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Studies on the Interaction of Paraffin-Chain Alcohols and Association Colloids

VII. Microscopic Investigation of the Interaction between some Liquid Alcohols and Sodium Laurate Solutions

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The formation of a mesomorphic phase as a result of the interaction between aqueous sodium laurate solutions and liquid paraffin-chain alcohols has been studied with the microscope. The first signs of this interaction occur at the L.A.C. The interaction product is predominantly hydrophilic and analyses show that it contains both alcohol and soap. The water content of this product seems to vary; the birefringence diminishes with increasing water content. When decanol interacts with laurate solutions, the molar ratio of alcohol to soap in the separated phase varies from about 1:2 to about 4-5:1, the alcohol content rising as more alcohol is added to the system. The interaction proceeds in several steps. The first amounts of alcohol added form soluble aggregates with the soap, mixed micelles or smaller aggregates. Then alcohol, soap and water separate as a mesomorphic phase. With further alcohol additions, more and more soap is transferred from the aqueous solution to the separated phase until the soap concentration of the solution decreases to a minimum value. Also after this point is reached, the separated phase takes up added alcohol. Finally this uptake reaches a limit and the alcohol appears in the free form. Soap solutions in equilibrium with the mesomorphic phase are not saturated with alcohol. Saturation is reached only when drops of free alcohol appear in the system.

As one of us has shown previously, microscopic observations can be used with advantage to study the interaction between an aqueous soap solution and fatty acid [1–4]. A method based on such observations was developed for the determination of the limiting concentration (L.A.C.) in soap solutions [3]. Subsequently the same method was found to be suitable for the study of the interaction between long-chain alcohols and association colloid solutions [5,6]. In the following we shall describe the results of further investigations in which

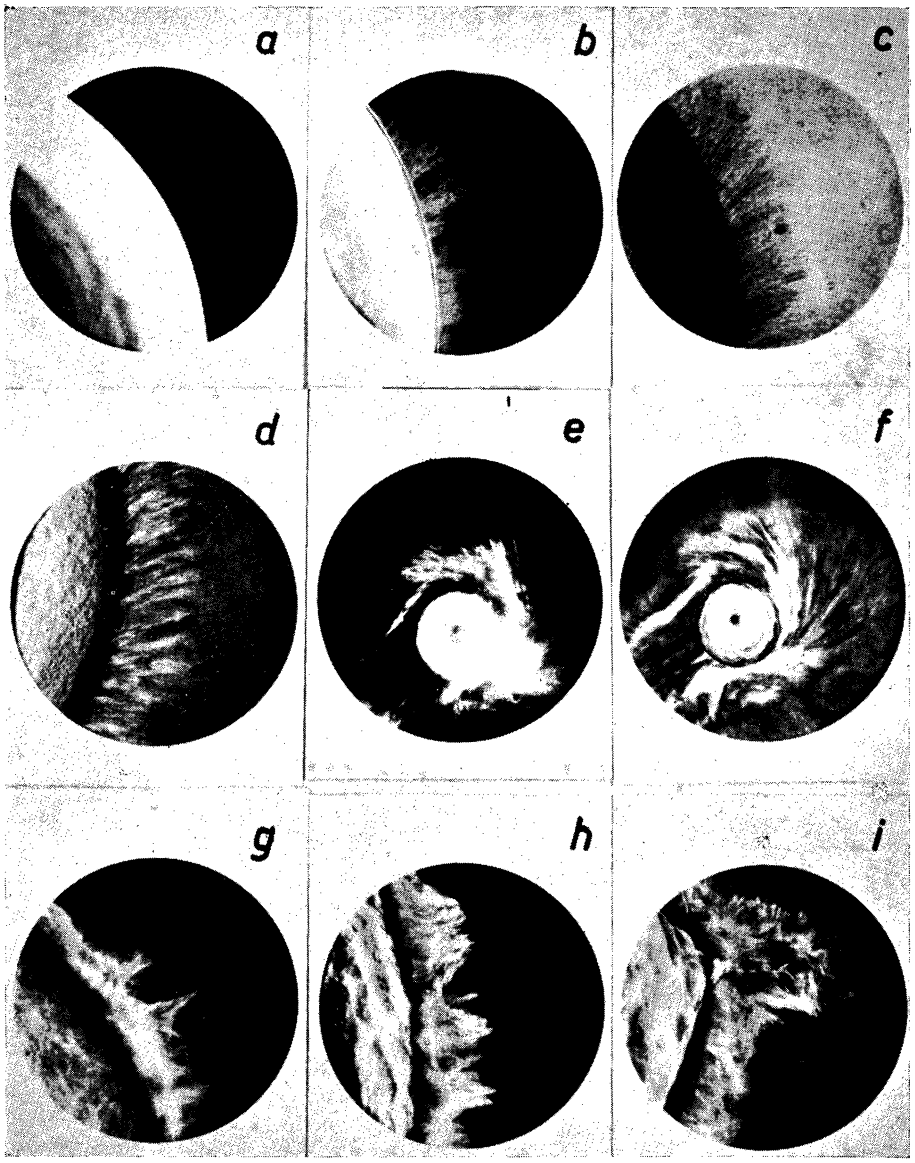

Fig. 1. Microphotographs of the first stages of the interaction between drops of decanol-1 and sodium laurate solutions at room temperature. In the photographs a—d and g—i the decanol drops are seen on the left and the laurate solutions on the right; in photographs e and f, the decanol drops are located near the centres of the photographs. 150 ×.

a) 0.001 M laurate; dark-field condenser
b) 0.006 M laurate; dark-field condenser
c) 0.006 M laurate; transmitted light
d) 0.006 M laurate; phase-contrast condenser
e) 0.006 M laurate; dark-field condenser
f) 0.006 M laurate; phase-contrast condenser
g) 0.014 M laurate; semidark-field condenser
h) 0.030 M laurate; dark-field condenser
i) 0.023 M laurate; dark-field condenser

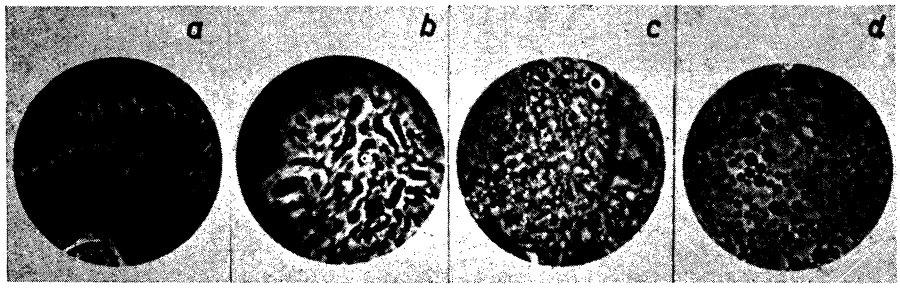

Fig. 2. Later stages of the interaction between decanol and a 0.04 M sodium laurate solution at room temperature.

a) Phase-contrast condenser. 300 ×. Decanol drop in the lower part. Upwards, there is first a layer of interaction product with filamentous structure, then a layer of sausage-shaped and spherical particles of interaction product. Laurate solution in the upper part.
b) Phase-contrast condenser. 600 ×. Myelinic interaction product. A small decanol drop near the centre.
c) Phase-contrast condenser. 150 ×. Sausage-shaped and spherical particles of interaction product streaming out into the solution.
d) Phase-contrast condenser. 300 ×. The interaction product is evenly dispersed in drops throughout the solution.

the same method has been used. In these investigations special attention was directed to the first stages of the interaction, but the appearance of the interaction product at later stages and its composition were also studied.

EXPERIMENTAL

Sodium laurate was prepared in the usual manner from pure lauric acid and sodium ethylate. Conductivity water with a specific conductance less than 1×10^{-6} $ohm^{-1}cm^{-1}$ was employed in the preparation of the soap solutions.

The paraffin-chain alcohols were the same as those used in the previous investigations of this series.

The concentrations of the soap solutions are given in moles per litre of solution, M.

The microscopic observations were made with a Leitz Dialux microscope equipped with phase-contrast and dark-field condensers. Some observations were made also in polarized light (between polaroid plates). While the observations were being made, care was taken to avoid evaporation from the aqueous solutions.

A. INTERACTION BETWEEN DECANOL AND SODIUM LAURATE

The first signs of interaction. The experiments were performed in such a manner that the interface between a decanol drop and the surrounding sodium laurate solution could be examined in the microscope from the moment when they came into contact with each other.

In extremely dilute solutions, when the laurate concentration is below 0.004—0.005 M, the interface between the drop and the solution remains sharply outlined and undergoes no change with time (Fig. 1 a). When the concentration exceeds 0.005—0.006 M, a pronounced change indicating inter-

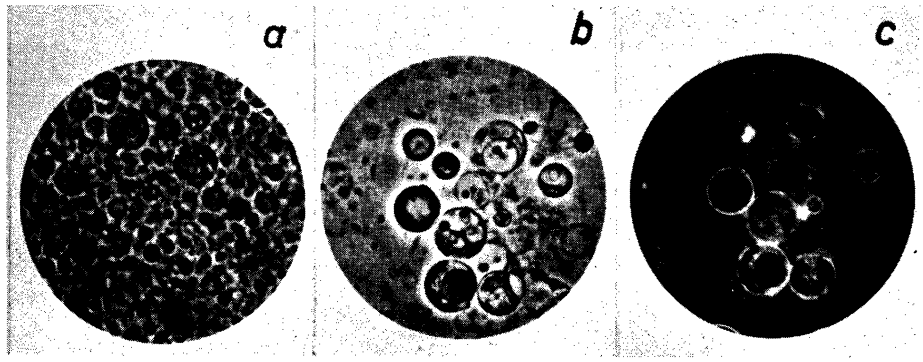

Fig. 3. Final stage of the interaction between decanol and laurate.

a) Laurate concentration 0.05 M + 1 mole of decanol per mole of laurate. Phase-contrast condenser. 600 ×.

b) Laurate concentration 0.014 M + 0.6 mole of decanol per mole of laurate. Phase-contract condenser. 600 ×.

c) The same sample as in b. Dark field condenser. 600 ×.

action between decanol and soap is observed. This change is noted immediately after decanol comes into contact with the laurate solution. The interface becomes uneven, cavities form on the surface of the decanol drop and small particles are dislodged. With the dark-field condenser numerous bright points are seen in vigorous motion in the vicinity of the drop surface. Very soon, however, a corona of hairlike filaments grows from the drop surface (Figs. 1 b, c, d,). Later this corona becomes uneven (Figs. 1 e, f), especially in solutions of high laurate concentration (Figs. 1 g, h, i). (The initial stages of the interaction, before the corona is formed, are difficult to observe, and we have not succeeded in photographing them.)

After the layer of interaction product is formed about the decanol drop, the interaction proceeds much more slowly, particularly in dilute laurate solutions. The outer ends of the filaments in the corona swell and form sausage-shaped figures (myelinic figures) which continue to expand (Figs. 2 a, b). Ultimately the expanded outer ends are disengaged and form clusters of spherical particles which stream out (Fig. 2 c) and are gradually dispersed uniformly in the solution (Fig. 2 d). In the concentration range, 0.02—0.03 M, on both sides of the C.M.C., it is observed that the solubility of the interaction product in the soap solution increases. This has been confirmed by quantitative measurements [6-7].

The final product of interaction. A laurate solution above the C.M.C. is able to solubilize a certain amount of decanol. When an excess of decanol is added, there results a turbidity caused by the separated interaction product. Below the turbidity point, no ultramicroscopic particles are seen on dark-field illumination in decanol-containing laurate solutions, but above this point there occur particles of ultramicroscopic and larger dimensions. The degree of dispersion depends on the mode of preparation and on the decanol and laurate contents of the system. When the decanol content is low, *e.g.* when a new phase

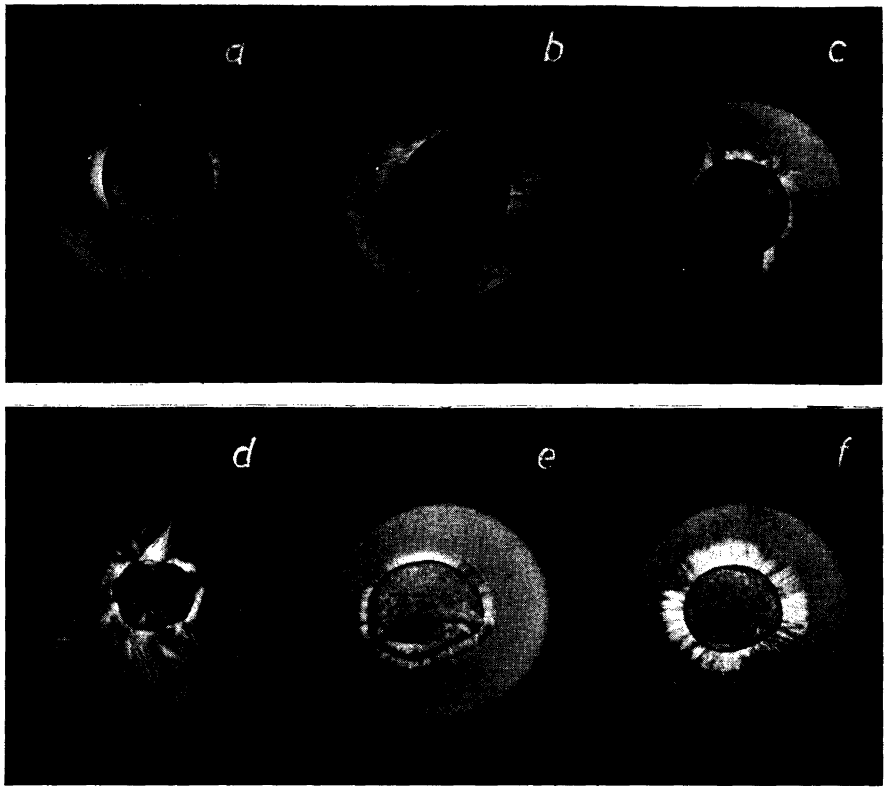

Fig. 4. Microscope observations between crossed polaroid plates of the interaction between decanol and laurate solutions at room temperature. 250×. An isomorphic decanol drop (innermost) surrounded by isomorphic laurate solution (outermost); a layer of birefringent interaction product at the interface.

a) *Laurate concentration 0.005 M · 2 min. from the start of the interaction.*
b) » » *0.005 M · 5* » » » » » » »
c) » » *0.01 M · 5* » » » » » » »
d) » » *0.02 M · 2* » » » » » » »
e) » » *0.04 M · 1* » » » » » » »
f) » » *0.04 M · 5* » » » » » » »

separates on cooling from solutions that are clear at higher temperatures, all the particles are very finely dispersed, ultramicroscopic. When larger amounts of decanol are added to the laurate solutions, the new phase separates in the form of particles of different sizes. The system resembles a semi-transparent emulsion.

In order to be able to examine the final products of the interaction, the following procedure was followed.

A 0.05 M sodium laurate solution containing one mole of decanol per mole of laurate was heated in a sealed ampoule in a water-bath to 75—80°C and shaken thoroughly to

promote the interaction of decanol and the soap. While the shaking was continued, the ampoule was allowed to cool to 40°C, and shaken for two days at this temperature. It was expected that in this way the interaction would be brought to completion.

As seen in Fig. 3 a, the solution now contained an agglomerate of spherical particles of different sizes, from 5—10 μ in diameter downwards. With oil immersion and 900-fold magnification, it was established that there was no lower limit to the sizes of the particles; the number of very small particles was exceedingly large. With the dark-field condenser it could be established that the solution contained numerous ultramicroscopic particles in vigorous Brownian motion.

In some cases another procedure was followed in preparing the solutions.

For example, a 0.014 M sodium laurate solution containing 0.6 moles of decanol per mole of laurate (and 0.05 moles of sodium hydroxide per mole of laurate to suppress the hydrolysis) was thoroughly shaken in a sealed ampoule at room temperature until the decanol was dispersed into small droplets barely visible to the naked eye. The solution was then allowed to stand for two months at room temperature to permit the interaction to continue to completion.

Also in this case the product of interaction was found to consist of spherical particles, but so that smaller particles often were embedded in the larger ones; sometimes one large particle contained many small spheres (Fig. 3 b, c). The refractive index of the substance appeared to differ from sphere to sphere; it seemed as if the decanol content was not the same in all spheres. Also some small drops of unreacted decanol could be seen alongside the interaction products.

It is thus evident that this latter mode of preparation cannot guarantee a complete interaction between the decanol and soap and therefore does not yield an uniform interaction product. The local decrease in the soap concentration of the solution and the accumulation of the separated interaction product, which hinders the contact between solution and decanol, must be prevented by shaking.

0.01—0.05 M sodium laurate solutions with different decanol additions prepared in the first-mentioned manner were investigated systematically. The appearance of the interaction product varied greatly. The sizes of the particles varied from very small particles in vigorous Brownian motion and observable only in dark-field illumination to large spheres about 10^{-2} mm in diameter; the refractive power of the separated phase varied from values near to values greatly deviating from that of the surrounding aqueous solution. At lower laurate concentrations, but above the L.A.C. (*e.g.* in the 0.01—0.014 M sodium laurate solutions) the separated phase appeared as a finely dispersed substance which was indistinct with both phase contrast and dark-field illumination and as fairly large spheres or drops of different sizes which were empty in dark-field and only weakly visible in phase contrast illumination. At higher laurate concentrations, above the C.M.C., (*e.g.* in the 0.04 M sodium laurate solution) and when the decanol additions were relatively small (up to 0.48 mole of decanol per mole of laurate), the separated phase appeared partly as a very finely dispersed substance, partly as small more or less compact spheres clearly outlined in phase contrast and dark-field illumina-

tion. With somewhat higher decanol additions, also in these cases the previously mentioned large, almost invisible spheres appeared. With increasing decanol content, the number of the large spheres increased, but the smaller distinctly outlined spheres did not disappear. There is thus a clear difference in the appearance of the particles of the separated phase above the L.A.C. (up to about 0.02 M sodium laurate) and above the C.M.C. The difference diminishes to some extent when larger amounts of decanol are added.

Observations on the properties of the interaction product. The interaction product is a viscous liquid. Decanol drops covered with a filamentous layer of interaction product approach each other until the ends of the filaments touch. When the drops are pressed together the filaments give way, but when the external force is removed they straighten out again and the drops separate from each other. The filaments are thus elastic. The same applies to the coarser myelinic figures and spherical particles. Examination in polarized light between polaroid plates showed that the interaction product is birefringent (Fig. 4). We have thus a liquid in the mesomorphic state [8,5,6].

In order to determine whether the interaction product is predominantly lipophilic or hydrophilic, the decanol was coloured with a typical fat-soluble dye, Sudan Red.

When the deep-red-coloured decanol interacted in the laurate solution, the dye remained in the decanol drops and the colour of the latter intensified until finally the dye separated as small granules. After all the decanol had been used up in the interaction, small dark red granules of Sudan Red remained among the interaction products at the points where the decanol drops had been earlier.

The dye facilitated the study of the various stages of the interaction. It was now found that sometimes a thin stream of dyed decanol flowed from the decanol drops into the layer of interaction product or into the solution where it more or less rapidly reacted with the soap. Sometimes the connection between the main drop was broken and the decanol formed a new drop that reacted further.

The interaction product was undyed. (A weak rose colour sometimes noted in the layer of the filamentous product was due to minute Sudan Red particles embedded here and there which had separated when the decanol had reacted.) No signs indicating that Sudan Red dissolves in the interaction product were seen. The conclusion was drawn that the interaction product was predominantly hydrophilic.

This was confirmed by experiments in which laurate solutions were coloured with the water-soluble dyes, Azo-blue and Wollecht-violet, which are insoluble in decanol. So far as we could determine, the interaction product was coloured in this case.

The phase formed at the interface between the decanol drop and the soap solution is thus a hydrophilic liquid in the mesomorphic state, probably of the smectic type. This phase seems to swell by taking up more water or soap solution, during which the birefringence diminishes and may disappear completely. The refractive index of the new phase approaches that of the surrounding solution. As mentioned above, this is especially the case in the concentration range above the L.A.C. up to a sodium laurate concentration of about 0.02 M.

Table 1. The decanol and sodium laurate contents of the interaction products formed in 0.014 M sodium laurate solutions to which various amounts of decanol had been added.

Decanol added, moles per mole of sodium laurate	Dried separated product mg	Decanol content of the dry product mg	Sodium laurate content (corrected *) of the dry product mg	Molar ratio of decanol and sodium laurate in the water-free reaction product
0.3	9.9	2.3	7.1	(0.5 :1)
0.3	145.0	29.2	106.4	0.44:1
0.3	89.6	21.3	61.9	0.48:1
0.6	46.9	13.3	29.0	0.64:1
0.6	105.5	31.0	66.9	0.65:1
0.6	416.6	139.0	256.3	0.76:1
1.0	68.4	28.6	35.1	1.2 :1
1.5	46.0	19.7	16.9	1.6 :1
1.5	102.0	42.1	35.8	1.6 :1
2.0	382.0	234.5	125.8	2.6 :1
3.0	425.0	310.5	93.4	4.7 :1

* The correction is based on the assumption that all the water of the isolated product is present as occluded sodium laurate solution. A part of the water belongs, however, to the separated phase itself. The correction is therefore somewhat too large and the decanol-soap ratios in the last column are thus maximum values.

The decanol content of the interaction product. An attempt was made to isolate for analysis the interaction product that appeared as a separate phase, but a complete separation from the solution was not achieved.

A series of 0.014 M sodium laurate solutions containing different additions of decanol were prepared as described above. The solutions were left to stand one month at 40°C, during which time the lighter interaction product gradually rose to the surface from which it was collected. This concentrate was passed through a membrane filter, first under slight pressure and finally by applying suction. The remaining highly viscous product still contained some of the laurate solution that could not be removed.

This product was dried and the water content calculated. Decanol was then removed from the dry residue by distillation and its amount determined. The distillation residue was acidified and the liberated lauric acid extracted with ether. Part of the fatty acid came from the soap dissolved in the occluded laurate solution. The amount of this lauric acid was subtracted and after this correction, the composition of the interaction product was calculated; the water content of the product could not be established. The calculated values are only approximate, but do, however, give an idea of the composition of the separated interaction product.

The data in Table 1 show that the interaction product contains both decanol and sodium laurate. They suggest that in the case of small decanol additions to the solution, the molar ratio of decanol to sodium laurate is near 0.4—0.5. With higher decanol additions, the decanol content of the separating phase increases, the ratio rising to about 1.6 when the amount of added decanol increases to 1.5 moles per mole of laurate. When further amounts of decanol are added, the decanol content of the separated phase increases more rapidly.

As will be shown below, free decanol occurs in the 0.014 M sodium laurate solution only after about 2.5 moles of decanol per mole of laurate have been added.

It is thus evident that the composition of the phase containing decanol and soap is a function of the total decanol content of the system. The interaction between the soap in solution and the decanol does not end when the new phase appears at the turbidity point. The interaction progresses further, but now the decanol is not incorporated in the micelles of the solution but in the separated phase and at the same time more and more soap is removed from the solution. Only after the soap concentration of the solution is decreased to a rather low value, does the interaction with the soap in the aqueous phase end.

Previously we have come to the same conclusion on the basis of conductance measurements.[9] These measurements showed that the decanol content of the separated phase increases with the amount of added decanol at the same time as the concentration of soap in the water phase decreases. The composition of the product which separates from 0.010—0.014 M sodium laurate solutions was calculated (from conductance values) to be 0.6—0.8 mole of decanol per mole of sodium laurate at the turbidity point, but was found to increase to about 4:1 after 1.5 moles of decanol had been added per mole of laurate. (These calculations, which were made on the assumption that the separated phase does not play any part in the transport of current, thus give higher decanol contents than the analyses.)

The calculations made on the basis of conductance measurements also showed that the composition of the separated phase varies with the concentration of the soap solution in which it is formed; in 0.1—0.5 M sodium oleate solutions the composition at the turbidity point was found to be 0.5 moles of decanol per mole of oleate, but at lower oleate concentrations the decanol content increased to 1 mole or more per mole of oleate.

In this connection it may be noted that it was previously found that the mesomorphic acid soap that separates from caprate solutions when capric acid is added has the composition 1 mole of capric acid to 2 moles of sodium caprate and 13—20 moles of water [4]. These acid soaps and the decanol-soap interaction products studied here resemble each other in many of their properties.

The maximum amount of decanol that dissolves in the system. We have previously found that the conductance of the system decreases to a constant value when sufficient decanol has been added. The composition of the separated phase at this point was calculated to be 3.0—3.5 moles of decanol per mole of soap in the 0.010—0.022 M sodium laurate solutions. We have also pointed out that drops of free decanol were observed in the range where the conductance was no longer altered by added decanol.

In a series of 0.010, 0.014, 0.023, 0.030 and 0.040 M sodium laurate solutions containing 0.1—10 moles of decanol per mole of laurate, a study was made of the amount of decanol that a known volume of the soap solution can transfer to the separated mixed phase. Microscopic examinations showed that drops of free decanol occurred in these solutions when the molar ratio of decanol to soap had risen in the respective cases to 2, 2.5, 3.5, 4.0 and 4.5. Considering that only a part (C_{tot}—$C_{L.A.C.}$) of the soap takes part in the formation of the

mesomorphic phase, the ratio in the new phase increases in all cases to 4—5 moles of decanol per mole of laurate. This shows that free decanol occurs in the investigated systems soon after the conductance has decreased to a constant value; small amounts of decanol seem to dissolve in the separated phase even after the interaction with soap in the aqueous phase has gone to completion. (At higher soap concentrations, *e.g.* in the 0.1—0.3 M sodium oleate solutions, the separated phase dissolves appreciable amounts of decanol between the point where the conductance becomes constant and the point where free decanol separates).

B. INTERACTION BETWEEN SODIUM LAURATE AND LIQUID ALCOHOLS OF VARYING CHAIN LENGTH

We have employed the above-described microscopic technique in a study of the interaction of sodium laurate solutions with octanol-1, heptanol-1 and hexanol-1. Similar effects were observed with all alcohols. The solubilities of the alcohols increase, however, with decreasing chain length of the alcohols, and likewise the solubilities of the products of the interaction with soap increase. As a result of this, the interaction proceeds more rapidly and some of the phenomena observed with decanol are weaker or are not observed at all.

On the surfaces of the octanol drops the characteristic layer of filamentous structure composed of birefringent liquid phase was formed. A similar layer developed also on the surfaces of the heptanol drops but did not retard the interaction to the extent noted in the case of decanol and octanol. No continuous layers were produced round the hexanol drops; the dissolution proceeded rapidly and led to complete disappearance of the drops. The end products of the interaction assumed in all cases similar filamentous, myelinic and spherical forms as in the case of decanol.

Separate experiments were made to determine the lowest laurate concentration at which the first signs of interaction with the different alcohols could be detected at 20°C. The laurate solutions employed contained 0.1 mole of sodium hydroxide per mole of laurate to suppress hydrolysis. For decanol, the laurate concentration was found to be 0.0045—0.0055 M; for octanol 0.0055—0.0061 M; for heptanol 0.0061—0.0068 M; and for hexanol 0.0061—0.0068 M. For all alcohols the reaction thus begins in the same relatively narrow laurate concentration range extending from 0.0045 to 0.0068 M. Within this range, the concentration where the first signs of interaction are noted with the microscope varies slightly with the chain length of the alcohol; this may be primarily due to the greater solubility of the reaction product with decreasing chain length of the alcohol.

The observed lowest laurate concentration range, 0.0045—0.0068 M, where interaction with alcohols occurs is in good agreement with the results of our previously published turbidity measurements.

C. INTERACTION WITH CRYSTALLINE ALCOHOLS

Some observations were also made on the interaction between sodium laurate solutions and crystalline dodecanol-1, tetradecanol-1, hexadecanol-1 and octadecanol-1. This interaction differs in principle from that observed with

the lower liquid homologues. The alcohol crystals swell rapidly when they come in contact with the soap solution; they seem to split into thin parallel layers which appear to be held together by a semisolid substance. The alcohol layers also expand in length and breadth; small reacting crystals often move forward quite rapidly, leaving behind a wide tail of interaction product with the layers parallel to the crystal surface. One gets the impression that the soap solution penetrates into the crystal between its double layers of parallel alcohol molecules and that soap concentrates there and also penetrates into the layers of alcohol molecules. The interaction product is birefringent and the interaction with alcohol crystals occurs at rather low laurate concentrations.

The study of this interaction is being continued.

DISCUSSION

In the previously described nephelometric measurements, the first sign of interaction between soap and alcohol at the L.A.C. was the disappearance of the excess of alcohol [10,11]. In the above-described microscopic method, on the other hand, one observes the formation of the mesomorphic phase. Neither of these methods gives information of the changes occurring in the solution, but with the aid of a third method (solubility measurements) we obtain an idea of what happens in the solution; we find that the solubility of the alcohol (decanol-1) increases somewhat above the L.A.C.[6,7]. These three methods give the same value for the concentration (L.A.C.) where the interaction begins; the small differences between the values depend on the fact that the three methods register different phenomena associated with the same process.

In the microscopic observations, the interaction between alcohol and soap solution appears as a reaction taking place at the interface. No changes or processes that take place within the alcohol phase are observed, whereas one gets an idea of the solution of the alcohol in the aqueous phase and of the conditions favouring the formation of the mesomorphic phase when the alcohol concentration increases locally to a certain value. In the interface (also on the alcohol side) there must occur an adsorption of soap and a formation of palisade layers composed of parallel alcohol molecules and soap ions. The interfacial tension must be very low. An extensive dispersion into very fine particles follows ("spontaneous emulsification") and the rapid solution of the alcohol in the water phase in the vicinity of the phase boundary is facilitated. These processes make it possible for the corona to grow out from the interface. The palisade layers of alcohol and soap formed in an environnement rich in alcohol but poor in water take up more water and perhaps more soap with swelling. We refer again to the swelling of the filaments; their strong birefringence decreases and spherical drops are produced. We wish to emphasize that the formation of the mesomorphic alcohol-soap-water phase does not presuppose the presence of soap solution-alcohol interfaces in the system, even if the formation of the corona-like structures does so. This phase can be formed directly from the components in the solution, *e.g.* on cooling the homogeneous solution. Soap solutions in equilibrium with the mesomorphic phase are not saturated with respect to alcohol and the concentration of free alcohol in them is much lower than in a saturated aqueous solution of the alcohol; conditions favouring the

formation of the phase mentioned are produced when the concentrations of soap and free alcohol increase over certain limits.

In the cases we have investigated the interaction between decanol and soap solution passes through several steps. The first amounts of added alcohol (in excess of that which dissolves in the water) form soluble aggregates with the soap; the alcohol solubilizes in micelles or forms smaller soap-alcohol aggregates. When more alcohol is added, a separate phase consisting of alcohol, soap and water is formed; with increasing alcohol additions, more and more soap is removed from the water solution to form more of the separated phase until the soap concentration of the solution is decreased to a minimum value. Also after this minimum value is reached and the interaction with soap in the solution ends, the separated alcohol-soap-water phase takes up added alcohol. Finally also this uptake attains a limit, and the alcohol appears in the free form. Only at this point does the system become saturated with alcohol. In sodium laurate and sodium oleate solutions at 20°C, the system at this point consists of three phases, the aqueous solution, the alcohol-soap-water phase and free decanol.

Both the alcohol-soap ratio and the water content of the alcohol-soap-water phase seem to vary between rather wide limits. If there is a continuous transition between the different compositions and forms of this interaction product or if the product possibly forms more than one phase is not clear. See, for example, the previously described rather sharp turbidity maxima which result when decanol is added to soap solutions in increasing amounts [9].

The character and composition of the substance that separates from association colloid solutions above the L.A.C. when alcohol is added in sufficient amount seems to have been unknown to most of the investigators in this field. This had led to a misinterpretation of the results of the solubility determinations in connection with studies of the solubilization of alcohols. Already in 1947 one of the present writers [8] postulated the difference in the solubilization mechanism of nonpolar and polar compounds and called attention to the fact that a liquid-crystalline product separates from sodium oleate solutions when octanol or hexadecanol is added and that this is accompanied by a fall in the conductance. In the same paper the solubilization of terpineol was also reported and it was shown that terpineol first dissolves readily in a 0.3 M oleate solution, but then causes the system to become heterogeneous when more than 4.5 % is added. The system becomes homogeneous again when still more terpineol is added. The solution was found to be definitely saturated with terpineol only after more than 26 % had been added. At the first turbidity point the viscosity passed through a very pronounced maximum, and after adding 13—16 % terpineol a second, rather low viscosity maximum was noted; the conductance was observed to decrease rapidly above the first turbidity point, but then passed through a minimum. In the saturated systems, both the viscosity and conductance remained constant. It was reported that many other substances effect similar phenomena. Menthol and decamethylene glycol were, however, found to solubilize normally in rather high oleate concentrations, *i.e.* the excess of these substances separated in pure form [8]. These investigations showed the necessity of making observations of the nature of the separated phase in solubilization studies.

Later [5,12] it was shown that a liquid-crystalline product is generally formed when paraffin-chain alcohols interact with aqueous association colloid solutions of the paraffin-chain type (fatty acid soaps, alkyl sulphates, alkyl trimethyl ammonium salts) and that the product contains both alcohol and colloid. It was emphasized that a large part of the colloid can be precipitated in this way from the solution, by adding sufficient amounts of the alcohol. It was also shown that the mesomorphic phase forms only above the L.A.C. and that the maximum solubility of the alcohol increases slightly somewhat above this point (before the system becomes heterogeneous). The great similarities between the interaction between alcohols and association colloid solutions and the formation of acid soaps in the interaction of soap and fatty acid were stressed. Ekwall, Passinen and Danielsson [6] reported on the formation of the mesomorphic alcohol-soap-water phase in a brief survey of their experimental work conducted during 1950—53 on the solubilization of alcohols, and pointed out the differences between the solubilization of alcohols and hydrocarbons. In the present series the results of this work is thoroughly discussed. In Part I [13] it was for instance emphasized that the solubility curves for paraffin-chain alcohols are not comparable with those obtained in studies of hydrocarbon solubilization.

In 1948 Winsor also reported on the separation of birefringent "gels" in systems which, however, contained besides a hydrotropic substance, alcohol, and water, also a hydrocarbon or a mixture of hydrocarbons and thus were rather complex; only in one case did Winsor give experimental data on the formation of a "gel" in a system containing no hydrocarbon (sodium-*n*-butyrate-octanol-water) [14]. Klevens, referring to his own observations and to Winsor's work, mentioned that added polar long-chain compounds and soaps readily form viscous birefringent "gels" [15]. However, in the same paper the solubility curves for alcohols were directly compared with those obtained for hydrocarbons. Lumb investigated the phase equilibria in mixtures of alcohols and aqueous potassium butyrate and octanoate solutions and showed clearly that in some cases a mesomorphic phase composed of soap alcohol and water separates over a wide concentration range [16]. Recently. Hyde, Langbridge and Lawrence, on the basis of extensive experimental observations, primarily on aqueous Teepol-alcohol systems, discussed "soap + water + amphiphile systems" [17]. In their work the study of the formation of a liquid-crystalline phase consisting of alcohol, association colloid and water holds a central place; also the disappearance of this phase on adding greater amounts of alcohol was studied. They showed that there occur two ranges of homogeneous systems (compare Ekwall's [8] observations on the sodium oleate-terpineol systems and Lumb's [16] on the above-mentioned soap-alcohol systems). The viscosities and conductances of the Teepol-systems pass through maxima and minima (somewhat similar to those previously observed in other association colloid-alcohol systems [8,6,9,18]). Lawrence and coworkers state that a similar phase equilibrium pattern has been found to apply to all soaps and all amphiphilic additives of the long-chain type. They emphasize the serious error incurred in many earlier studies when "the initial separation of the liquid-crystalline phase was taken to be emulsion and excess of the amphiphile above saturation . . ."

Summarizing it can be said that Ekwall and coworkers have studied the changes in the aqueous association colloid solutions when alcohol is added both before and after the mesomorphic phase has formed and have attempted an exact determination of the conditions favouring the formation of this phase. They have also studied the properties and composition of this phase, but their investigations were in only a few cases extended to the addition of more than 5 moles of the alcohol per mole of the colloid. The English investigators have studied the systems from the viewpoint of the phase equilibria and have been interested also in those systems where the polar substance predominates; they have attempted to draw equilibrium diagrams for the ternary systems. Only in a few cases have the same systems been studied in these different investigations. They complement each other and give a fairly good idea of the interaction between polar substances and aqueous association colloids, even if there still are many unsolved problems in this field.

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