Properties and Structure of the Decanolic Solutions in the Sodium Caprylate-Decanol-Water System

I. The Region of Existence of the Isotropic Decanolic Solutions

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Caprylate-free decanol dissolves rather small amounts of water, and water-free decanol extremely little sodium caprylate. The caprylate and water enhance the solubility of each other in decanol so that one is able to get solutions containing more than 20 % caprylate or water, respectively, in decanol. At 20°C these solutions are obtained when the water content exceeds about 5 to 6 and is below about 27 moles of water per mole of caprylate. An increase of the temperature does not displace at all the position of the latter boundary, but the former is somewhat displaced towards lower water contents. On the opposite, the lower boundary of the solution region is markedly displaced towards lower decanol contents.

Preliminary conductance measurements show that one does not have to do with solutions with free ion migration, and small-angle X-ray diffraction studies show that these solutions are of micellar character. On the basis of these circumstances and from the fact that these solutions at the lower boundary are in equilibrium with a two-dimensional hexagonal mesophase consisting of water cylinders in a continuous amphiphilic environment the preliminary conclusion is drawn that the micelles of the isotropic decanolic solutions are composed of sodium caprylate and decanol molecules around a water core and with decanol as intermicellar solution.

REGION OF EXISTENCE AT 20°C

It has been shown earlier that there exist, at 20°C in the three-component system sodium caprylate-decanol-water, five mesomorphous phases and two isotropic solutions.[1,2] One of the last mentioned appears in the part of the system with a high water content and consists of aqueous solutions of sodium caprylate with and without solubilized decanol, and the other in the part of the system with a high decanol content consists of sodium caprylate and water dissolved in decanol. In the phase diagram in Fig. 1 the region of the existence of the last mentioned solution is denoted L_2.
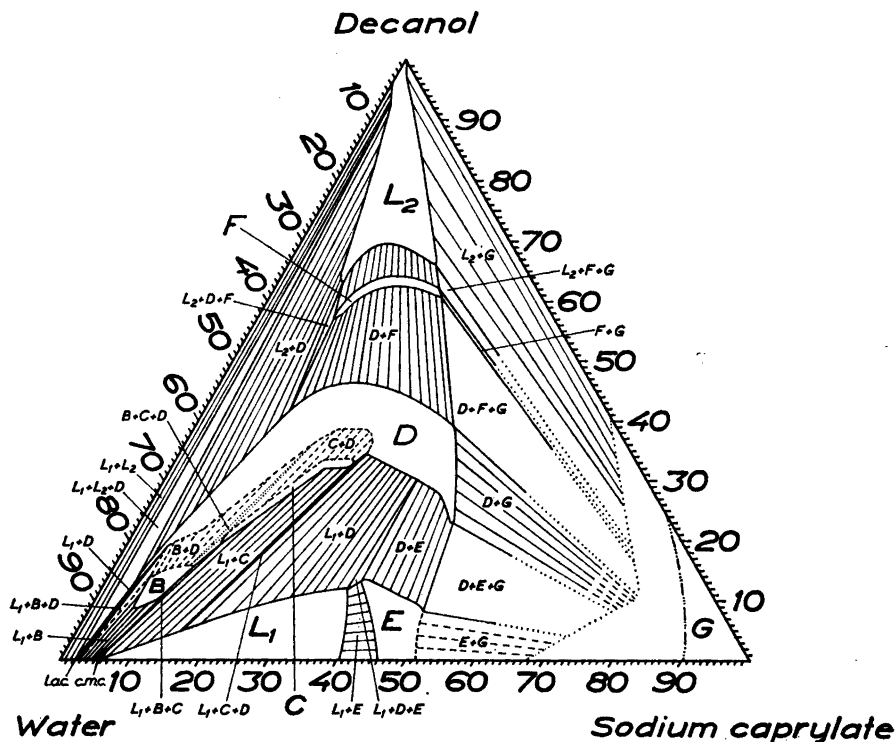
Fig. 1. Phase diagram for the three-component system sodium caprylate-decanol-water at 20°C. B—F regions with homogeneous mesomorphous phases; G region with solid substances; L_1 region with homogeneous isotropic aqueous solution; L_2 region with homogeneous isotropic decanolic solution.

The region L_2 extends from the decanol corner (at 100 % decanol) almost down to 66—69 % decanol. The region widens as the decanol content decreases.

Caprylate-free decanol dissolves only 3.8 % of water, and water-free decanol only 0.35 % of sodium caprylate. The caprylate and the water, however, increase the solubility of each other in decanol. For a water-to-caprylate ratio of 58/100 by weight the solubility of the caprylate increases to 21.4 %, and that of the water to 12.5 %; at a ratio of 304/100 the corresponding solubilities are 9.4 and 27.5 %. The region of existence of the solutions in question lies largely between these ratios.

At lower ratios than 58/100 the L_2 solutions did not exist and a two-phase region is entered where L_2 solution is in equilibrium with fibrous solid sodium caprylate. The boundary with this two-phase zone is quite linear, except at extremely high decanol contents (between 95 and 100 %), where it curves inwards toward a water-to-caprylate ratio of about 82/100.

There is also an upper limit of the water content at which the L_2 solution can exist; when the ratio 304/100 is exceeded a two-phase region is entered in

which the L_2 solution is in equilibrium with a mesomorphous phase of lamellar structure designated type D. Also this boundary is quite linear, except at higher decanol contents above about 95 %, where the boundary curves out-wards, and here the L_2 solution exists down to zero caprylate. This last sec-tion of the L_2 region borders a two phase zone where the L_2 solution is in equilibrium with dilute aqueous solutions of caprylate.

The lower limit of the region is curved; below it there is a two-phase zone, in which the L_2 solution is in equilibrium with a mesomorphous phase with a two-dimensional hexagonal structure, denoted as type F.

The experimental data on which these results are based have been published earlier.[2]

THE REGION OF EXISTENCE AT HIGHER TEMPERATURES

To examine the displacement of the boundary of the L_2 region with tem-perature a series of specimens were prepared with constant weight ratios
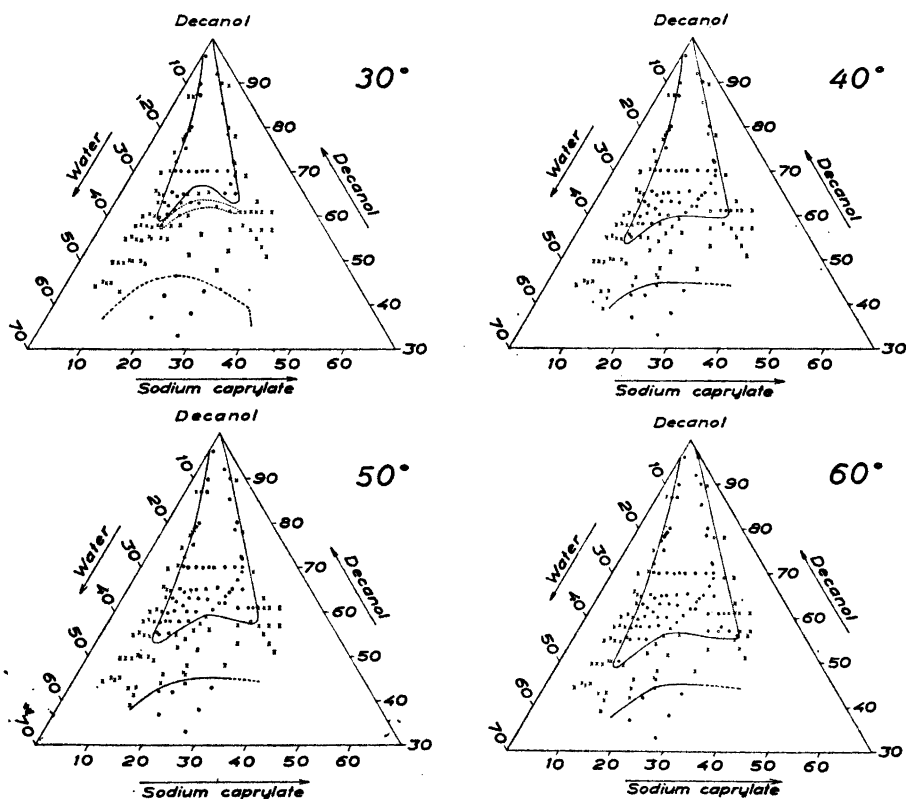

Fig. 2. Observations concerning the extent of the region with isotropic decanolic solu-tions at different temperatures. ○ Homogeneous isotropic solutions; × two phases; ● homogeneous mesophase.

between decanol and sodium caprylate and varied proportions of water, and with constant ratios between water and caprylate and varied proportions of decanol. The composition of the specimens was chosen so that it fell within the region for the homogeneous L_2 solutions and in the two-phase zones outside this. The specimens were preserved in a thermostat, the temperature of which was raised from 20° to 60° in 10° steps at intervals of few days. They were examined visually and under the microscope between crossed nicols. The results are reproduced in the form of graphs, one for each temperature (Fig. 2a-d). On the basis of these observations the boundaries were drawn for the L_2 region at different temperatures.

It was found that the region L_2 increased in area with temperature. The lower boundary of the region was above all displaced downwards towards lower decanol contents. At the same time the mesophase F disappeared; it still occurred at 30° but not at 40°. The upper limit of mesophase D seemed not to be noteworthy affected by the rise in temperature. As a result the L_2 solution, that at lower temperatures along its lower border boundary was in equilibrium with mesophase F, was from 40° in equilibrium with mesophase D along this border.

Fig. 3 surveys the effect of the rise in temperature. The region of existence of mesophase F at 20° is also indicated, as is the upper limit for mesophase D. As already mentioned, the lower limit of region L_2 was displaced with rising temperature towards lower decanol contents; at as low as 40° it lays below the lower boundary of region F at 20°, and at 60° it lays between 50 and 57 % of decanol. At the same time the right boundary of the region was displaced
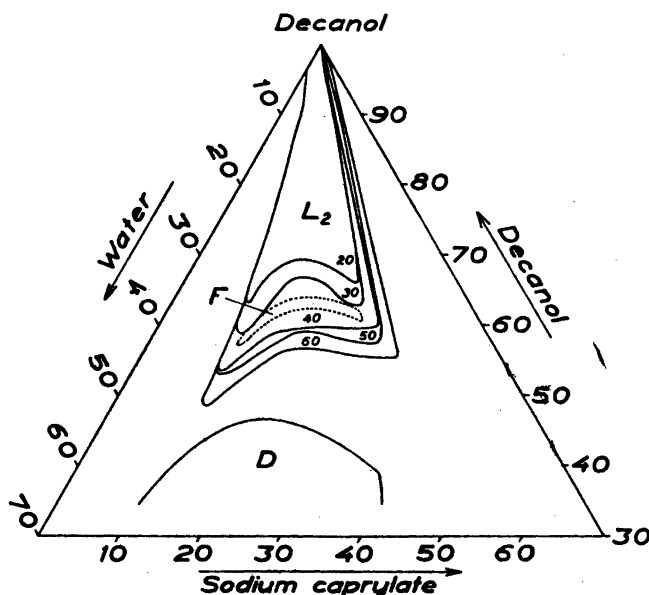

Fig. 3. The location of the boundaries of the L_2-region at temperatures between 20° and 60°C.

towards lower water contents, but more slowly. At 30° it was at about the same site as at 20°, that is at the water/caprylate ratio 58 to 100, and at 40°, 50°, and 60° at about 48, 45, and 39 to 100. Thus, throughout the temperature range examined a minimum proportion of water is needed for the formation of the L_2 solution. The main part of the left boundary of the region remained completely unaffected by the rise in temperature at the water/caprylate ratio 304/100; only the boundary of the new lower part of the region tends to move towards higher water ratios, about 375/100 at 60°. The L_2 solution thus cannot exist above a certain ratio of water to caprylate and over a large part of the region this maximum is rather independent of temperature.

DISCUSSION

The fact that water-free decanol per mole dissolves only about 0.035 moles of sodium caprylate shows that the formation of L_2 solutions is not due appreciably to formation of complexes directly between the two components. On the other hand, the fact that pure decanol per one mole dissolves about 0.3 moles of water, shows that only a small part of the large water content of the L_2 solutions can be ascribed to the hydration of the decanol molecules. However, as the caprylate and water increase each other's solubility in decanol some kind of caprylate-water or caprylate-water-decanol complexes must be formed, that are highly soluble in decanol. The existence of these complexes is restricted to certain water-caprylate ratios; at 20° this ratio ranges from 5—6 moles to about 27 moles of water per mole of caprylate.

The minimum required amount of water, 5—6 moles per mole of sodium caprylate, could suffice for complete hydration of the sodium ions of the soap and this was already some years ago taken as a sign that the L_2 solutions contain sodium ions in the hydrated state.[1,6] The fact that the hydration of the ions diminishes with temperature might account for the displacement on raising the temperature of the right boundary of the L_2 region towards lower water contents; at 60° the minimum required is 3.6 moles of water per mole of sodium caprylate. Support for the view that there is a connection between the minimum content of water and the hydration of the soap is found in the fact that the right border of the L_2-region at 20° in all three-component systems consisting of sodium caprylate, alcohol and water is found to be constant at 5—6 moles of water per mole of sodium caprylate, irrespective of the alcohol used (from decanol down to ethanol).[3-5] Further proof is the fact that the minimum amount of water required for formation of the L_2 solutions in three-component systems of alkali soap-alcohol-water varies with the nature of the alkali ion of the soap in the same direction as the hydration number of the ion. For lithium caprylate the minimum water content at 20° was found to be 7.5 moles, for sodium caprylate 5.4 moles, and for potassium caprylate 2.5 moles of water per mole of soap.[3-5]

The maximum water content at which the L_2 solutions can exist at 20° is, as we have seen above, about 27 moles of water per mole of sodium caprylate. This is a large amount but not more than could be bound to the hydrophilic groups of the amphiphilic components by means of hydrogen bonds and ion dipole attraction. It is conceivable, therefore, that the left border of the L_2

region is determined by the maximum number of water molecules that could be bound in this way to the caprylate-decanol complexes of the solution.

A preliminary investigation showed that the conductance of the L_2 solutions was very low; from the extremely low value for pure decanol the specific conductance rose with increasing sodium caprylate and water content but did not exceed 35×10^{-5} ohm^{-1} cm^{-1} even for the strongest solutions, where the soap content had risen to $0.5-1.2$ moles of sodium caprylate per 1000 g of solution and the water content to $14-28$ %.[7] In ordinary electrolyte solutions in water such values are reached at only about 4×10^{-4} molar solutions. A 0.005 molar aqueous solution of sodium caprylate has a conductivity about 100 times greater.[8] It is evident from this that the structure of the decanolic solutions in the L_2 region differs appreciably from that of ordinary electrolyte solutions with their free ionic migration.

The low angle X-ray diffraction patterns of the L_2 solutions show at certain concentrations similarity to those of micellar aqueous caprylate solutions.[1,6] The pattern displays the existence of a diffuse scattering maximum, the intensity of which increases greatly when the sum of the caprylate and water content exceeds about 10 %.[7] That shows that particles of colloidal dimensions here are formed. The complexes of amphiphilic molecules and water that exist in the L_2 solutions thus probably give rise to micelles; from the low conductance it is resonable to suppose that sodium caprylate and water are present in the micelles in such a state that free ions cannot be split off and hence no electrically charged particles can be formed.

A study of the conditions in the two-phase zone between the L_2 solution and the mesophase in region F (Fig. 1) showed that the tie lines joining these two phases agree closely in direction with the lines joining the decanol corner of the diagram with various points on the water-caprylate axis.[1,2] This means that the molar ratio between water and the caprylate was the same for the L_2 solution and for the mesophase and thus the aggregates of the mesophase have about the same composition as the micelles of the L_2 solution. We have supposed that the transition from the micellar L_2 solution to the mesomorphous phase in F has a similar mechanism as that from the micellar L_1 solution to mesophase in E.[5,6] In the latter case the transition is characterized by the fact that the micelles in a fairly unchanged state pass from the unordered micellar state to the ordered mesophase as soon as the volume fraction of the micellar matter of the solution exceeds a critical value, the magnitude of which depends on the axis ratio of the anisometric micelles.[1,3,6,9] If this is the case, it is possible to derive the probable structure of the micelles in the solution close to the lower boundary of the L_2 region from the aggregate structure in mesophase in the F-region.

Mesophase F has a two-dimensional hexagonal structure. Calculations on the basis of X-ray diffraction studies and density measurements showed it to be composed of hexagonally arranged, long parallel cylinder aggregates.[1,2,8] These consist of a water core closely surrounded by the hydrophilic groups of amphiphilic molecules, that is the carboxylate groups and the sodium ions of the caprylate, and the hydroxyl groups of the decanol molecules. The paraffin chains of the amphiphiles form a continuous, semi-liquid hydrocarbon environment between the cylinders. The packing density within the hydro-

philic layer is high — about 18.5—25 Å^2 per hydrophilic group — but considerably less within the hydrocarbon layer. In the part of the mesophase F that is in equilibrium with the outermost right corner of the L_2-region, the aggregates are composed of about 5.5 moles of water and about 1.8 moles of decanol per mole of sodium caprylate, and in the part far to the left, the composition is about 27 moles of water and about 3—5 moles of decanol per mole of sodium caprylate.

It has been stressed above that the micelles of the L_2 solution have the same water content, ranging from about 5.4 to 27.0 moles per mole of sodium caprylate, as the aggregates of the mesophase. Provided that the decanol content is also the same for the micelles next to the lower border of the L_2 region it should vary between about 1.8 and 3—5 moles of decanol per mole of caprylate. The rest of the decanol would then form an intermicellar liquid between the micelles. It seems likely that also the micelles at the lower border of region L_2 are cylindrical but that they further into the region become more spherical, as in the case of the micellar aqueous solutions in the L_1 region.

The above experimental results thus suggest a micelle structure with a central water core surrounded immediately by the hydrophilic groups of amphiphilic molecules, and, further out, by a layer consisting of the paraffin chains of these molecules. The cohesion in the micelles is probably provided chiefly by the interaction between the water molecules and the hydrophilic groups of the sodium caprylate, and decanol of the micelles. The water content of the micelles does not fall below that required for complete hydration of the sodium ions of the caprylate, and is probably not more than can be bound on the hydrophilic groups through hydrogen bonds and ion-dipole attraction. The micelles are not electrically charged. They are surrounded by an intermicellar solution consisting chiefly of decanol.

New experimental studies have been carried out to check, modify or possibly extend this hypothesis on the micellar structure of the decanol-sodium caprylate-water solutions. These studies will be dealt with in the following articles in this series.

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