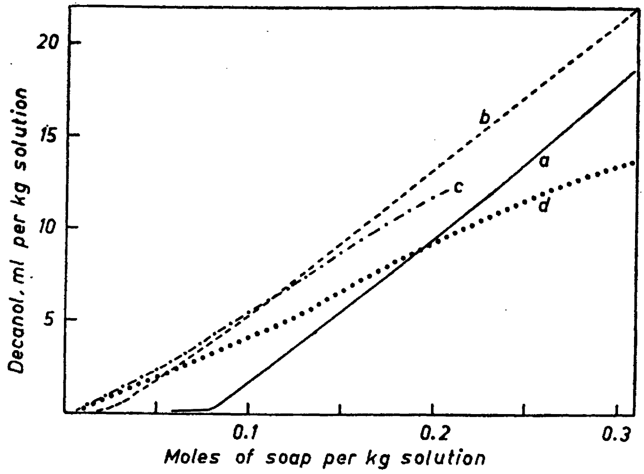

Fig. 4. The maximum amounts of decanol dissolved at the turbidity point. 40°C. a) Sodium caprate solutions, b) Sodium laurate solutions, c) Sodium myristate solutions, d) Sodium oleate solutions.

solutions above about 0.03 *M* in concentration [11]. The solubility of the soap increases, however, when decanol is added to the system. The dotted curve in Fig. 3 has been drawn on the basis of some scattered observations; it gives the approximate amounts of decanol needed to prevent the separation of myristate. Below the dotted curve, the system is heterogenous owing to separated myristate. Between the dotted and the continuous curves, the system is homogeneous but becomes heterogeneous again above the latter curve owing to the separation (above the L.A.C.) of the decanol-myristate-water phase.

The solubility of decanol in potassium myristate solutions was determined at only four soap concentrations (Fig. 3, curve b).

With the purpose of making possible a direct comparison of the solubility curves, the curves for the three soaps and the corresponding curve for sodium oleate have been plotted in the same diagram, Fig. 4. It can be seen that the slopes of the first linear parts of the curves for laurate, myristate and oleate between the C.M.C. and the break point A decrease with increasing number of carbon atoms in the soap; the result is that the curves intersect.

DISCUSSION

The solubility of decanol and its relationship to the molecular structure of the soap and the concentration of the soap solution. It is believed that the molecules of solubilized higher alcohols enter into the palisade layers of the micelles, whereupon mixed micelles are formed. The solubility which results from the solubilization in the micelles is, however, limited by the separation of a new phase composed of decanol, soap and water. As we have already pointed out, the appearance of the new phase does not mean that the system as a whole is

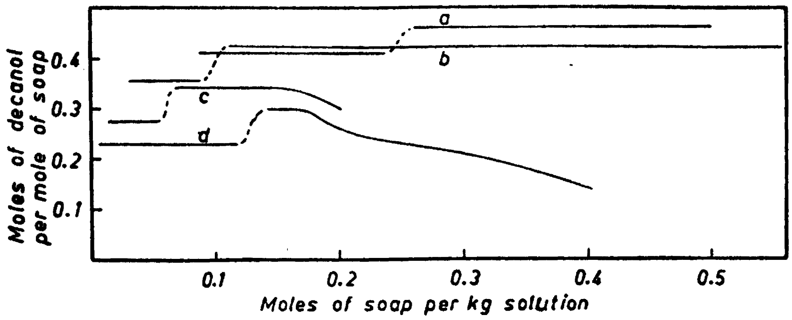

Fig. 5. The decanol content per mole of soap in the mixed micelles. 40°C. a) Sodium caprate solutions, b) Sodium laurate solutions, c) Sodium myristate solutions, d) Sodium oleate solutions.

saturated with decanol. The solubility curves drawn in the figures give only the maximum amounts of decanol which the micelles are able to dissolve before the new phase separates. Hence the solubility values measured at the turbidity point when a polar substance such as a long chain alcohol or fatty acid is solubilized are not comparable with the solubility values obtained in the solubilization of nonpolar compounds since the latter values give the real saturation points above which the pure solubilizate separates [2,7,8]. This difference has been recently stressed also by Hyde, Langbridge and Lawrence [12].

It has previously been customary to compare the solubilities of alcohols (and also hydrocarbons) at the same and often only one concentration of different soaps [13]. Since, as shown by the curves in Fig. 4, the solubility curves have different slopes for different soaps, the results of the comparison depend on the soap concentration chosen. A better survey is obtained when, as has been done in the present study, the slopes of the solubility curves are compared.

The slope of the solubility curve at a certain soap concentration, ∂(solubility)/∂(soap concentration), gives the ratio of decanol and soap in the mixed

Table 1. The compositions of the mixed micelles at the turbidity point expressed as moles of decanol per mole of micellar soap.

Association colloid	Concentration range	Composition, moles of decanol per mole of soap	Break point A	Concentration range	Composition, moles of decanol per mole of soap	Increase of the decanol content of mixed micelles above the break point A (%)
Na-caprate	0.08–0.22 *M*	0.41	0.23 *M*	0.24–0.5 *M*	0.46	12
Na-laurate	0.03–0.10 *M*	0.36	0.11 *M*	0.12–0.6 *M*	0.42	19
Na-myristate	0.01–0.05 *M*	0.28	0.06 *M*	0.07–0.16 *M*	0.34	24
				0.2 *M*	0.30	
K-myristate	0.01–0.05 *M*	0.36				

micelles formed at the soap concentration in question when the turbidity appears. The composition of the mixed micelles is different in different soap concentration ranges, as shown in Fig. 5 and Table 1. The decanol content of the mixed micelles is seen to decrease with the number of carbon atoms in the hydrocarbon chain of the soap both in the range between the C.M.C. and the break point A and in the range above the latter point. The relative increase in the decanol content of the mixed micelles varies in a similar manner in both ranges (Table 1, last column). From Fig. 5 it is also seen that the compositions of the decanol-caprate and decanol-laurate mixed micelles remain constant above the break point over the range studied, whereas the decanol content of the decanol-myristate micelles remains constant at first, but decreases at the higher myristate concentrations. In the case of sodium oleate and sodium myristyl sulphate[2], there is practically no concentration range above the break point where the composition of the mixed micelles remains constant; the decrease in the decanol content of the mixed micelles begins after a very short linear range of fairly high solubility values.

That the decanol content of the mixed micelles at the turbidity point is not dependent solely upon the length of the hydrocarbon chain of the soap is shown by the collected experimental data and has also been emphasized earlier[2]. The nature of the ionic group of the colloid and the presence of a double bond influence the mixed micelle composition. For instance, the decanol content of the mixed decanol-myristyl sulphate micelles in moles per mole of colloid is about 47 % higher than that of the decanol-myristate mixed micelles in both ranges above and below the break point. If the decanol content decreases in the same proportion with increasing chain length as in the series caprate, laurate and myristate, the decanol-stearate mixed micelles should contain 0.12 and 0.18 mole of decanol per mole of soap in the ranges below and above the break point, respectively. For oleate with 18 carbon atoms, considerably higher values, 0.23 and 0.30 mole of decanol per mole of oleate, are obtained[2]; this is evidently to be ascribed to the presence of the double bond in the oleate molecule. Also the gegenion appears to exert some influence since the decanol content on the mixed micelles is higher in potassium myristate solutions than in sodium myristate solutions.

It can be further seen from Fig. 5 that the break point A in the solubility curve shifts to lower soap concentrations as the number of carbon atoms in the soap increases in the homologous series. Also other factors seem to operate here, since the break points lie higher in the curves for oleate and myristyl sulphate than in the myristate curve.

The "Second Critical Concentration". As mentioned in the introduction, we have previously observed that the break point in the solubility curve for decanol lies in oleate and myristyl sulphate solutions in the same narrow concentration range in which also other properties of these solutions undergo marked alterations. We have therefore considered it appropriate (for the lack of a better name) to call this narrow concentration range the "second critical concentration" (*2nd* C.M.C.). Since a similar variation has now been observed in the alcohol solubility in solutions of the saturated fatty acid soaps, it is of interest to examine on the basis of previously reported experimental data whether also other properties of the solutions of these soaps undergo a change in the concentration range where the break point occurs. It should be noted in this connection that the break points in the decanol solubility curves occur at soap concentrations that are a little lower than those in which changes can be expected to occur in pure soap solutions. This was found to be the case for the oleate and the myristyl sulphate solutions; similarly as decanol lowers the C.M.C. slightly, the "second critical concentration" is evidently also shifted to a lower concentration in the presence of decanol.

One of us has previously shown that the amount of *p*-xylene solubilized at 40°C by sodium myristate solutions increases linearly with the colloid concentration (*i.e.*, the saturation capacity of the micellar substance remains constant) in the concentration range between 0.03 *M* and 0.06 *M*, but increases more rapidly (the saturation capacity has a greater value) above the latter concentration [7]. It has also been found that the equivalent conductance of sodium myristate passes through a shallow minimum at the approximately 0.14 *M* soap concentration (35—80°C) (the change in equivalent conductance is very slight above the 0.08 *M* concentration) [14]. An inspection of the $\partial\varkappa/\partial c$-concentration curve shows that after a rapid fall above the C.M.C. the curve continues horizontally up to the approximately 0.1 *M* concentration and then bends upwards. The break point in the decanol solubility curve is situated in the range from 0.055 *M* to 0.065 *M*.

McBain, Laing and Titley [15] found that a conductance minimum occurs in potassium laurate solutions at the approximately 0.13—0.15 *M* concentration; the horizontal part of the $\partial\varkappa/\partial c$-curve terminates already when the soap concentration is about 0.10 *M*. The break point in the decanol solubility curve occurs approximately in the 0.10—0.12 *M* range.

It is thus seen that also other changes typical of the *2nd* C.M.C. occur in the properties of solutions of at least two of the three soaps in the concentration range where the break point A in the decanol solubility curve is located.

According to Mysels and Dulin [16], the minimum in the equivalent conductance curve (Λ *vs.* $\sqrt{c}$) cannot be taken as an indication that the nature of the solution changes in this region. They emphasize that the specific conductance-concentration curves for soap solutions above the C.M.C. show a continuous upward curvature and that this curvature is almost constant but increases slightly and regularly. We have inspected from this viewpoint numerous conductance measurements of different association colloids by different investigators [4,5,11,14,15,17-22] and found that in nearly all cases the $\varkappa$-c-curve is linear and the $\partial\varkappa/\partial c$-curve consequently horizontal over a fairly wide concentration range above the C.M.C. The $\varkappa$-c-curve bends upwards at a concentration only slightly below that at which the minimum occurs in the Λ-$\sqrt{c}$-curve; consequently also the $\partial\varkappa/\partial c$-curve deviates from the horizontal at this point. (This applies also to sodium myristate, potassium laurate, sodium oleate and sodium myristyl sulphate.) The conclusion of Mysels and Dulin thus appears to be based on an erroneous interpretation of the experimental data. For the present it seems to us that the course of the conductance curve in the neighbourhood of the minimum of the equivalent conductance (Λ) must be considered a sign that a new factor begins to operate and effects a change in the process of micellization. This is supported by the changes observed in the decanol solubility. New conductance measurements are required before any further conclusions can be drawn.

As the number of micelles increases, a point is sooner or later reached where the electrical double layers of the micelles approach each other so closely that their charged surface layers begin to interfere with each other. This type of interaction may be considered the primary cause of the changes observed in the properties of colloid solutions at the *2nd* C.M.C. Even if this explanation is sufficient for some of the changes, it can hardly apply to others, *e.g.*, to the variation of the solubilizing power. It is difficult to understand how the interaction between the charged micelle surfaces can alone effect a greater solubilization of hydrocarbons or an increase of the alcohol content of the mixed micelles without the occurrence of a parallel change in the micellar structure. On the basis of various observations many investigators have concluded that only one type of micelle exists, namely, that which is produced in the concentration range immediately above the C.M.C.[23-25] The available experimental evidence relating to this hypothesis is still somewhat uncertain. It seems that the changes in the properties of the micellar substances which have become clearly evident in solubilization studies have not received adequate attention. It must therefore be permissible, until further evidence for the electrical interference theory has been collected, to assume that the changes in the properties of the solutions at the *2nd* C.M.C. are primarily due to changes in the structures and/or sizes of the micelles. Starting from the assumption that the interaction between the micelles leads to further aggregation and rearrangement of the ions and molecules of the micelles (whereupon energetically more stable micelles are formed), one may offer a plausible explanation for the changes noted in the solubilizing power. If the charge density in the outermost palisade layer of the large micelles against the surrounding solution remains sufficiently high when decanol is incorporated in the inner parts of the micelle, the stability of the large micelle in the solution will remain practically unaltered. In this way larger amounts of alcohol per mole of soap can be brought into the solution by the large micelles than by the small micelles. Similarly the micelle aggregation would be expected to increase the solubilization of hydrocarbons.

Irrespective of whether it will be established that either micelle aggregation (or some other change in the micelle) occurs, or if only one type of micelle exists and the changes in the properties of the solutions are due to other yet unknown factors, it is necessary to conclude that a concentration limit is reached in the highly concentrated solutions above which the properties of the association colloid differ from the properties below this limit.

Factors determining the formation of the mesomorphic phase. In all the cases we have studied, the alcohol-soap-water phase separates from solutions that contain higher or lower concentrations of soluble aggregates consisting of soap ions and alcohol molecules; between the L.A.C. and the C.M.C. the aggregates are very small, but above the C.M.C. we have to do with the much larger mixed micelles. There must thus be some relationship connecting the occurrence of the soluble aggregates and the formation of the mesomorphic phase. The question arises whether the association of soap ions and alcohol molecules to soluble aggregates, on one hand, and the association of the components to form the mesomorphic phase, on the other, are two parallel phenomena in which similar factors play a part or whether the presence of soluble soap ion-alcohol aggregates of some kind is a necessary condition for the formation of the phase mentioned. In the latter case it seems probable that the aggregates directly take part in the formation of the new phase and that the shift in the hydrophilic-lipophilic balance of the aggregates caused by the incorporation of alcohol is of importance.

It has previously been established that there is evidently some relationship connecting the balance between the hydrophilic and lipophilic properties of the molecules and ions taking part in mixed micelle formation and the maximum amount of alcohol that the micelles can incorporate before the system becomes turbid due to the separation of the mesomorphic phase [2]. The balance shifts in favour of the hydrophilic properties as the chain length decreases in a homologous series. A similar shift occurs when a double bond is introduced into the hydrocarbon chain of the soap or when the carboxyl group in a fatty acid soap is replaced by a sulphate group. In such cases we have established that the decanol content of the mixed micelles at the turbidity point increases; this result is in agreement with observations of other investigators [26,27]. A similar shift occurs also when the solubilizate is changed: the alcohol content of the micelles at the turbidity point decreases with the chain length of the alcohol (for the heptanol-caprate system the content of heptanol is 1.0 mole of heptanol per mole of soap [28] and for decanol-caprate, 0.43 mole of decanol per mole of soap).

As the hydro-lipophilic balance of the mixed micelle is shifted sufficiently in the direction of the hydrophilic properties, we finally come to a system in which the solubilization of the polar compound is not limited by the separation of a mesomorphic phase but increases to its highest possible value, after which the excess of the polar compound separates in pure form. This has been found to occur, for example, when caproic acid is solubilized in sodium caproate solutions [28], when caprylic acid is solubilized in sodium caprylate solutions [28], when decanediol-1,10 is solubilized in solutions of various soaps [7,28,29], and when decanol-1 is solubilized in solutions of the potassium salts of the α,ω-alkanedioic acids (in some cases a mesomorphic phase appears at higher colloid concentrations; the concentration at which this occurs decreases as the temperature is lowered)[30]. When pure polar substance separates, the solubility values obtained are comparable with those for hydrocarbons, contrary to the solubility values obtained when the phase composed of polar substance, soap and water separates.

We have previously pointed out that the penetration of alcohol molecules between the soap ions in the palisade layers of the micelle leads to changes in the surface of the micelle [2,5]. Weakly hydrophilic groups become located between the strongly hydrophilic ionized carboxylic or sulphate groups. This leads to a decreased charge density on the micelle surface. The decrease should at first be compensated to some degree by a decrease in the number of gegenions bound to the micelle. As more alcohol is solubilized, the hydrophilic properties of the micelle surface will weaken while the number of lipophilic groups in the inner region of the micelle (per unit surface area) will remain practically unaltered (depending on the relative chain lengths of the alcohol and soap). The balance between the lipophilic and hydrophilic properties of the micelle will thus be shifted in favour of the lipophilic properties. As the hydrophilic properties of the micelle surface weaken in this manner, the stability of the micellar solution will decrease and the tendency of the micelles to adhere to each other will increase although the micelles are still charged (this must be true both below and above the *2nd* C.M.C.). The decrease in the hydrophilic properties of the micelle surface must therefore sooner or later lead to the separation of a new phase. The process is the same for the small soap ion-alcohol aggregates at concentrations below the C.M.C. when the alcohol-soap ratio increases. As we have pointed out previously (Part VIII), the limits in which this ratio can vary are very narrow, and the hydrophobic properties increase rapidly as the ratio increases.

With the purpose of elucidating the formation of the mesomorphic phase, we have applied the law of mass action to the system containing alcohol, soap and water, irrespective of the fact that considerable errors must be introduced through the neglect of the activity coefficients. As was pointed out above, the formation of the mesomorphic phase can be assumed to occur by either of two ways: A) soap ions and alcohol molecules associate to soluble aggregates which form the mesomorphic phase by aggregation when their alcohol content attains a certain value, or B) soap ions and alcohol and water molecules form the mesomorphic phase directly when the decanol content of the mixed micelles attains a certain value. The calculations must, of course, lead to the same result irrespective of the mechanism chosen.

A. The formation of mixed micelles may be considered a process in which alcohol molecules are incorporated in the ordinary soap micelles or one in which new alcohol-containing micelles are produced. Under certain conditions (concentration, temperature and salt concentration) the molar ratio of alcohol and soap ions in the mixed micelles does not exceed a certain value (y/x). When this value is reached, further addition of alcohol leads to the formation of the mesomorphic phase. At the turbidity point where the soap solution is in equilibrium with the mesomorphic phase, the formation of the mixed micelles in the aqueous phase may be expressed by an equation of the following general type:

$$x\,\mathrm{R'COO^-} + y\mathrm{R''OH} + z\,\mathrm{Me^+} \rightleftharpoons ((\mathrm{Me^+})_z(\mathrm{R'COO^-})_x(\mathrm{R''OH})_y)^{-(x-z)} \qquad (1)$$

$$\frac{[((\mathrm{Me^+})_z(\mathrm{R'COO^-})_x(\mathrm{R''OH})_y)^{-(x-z)}]}{[\mathrm{R'COO^-}]^x\,[\mathrm{R''OH}]^y\,[\mathrm{Me^+}]^z} = K \qquad (2)$$

R'COO$^-$ denotes a soap anion, R''OH an alcohol molecule and Me$^+$ a metal ion. The values of x, y and z need not be the same as for the pure soap micelles. (The formation of the small soap ion—alcohol aggregates occurring in the concentration range between L.A.C. and C.M.C. can be treated in the same way in principle.)

Eqn. (2) may be rewritten as follows:

$$[\mathrm{R'COO^-}][\mathrm{R''OH}]^{y/x} = \frac{[((\mathrm{Me^+})_z(\mathrm{R'COO^-})_x(\mathrm{R''OH})_y)^{-(x-z)}]^{1/x}}{K'\ [\mathrm{Me^+}]^{z/x}} \qquad (3)$$

The soap anion concentration may be taken to be approximately equal to the soap concentration at the C.M.C. of the alcohol-containing solution. The alcohol concentration is less than its solubility in water. The decanol content y/x of the mixed micelles at the turbidity point has been determined experimentally and found to be constant below the break point A. When the ratio y/x exceeds a certain value, the mesomorphic phase appears.

If we assume that about 50 % of the gegenions are bound by the micelles, *i.e.* $z/x = 0.50$, it will be seen that the right member of eqn. (3) decreases with increasing soap concentration. Consequently also the concentration of free alcohol, [R″OH], at which the mixed micelles characterized by the ratio y/x are formed, will decrease with increasing soap concentration, at least in the concentration range below the break point A. This may be the explanation for the observation that the alcohol content of the mesomorphic phase decreases with increasing soap concentration below the break point A (see Part II [4]).

B. The conditions resulting in the formation of the mesomorphic phase can also be defined by means of an equation of the solubility product type:

$$[\mathrm{R'COO^-}][\mathrm{R''OH}]^{y/x}[\mathrm{Me^+}]^{z/x} = \mathrm{P} \qquad (4)$$

where y/x and z/x denote the molar ratios of alcohol to soap and of gegenions to soap in the mesomorphic phase. The ratios do not have the same values as in eqns. (1)—(3). It has been found that the ratio y/x has a smaller value for the mixed micelles in solution than for the separated phase. Furthermore, the ratio y/x does not remain constant in the separated phase but decreases with increasing soap concentration, at least up to the break point A. According to eqn. (4), the concentration of free alcohol should also decrease with increasing soap concentration.

The ratio z/x has been assumed to have values different from unity and it may hence seem at first sight that the particles of the mesomorphic phase should therefore have an enormously high electrical charge. This is of course not true. The gegenions in the water layers in the mesomorphic phase must be assumed to be partly bound to the soap ions, partly free (analogously as in the micellar solution) so that their activity is the same as in the micellar solution. In the expression for the law of mass action there remains only the activity of the bound gegenion, the activities of the free ions in solution and in the mesomorphic phase cancelling each other. Considerable errors are involved through the neglect of the activity coefficients, which must differ much from unity, especially in the mesomorphic phase.

It should finally be emphasized that the conditions for both equilibria mentioned above, *i.e.* the equilibrium between soap ions, alcohol and mixed micelles and the equilibrium between soap ions, alcohol and mesomorphic phase, must be fulfilled simultaneously.

In the qualitative respect the equations written above seem to be in accord with the observed phenomena. The available experimental data are yet so limited that a quantitative confirmation of the theory is not possible. It seems probable, however, that the soluble small soap ion-alcohol aggregates occurring between the L.A.C. and the C.M.C. and the mixed micelles occurring at concentrations above the C.M.C. partake in the formation of the separating alcohol-soap-water phase and that the increase in hydrophobic properties of these soluble aggregates caused by the incorporation of alcohol is an important factor in this process.

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