# FINSKA KEMISTSAMFUNDETS MEDDELANDEN

# SUOMEN KEMISTISEURAN TIEDONANTOJA

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# Mesomorphous Phases in Association Colloid Systems

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A number of crystalline organic compounds with extended or platelike molecules are transformed by warming into a mesomorphous (liquid-crystalline) state. It is customary to distinguish between nematic, smectic and cholesteric mesophases. Fig. 1 shows schematically the arrangement of the molecules in the two first-mentioned cases.

In addition to this so-called thermotropic mesomorphism, there is a lyotropic mesomorphism which involves a solvent as a participating reactant. Both types of mesomorphism are displayed by many surface-active substances.

In the following we shall consider lyotropic mesomorphism.

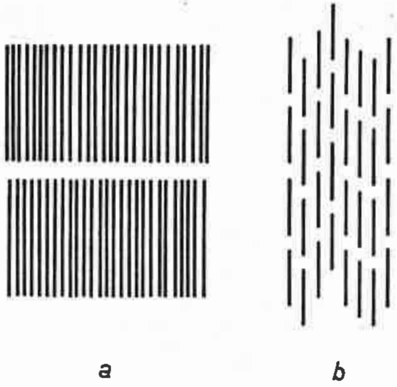

*Fig. 1.* Schematic arrangement of the molecules in a smectic mesophase (a) and in a nematic mesophase (b).

It has long been known that lyotropic mesomorphism is displayed by two-component systems of salts of the higher fatty acids and water. Fundamental studies of the phase equilibria in such systems were carried out by McBain and his co-workers. Phase equilibria diagrams similar in principle were found to be valid for aqueous systems of many soap-like compounds. Fig. 2 shows the phase equilibria of the potassium oleate-water system at different temperatures (1). The soap that separates from the oleate solutions when the soap concentration exceeds 20 per cent is not the crystalline soap, but a mesomorphous, water-containing phase which is called middle soap. When examined between crossed nicols under a microscope, the phase exhibits a marked double refraction and a characteristic texture. By X-ray studies Luzzati (2, 3, 4, 5) has recently found that the middle soap derived from oleates and other higher (C12—C18) soaps consists of extremely long hexagonally packed cylinders surrounded by water. The hydrocarbon chains of the fatty acid anions in the cylinders project inwards and the hydrophilic ionized carboxyl groups outwards into the water. The hydrocarbon core of the cylinders is semiliquid. At high soap concentrations another mesomorphous phase, the so-called neat soap, separates. This phase is more fluid than the middle soap and differs from the latter in microscopic appearance. Luzzati has shown that this mesophase has a layer structure comprising double layers of fatty acid anions separated by layers of water. The hydrophilic end groups of the fatty acid anions in the double layer point toward the water layer. Also in this case the hydrocarbon part of the double layer is in a semiliquid state.

If a third component of amphiphilic character is introduced into the association colloid-water system, the tendency to form mesomorphous phases may be even greater than in the two-component system. Such is the case when compounds like long chain fatty acids, aliphatic alcohols and alkylamines are introduced.

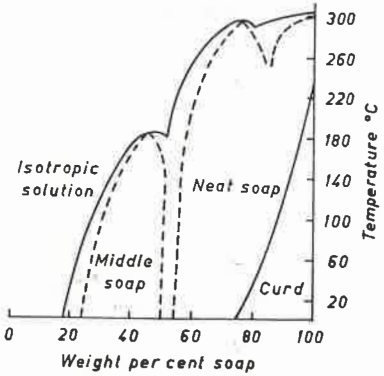

*Fig. 2.* Phase diagram for the two-component system of potassium oleate and water. (McBain and Sierichs).

Already in 1933 McBain (6) described the results of an extensive investigation into the phase equilibria of the three-component system potassium laurate-lauric acid-water at temperatures between 100 and 360°C. The triangular phase diagram in Fig. 3 shows his results at 100°C. At this temperature there are two regions of homogeneous, isotropic solutions, one, L 1, in which water and another, L 2, in which lauric acid is the solvent. Both mesomorphous phases, the middle soap and the neat soap, are observed; the regions where they exist are expanded because the phases can incorporate lauric acid. Between these four regions there are large two-phase regions and three-phase triangles (between L 1, L 2 and the middle soap; between L 2, the middle soap and the neat soap; between L 2, the neat soap and solid crystalline potassium laurate). When the temperature increases the ranges where isotropic solutions exist expand, whereas the mesomorphous regions diminish in size and finally disappear completely.

Since the late forties the conditions favouring the formation of mesophases in three-component systems have been studied by many groups of investigators.

In 1951 Lumb (7) published a paper describing several systems of this nature. Fig. 4 shows the triangular phase diagram for one of these systems, potassium caprylate-octanol-water, at 25°C. In this diagram we see two regions of isotropic solutions, one (L 1) consisting of solutions in water and the other (L 2) consisting of solutions in octanol. Between these there is a so-

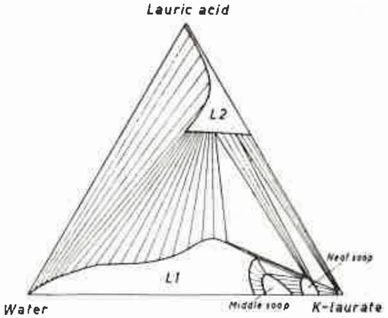

*Fig. 3.* Phase diagram for the three-component system potassium laurate-lauric acid-water at 100°C. (McBain and Field).

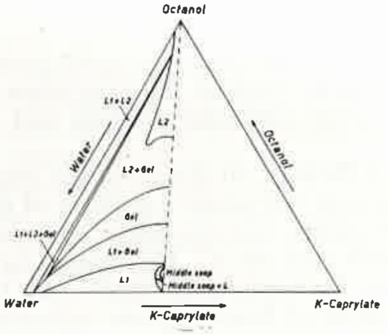

*Fig. 4.* Phase diagram for the three-component system potassium caprylate-octanol-water at 25°C. (Lumb).

called "gel" region containing mesomorphous matter. There is also a vague indication of a region of mesomorphous middle soap. Between these regions of homogeneous phases there are two-phase regions and a three-phase triangle (between L 1, L 2 and the central "gel" region).

Winsor (18), who carried out several studies of the phase transitions in systems of this type, but who did not construct complete phase diagrams, also concluded that there exists a central mesomorphous "gel" region.

In 1957—60 Dervichian (9) published several diagrams relating to three-component systems, among them the potassium caprate-octanol-water system at 21-22°C (Fig. 5). Two regions of homogeneous, isotropic solutions L 1 and L 2 were present and also a region of mesomorphous matter (paracrystalline phase) in the part of the diagram where middle soap is expected to exist according to McBain's studies. Several two-phase regions and two three-phase triangles were evident in the phase diagram.

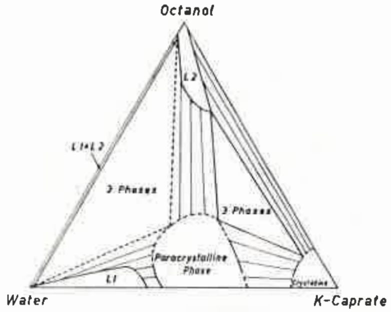

*Fig. 5.* Phase diagram for the three-component system potassium caprate-octanol-water at 21—22°C. (Dervichian).

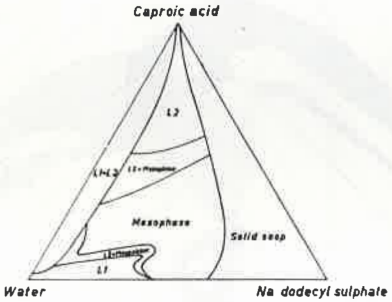

*Fig. 6.* Phase diagram for the three-component system sodium dodecyl sulphate-caproic acid-water at 25°C. (Lawrence).

Lawrence (10, 11) also conducted a number of studies on the formation of mesomorphous phases in three-component systems of this type and published in 1958 a diagram for the sodium dodecyl sulphate-caproic acid-water system at 25°C (Fig. 6). The regions L 1 and L 2 of homogeneous isotropic solutions occur again and also one extended region of mesomorphous substance comprising both the "gel" region in Lumb's diagrams and the paracrystalline region in Dervichian's diagrams. No three-phase triangles are marked in the diagram although such should exist according to the phase rule.

These studies performed in different laboratories seemed to indicate that only one type of mesomorphous substance occurs (in addition to the neat soap that in many cases exists at high association colloid concentrations) in the systems in question. This view has been presented with increasing conviction (Winsor,

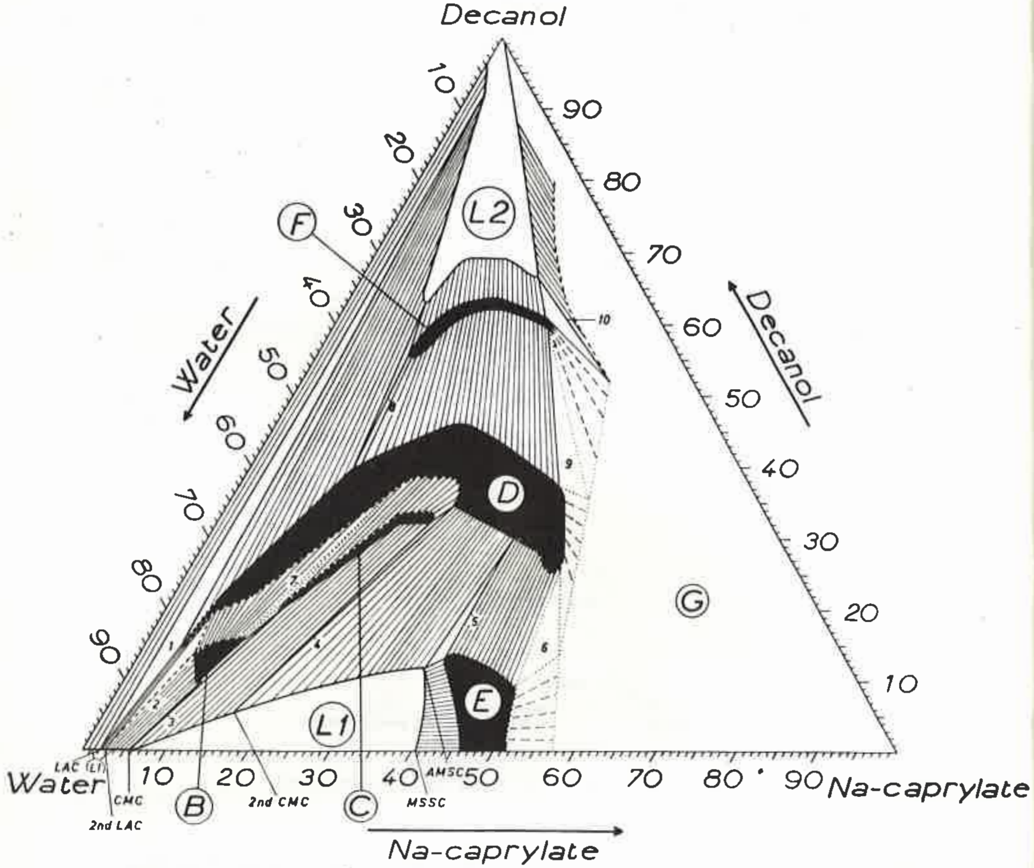

*Fig. 7.* Phase diagram for the three-component system sodium caprylate-decanol-water at 20°C. (Ekwall, Danielsson and Mandell). The concentrations are given in per cent by weight. L 1, homogeneous, isotropic solutions in water. L 2, homogeneous, isotropic solutions in decanol. B, C, D, E, F, homogeneous mesomorphous phases. 1—10, three-phase triangles. AMSC; Alcohol Middle Soap Corner. MSSC, Middle Soap Separation Concentration. CMC, Critical Micelle Concentration. LAC, Limiting Association Concentration. G, solid crystalline sodium caprylate and hydrated sodium caprylate with fibre structure.

Dervichian, Lawrence). In addition, Winsor has claimed that this mesophase can possess only a layer structure.

In 1959 a paper appeared from our laboratory that contained results obtained for the three-component system sodium caprylate-decanol-water at 20°C which were at variance with these views (12). A phase diagram for this system is shown in Fig. 7. In addition to two regions of homogeneous, isotropic solutions

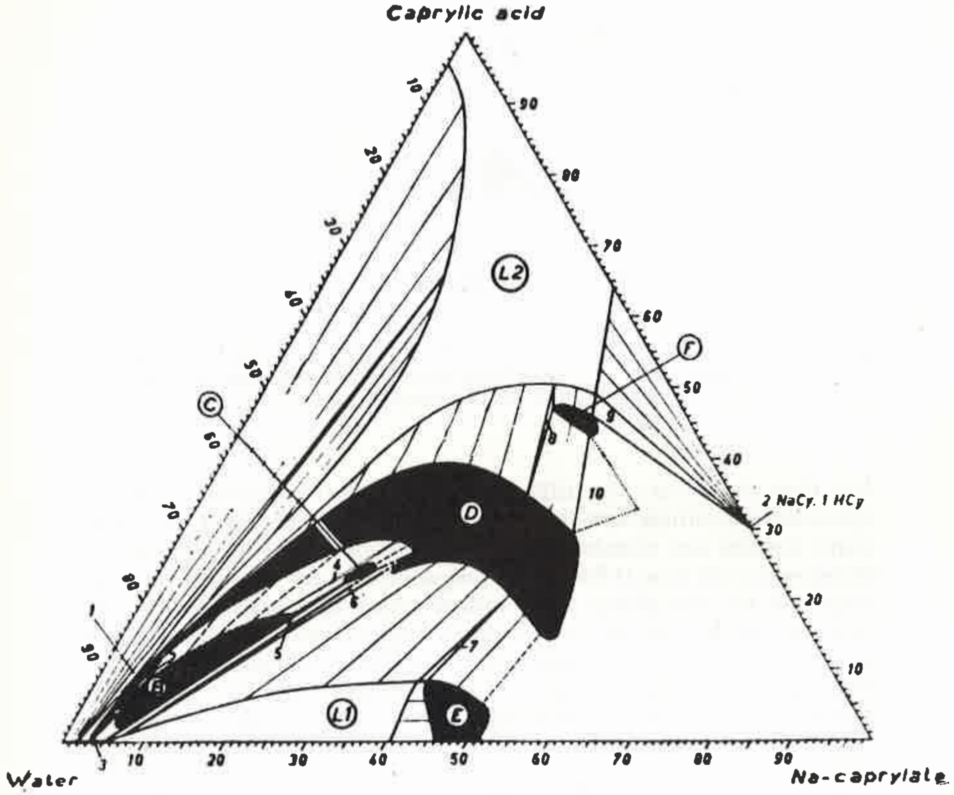

*Fig. 8.* Phase diagram for the three-component system sodium caprylate-caprylic acid-water at 20°C. (Ekwall, Mandell and Gyllenberg). L 1, homogeneous, isotropic solutions in water. L 2, homogeneous, isotropic solutions in decanol. B, C, D, E, F, homogeneous mesomorphous phases. 1—10, three-phase triangles.

L 1 and L 2, there occur no less than five mesomorphous phases designated B, C, D, E and F, and between these several two-phase regions and ten three-phase triangles. Our conclusions were based primarily on the results obtained by separating the different phases by centrifugation and analysing them, but the results were also confirmed by macro- and microscopic observations and X-ray diffraction studies. All these methods revealed that a mesomorphous phase has the same properties and the same structure over the whole range where it occurs,

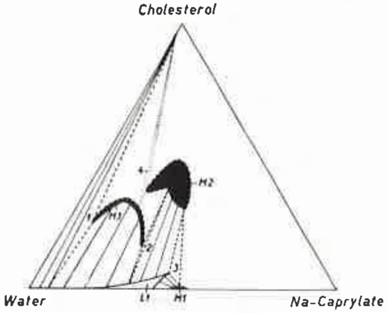

*Fig. 9.* Phase diagram for the three-component system sodium caprylate-cholesterol-water at 20°C. (Ekwall and Mandell). L 1, homogeneous, isotropic solutions in water. M 1, M 2, M 3, homogeneous mesomorphous phases. 1—4, three-phase triangles.

but that these vary for different phases. That reversible thermodynamic equilibria are involved is shown by the fact that the same results are obtained for a system of a given composition irrespective of how it has been prepared and by the fact that, as required by the phase rule, independent of where the system lies on a tie line within a two-phase region, the two phases have constant compositions and that the three phases within each three-phase triangle also have constant compositions. X-ray diffraction data show that the various phases have different structures. These data will discussed later to-day (Ekwall, Fontell) (13, 14).

It may hence be concluded that several mesomorphous phases of different structures are formed in the sodium caprylate-decanol-water system. The "middle soap" phase is clearly different from the central "gel" region and there occur several mesophases in the central region. We believe that this system is a model representing a large number of three-component systems comprising an association colloid, an amphiphilic compound with predominantly lipophilic properties, and water that are of interest from the point of view of theory, technology and biology. Obviously we have to a allow for modifications caused by the structure, form and properties of the lipophilic and hydrophilic parts of the molecules and by the specific solubilities of the components.

Our later studies of a number of other three-component systems have confirmed these conclusions.

We have replaced the sodium caprylate of our model system by another soap, sodium caprate, and have confirmed the existence of the mesophases E, D, C, and B in this system (40°C) (15). Also three-component systems containing water, decanol and sodium laurate, sodium myristate or sodium oleate have been found to form various mesomorphous phases (16, 17, 18, 19, 20). In the sodium caprylate-octanol-water system we have hitherto observed at least the two mesomorphous phases E and D (15).

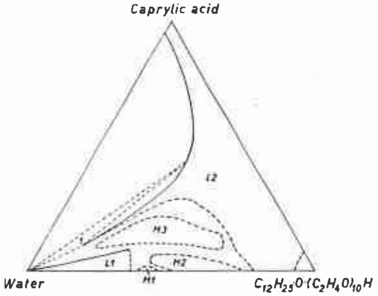

*Fig. 10.* Tentative phase diagram for the three-component system polyoxyethylene glycol monolauryl ether ($C_{12}H_{25}-O-(C_2H_4O)H)_{10}$-caprylic acid-water at 20°C. (Ekwall, Mandell and Gyllenberg). L 1, homogeneous, isotropic solutions in water. L 2, homogeneous, isotropic solutions in caprylic acid. M 1, M 2, M 3, homogeneous mesomorphous phases. 1, three-phase triangle.

We studied in detail at 20°C a system, the sodium caprylate-caprylic acid-water system, which contains a fatty acid instead of the paraffin chain alcohol of the model system (Fig. 8). Also in this system we find two regions L 1 and L 2 of homogeneous, isotropic solutions. In this system, however, the phase L 2 extends to the right to a zero water content and down toward the water corner as a long wedge. In these respects the system resembles the potassium laurate-lauric acid-water system studied by McBain. In the sodium caprylate-caprylic acid-water system, moreover, we established the existence of an equal number of different mesophases as in the sodium caprylate-decanol-water system; the mesophases are of the same type and structure as in the model system.

The liquid decanol of the model system has also been replaced by the solid cholesterol with its large and rigid hydrocarbon skeleton, but we have studied to date only the equilibria between the aqueous solutions and the mesomorphous phases (Fig. 9) (21). We have confirmed in this system the existence of one homogeneous, isotropic aqueous solution L 1 and at least three mesomorphous phases.

A preliminary investigation of a three-component system composed of a nonionic association colloid of the polyoxyethylene type, caprylic acid and water at 20°C (Fig. 10) is in progress. We have already established the existence of two regions of homogeneous, isotropic solutions and three mesomorphous phases.

It may be appropriate to stress finally the fact that all the investigated systems fulfill the requirements imposed by the phase rule.

## References

1. *McBain, J. W.* and *Sierichs, W. C.* J. Am. Oil Chemists' Soc. *25* (1948) 221.
2. *Luzzati, V., Mustacchi, H., Skoulios, A.* and *Husson, F.* Acta Cryst. *13* (1960) 660.
3. *Husson, F., Mustacchi, H.* and *Luzzati, V.* Acta Cryst. *13* (1960) 668.
4. *Luzzati, V., Mustacchi, H.* and *Skoulios, A.* Faraday Soc. Disc. *25* (1958) 43.
5. *Luzzati, V., Mustacchi, H.* and *Skoulios, A.* Nature *180* (1957) 600.
6. *McBain, J. W.* and *Field, M. C.* J. Am. Chem. Soc. *55* (1933) 4776.
7. *Lumb, E. C.* Trans. Faraday Soc. *48* (1951) 1049.
8. *Winsor, P. A.* Chem & Ind. (1960) 632. Trans. Faraday Soc. *44* (1948) 376.
9. *Dervichian, D. G.* Proc. Second Intern. Congr. Surface Activity (London 1957), Vol. I, p. 326. Faraday Soc. Disc. *25* (1958) 58. Kolloid-Z. *169* (1960) 107.
10. *Boffey, B. J., Collison, R.* and *Lawrence, A. S. C.* Trans. Faraday Soc. *55* (1959) 654.
11. *Lawrence, A. S. C.* Nature *183* (1959) 1491.
12. *Ekwall, P., Danielsson, I.* and *Mandell, L.* Kolloid-Z. *169* (1960) 113. Proc. Third Intern. Congr. Surface Activity (Cologne 1960) Vol. I, 193.
13. *Ekwall, P.* Scandinavian Symposium on Surface Activity, Åbo 1962. This volume, p. 59.
14. *Fontell, K.* Scandinavian Symposium on Surface Activity, Åbo 1962. This volume, p. 99.
15. *Ekwall, P.* and *co-workers.* Unpublished results.
16. *Passinen, K. and Ekwall, P.* Acta Chem. Scand. *9* (1955) 1098.
17. *Passinen, K.* and *Ekwall, P.* Acta Chem. Scand. *10* (1956) 215.
18. *Ekwall, P., Salonen, M., Krokfors, I.* and *Danielsson, I.* Acta Chem. Scand. *10* (1956) 1146.
19. *Ekwall, P.* and *Vittasmäki, T.* Acta Chem. Scand. *10* (1956) 117.
20. *Ekwall, P.* and *Passinen, K.* Acta Chem. Scand. *10* (1956) 1215.
21. *Ekwall, P.* and *Mandell, L.* Acta Chem. Scand. *15* (1961) 1407.

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# Properties and Structures of Systems Containing Association Colloids

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It is not possible to present here a complete surwey of the properties of association colloids and therefore I must confine myself to drawing attention to certain problems of current interest.

## *The Concentration Range above the CMC*

We all know that in dilute aqueous solutions association colloids mainly behave like simple electrolytes or molecular species, but that marked deviations from this behaviour are noted when the concentration attains the critical concentration for micelle formation (CMC), where an association of individual ions or molecules to larger aggregates, micelles, takes place. This association equilibrium obeys the law of mass action. The difficulties associated with an exact treatment of this problem will become evident later during this symposium (Danielsson [44]). Here I shall only present the fundamental equations:

$$\mathrm{mRA} \rightleftharpoons (\mathrm{RA})_{\mathrm{m}} \qquad ; \quad \frac{a_{(\mathrm{RA})_\mathrm{m}}}{a^{\mathrm{m}}_{\mathrm{RA}}} = K_{\mathrm{mic}}$$

$$\mathrm{mRA}^- + \mathrm{nMe}^+ \rightleftharpoons (\mathrm{Me}^+_\mathrm{n}\mathrm{RA}^-_\mathrm{m})^{(\mathrm{m-n})-} \qquad ; \quad \frac{a_{(\mathrm{Me}^+_\mathrm{n}\mathrm{RA}^-_\mathrm{m})^{(\mathrm{m-n})-}}}{a^{\mathrm{m}}_{\mathrm{RA}^-} \cdot a^{\mathrm{n}}_{\mathrm{Me}^+}} = K_{\mathrm{mic}}$$

*m* denotes the aggregation number, the number of single amphiphilic molecules or ions that form the micelle. This number is determined primarily by the dimensions, form and structure of the hydrocarbon part R and the nature of the hydrophilic group A. Every association colloid seems to have a characteristic aggregation number, which most frequently lies between about twenty and two hundred. In the case of association colloids of the paraffin-chain type, the number increases with the length of the chain.

$n$ again denotes the number of gegenions that are bound in the micelle.

When the concentration is increased over the CMC, all the added amphiphilic substance forms micelles. The small transition range at the CMC is narrower, the higher the aggregation number. This rapid transition from a molecule-disperse solution to a micellar solution is accompanied by marked changes in the properties of the system. Some of the most typical of these changes are seen in Fig. 1 in which data for sodium caprylate, a soap with eight carbon atoms, are plotted [1]. Above the CMC the osmotic coefficient decreases rapidly in value, which means that the number of osmotically active particles per mole of compound diminishes as a result of aggregation (Fig. 1, *5*b). At the same time the partial specific volume of sodium caprylate increases (Fig. 1, *1*); this has been taken to indicate that the caprylate occupies a larger volume in the micelles than in the ion-disperse solution. The viscosity of the solution, which varies like that of a normal electrolyte below the CMC, increases rapidly above the latter concentration (Fig. 1, *2*a). An altogether new property becomes evident above the CMC; the solution is now able to dissolve, i.e. solubilize, hydrocarbons and other lipophilic compounds insoluble in water (Fig. 1, 3).

Energy and structural considerations lead to the conclusion that the micelles which form above the CMC are spherical or closely so, at least in solutions of paraffin-chain colloids. This opinion is supported by experimental data on, e.g., diffusion, light scattering and viscosity. It has, it is true, proved difficult

2b Schematic representation of the occurrence of structural viscosity at high sodium caprylate concentrations. The curve shows in arbitrary units the deviation of the shear rate — shear stress curve at 600 sec$^{-1}$ from the equilibrium curve obtained after rotation at high shear rates.

3. The solubilization of p-xylene. The solubilization capacity in grams of xylene per mole of caprylate.

4. X-ray scattering. The curves shows the concentration ranges where X-ray scattering is observed.
   4a Low-angle X-ray diffraction maximum.
   4b Wide-angle X-ray diffraction maximum.

5. The osmotic behaviour of the solutions.
   5a The activity of water.
   5b The osmotic coefficient $f_o$ of sodium caprylate
   5c The function $\frac{1 - f_o}{\sqrt{\mathcal{M}}}$

6a The calculated total number of moles of free ions in the intermiceller solution.
6b The calculated percentage of bound gegenions.

(Ekwall and co-workers)

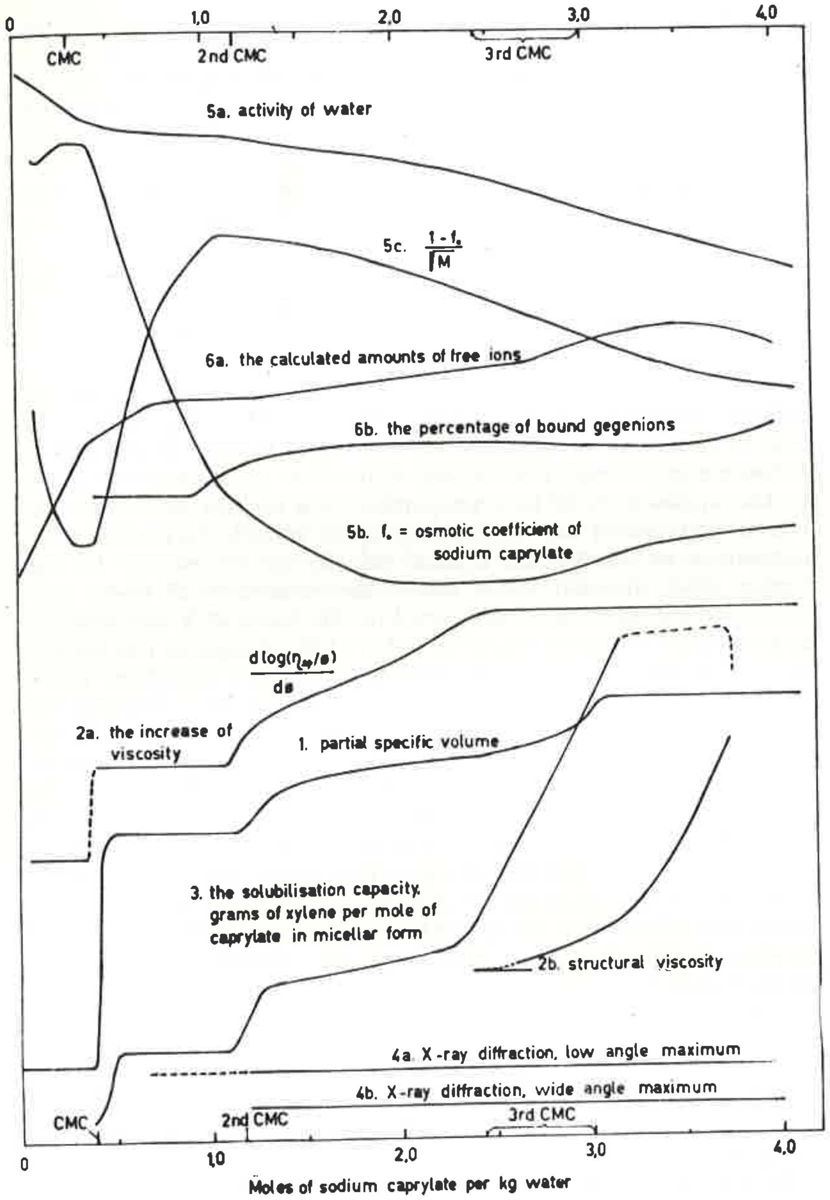

*Fig. 1.* Properties of sodium caprylate solutions at 20°C.

1. The partial specific volume of sodium caprylate.
2. The viscosity of the solutions.
   2a The increase in viscosity with concentration, $\frac{d \log(\eta_{sp}/\Phi)}{d\,\Phi}$
   $\eta_{sp}$ = specific viscosity
   $\Phi$ = volume fraction of hydrated caprylate.

to determine the exact sizes of the micelles, but as various methods have afforded values that are in relatively good agreement with one another, at least the order of magnitude may be considered established. As far as the number of gegenions bound in the micelles is concerned, it is known that in the case of paraffin-chain salts with small ionized end groups, such as the carboxylate, sulphate, sulphonate and primary amine groups, it is somewhat more than 50 per cent of the number of the ionized groups.

We thus have a fairly clear picture of the components in the solutions over a range of concentration immediately above the CMC, but the opinions about the conditions in the more concentrated solutions are both vague and contradictory.

McBain already observed that the properties of association colloid solutions undergo marked changes when the concentration is increased to high levels. In the late thirties investigators in Germany claimed that X-ray diffraction measurements point to the appearance of new properties at a certain concentration which they called the roentgenographic micelle formation concentration or the second critical micelle concentration. In the forties more detailed views about the structures of these concentrated solutions were presented on the basis of X-ray studies; among other things it was concluded that, alongside the spherical small micelles, large micelles with a layer structure make their appearance at and above the second CMC. Toward the end of the decade, however, the interpretation of the X-ray data was severly criticized and at the same time new experimental data were collected that were not consistent with the proposed structures; it was therefore necessary to relinquish these ideas about the structures of the solutions. Most investigators now believe that the changes that occur appear gradually without it being possible to determine any definite concentration limit where they set in. Only one type of micelle is assumed to exist, but both the size and shape may change. The idea of a layered micelle has been abandoned by many investigators but cylindrical micelles are believed to exist since light scattering studies have shown that the micelles may under certain conditions, in the presence of salts, for instance, grow out to cylindrical particles[2] and since observations of the so-called conductance anisotropy have revealed that micelles of the latter form exist in highly concentrated solutions[3].

It may be underlined, however, that conclusive experimental evidence has been collected which shows that the properties of the micellar substance remain constant over a relatively wide range of concentration above the CMC. The rate of diffusion[4], the partial specific volume[1] (Fig. 1, *1*) and the amount of matter solubilized per mole of association colloid[1,5] (Fig. 1, *3*) remain

constant and the viscosity increases linearly in proportion to the content of micellar matter[1] (Fig. 1. *2*a). All these observations indicate that not only the properties of the micellar matter but also the dimensions, form and gegenion content of the micelles remain largely constant. Furthermore, recent experiments have revealed that this so-called small micelle range has a definite upper limit above which a number of properties change[1,6]. The partial specific volume undergoes an abrupt increase (Fig. 1, *1*) the viscosity increases more rapidly than at lower concentrations (Fig. 1, *2*a), the very rapid decrease of the osmotic coefficient comes to an end (the function $\frac{1-f_o}{\sqrt{\mathcal{M}}}$ passes through a maximum (Fig. 1, *5*b, *5*c) and the amounts of hydrocarbons solubilized per mole of colloid increases (Fig. 1, *3*). All this points to a marked change in the structure of the solution and to the presence of a concentration limit that actually can be called the second critical concentration. Above this 2nd CMC most of the properties of the micellar system continue to change slowly. In contrast to the region above the first critical concentration, there is thus no range immediately above the 2nd CMC where the properties are constant. Only after the concentration increases to a high value do we come to a such a range with constant properties. This begins, however, only after a new narrow transition range, where pronounced, sometimes abrupt, changes occur and which may possibly be accepted as a third critical concentration. After this transition range the partial specific volume is again constant, the viscosity increases linearly, and the specific conductance decreases[1].

At these last-mentioned very high concentrations the system exhibits a structural viscosity that becomes more and more marked the more concentrated the solution (Fig. 1, 2b)[1]. This shows that anisodimensional particles, rod-shaped or platelike micelles, appear in the solution. Comparative studies of partial specific volumes and the diffraction of X-rays in these highly concentrated caprylate solutions and in the mesomorphous middle soap in equilibrium with these solutions had already before the viscosity measurements were performed led us to the conclusion that the micelles in this range are cyclindrical[7]. This conclusion has now been confirmed by a study of the conductance anisotropy that showed that cylindrical micelles exist in 40 per cent sodium caprylate solutions[8].

There is hence no doubt that the spherical micelles which begin to form at the critical concentration grow out to cylindrical aggregates above the third CMC. Calculations based on X-ray[7] and viscosity[1] data in which the relative volume occupied by the micellar matter is taken into account show that the length of the micelle increases up to a value of about 1500 Å in a 38 per cent sodium caprylate solution if the micelle diameter is assumed to remain the same as that of the spherical micelle.

The X-ray diffraction that is caused by sodium caprylate, as well as by other association colloid solutions, becomes evident in the range about the 2nd CMC [1]. A very weak, diffuse scattering in the small-angle range is seen already at somewhat lower concentrations, but above the 2nd CMC a relatively distinct scattering maximum pointing to a distance of 33—34 Å (as found by radial distribution analysis [7]) within the system is recorded. This is accompanied by a reflection in the wide angle range at 4.5 Å.

Full agreement has not yet been reached about how these interference phenomena should be interpreted. It is obvious that they point to the existence of particles, aggregates, micelles in the systems. The distance of 4.5 Å is taken to relate to the liquid or semiliquid state in their hydrocarbon cores. Furthermore, it may be anticipated that if the number of micelles in a system of spherical micelles increases until they approach so close to one another that their electrically charged surface layers begin to interact the previous random distribution of aggregates must be replaced by a relatively ordered spacing. These would be expected to lead to a more distinct small-angle X-ray diffraction. The distance 34 Å could then be taken to be the distance between the micelle centres. The difficulties in the interpretation of these phenomena will be reviewed later at this symposium (Fontell [45]).

The mentioned close approach of the micelles provides one possible reason for the changes in the properties of the system at the 2nd CMC. The charged surfaces interact so strongly that they bring about changes in the structures of the surface layers and perhaps also in the form and size of the micelles.

There exist, however, experimental data that seem to be contradictory. The osmotic activity (as revealed by the lowering of vapour tension and the activity of water and the variation of the osmotic coefficient of sodium caprylate) increases with increasing caprylate concentration more rapidly above than below the 2nd CMC, although the aggregation continues, i.e. all added substance forms micelles. (Fig. 1, *5a*, *5b*.)

The effect of solvation on the properties of the micellar solutions must be taken into consideration in this connection. On the basis of viscosity data it has been possible to determine the extent of solvation; the solvation number was found to be 9—10 moles of water per mole of micellar sodium caprylate over the whole range from the first CMC up to high concentrations [1]. This water is bound partly by the sodium ions and partly by the ionized carboxyl groups. The micelles are thus surrounded by a layer of bound water molecules that approximately doubles their weight *. Hence a part of the water in the system is immobilized. The remaining water forms an intermicellar solution in which the free ions are found. One would therefore expect that the effect of solvation on the properties of a system must be more extensive in micellar systems of this type than in solutions of ordinary electrolytes.

With respect to the osmotic activity, the micelles may be taken to represent a separate phase with the same vapour tension as the intermicellar solution and it may be assumed that the vapour tension of the latter is primarily a function of the concentration of free ions in it. It is hence possible to distinguish between properties that are mainly determined by the micellar substance (lower part of Fig. 1) and those that are mainly attributable to the intermicellar solution (upper part of Fig. 1).

On the basis of vapour pressure and other data and by comparing caprylate solutions and isopiestic solutions of an unassociated salt, we have attempted to draw a picture of how the total volume, the ion concentration of the intermicellar solution and the binding of gegenions on the micelles vary [1]. The volume of the intermicellar solution and hence the amount of free, non-micellar sodium caprylate decreases rapidly with increasing concentration of the micellar substance; at the same time the total number of free gegenions and their concentration in the intermicellar solution increase (Fig. 1, *6*a). This increase is found to be more rapid above than below the 2nd CMC although the binding of gegenions also increases at this concentration limit (Fig. 1, 6b). In the most concentrated solutions, above the 3rd CMC, however, the increase in the concentration of free ions becomes weaker and the binding of gegenions increases again.

These changes in the ion concentration of the intermicellar solution provide an explanation for the observed variations of the vapour tension and osmotic activity above the 2nd CMC. The fact that the binding of gegenions increases at this concentration limit means that more gegenions together with their hydrate shells enter the micelles and thus increase the volume of the latter. This may be one reason for the observed more rapid increase in the viscosity and possibly also for the increase in the partial specific volume (Fig. 1, *2*a, *1*). Whether there occurs also an increase in the aggregation number or a deformation of the micelles is not known; the increased uptake of gegenions would be expected to promote such changes and certain experimental data point to such a possibility. Viscosity data show, however, that the micelles are spherical or practically so up to a sodium

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* This means that the paraffin-chain ions and bound gegenions of the micelles seem to bind about the same amount of water as they do as free ions. If the association to micelles causes any change in the solvation, this change may be very small.

caprylate concentration of about 28 % and therefore any deformation that takes place must be limited in scope[1].

There thus seems to be mainly two kinds of underlying reasons for the changes in the micellar structure of the solution with increasing concentration: the solvation of the micelles that leads to changes in the volume and concentration of the intermicellar solution and the fact that the micelles approach so close to each other that their surface layers begin to interact. On the basis of the available experimental data the following picture of the changes in the structure of the micelles above the CMC may be drawn. After a well-defined concentration range above the CMC where the micelles have constant properties and are spherical and constant in size, a new range begins at the 2nd CMC where the properties of the micelles change in such a way that the binding of gegenions and hence the micelle volume increases but perhaps there occurs also an increase in the aggregation number and some alteration in form. The micelles remain, however, largely spherical up to a concentration, which may be called the 3rd CMC, where the binding of gegenions again increases and the micelles grow out to cylinders and perhaps undergo other changes too.

It is obvious that reliable experimental methods for the direct determination of the number of bound water molecules and gegenions and of the size and form of the micelles would be highly desirable.

### *The Concentration Range below the CMC.*

The conditions in the dilute solutions below the CMC is another question that has been controversial until quite recently. It is obvious that an association to large aggregates consisting of, say, 50 to 100 ions or molecules must proceed by way of smaller aggregates, dimers, trimers, etc. The question is, however, whether these aggregates occur in amounts sufficient to influence the properties of the solutions in such a degree that changes in properties become observable or whether the aggregation proceeds to micelles in a narrow concentration range so rapidly that no premicelles can be detected. During the past three decades the opinion has prevailed that micelles are so much more favoured energetically that no preliminary stages of association can be detected. Only a few investigators have supported the opinion that in the concentration range below the CMC the properties deviate from those typical for solutions of normal uni-univalent electrolytes and that these deviations indicate an association to small premicelles.

It must now be considered conclusively established that an association of the latter type really takes place when the solutions contain besides paraffin-chain ions small amounts of organic amphiphilic molecules such as paraffin-chain alcohols, fatty acids and alkylamines. The latter may be compounds added to the solutions or compounds that result from the hydrolysis of association colloids themselves. Aggregates are formed by these molecules and the ions of the colloid; ion-dipole interaction and hydrogen bond formation between the ionic and polar group play major roles in binding these parts together.

The fact that the solubility of sparingly soluble alcohols in association colloid solutions increases as soon as the colloid concentration exceeds a certain value shows that soluble aggregates of alcohol molecules and association colloid ions are formed. (Figs. 2 and 3)[9]. A common feature of solubility curves of this type is that there first occurs a slight increase in the solubility at a concentration far below the CMC and then a very marked increase from the CMC upwards when micelle formation begins. These investigations thus show that soluble ion-molecule complexes are formed only to a small extent below the CMC and calculations reveal that these complexes are small in size and consist of only two to four association colloid ions and one or two alcohol molecules.

Also the solubility of fatty acid increases in soap solutions below the CMC when the soap concentration exceeds a certain value; this shows that soluble aggregates composed of fatty acid ions and fatty acid molecules are formed. The existence of these aggregates was detected already long ago in studies of the hydrolysis of soap solutions[10,11] and confirmed by potentiometric titrations of these solutions[12]. Such aggregates are formed also in the case of the lower fatty acids and their salts. Thus Davies and Griffith proved that ionized aggregates of this type, from dimers up to micelles, are formed in solutions of butyric acid and probably of other lower fatty acids too[13]. The occurence of an association to small aggregates in solutions of butyrate containing only a small excess of butyric acid has recently been shown by means of potentiometric titrations by Rosotti[40] as well as by Danielsson[41].

Usually the existence of this type of aggregation in association colloid solutions is observed experimentally within a rather narrow concentration range. Very interesting is that for a given soap this range is the same quite irrespective of whether the interaction involves a fatty acid, a monohydric alcohol or a dihydric alcohol and whether the alcohols are more or less soluble in water (Fig. 4 A)[14,9]. The location of this concentration range is determined by the number of carbon atoms in the soap and is lower the longer the carbon chain of the soap (Fig. 4 B)[15,1]. These observations show that although ion-dipole interactions and the formation of hydrogen bonds between the ionized carb-

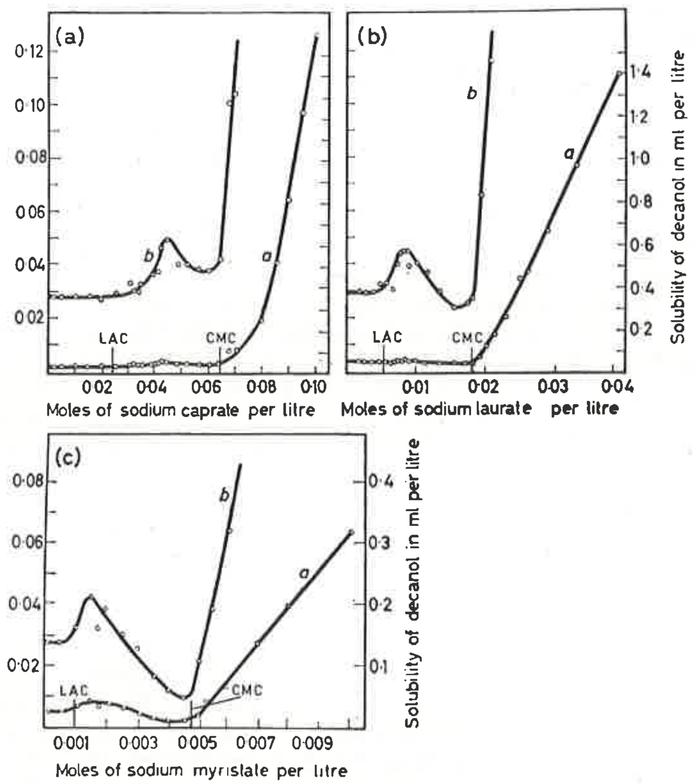

*Fig. 2.* The solubility of n-decanol in soap solutions at 40°C. In presence of decanol in the solution the CMC is shifted to a lower concentration than in decanol-free solutions.

2a The solubility in sodium caprate solutions. a) The solubility around the CMC (scale on the right). b) The solubility between the LAC and the CMC (scale on the left).

2b The solubility in sodium laurate solutions. a) The solubility around the CMC (scale on the right). b) The solubility between the LAC and the CMC (scale on the left).

2c The solubility in sodium myristate solutions. a) The solubility around the CMC (scale on the right). b) The solubility between the LAC and the CMC (scale on the left). (Ekwall and Wittasmäki)

oxyl groups of the soap ions and the hydroxyl groups of the molecules play a part in binding the parts together, it is the chain length of the soap ion that determines the concentration at which the aggregate formation begins to be noticeable. The lowest concentration at which deviations from the behaviour of normal uni-univalent electrolytes are observed as a result of this aggregate formation we have chosen to call the limiting association concentration (LAC)[16,11,10,17,15,14,9].

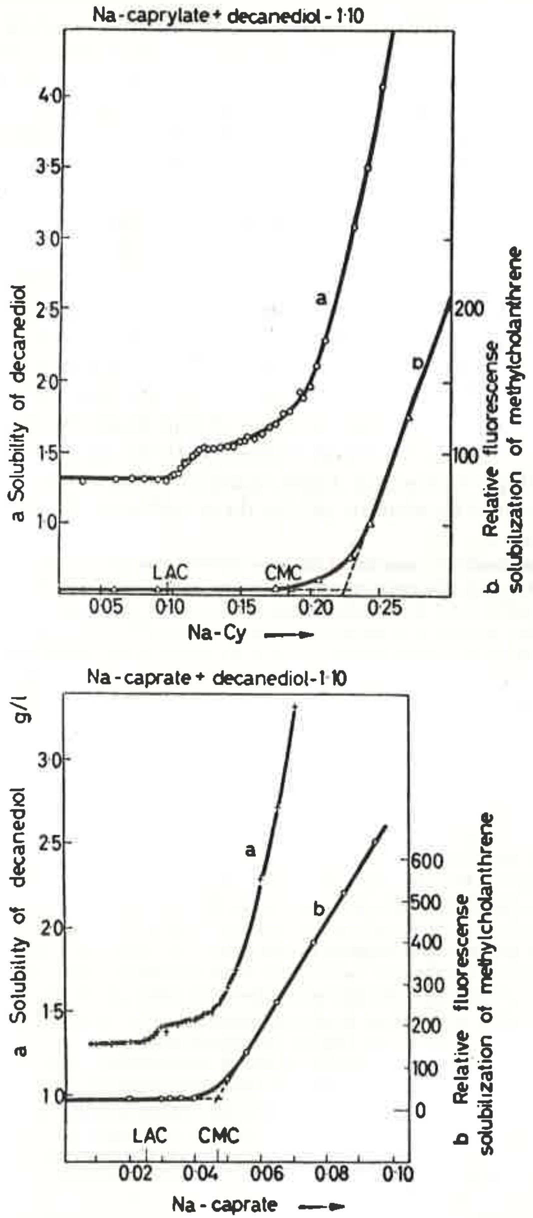

*Fig. 3.* The solubility of decanediol-1,10 and methylcholanthrene in soap solutions at 40°C. In the presence of decanediol in the solution the CMC is shifted to a lower concentration than in decanediol-free solutions.

3a Sodium caprylate solutions. a) The solubility of decanediol-1,10. b) Solubilization of methylcholanthrene in caprylate solutions saturated with decanediol.

3b Sodium caprate solutions. a) The solubility of decanediol-1,10. b) Solubilization of methylcholanthrene in caprate solutions saturated with decanediol.

(Ekwall and Henriksson).

In order to explain the observed abnormal courses of the hydrolysis curves from the LAC upwards to the CMC (Figs. 5, 6, 7, 8), a hypothesis was made many years ago that the fatty acid ions associate to double ions and that these double ions undergo hydrolysis more readily than the simple ions as a result of which their hydrolysis will dominate [11,10,18]. Both phenomena are superimposed; over a transition range at the LAC the double ions increasingly promote the hydrolysis and are themselves revealed by the latter. The form of the hydrolysis curve indicates that the hydrolysis immediately above the LAC proceeds over double ions but at higher concentrations over somewhat larger ion aggregates *. By means of potentiometric measurements it was later confirmed that the values of the apparent dissociation constants of the fatty acids actually decrease above the LAC (Fig. 9) [19,1]. In the earlier studies of the hydrolysis, the solutions regularly contained a small excess of fatty acid which made the mentioned phenomenon more readily observable, but rendered the theoretical treatment of the data difficult. Recently Eagland and Franks measured the pH values of laurate solutions containing no excess fatty acid and were able to confirm that the hydrolytic equilibrium deviates from the normal at concentrations far below the CMC [20].

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* Between the LAC and the CMC the hydrolysis phenomena do not depend, as Alexander and Stainsby proposed some years ago, on the presence in the solution of fatty acid in micellar form and on the fact that acid soap would be formed by the uptake of soap ions by these micelles[46]. Only butyric acid dissolves in water in such an extent that micelles are formed, and this happens as known only at concentrations above 0.85—1.35 M [47,48]. As Ekwall and Sjöblom have shown for caproic, caprylic, nonylic, capric and oleic acids, their solubility is so low that no micelle formation occurs in their solutions [48]. Below the CMC the well-defined hydrolysis equilibria involve reactions in molecule-disperse solutions between ions and molecules. Only from the CMC upwards when the soap forms micelles do colloid aggregates take part in the hydrolysis process. Thus the problem is whether the hydrolysis is a reaction in solution between fatty acid molecules and simple fatty acid anions to anions of an acid soap or if the latter are formed directly by the hydrolysis of double anions and larger ion aggregates. The experimental data support the latter interpretation [11,10,18].

According to McBain it seems probable that the hydrolysis alone is not sufficient to produce precipitating hydrolysis products. Such products separate, however, in many cases already in the presence of a very small excess of fatty acid. The solid, crystalline acid salts that in some cases separate at room temperature represent well-defined molecular compounds of constant composition, a fact that sometimes is still overlooked. The mesomorphous acid soaps that separate at somewhat higher temperatures, and from the solutions of caprate and lower soaps already at room temperature, are of different types and compositions. Their type and composition depends, however, on the soap ion concentration of the solution. Finally there separates in some cases a liquid isotropic fatty acid-water-soap phase (at room temperature in solutions of caprylate and lower soaps, at higher temperatures in solutions of higher soaps). Also the composition of this phase is determined by the soap ion concentration in the solution.

In studying the hydrolysis equilibria of solutions containing separated products of the mentioned types a knowledge of their composition and character is, of course, necessary. On the other hand, this knowledge gives in some cases directly an idea of the character of the hydrolysis equilibria in solution and a knowledge of the latter gives an idea of the association equilibria in a solution in general [11].

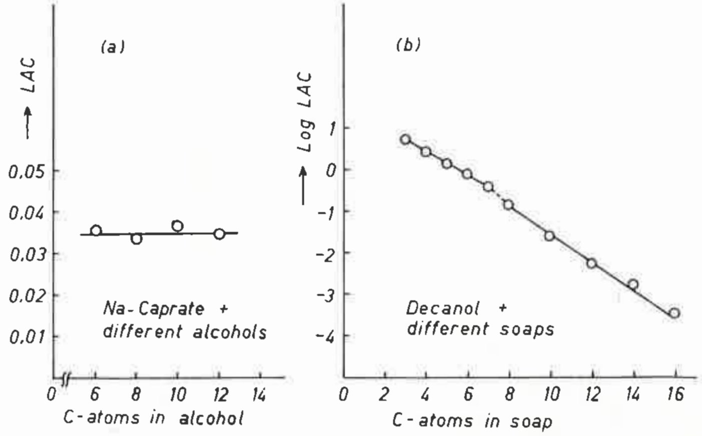

*Fig. 4.* The dependence of the LAC on the chain length.

4a The dependence of the LAC of sodium caprate on the chainlength of alcohol at 50°C.

(Ekwall and Aminoff).

4b The dependence of the LAC on the chain-length of the soap at 20°C.

(Ekwall, Söderberg and Lemström).

There are also other experimental observations that point to a weak association in fatty acid salt solutions below the CMC. Activity measurements (e.m.f.) on sodium laurate solutions have shown that from the LAC upwards to the CMC the activities deviate from the values typical for normal uni-univalent electrolytes (Fig. 10) [21]. From these data a dimerisation constant, $K = \frac{\text{activity of dimer}}{(\text{activity of monomer})^2}$ with a value of 2—3.5 was obtained for sodium laurate. From vapour pressure data Smith and Robinson have concluded that an association leading to small aggregates takes place in solutions of lower fatty acid salts which do not have any critical concentration and evidently do not form micelles [22]. Later we have found, with the same experimental technique, deviations in the osmotic coefficient of sodium caprylate below the CMC that point to a limited association already before the micelle formation begins (Fig. 11) [1]. (Also Stokes and Robinson's measurements point in the same direction). Our experimental data give a dimerisation constant of about 0.2—0.4 for sodium caprylate.

Premicelles are formed also in solutions of other association colloids. From absorption measurements on cetylpyridinium

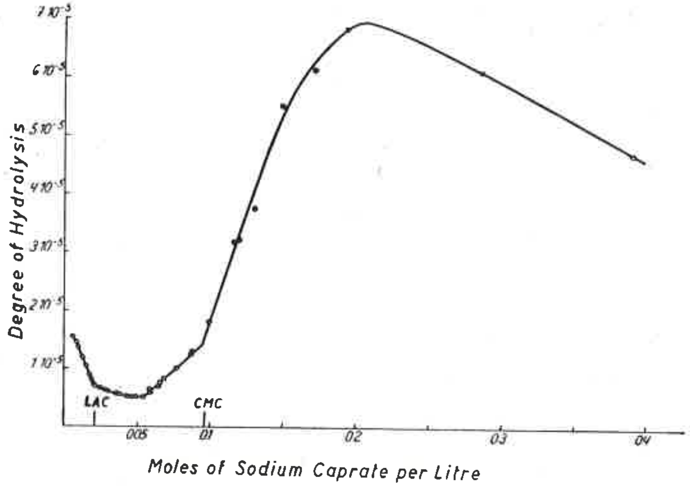

*Fig. 5.* Hydrolysis curve of sodium caprate at 20°C. The solutions contained an excess of about 0,1 mole of capric acid per 100 moles of sodium caprate. The carbon dioxide content of the water was 0,4—0,5.$10^{-6}$ M. Between 0.055 C and 0.095 C the solutions were weakly turbid owing to a small amount of separated mesomorphous acid soap; at all other concentrations they were quite clear. Note the different course of the hydrolysis curve below and above the LAC although there are no separated hydrolysis products in the solutions!

(Ekwall and Franzén).

chloride solutions Sata and Sasaki recently concluded that a weak aggregation occurs already below the CMC[23]. Long ago the conductance curves and the variation of transport numbers in solutions of alkylsulphonic acids and salts of alkylamines below the CMC were explained to be due to premicelle formation [24,25,26]. A short time ago Mukerjee and Mysels concluded from similar data that dimerisation takes place in alkyl sulphate solutions below the CMC [27]. Bortré came to a similar conclusion from a study of activities in solutions of the last-mentioned colloid [28]. Quite recently van Voorst Vader [29] calculated from e.m.f. measments a value of 10 for the dimerisation constants of potassium dodecyl sulphonate and sodium dodecylsulphate. The systems studied in the last three investigations did not contain any unionized amphiphilic molecules. Some authors, however, believe that these experimental observations can be better interpreted in another manner [42,43].

Premicelle formation is very pronounced in solutions of association colloids of the bile acid salt type. The association leads first to small amounts of aggregates with an aggregation number increasing from 2 to 5, then to aggregates of the last-mentioned size alone and above a well-defined concentration limit to small micelles with an aggregation number of 15—20.

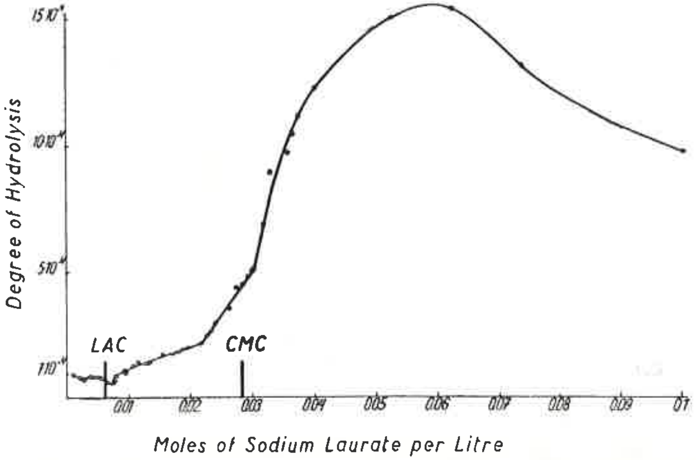

*Fig. 6.* Hydrolysis curve of sodium laurate at 20°C. The solutions contained an excess of about 0,1 mole of lauric acid per 100 moles of sodium laurate. The carbon dioxide content of the water was 0,4—0,5.$10^{-6}$ M. Below 0,006 C the solutions contained lauric acid crystals and above 0,008 C crystals of the acid soap $NaHL_2$. Between 0,0065 and 0,008 C and from about 0,028 C upwards the solutions did not contain any separated hydrolysis product. Note (1) that the crystallised lauric acid disappears at the LAC, although the total amount of the hydrolysis products increases and no other hydrolysis product separates and (2) that the course of the hydrolysis curve alters at the LAC!

(Ekwall and Lindblad).

At higher concentrations there are two more concentration ranges where larger micelles exist; in the higher range the micelles seem to be very large. These results are based upon measurements of partial molar volumes, conductance, hydrolysis, solubilisation of hydrocarbons and amphiphilic compounds, viscosity and X-ray diffraction [30,31]. It should, however, be noted that interactions between the different hydrophilic groups of the bile acid molecules seem to play a part in the micellisation in solutions of this group of association colloids and lead to other structures of the micelles than in the case of the paraffin-chain salts.

Although the idea of dimerisation of ions in association colloid solutions and the further aggregation to premicelles below the CMC is thus supported by extensive experimental data, it must be admitted that the existence of these small ion aggregates in the case of long paraffin-chain colloids has not been proved with the same degree of certainty as the existence of small mixed aggregates. This is understandable owing to the low concentrations in question and the small amounts of aggregates that are consequently formed.

The most important objection to the existence of double ions is, however, theoretical. It has been stated that the probability

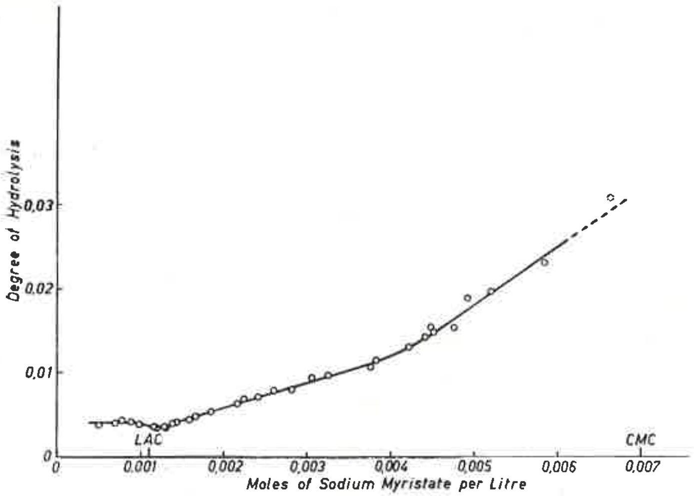

*Fig. 7.* Hydrolysis curve of sodium myristate at 20°C. The solutions contained an excess of about 0,1 moles of myristic acid per 100 moles of sodium myristate. The carbon dioxide content of the water was $0{,}4-0{,}5.10^{-6}$ M. All solutions contained separated hydrolysis products; below the LAC this consisted of myristic acid crystals, above the LAC of acid sodium myristate crystals, $NaHMy_2$. (Ekwall and Birck).

of the formation of dimeric ions must be extremely low because the energy released in the process is small. This conception has been based on the fact that two ionized groups with charges of like sign repel each other, but the possibility that a gegenion may also be bound has been disregarded. If a gegenion is simultaneously bound, the free energy change will be appreciably greater. An observation recently made in our laboratory may be of interest in this connection. When the vapour pressures over solutions of $\alpha,\omega$-dicarboxylates were measured, it was found that, whereas the osmotic coefficients of salts with 2—8 methylene groups gave values of the same magnitude as the osmotic coefficients of compounds that dissociate to three ions, the osmotic activity of potassium oxalate was unexpectedly found to be very low and of a magnitude typical for a uni-univalent salt at concentrations exceeding 0.2 M[32]. It would seem that only one potassium ion is released and the other cation remains bound to the two adjacent carboxylate groups. The release of the second cation becomes evident only after the salt concentration decreases below about 0.1 M. I am inclined to draw the conclusion that if double ions with two carboxylate groups as close to each other as in an oxalate ion are formed in a solution, the conditions are favourable for the retention of an alkali metal ion by these double ions already at low concentrations.

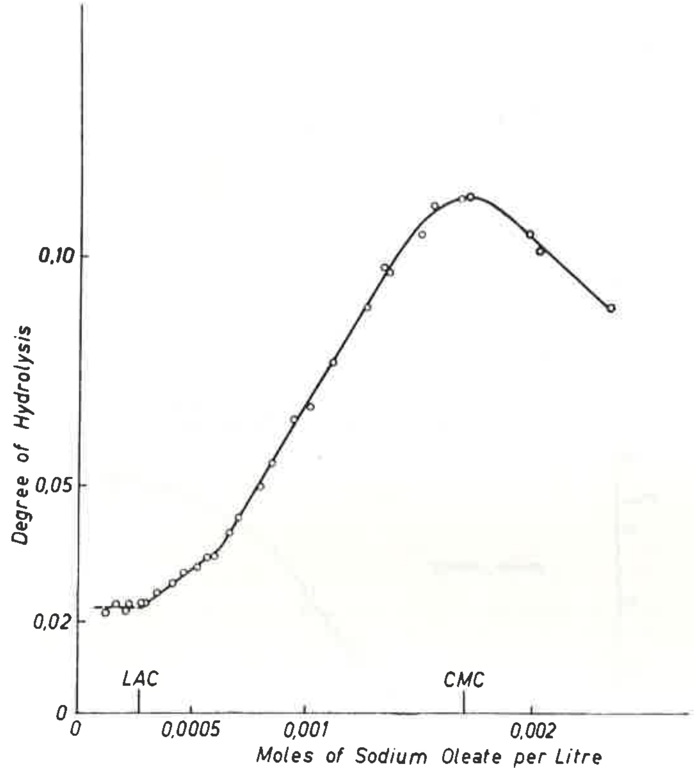

*Fig. 8.* Hydrolysis curve of sodium oleate at 20°C. The solutions contained an excess of about 0,1 moles of oleic acid per 100 moles of sodium oleate. The carbon dioxide content of the water was $0{,}4-0{,}5.10^{-6}$ C. Up to 0,006 C all solutions were turbid owing to small amounts of separated hydrolysis products. Up to 0,00027 C, the LAC, the separated substance consisted of emulsified oleic acid, above the LAC, from 0,0003 C to 0,0007 C, of mesomorphous acid soap with a relatively high ratio of oleic acid (about 1,5—2 HOl: 1 NaOl) and from 0,0008 C upwards of mesomorphous acid soap with a lower ratio of oleic acid (about 1 HOl: 2 NaOl). (Ekwall and Birck).

On the basis of the limited data available, the decrease in free energy associated with the binding of an alkali metal ion to two adjoining ionized carboxyl groups of a double ion can be estimated to be about 2000 cal/mole. This decrease in free energy is so large that the formation of dimers with one bound gegenion would be possible already in soap solutions of rather low concentrations. The association energy for a dimer formation of this type can be expressed by the equation

$$\Delta G_{ass_2} = -\eta \cdot \Delta G_{CH_2} - 2000 + \Delta G_2$$

where $\eta$ is the number of methylene groups in the straight paraf-

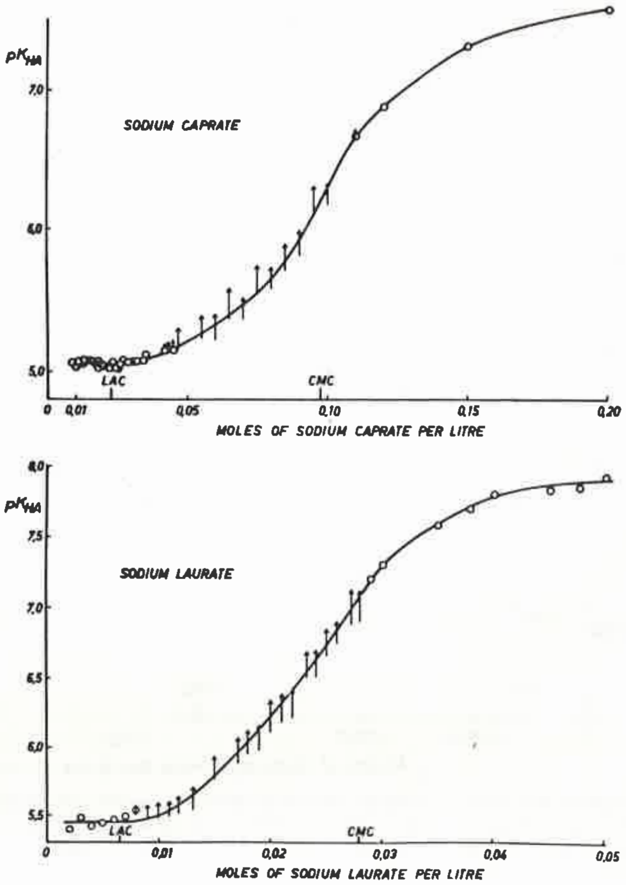

*Fig. 9.* The dissociation constants of fatty acids determined by potentiometric titration of soap solutions with hydrochloric acid at 40°C. The determinations were made on quite clear solutions not containing any separated hydrolysis products. Only below the LAC do the titrations give the correct value of the constant. Above this concentration the value of $pK_{HA}$ increases; between the LAC and the CMC there is in addition a drift in the $pK_{HA}$ values (the arrows indicate this drift).

(Ekwall and Rosendahl).

fin chain and $\Delta G_2$ is a constant, the magnitude of which depends on the electrical repulsion between the negative charges of the carboxyl groups. Calculations show that a small but definite amount of dimers of the mentioned type may be formed at the limiting association concentration of a soap.

The above would mean that the first step in the association is the formation of dimers as follows.

$$2RA^- + Me^+ \rightleftharpoons (Me^+ \cdot 2RA^-)^-$$

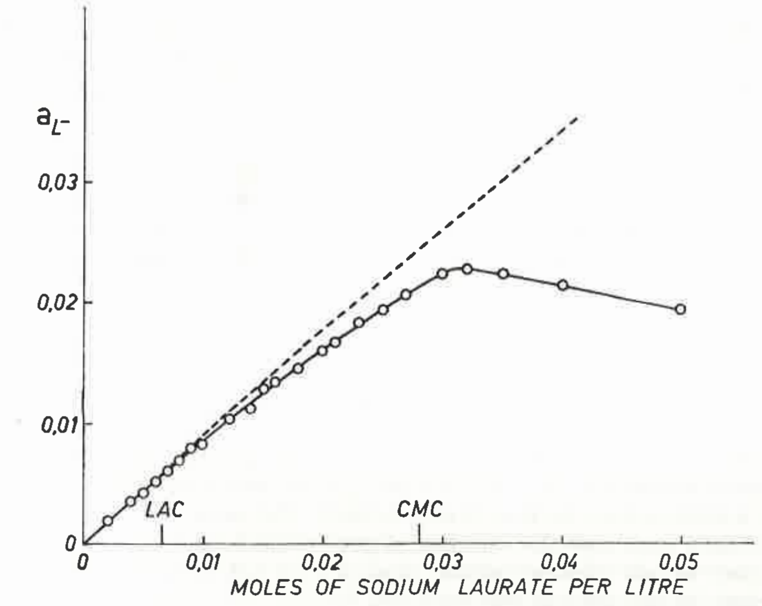

*Fig. 10.* The activities of laurate ions in sodium laurate solutions at 20°C. Measurements with the Ag/Ag laurate electrode. The dotted line gives the activities of typical organic anions (calculated using the equation of Kielland).

(Ekwall and Harva).

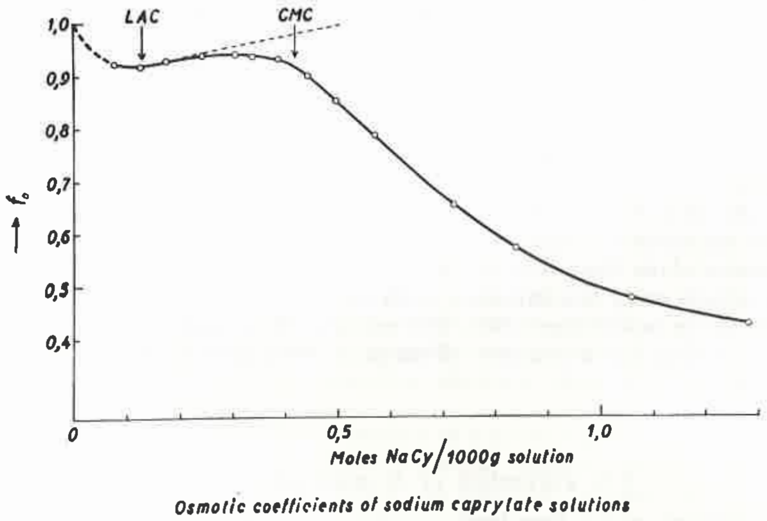

*Fig. 11.* The osmotic coefficient of sodium caprylate in the concentration ranges below and above the CMC. The dotted line gives the osmotic coefficient of a fatty acid salt which does not associate above 0,1 M.

(Ekwall and Lemström).

If the formation of soluble aggregates by association colloid ions and alcohol or fatty acid molecules proceeds over such dimers above the LAC, this would explain why these aggregates are formed to such a limited extent and why the concentration, the LAC, where these aggregates are observed to be formed is a function of the chain length of the association colloid although ion-dipole forces between the end groups are operative.

If such a dimerisation takes place, our views about the formation of micelles must be modified. The micelles must then be formed from dimers each with one bound gegenion. In this aggregation step the repulsion between the end groups of the dimers must be overcome and this seems to be possible only when more gegenions are bound to the micelle surface. A fact supporting this view of micelle formation is that in general the number of bound gegenions in the micelles does not decrease below 50 per cent. Up to one gegenion should consequently be relatively firmly bound for every two ionized groups and a variable number in addition may be less firmly bound. The same is indicated by the fact that also the number of gegenions bound in the ionized layers within mesomorphous phases does not as a rule decrease below 50 per cent of the maximal [1].

We have here a problem which will require further investigation before it can be solved. Here again there is a need of more reliable experimental methods for the determination of the degree of binding of gegenions. I have drawn attention to these questions not only to point out a research problem which is of importance for our understanding of the structure of association colloid solutions, but also because a knowledge of aggregate formation in dilute solutions is essential before we can understand the formation of mesomorphous phases in them and before we can clarify many physiological and technical processes where solutions below the CMC play a part.

As far as the structures of aqueous association colloid solutions are concerned, it may be said in the light of the available experimental data that it is difficult to assert that the properties of solutions vary continuously with increasing concentration either above or below the CMC. The concept of an association process proceeding by a number of steps is becoming more and more evident.

## *The Formation of Mesomorphous Phases*

A third group of problems that I wish to discuss are the conditions favouring the appearance of water-containing mesomorphous phases and the factors that determine the structures of these phases.

We shall first review the conditions promoting the formation of these phases in aqueous solutions. Solubility is one important factor. In the two-component soap-water systems, mesophases separate only at high soap concentrations. This concentration decreases, however, with increasing chain length of the soap. When we are dealing with more lipophilic compounds like the fatty acid monoglycerides and phosphatides, the concentration at which a mesophase appears is particularly low.

The presence of a third component, amphiphilic but yet predominatingly lipophilic in nature, in the system greatly promotes the formation of water-containing mesomorphous phases. This applies also to systems of association colloids that themselves are highly soluble in water. Sodium caprylate, for instance, which in a two-component system with water forms a liquid-crystalline phase only when its concentration is as high as 40 per cent, does so in the presence of a third component such as a paraffin-chain alcohol, caprylic acid or cholesterol already when the caprylate concentration exceeds 2.1 per cent. In the case of potassium oleate the concentration decreases from about 19 per cent to only 0.008 per cent. In these cases, in addition, a series of different phases are formed as we heard in the preceding lecture (Mandell [33]). In the following, I will illustrate my views with examples from the model system consisting of sodium caprylate, decanol and water that was discussed in that lecture (Fig. 12) [34,35].

As far we know at present, it seems that mesomorphous water-containing phases separate only from aqueous solutions of association colloids where micelles or smaller aggregates exist. We have never observed that such phases separate from solutions below the limiting association concentration [34,36]. From the solutions below the LAC, alcohols, cholesterol and fatty acids separate in pure form or as isotropic solutions. We have drawn the conclusion that one of the conditions necessary for the formation of mesomorphous phases in aqueous solutions is that aggregates are present and that these hence take an active part in promoting the formation of the mesophases. On the other hand, this does not, of course, mean that the substance which separates from a solution where such aggregates are present is always mesomorphous. Numerous examples showing that this is not the case are known [36].

The factors promoting the formation of a mesophase in aqueous solutions seem to be of two types. In some cases it is simply so that the mesophase separates when the solution becomes saturated with micellar substance. This is the case when the so-called middle soap (Phase E in Fig. 12) separates. Our experiments have revealed that the mesomorphous substance and the micellar substance in equilibrium with each other have the same composition, that their partial specific volumes are almost equal, and that the aggregates present in both phases are cylindrical in form. In addition, the binding of gegenoins by the micelles seems to be practically complete. We have therefore concluded that the micelles are transferred relatively unchanged together with their gegenions and water of hydration from the aqueous phase to the mesomorphous phase.

In other cases the solutions do not become saturated in such a way that the concentration of the association colloid exceeds a certain value, but as a result of the addition of a foreign compound that alters the micelles or aggregates so much that they no longer can remain in solution. This is effected by amphiphilic compounds of predominating lipophilic character such as long-chain alcohols, fatty acids, etc. When these compounds are added to a solution containing micelles, they become solubilized and incorporated in the micelles with their hydrocarbon chains projecting into the micelles and the hydrophilic groups at the surface of the micelle. When, for example, a caprylate micelle solubilizes decanol, the micelle thereby becomes loaded with relatively more lipophilic matter than it contained before and the lipohilic-hydrophilic balance of the micelle is shifted in the lipophilic direction. The strongly hydrophilic ionized groups in the surface layer of the micelle and the associated gegenions are replaced by less hydrophilic hydroxyl groups. The charge density and the electrokinetic potential at the micelle surface diminishes. As a consequence the solubility of the micellar substance decreases and the micelle separates as a new phase. Our studies indicate that this can take place although the binding of gegenions by the micelle is less than 100 per cent, i.e. despite the fact that the micelle carries free negative charges. However, when the micelles separate, they take with them, owing to the principle of electroneutrality, gegenions in an amount sufficient to neutralize the free electric charges. Also the water of solvation of the micelles and the gegenions is transferred to the new phase. A mesomorphous structure containing the separated micelles in unchanged form seems to be unstable in most cases and a rearrangement to a more stable structure therefore takes place. This mechanism occurs, e.g., when on adding decanol to caprylate solutions mesomorphous phases separate between the concentrations marked AMSC and LAC in Fig. 12.

Although the separated micelles do not enter the mesomorphous phase unchanged it nevertheless seems that there is a correlation between the micellar structure of the aqueous solution and the structure of the mesophase in equilibrium with the solution [34,36]. In each concentration range where caprylate solutions contain a certain type of aggregate, the mesomorphous phase that separates is also of a definite type. We have found that a phase E containing cylinders in hexagonal array separates from the concentrated colloid solutions that contain cylindrical micelles. From the point AMSC (see Fig. 12) down to the 2nd CMC, the phase D that separates has altogether different pro-

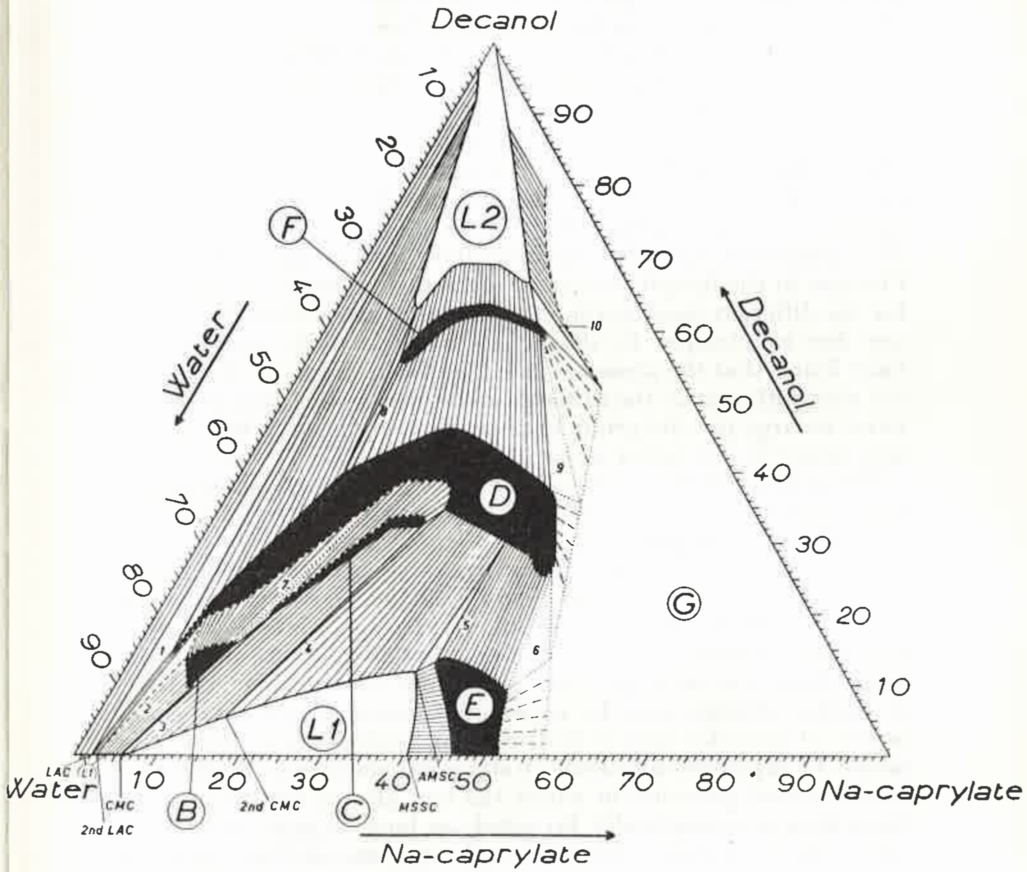

*Fig. 12.* Phase diagram for the three-component system sodium caprylate—decanol—water at 20°C. The concentrations are given in per cent by weight.
L 1 Homogeneous isotropic solutions in water.
L 2 » » » in decanol.
B,C,D,E,F. Homogeneous mesomorphous phases.
G. Solid crystalline sodium caprylate and hydrated sodium caprylate with fibre structure.
1—10 Three-phase triangles.
MSSC = Middle Soap Separation Concentration.
AMSC = Alcohol Middle Soap Corner.
CMC = Critical Micelle Concentration.
LAC = Limiting Association Concentration.
(Ekwall, Danielsson and Mandell).

perties and a quite different layer structure. Between the 2nd CMC and the 1st CMC where the solution contains spherical micelles, a third mesophase C with still other properties and a partly less dense layer structure separates. And below the CMC down to a point somewhat above the LAC, where small aggregates of decanol and caprylate ions, premicelles, exist, a phase B of unknown structure is formed that differs completely from the foregoing. Between this latter point and the LAC where the solutions contain very small aggregates, a mesophase with the same structure as phase D separates.

About the factors that determine the structures of mesomorphous phases the following is known [34,36,37]. All mesophases of paraffin chain compounds, like the micellar solutions of these compounds, give a diffuse X-ray diffraction maximum at 4.5 Å. This indicates that the hydrocarbon regions are semiliquid. Changes in the lipophilic regions are therefore hardly responsible for the different mesomorphous structures; more likely the latter are due to changes in the layers of hydrophilic groups. We have found that the areas occupied by the hydrophilic end groups are very different in the different mesophases; this area is almost twice as large per end group in phase E as in phase D, and definitely larger in the latter phase than in phase F [37].

The reason for this difference is to be found in the interaction between the end groups. It has been known for a long time [38,39] that when a compound with a hydroxyl group (an alcohol or unionized carboxyl group) is incorporated between the ionized carboxyl groups in the monolayer of a fatty acid salt the cohesion in the monolayer increases owing to ion-dipole interaction and hydrogen bonding between the end groups (Fig. 13 a); at the same time the area per end group diminishes (Fig. 13 b) [39]. A similar change may be expected to occur in the end group layers of micelles and cylindrical aggregates when decanol is added to caprylate solutions. A structure composed of spherical or cylindrical particles in which the end groups occupy a fairly large area is energetically favoured, as long as most of the end groups have charges of like sign and repel one another (Solution L 1 and mesophase E). (Fig. 14). When decanol is incorporated and hydrogen bonds draw the end groups together, the preceding structure becomes less favoured. Evidently it can persist only up to a certain mole ratio of decanol to caprylate. At higher mole ratios another structure with a denser packing is favoured; this is a structure composed of double layers of amphiphilic matter separated by layers of water (Phase D) (Fig. 15). Such a layer structure is favoured only as long as the mole ratio of decanol to caprylate lies within certain limits. When this ratio and the possibility of hydrogen bonding between the end groups increases further and the water content decreases, a new struc-

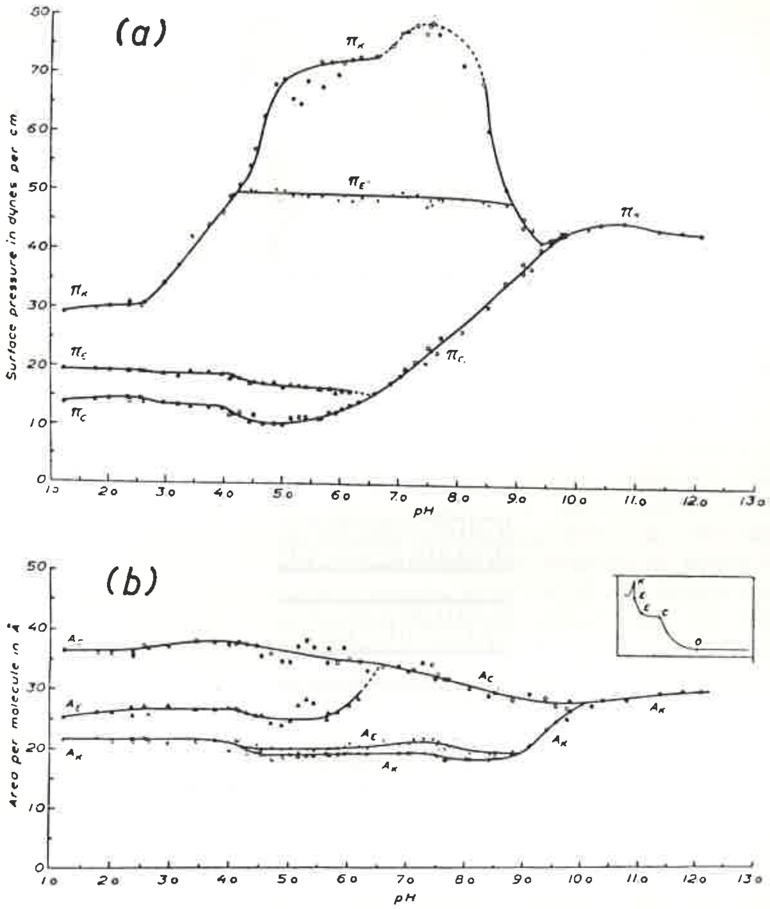

*Fig. 13.* Monolayers of myristic acid on 3 M sodium chloride solutions at different pH 20°C.

13a The dependence on pH of the surface pressure at the transition points in the myristic acid monolayer when it is compressed. The stability of the monolayer increases ($\pi_K$ and $\pi_{E'}$ increase) when the pH decreases below about 10 and molecules of undissociated myristic acid are formed in the monolayer between the myristate anions.

13b The dependence on pH of the areas per molecule corresponding to the transition points in the myristic acid monolayer when it is compressed. The area per molecule decreases ($A_K$, $A_{E'}$) when the pH decreases below about 9,5 and molecules of undissociated myristic acid are formed in the monolayer between the myristate anions.

(Ekwall, Groth and Lönegren).

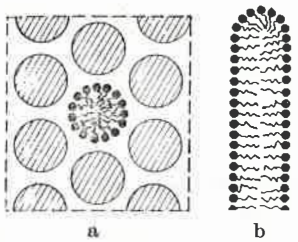

*Fig. 14.* Schematic drawing of the mesomorphous structure in the phase E. Cylinders in hexagonal array. The cylinders are surrounded by water (white areas) and consist of a hydrocarbon core with a surface layer of hydrophilic end groups of the amphiphilic ions and molecules (black) at the interface against water.

a) Cross section perpendicular to the axes of the cylinders.
b) Longitudinal section of a cylinder.

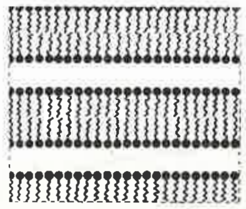

*Fig. 15.* Schematic drawing of the mesomorphous structure in the phase D. Layer structure with alternating double layers of amphiphilic ions and molecules separated by water layers (white area). The double layers consist of ions and molecules which are oriented with their hydrocarbon parts pointing inwards and the hydrophilic end groups (black) pointing towards the water.

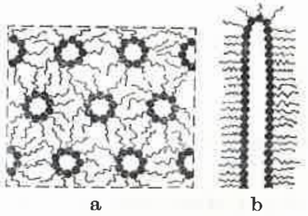

*Fig. 16.* Schematic drawing of the mesomorphous structure in the phase F. Cylinders in hexagonal array. The cylinders have a water core (white areas) which is surrounded by a layer of hydrophilic groups of the amphiphilic ions and molecules (black). The hydrocarbon parts of these ions and molecules are oriented outwards from the water core and form a continuous hydrocarbon region between the cores.

a) Cross section perpendicular to the axes of the cylinders.
b) Longitudial section of a cylinder.

ture with even more densely packed end groups is favoured. This leads again to a cylindrical structure, but now to a reversed one in which the hydrophilic end groups of the radially oriented caprylate ions and decanol molecules project inwards toward the middle of the cylinder where there is a core of water molecules (Phase F) (Fig. 16)[37].

A similar reversed structure is possessed also by the micelles present in the decanol solution in region L 2. Along the boundary of this region against the phase F the micelles evidently are cylinders with a water core and they separate from the solution L 2 to form the mesophase F similarly as the cylindrical micelles in the aqueous solution L 1 separate to form phase E. On dilution with decanol the cylindrical micelles in solution L 2 probably change to spherical micelles as the micelles in solution L 1 do when water is added.

Finally something must be said about the effect of water on the structures of the mesophases. In the opening address to this symposium I mentioned the fundamental significance of the polarity of water and the results of breaking down its "iceberg" structure. We should not either forget the binding of water by hydrophilic end groups that results from ion-dipole interaction and hydrogen bonding. It has been calculated that at most about eleven molecules of water are bound by a sodium ion and an ionized carboxyl group. This number of water molecules per mole of sodium caprylate is found in the mesophase E that separates from concentrated solutions of the soap. The experiments give, as already mentioned, a hydration number of 9—10 moles of water per mole of micellar caprylate, which points to an almost maximal hydration of the micelles. In mesomorphous phases in equilibrium with aqueous caprylate solutions the water contents per mole of sodium caprylate are at least of the same magnitude. These phases, however, contain also decanol; a hydroxyl group is believed to bind three molecules of water by hydrogen bonding. If hydrogen bonds are formed with other groups, the number of bound water molecules should decrease proportionately.

In the middle of the phase diagram, the water contents of the mesophases are so low that all the water may be bound as water of hydration. Only when the mole ratio of decanol to caprylate increases over about 1.5—2 do some mesophases become able to incorporate larger amounts of water. This is connected with the fact that the charge density diminishes with the number of ionized groups in the hydrophilic layers. This again leads to a release of previously bound gegenions that become more or less free to move about in the water of the mesomorphous phase. A Donnan equilibrium may thereby develop in which increasing amounts of water are taken up and bound by the mesomorphous phase without the structure of the latter being broken down. In the most water-rich mesophases (D and B) the water content may be as high as 70—90 per cent, which means that about 30 molecules of water are present for each hydrophilic group. But even in these cases the binding of gegenions does not fall below 50 per cent of the maximum.

By taking up water in this way the conditions in the mesophases approach those in the micellar systems with their intermicellar solutions containing mobile gegenions. This is the case in some parts of the phases D and C although their layer structure is preserved. Even more is this the case in phase B, which possibly has some kind of particle structure and is one step closer to the micellar solutions.

I would summarize the situation as follows.

One may start with the solid, crystalline association colloid (in the right lower corner of our triangular diagram in Fig. 12) with its layer lattice and introduce water between the double layers without destroying the layered structure. The transition from a solid to a liquid-crystalline state takes place, however; the thickness of the water layers increases as we proceed to higher water contents (to the left in our diagram) and the character of these layers becomes like that of an intermicellar solution.

These layer structures in the middle of the diagram, on the other hand, are connecting links between the particle structures in the water-rich and in the lipophilic regions of the system (along the base-line and in the upper corner of the triangular diagram). From the aqueous solutions L 1 with their small aggregates and spherical and cylindrical micelles and from the mesophase E with its long cylindrical aggregates, all with a hydrocarbon core innermost surrounded by hydrophilic groups and a water region, one enters, after passing through the layered structures, the lipophilic parts of the system (mesophase F and solution L 2) with similar but reversed particle structures, all with a water core surrounded by a hydrocarbon region.

In this scheme the association to small aggregates and micelles and the formation of mesomorphous structures are different stages of one and the same process where the major energy-liberating factor is the restoration of the disrupted water structure. This scheme can obviously be extended also to the formation of monolayers and double layers at interfaces.

Systems of the types we just have examined are common in the lipoid regions of living organisms. A difference is that in these cases we have to do not only with two or three components but often with multicomponent systems. Systems of the mentioned type are encountered also in numerous manufacturing

processes in the form of ointments, pastes, creams, gels and emulsions.

I should like to draw your attention particularly to the close relationship that exists between the phenomena discussed above and emulsification. In many cases when we talk about emulsions or spontaneous emulsification, we are actually dealing with mesomorphous phases and their formation. On the other hand, pairs of compounds of the type we have considered above have often been recommended as excellent emulsifiers; they include an association colloid and an amphiphilic compound with a pronounced lipophilic character. The ion-dipole interactions and hydrogen bond formation between end groups which we found to be active in the formation of mixed small aggregates, mixed micelles and mesomorphous structures play a part also in the formation of the stabilizing adsorbed layers around the emulsified droplets. There may, as we have seen, exist a certain relationship between the inner structures of two phases in equilibrium with each other and the same is naturally the case between the structures within a phase and the structure of the interface layer. This has not always been recognized to a sufficient extent in studies of emulsions. Any research relating to emulsions must start from a knowledge of this relationship and be based on a knowledge of the structures, and not only the compositions, of the phases.

As an extension of pure phase boundary phenomena and the conditions in relatively dilute aqueous solutions which were previously the main objects of interest, more and more attention has been directed in the last decade to more concentrated and in many cases heterogeneous systems containing amphiphilic compounds. We have here an extensive field of investigation that has up to now been characterized by many unexplored areas and a confusing variety of random empirical observations. An ordered pattern has begun to emerge and in this can be distinguished a relatively small number of fundamental factors.

## **References**

1. *Ekwall, P.*, Unpublished experiments.
2. *Debye, P.* and *Anaker, E. W.*, J. Phys. and Colloid Chem. *51*, (1947) 18. Ibid. *55* (1951) 644.
3. *Heckmann, K.*, Naturwiss. *40* (1953) 478; Z. phys. Chem. 9 (1956) 318; *Götz, K. G.* and *Heckmann, K.*, Z. phys. Ch. *20* (1959) 42; *Götz, K. G.*, Dissert. Göttingen, 1961.
4. *Lamm, O.* and *Högberg, H.*, Kolloid-Z. *91* (1940) 10; *Lamm, O.*, Ibid *98* (1942) 45.
5. *Ekwall, P.*, Sjätte Nordiska Kemistmötet, Lund, 1947, p. 179;
*Ekwall, P.*, *Hasan, A.* and *Danielsson, I.*, Acta Chem. Scand. *6* (1952) 440;
*Ekwall, P.* and *Smeds, K.* Acta Chem. Scand. *6* (1952) 441.

6. *Ekwall, P.*, *Eikrem, H.* and *Mandell, L.*, Acta Chem. Scand. *17* (1963) 111.
7. *Ekwall, P.*, *Danielsson, I.*, *Fontell, K.* and *Mandell, L.*, Finska Kemistsamf. Medd. *70* (1961) 51.
8. *Danielsson, I.*, Scandinavian Symposium on Surface Activity, Åbo, 1962. This volume, p. 90.
9. *Ekwall, P.* and *Vittasmäki, P.*, Acta Chem. Scand. *10* (1956) 1177; *Ekwall, P.*, Second Intern. Congr. Surface Activity, London, 1957. I, 405.
10. *Ekwall, P.* and *Lindblad, L. G.*, Kolloid-Z. *94* (1941) 42. *Ekwall, P.* Kolloid. Z. *97* (1941) 71.
11. *Ekwall, P.*, Kolloid-Z. *80* (1937) 77; Ibid. *92* (1940) 141; *Ekwall, P.*, Tekn. Fören. Finland, Förhandl. *60* (1940).
12. *Ekwall, P.* and *Rosendahl, T.*, Unpublished experiments.
13. *Davies, M.* and *Griffiths, D. M. L.*, Z. phys. Chem. N. F. *6* (1956) 143.
14. *Ekwall, P.* and *Aminoff, F.*, Acta Chem. Scand. *10* (1956) 237.
15. *Ekwall, P.* *Söderberg, O.* and *Danielsson, I.*, Acta Chem. Scand. *10* (1956) 227.
16. *Ekwall, P.*, Kolloid-Z. *77* (1936) 320.
17. *Ekwall, P.*, Svensk Kem. Tidskr. *63* (1951) 277; *Ekwall, P.* and *Danielsson, I.*, Acta Chem. Scand. *5* (1951) 973.
18. *Stauff, J.*, Z. physik. Chem. Abt. B *183* (1938) 76.
19. *Ekwall, P.*, J. Colloid. Sci. *Suppl. 1* (1954) 66.
20. *Eagland, D.* and *Franks, F.*, Nature *191* (1961) 1002.
21. *Ekwall, P.* and *Harva, O.*, Finska Kemistsamf. Medd. *52* (1943) 257.
22. *Smith, E. R.* and *Robinson, R. A.*, Trans. Faraday Soc. *38* (1942) 74.
23. *Sata, N.* and *Sasaki, H.*, Second Int. Conf. Surface Activity, London 1957, Vol. 1, p. 340.
24. *McBain, J. W.* and *Huff, H. J.*, Am. Chem. Soc. *70* (1948) 3838; *McBain, J. W.* and *Hoffman, O. A.*, J. Phys. and Colloid Chem. *53* (1949) 39; *McBain, J. W.*, J. Colloid Sci. *10* (1955) 224.
25. *Ralston, A. W.*, N.Y. Acad. of Sciences *46*. Art 6 (1946) 351.
26. *Kuhn, D. W.* and *Krauss, C. A.*, J. Am. Chem. Soc. *72* (1950) 3676; *McDowell, M. J.* and *Krauss, C. A.*, J. Am. Chem. Soc. *73* (1951) 1129; *Krauss, C. A.*, Proc. Nat. Acad. Sci, N.Y. *39* (1953) 1213.
27. *Mukerjee, P.* and *Mysels, K. J.*, J. Phys. Chem. *62* (1958) 1390, 1397, 1400, 1404.
28. *Bortré, C.*, *Crescenzi, V.* and *Melé, A.*, J. Phys. Chem. *63* (1959) 650.
29. *van Voorst Vader, F.*, Trans. Faraday Soc. *56* (1960) 1067.
30. *Ekwall, P.*, *Fontell, K.* and *Sten, A.*, Second Intern. Congr. Surface Activity, London, 1957, Vol. I. p. 357; *Ekwall, P.*, Unpublished experiments.
31. *Fontell, K.*, Unpublished measurements.
32. *Danielsson, I.*, Finska Kemistsamf. Medd. *69* (1960) 89.
33. *Mandell, L.*, Scandinavian Symposium on Surface Activity. Åbo, 1962. This volume, p. 49.
34. *Ekwall, P.*, *Danielsson, I.* and *Mandell, L.*, Kolloid-Z. *169* (1960) 113.
35. *Ekwall, P.*, *Danielsson, I.* and *Mandell, L.*, Third International Congr. Surface Activity. Cologne, 1960, Vol. I, p. 193.
36. *Ekwall, P.*, *Danielsson, I.* and *Mandell, L.* Third Intern. Congr. Surface Activity, Cologne, 1960. Vol. I. p. 189.
37. *Fontell, K.*, *Ekwall, P.*, *Mandell, L.* and *Danielsson, I.*, Acta Chem. Scand. *16* (1962) 2294.
38. *Schulman, J. H.* and *Rideal, Erik.*, Proc. Roy. Soc. B *122* (1937) 29, 46; *Schulman, J. H.* and *Cockbain, E. G.*, Trans. Faraday Soc. *36* (1940) 651, 661.
39. *Ekwall, P.*, Svensk Kemisk Tidskr. *63* (1951) 277; Kolloid-Z. *125* (1952) 129.
40. *Rosotti, J. C.* and *Martin, D. L.*, Proc. Chem. Soc. 1959, 60.
41. *Danielsson, I.* Elfte Nordiska Kemistmötet, Åbo, 1962, p 238.
42. *Pethica, B. A.* Third Intern. Congr. Surface Activity, Cologne, 1960, Vol. I, p. 212.
43. *Parfitt, G. D.* and *Smith, A. L.*, Journ. Phys. Chem. *66* (1962) 942.

44. *Danielsson, I.*, Scandinavian Symposium on Surface Activity, Åbo, 1962, This volume, p. 108.
45. *Fontell, K.*, Scandinavian Symposium on Surface Activity, Åbo, 1962, This volume, p. 99.
46. *Alexander, A. E.* and *Stainsby, G.*, Trans. Faraday Soc. *45* (1949) 585.
47. *Bury, Ch. R.* and *Grindley, J.*, J. Chem. Soc. (1929) 679.
48. *Ekwall, P.* and *Sjöblom, L.*, Acta Chem. Scand. *6* (1952) 96.

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# Thermodynamic Aspects of Micelle Formation

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It is typical of association colloids that, whereas they exist in the molecule-disperse form in dilute solutions, they undergo association to larger aggregates over a relatively narrow concentration range known as the critical concentration for micelle formation (CMC). This micelle formation takes place so abruptly that the process resembles in many respects the production of a new phase such as the formation of a precipitate. But, as it is not possible to isolate the micelles from the intermicellar liquid without causing a shift in the equilibrium, the micelle formation must be considered to be a process taking place in a homogeneous solution.

In recent years many authors have discussed the thermodynamics of micelle formation [1,2,3,4]. The association equilibrium can be formally defined by the expression

$$\frac{a_{mic}}{a^n_{Na} \cdot a^m_{RA}} = K_{mic}$$

As the exponents n and m have high values, small errors in measured activities lead to large errors in the value of the micelle formation constant and hence the value cannot readily be determined experimentally[5–9].

Corrin, however, has shown that the proportion of gegenions bound by the micelles can be estimated from the slope of the curve plotting log CMC against log ($C_{soap} + C_{salt}$), where $C_{salt}$ denotes the concentration of a neutral salt of the same cation present in the colloid solution [10]. Attempts have also been made to evaluate by this route the "standard" free energy of micelle formation $\Delta G_{ass} = RT \ln K_{mic}$ [11,12]. As log CMC is a linear function of the chain length for a series of homologous association colloids, the standard free energy of micelle formation is also a function of the chain length. The increase in free energy per methylene group has been estimated at about 600 cal.

When applying the mass-action law it is necessary to choose a "charged" standard state for the ions and micelles which has no physical counterpart. It is also unknown how the gegenions in the electrical double layer surrounding a micelle are to be introduced into the equilibrium expression. There is furthermore the inconsistency that the activity of water is not included in the expression although this activity varies considerably with the solute concentration.

These difficulties can in some degree be avoided by considering the micelle as a separate phase [13–17]. The application of the phase rule to micellar systems has recently been discussed by Pethica [4,9]. He stressed that the micelles are not composed solely of association colloid, but contain also water molecules and in certain cases hydronium or hydroxide ions, and that these should be taken into account. The introduction of another compound (e.g. $H_2O$) than the colloid in the micelle phase leads according to Pethica to a micelle which should be considered as a new component in the system. He took as an example the formation of a micelle M by a nonionic association colloid ROH. If we take the equilibrium reaction to be

$$(2) \qquad n\,ROH = M \qquad\qquad (M = \text{micelle})$$

without including water or its ions in the micelle, the number of components in the system is the same whether we assume the micelle to be a solute or a separate phase. If we assume the micelle to represent a separate phase, we have three phases (P), the micelle, the solution and water vapour. By the phase rule, the number of degrees of freedom of the system is then

$$F = C - P + 2 = 2 - 3 + 2 = 1.$$

This means that if the temperature is defined, the composition of the intermicellar solution and also the vapour pressure is invariant. This is not in accord with the experimental observation that the vapour pressure varies slightly with increasing concentration above the CMC. The correct number of degrees of freedom, two, is obtained if the micelle is taken to be a solute and not a separate phase. It is therefore unwarranted to consider the micelle as a separate phase as implied by the equilibrium (2), which neglects the participation of water in the association process.

If we now assume that micelle formation results from an interaction of the association colloid with water or its ions in accordance with equation

$$(3) \qquad n\,ROH + h\,H_2O = M,$$

we have a slightly different situation. (h represents the difference in hydratation of the micellar and free species). If the micelle M is a solute, the number of components is two although the number of constituents in the system is three. This is because the three constituents are in equilibrium. If, however, the micelle M were a separate phase, the number of components would be three. The number of degrees of freedom of the system is hence two irrespective of whether the micelle is a separate phase or not. From this Pethica concluded that when applying the phase rule, it is permissible to consider the micelle as a separate phase, but only if it is noted that water participates in the formation of the micelle.

Pethica compared the micellar system with an aluminium chloride solution from which hydrated aluminium hydroxide has precipitated and where the number of components is hence three. He extended his views not only to solutions of nonionic association colloids, but also to solutions of paraffin-chain salts. Pethica concluded that the choice between the mass-action approach and the phase rule approach is one of convenience rather than of principle. If the association colloid solution is treated as a twocomponent system, the mass-action approach may be applied, but if the micelle is considered to be a third component in the system, the phase rule approach may be applied.

Similarly as the equilibrium between two liquids containing the same solute is determined by the chemical potential of the solute, so also the micelle formation equilibrium is determined by the chemical potential of water according to Pethica. It should be noted that this way of viewing the problem does not imply that the vapour pressure of water above the two phases remains constant when the soap concentration in the system increases. It is sufficient that the activity of water varies in a similar manner in both the micelle and the intermicellar liquid.

The shift in the micelle formation equilibrium effected by neutral electrolytes Pethica attributed to the influence of these electrolytes on the activity of water.

A review of the properties of soap solutions containing no additives reveals, as Pethica pointed out, that the osmotic pressure and hence the activity of water is nearly constant above the CMC [18,19,20]. The measurements of Robinson and co-workers and Ekwall and Danielsson have, however, shown that the vapour pressures over solutions of typical association colloids and lower paraffin-chain salts decrease with increasing colloid concentration although micelles or other aggregates are present in these solutions [21,22,23,24]. The decrease in vapour pressure is, it is true, very slow immediately above the CMC but is more pronounced at higher concentrations. Pethica claims that according to the phase rule approach such effects are to be expected at high concentrations owing to the effects of ions on the activity of water [4].

According to the classical phase rule the vapour pressure of the solution should change suddenly at the concentration, the CMC, where the micellar phase is formed. Immediately above this concentration the vapour pressure should be independent of the amount of micellar phase. The vapour pressure changes gradually both in the case of lower paraffin-chain salts and in the case of typical association colloids in the range about the CMC. The same is in principle the case with all other properties of paraffin-chain salt solutions such as, for example, hydrolytic equilibria and solubilisation [25]. These effects seem to be in contradiction to the phase rule approach, at least in the case of lower paraffin-chain salts. Under these circumstances the micellar solutions should be considered homogeneous. The observed changes in vapour pressure with increasing concentration are probably to be attributed to an increase in the concentration of the free gegenions in the intermicellar solution.

The hypothesis that the micelles form a separate phase offers, however, many formal adventages; one of these is that the gegenions may be assumed to be incorporated in the micellar phase.

On the assumption that the micelles may be taken to be a separate phase with an invariant water activity, Hutchinson and later Pethica derived a Clausius-Clapeyron equation for the determination of the heat of micelle formation from the temperature dependence of the CMC [13,14,15,26,27]. In the equation

$$\frac{-\Delta H_{mic}}{RT^2} = k \frac{d \ln CMC}{dT}$$

derived by Pethica k is a factor which is a measure of the ion exchange at the micelle surface. In acid solutions of paraffin-chain salts a relatively extensive exchange of hydrogen and sodium ions may be assumed to have taken place; when all the ions have been replaced, the value of k is unity. If no cation exchange occurs, the alkali metal ions take part formally in the micelle formation in the same way as the paraffin-chain ions and the value of k is then 2 according to Pethica. This is probably the case in a neutral soap solution where the number of hydrogen ions is negligibly small compared with the number of sodium ions. If we consider soap solutions containing a high invariant excess concentration of neutral salt, the value of k is unity. In this case the activity of the alkali metal ions is invariant and may be "included in the solvent medium".

Since the CMC decreases with increasing temperature when this is low and increases when it is high, the heat of micelle formation will vary greatly with temperature according to the Clausius-Clapeyron equation [9,28-35].

It should be also possible to apply the Clausius-Clapeyron equation to the variation of the activity of an individual ion, but the variation has not been evaluated with sufficient accuracy for micellar solutions. The only quantity susceptible to accurate measurement is the vapour pressure of water. From the temperature dependence of the vapour pressure of water over potassium octanoate solutions, Benson derived the value 5.5 eu/mole for the entropy change in micelle formation [36].

Many investigators have attempted to evaluate the heat of micelle formation directly by calorimetric methods [34,38,39,40]. The measured values are small and may differ also in sign depending on the nature of the paraffin-chain salt and the electrolyte content of the solution. From the decrease in the heat of micelle formation with increasing salt content Benson drew the conclusion that the depolymerization of water is the decisive factor [41].

The complex of forces that bring about association may be schematically divided into three groups:

a. Forces arising from the polarity of water.

b. Electrostatic forces.

c. Attractive forces between the lipophilic parts of the molecules.

We include in the first group all the forces arising from the polar properties of the association colloid molecules and the water molecules. It has long been known that the forces arising from the polarity of water and the electrostatic forces are decisive and that, in comparison, the weak forces of attraction between the lipophilic parts of the molecules can be neglected.

The influence of the polarity of water should be understood so that the lipophilic parts of the molecules in molecule-disperse solutions prevent the water molecules from coming into contact with one another. When these lipophilic parts are incorporated in micelles, the water molecules come into contact, hydrogen bonds are formed, and energy is released. This energy change represents the greater part of the energy change associated with micelle formation. These energy changes are always coupled with electrostatic interactions on the charged surfaces of the micelles and cannot be evaluated separately. Also their theoretical calculation presents difficulties. However, the influence of the polarity of water is a linear function of the size of the lipophilic part of the colloid molecule. When several water molecules have an opportunity to associate, as result of the incorporation of large hydrophobic surfaces in the micelles, a large quantity of energy is released and the CMC shifts to lower values. This is reflected in the observation that log CMC decreases linearly with increasing chain length in a homologous series of association colloids [1,10,11,42,43].

The electrostatic forces between the like-charged paraffin-chain ions oppose the association, but this effect is partly counteracted by the binding of gegenions. Many observations suggest that the degree of gegenion binding is nearly constant; for example, one alkali metal ion to two carboxyl groups in soaps near the CMC [10,11]. Despite this, it is generally held that the gegenions are only bound by electrostatic forces at the micelle surface [10,43-52].

Shinoda has calculated the contribution of the electrostatic forces to the energy of micellar association by starting from the theory of the electrical double layer. The values he derived for myristate and caprylate are of the order of 4 kT per ion [53,54].

Overbeek's theoretical work represents a new step forward in the quantitative evaluation of the electrostatic effects in the electrical double layer [55]. Overbeek and Stitger include in one term all the contributions to the chemical potential which are due to the charges of the various species in an association colloid solution. The evaluation of this electrostatic energy term $\Delta G_{el}$ takes place in three stages. The electric work done in discharging the free paraffin-chain ions and gegenions is first calculated in accordance with the Debye-Hückel theory. The surface of a spherical micelle is then charged with an electrical double layer and the associated energy change is calculated assuming the charge to be uniformly distributed over the micelle surface. The last stage in the calculations involves the concentration of the resulting homogeneous surface charge into point charges. The micelle surface is taken to be only two-dimensional, the ions in the micelle surface being assumed to have no dimension in the direction of the radius. The sum of the energy changes in the three steps gives the total electric contribution $\Delta G_{el}$ to the free energy of micelle formation.

As Overbeek and Stitger pointed out, their calculations are complicated by the following factors. First, they have to assume a certain aggregation number for the micelles. This number cannot be determined accurately by experiment; both the sizes of the micelles and their size distribution at different concentrations may vary with different association colloids. Secondly, they have assumed that the micelles are spherical. The influence of these simplifying assumptions on the results of the calculations should not be very great. More serious is the assumption that the volumes of the ions can be neglected. The fact that in many cases about 50 per cent of the maximal number of gegenions are bound to the micelle surface implies almost a "chemical" bonding of anions and cations at the micelle surface. Overbeek and Stitger do not taken into account any binding of gegenions at the micelle surface. Uncertainty arises also from the fact that when concentrating the uniformly spread surface charge on points, the authors have been forced to operate with a two-dimensional model. This is a consequence of the fact that very little is known about the topography of an electrical double layer.

It should be noted, however, that despite the limitations Overbeek and Stitger mention, their calculations of the electrical contribution to the energy of micelle formation represents an important step in the development of a thermodynamical theory for the process of micelle formation. Unfortunately, the calculations have been carried out for only a few association colloids. Values derived by Overbeek and Stitger for sodium dodecyl sulphate are $\Delta G_{el} = 3.41$ kT for salt-free solutions and $\Delta G_{el} = 0.59$ kT for a solution 0.4 molar in sodium chloride. The experimental value found for dodecylammonium chloride is 3.75 kT and that for sodium dodecyl sulphate 3.4 kT. Especially the data for alkylammonium chlorides are of great interest because Veis and Hoerr developed a method for the evaluation of $\Delta G_{el}$ from the acidity constant [56,57]. For dodecylammonium chloride they derived the value 2.53 kT.

The reasons why the association does not continue until infinitely large aggregates are formed (phase separation) have been discussed by many investigators, among them Stitger and Reich [58–61]. The limiting factor can hardly be a purly geometric one nor can it be the electrostatic forces, because also nonionic association colloids form micelles of limited size. Benson and Hoeve have considered the problem of the limited size of the micelles by applying methods of statistical mechanics to the formation of micelles. They have examined primarily nonionic association colloids in which case the electrostatic forces can be disregarded. The theory can, however, be extended to ionic association colloids. Benson and Hoeve assumed that the micelles first formed above the CMC are spherical with a liquid core. Also other types of micelles formed at high concentrations were considered. It was assumed that the polar groups are located only at the surface of the micelles and that their state is the same on the surface as in the surrounding solution. Their approach does not take into account the changes in the "iceberg" structure of water. The final results are that the size distribution of the micelles is large and that the average size varies with the concentration. Benson and Hoeve strongly stress their opinion that neither the size of the micelle nor the concentration of the monomeric colloid remains constant above the CMC. The results are, however, uncertain in that these authors were unable to take into account some of the effects of the solvent, but nevertheless their method has opened up new possibilities for the treatment of systems containing a whole series of particles of different size.

The application of statistical methods to micelle formation is rendered difficult by the smallness of the entropy changes associated with micelle formation, which in turn is due to the superposition of many different factors.

Since the polarity of water is the deciding factor in micelle formation, any attempt to study the thermodynamics of association requires a knowledge of the heat and entropy associated with the association of water molecules. It is necessary to take into consideration the changes in the "iceberg" formation in the immediate vicinity of the hydrocarbon chains and the polar groups at the micelle surface. As a theoretical treatment of these problems is not possible at present, the only way to proceed is to "consolidate" the associated state of water by means of a high ionic strength. At the same time the activity coefficients of the various ions will be maintained nearly constant. The use of a high ionic strength will naturally greatly alter the conditions from those prevailing in solutions of low ionic strength, i.e. additive-free association colloid solutions.

Before experimental data can be collected that will provide a basis for a more accurate treatment of the thermodynamics of micelle formation, it is hence necessary to carry out measurements on solutions of high invariant ionic strength. This seems to be one of the most urgent problems in the field of association colloids now that many of the phenomena taking place at the CMC have been clarified.

## References

1. *Phillips, J. N.*, Trans. Faraday Soc. *51* (1955) 561.
2. *Hutchinson, E.*, Z. phys. Chem. N.F. *2* (1959) 143.
3. *Overbeek, J. Th. G.*, Chem. Weekblad *54* (1958) 687.
4. *Pethica, B. A.*, Third Intern. Congr. Surface Activity, Cologne, 1960, Vol. I, p. 212.
5. *Hartley, G. S.*, Aqueous Solutions of Paraffin-Chain Salts. Paris 1936.
6. *Bury, C. R.* and *Grindley, J.*, J. Chem. Soc. (London) *1929* 679.
7. *Jones, E.* and *Bury, C. R.*, Philos. Mag. *4* (1927) 841.
8. *Murray, R. C.* and *Hartley, G. S.*, Trans. Faraday Soc. *31* (1935) 183.
9. *Matijevic, E.* and *Pethica, B. A.*, Trans. Faraday Soc. *54* (1958) 587.
10. *Corrin, M. L.*, J. Colloid Sci. *3* (1948) 333.
11. *Ekwall, P.* and *Danielsson, I.*, Acta Chem. Scand. *9* (1955) 1661.
12. *Alexander, A. E.*, Trans. Faraday Soc. *33* (1942) 54.
13. *Stainsby, G.* and *Alexander, A. E.*, Trans. Faraday Soc. 46 (1950) 587.
14. *Hutchinson, E.*, *Inaba, A.* and *Bailey, L. G.*, Z. phys. Chem. N.F. *5* (1955) 344.
15. *Hutchinson, E.* and *Bailey, L. G.*, Z. phys. Chem. N.F. *21* (1959) 24.
16. *Hutchinson, E.* and *Bailey, L. G.*, Z. phys. Chem. N.F. *21* (1959) 30.
17. *Hutchinson, E.* and *Shinoda, K.*, J. Phys. Chem. *66* (1962) 577.

18. *McBain, J. W.*, *Huff, M.* and *Brady, A. P.*, J. Phys. Chem. *55* (1951) 311.
19. *McBain, M. E. L.*, *Dye, W. B.* and *Johnson, S. A.*, J. Am. Chem. Soc. *61* (1939) 3210.
20. *Johnson, S. A.* and *McBain, J. W.*, Proc. Roy. Soc. (London) *A181* (1942) 119.
21. *Smith, E. R.* and *Robinson, R. A.*, Trans. Faraday Soc. *38* (1942) 74.
22. *Danielsson, I.*, Acta Academiae Aboensis Math. & Phys. XXI (1960).
23. *Danielsson, I.*, Finska Kemistsamfundets Meddelanden *69* (1960) 89.
24. *Ekwall, P.*, Scandinavian Symposium on Surface Activity, Åbo 1962, This volume, p. 59.
25. *Ekwall, P.*, J. Coll. Sci. Suppl. *1* (1954) 66.
26. *Hutchinson, E.* and *Winslow, L.*, J. Phys. Chem. *60* (1956) 122.
27. *Shinoda, K.*, *Yamaguchi, T.* and *Hori, R.*, Bull. Chem. Soc. Japan *34* (1961) 237.
28. *Nagakama, T.* and *Shinoda, K.*, Colloidal Surfactants, New York, 1962, chapter II.
29. *Nagakava, T.*, *Tori, K.*, *Inoue, H.* and *Kuryiama, K.*, J. Chem. Soc. Japan *79* (1958) 1194.
30. *Hoeve, C. A. J.* and *Benson, G. C.*, J. Phys. Chem. *61* (1957) 1149.
31. *Klevens, H. B.*, J. Phys. Coll. Chem. *52* (1948) 130.
32. *Goddard, E. D.* and *Benson, C. G.*, Canad. J. Chem. *35* (1957) 986.
33. *Flockhart, O. B.* and *Ubbelohde, A. R.*, J. Coll. Sci. *8* (1953) 428.
34. *Betts, I. J.* and *Pethica, B. A.*, Second Intern. Congress Surface Activity London, 1957, Vol. I, p. 000.
35. *McGinn, Kinney, F. B.* and *Harris, J. C.*, J. Am. Oil Chem. Soc. *37* (1960) 183.
36. *Moule, D.*, *White, P.* and *Benson, C. G.*, Canad. J. Chem. *37* (1959) 2086.
37. *White, P.* and *Benson, C. G.*, J. Colloid Sci. *13* (1958) 584.
38. *Goddard, E. D.*, *Hoeve, C. A. J.* and *Benson, C. G.*, J. Phys. Chem. *61* (1957) 593.
39. *White, P.* and *Benson, C. G.*, Trans. Faraday Soc. *55* (1959) 1025.
40. *Hutchinson, E.*, *Manchester, K. E.* and *Winslow, L.*, J. Phys. Chem. *58* (1954) 1124.
41. *White, P.* and *Benson, C. G.*, J. Phys. Chem. *64* (1960) 599.
42. *Klevens, H. B.*, J. Am. Oil Chem. Soc. *30* (1953) 74.
43. *Kling, W.* and *Lange, H.*, Second Intern. Congr. Surface Activity, London 1957, Vol. I p. 295.
44. *Corrin, M. L.* and *Harkins, W. D.*, J. Am. Chem. Soc. *69* (1947) 683.
45. *Lange, H.*, Kolloid Z. *117* (1950) 48.
46. *Vold, M. I.*, Kolloid Z. *119* (1951) 54.
47. *Kenjuro Meguro* and *Tamotsu Kondo*, Nippon Kagaku Zasshi, *80* (1959) 818.
48. *Moresuke Kashiwagi* and *Heichachi Ezaki*, Bull. Chem. Soc. Japan *32* (1959) 624.
49. *Hobbs, M.*, J. Coll. Sci. *5* (1951) 675.
50. *Stitger, D.* and *Mysels, K.*, J. Phys. Chem. *59* (1955) 45.
51. *Stitger, D.*, Rec. Trav. Chim. Pays Bas 73 (1954) 771.
52. *Parreira, H. C.*, Thesis 1958 Cambridge University, England.
53. *Shinoda, K.* and *Kimoshita, K.*, Bull. Chem. Soc. Japan *27* (1954) 73.
54. *Shinoda, K.*, J. Phys. Chem. *60* (1956) 1439.
55. *Overbeek, J. Th. G.* and *Stigter, D.*, Rec. Trav. Chim. Pays Bas *75* (1956) 1263.
56. *Veis, A.* and *Hoerr, C. H.*, J. Coll. Sci. *15* (1960) 427.
57. *Tartar, H. V.*, J. Coll. Sci *14* (1959) 115.
58. *Reich, I.*, J. Phys. Chem. *60* (1956) 257.
59. *Debye, P.*, Ann. N.Y. Acad. Sci. *51* (1949) 575.
60. *Nakagaki, M.*, J. Chem. Soc. Japan *72* (1951) 113.
61. *Ooshika, Y.*, J. Coll. Sci. *9* (1954) 254.

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# X-ray Studies of Association Colloid Systems

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The dualistic nature of association colloid molecules becomes apparent also when their diffraction of X-rays is studied. The solid compounds give rise to sharp X-ray reflections from which the crystal structures can be deduced in the usual way. Polymorphism is, however, observed; the crystals are either triclinic or monoclinic but with the common feature that one axis is always much longer than the other two. A consequence of this is that these compounds possess a layer structure.

Previous lectures delivered at this symposium (5, 20) have revealed that mesophases frequently occur in systems containing association colloids. Two types of mesomorphism, thermotropic and lyotropic, exist. An example is shown by the phase diagram of the sodium palmitate-water system in Fig. 1. The anhydrous soaps exhibit five different mesomorphous states in the temperature range from room temperature up to about 350°C. These phases are called subwaxy, waxy, superwaxy, subneat and neat. This is thermotropic mesomorphism. Several lyotropic mesomorphous phases exist between the curves $T_c$ and $T_i$; above curve $T_i$ the solutions are isotropic. The sharp knee on the curve $T_c$ indicates the so-called Krafft point, the temperature above which the solubility suddenly increases.

Fig. 2 shows the phase diagram of the three-component system sodium caprylate-decanol-water already described today. The crystalline soap with its layered structure is in the right corner. Water and/or decanol can be added to the soap without its crystalline character being lost. When the water concentration increases on going to the left along the base of the triangle, the system finally divides into two phases, one identical with the original one (region G in the diagram) and one consisting of mesomorphous matter, the middle soap (the base line of the region E). A general characteristic of X-ray diffraction patterns of

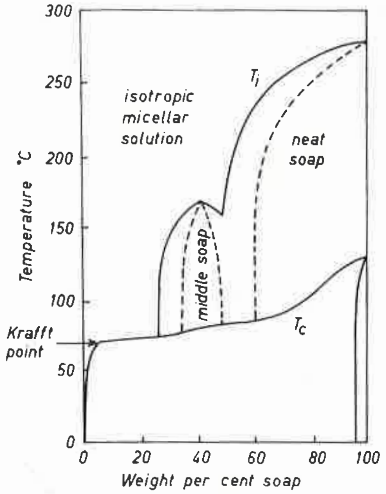

*Fig. 1.* Phase diagram for the two-component system of sodium palmitate and water.

mesomorphous phases of various soaps is that there is a series of from 2 to 7 distinct reflections, equal in sharpness to those obtained with crystalline substances, in that part in the centre of the diagram which corresponds to values of s less than 0.1 Å$^{-1}$ ($s = \frac{2 \sin \Theta}{\lambda}$). Outside these sharp reflections there are one or two diffuse reflections in the region from s = 0.2 Å$^{-1}$ to s = 0.33 Å$^{-1}$. In the case of the middle soap of sodium caprylate we have found three sharp reflections corresponding to the identity distances 25.9, 15.0 and 13.0 Å. These distances are in the ratio $1:1/\sqrt{3}:1/\sqrt{4}$ which is the condition for a two-dimensional hexagonal structure. Luzzati [15,17,18,19] has interpreted similar results for the higher soaps, $C_{12}-C_{18}$, as follows. The soap molecules are arranged radially in "infinitely" long rodlike aggregates which are hexagonally packed as shown in Fig. 3. The cores of the rods are in a semiliquid state as is proved by, among other observations, the broad diffuse reflection at s = 1/4.5 Å$^{-1}$. As the water concentration of the mesomorphous phase is increased, the "crystalline" reflections shift to smaller angles, which implies that the unit cell dimension of the two-dimensional cell increases. Luzzati showed that the dimensions of the rodlike aggregates remain unchanged and that the increased unit cell dimension is due to the water. Our results for the middle soap of sodium caprylate are not exactly the same, as we have not been able to establish any change in the unit cell dimension. This would imply that the diameters of the rod-like aggregates vary slightly or that

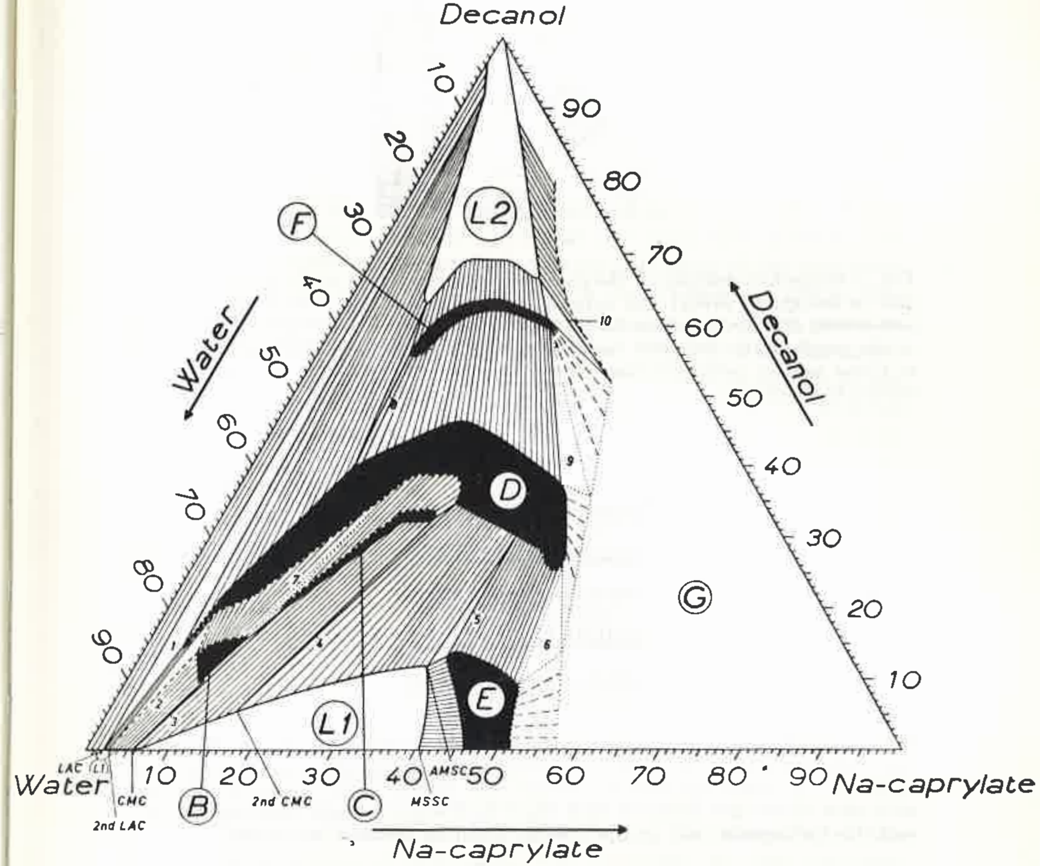

*Fig. 2.* Phase diagram for the three-component system sodium caprylate — decanol — water at 20°C. The concentrations are per by weight.
L 1 Homogeneous isotropic solutions in water.
L 2 » » » in decanol.
B, C, D, E, F. Homogeneous mesomorphous phases.
G. Solid crystalline sodium caprylate and hydrated sodium caprylate with fibre structure.
1 — 10. Three-phase triangles.
MSSC Middle Soap Separation Concentration
AMSC Alcohol Middle Soap Corner
CMC Critical Micelle Concentration
LAC Limiting Association Concentration.

(Ekwall, Danielsson and Mandell)

the aggregates are not "infinitely" long. In other respects our results are in full agreement with those of Luzzati.

When decanol is added to the middle soap, it is built into the structure and the macroscopic and microscopic appearance of

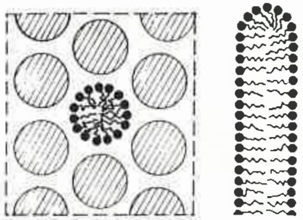

*Fig. 3.* Schematic drawing of the mesomorphous structure in the phase E. Cylinders in hexagonal array. The cylinders are surrounded by water (white areas) and consist of a hydrocarbon core with a surface layer of hydrophilic end groups of the amphiphilic ions and molecules (black) at the interface against water. a) Cross section perpendicular to the axes of the cylinders. b) Longitudinal section of a cylinder.

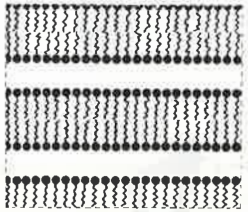

*Fig. 4.* Schematic drawing of the mesomorphous structure in the phase D. Layer structure with alternating double layers of amphiphilic ions and molecules separated by water layers (white areas). The double layer consist of ions and molecules which are oriented with their hydrocarbon parts pointing inwards and the hydrophilic end groups (black) pointing towards the water.

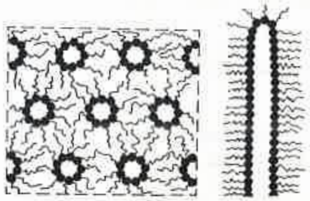

*Fig. 5.* Schematic drawing of the mesomorphous structure in the phase F. Cylinders in hexagonal array. The cylinders have a water core (white areas) which is surrounded by a layer of hydrophilic groups of the amphiphilic ions and molecules (black). The hydrocarbon parts of these ions and molecules are oriented outwards from the water core and form a continuous hydrocarbon region between the cores. a) Cross section perpendicular to the axes of the cylinders. b) Longitudinal section of a cylinder.

the phase undergoes no change (region E in the diagram). The X-ray diffraction pattern remains unaltered in the main except that the unit cell dimension of the two-dimensional hexagonal cell increases slightly. The calculated area occupied by a hydrophilic group on the surface of the cylindrical aggregate (area calculated similarly as was done by Luzzati [19] decreases from about 47 Å$^2$ to about 40 Å$^2$ with increasing decanol content. When the decanol content exceeds about 13 per cent, the system consists of two phases, one of which is the middle soap of the composition at the borderline and the other a new phase of altogether different macroscopic and microscopic appearance which gives an X-ray diffraction pattern of another type. The identity distances of the sharp centrally located X-ray reflections of this new phase (region D in the diagram) are in the ratio 1:2:3, the innermost reflection being much stronger than the other two. A pinhole pattern shows, moreover, a preferred orientation in that the diffraction rings vary in intensity around their circumference with maxima in the plane perpendicular to the axis of the capillary tube containing the sample. Further out from the centre of the pattern, the broad, diffuse, unoriented hydrocarbon and water reflections similar to those observed with phase E are located. The Bragg spacing of the innermost reflection varies within fairly wide limits, from 25 Å to 120 Å, with increasing volume fraction of water in the system. A lamellar structure composed of double layers of amphiphilic molecules separated by layers of water is in question (Fig. 4). The hydrocarbon interiors of the lamellae are semiliquid. Calculations similar to those mentioned above show that the area per hydrophilic group at the interface is of the order of 25 Å$^2$ and that the thickness of the double layer remains constant, the increase in the identity distance being solely due to the greater thickness of the water layers.

Below the region D there is a narrow, elongated region C where a phase with a different macroscopic and microscopic appearance exists. The X-ray diffraction pattern of this phase exhibits, like phase D, up to three sharp reflections in the central part. The pinhole pattern, however, contains diffraction rings of uniform intensity around their circumference. The Bragg spacings are again in linear ratio but vary differently with the water content. Also this phase has a lamellar structure comprising double layers with a semiliquid hydrocarbon interior and water layers; possibly the lamellae have a smaller lateral dimension. The calculated area per hydrophilic group at the interface is about 35 Å$^2$.

When the decanol content of the system is increased still further, two phases appear of which one is phase D and the other is a new phase marked F in the diagram. Both the macros-

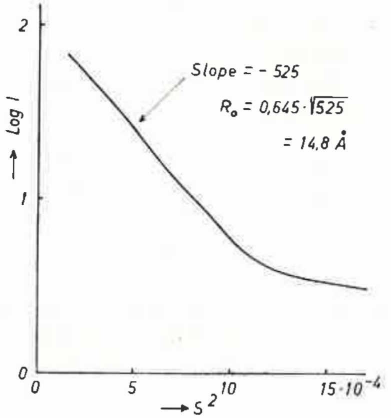

*Fig. 6.* Plot of log I versus s² ($s = \frac{2 \sin \Theta}{\lambda}$) for 0.12 molal sodium desoxycholate. The radius of gyration ($R_0$) is calculated according to ref. 12, p. 127. The radius of the micelle, assumed spherical, is about 19 Å.

scopic and microscopic appearances of this phase are similar to those of phase E, the middle soap. The X-ray diffraction patterns of the two phases resemble each other greatly; there are up to three sharp reflections in the central part of the pattern with Bragg spacings in the ratio $1{:}1/\sqrt{3}{:}1/\sqrt{4}$ and the same feeble outer reflections as in the previous cases. This is consistent with a two-dimensional hexagonal structure but one in which "water cylinders" are hexagonally arranged as shown in Fig. 5. The calculated area per hydrophilic group at the cylindrical interface is of the order of 18 Å².

Regions L 1 and L 2 consisting of isotropic solutions are located at the water and the decanol corners of the diagram, respectively. The solutions of micellar sodium caprylate are in region L 1. The X-ray diffraction pattern of a soap solution exhibits one or a few diffuse maxima in the central region ($S < 0.1$ Å⁻¹), one diffuse band at $s = 1/4.5$ Å⁻¹ due to hydrocarbon and reflections due to water. The positions and intensities of the inner reflections are influenced by the nature of the soap, its concentration and the presence of foreign solubilised substance. These experimental observations are well known from the work of Hess, Kiessig, Harkins and others (for a review see, for example, ref. 22). The solutions of region L 2 give similar patterns. The results for aqueous soap solutions have been interpreted with the aid of Bragg's equation as if crystal reflections were in question and the derived identity distances were used in discussions of the sizes and structures of the micelles and it was concluded from the absence or presence of interference maxima whether or not micelles were present in a solution [21]. In the late forties, however, this way of interpreting X-ray diffraction patterns of soap solutions was severely criticized [3,12,14,22]. It was pointed out that it is not permissable to select some separate details of a diffuse scattering curve; the whole curve must be taken into consideration. The shapes of the experimental curves indicate gas-type or liquid-type scattering.

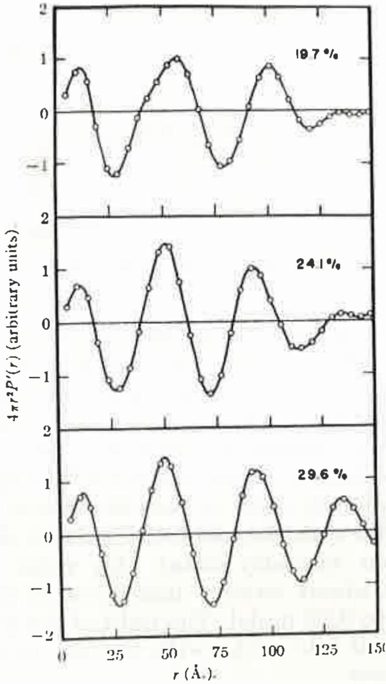

*Fig. 7.* Radial distribution functions for three concentrations of potassium laurate. (Andersen, D. E., and Carpenter, G. B. (1)).

It is the heterogeneities of colloid dimensions in the systems that give rise to the scattering of X-rays in the small angle region. Theoretically the X-rays scattered by the colloid particles, micelles, should give rise, when they do not interfere, to a monotonically decreasing intensity curve with increasing scattering angle that could be interpreted according to the methods developed by Guinier, Hosemann and Kratky [11,13,16].

As to soaps, the scattering by their aqueous solutions can not be interpreted in this way but the methods may possibly be applied to the X-ray diffraction patterns of aqueous solutions of another group of association colloids, the sodium salts of bile acids. In contrast to earlier reports [21], these solutions give

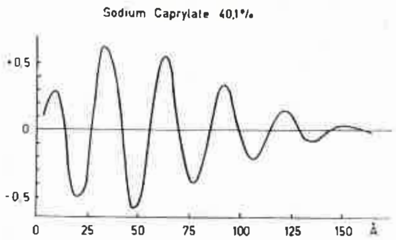

*Fig. 8.* Radial distribution function for 40.1 % sodium caprylate solution.

rise to X-ray scattering in the small angle region [7–10]. The scattering by dilute solutions might be interpreted according to the mentioned theories, but the intensities are very feeble and hence the accuracy of the data is not high; the values are, however, fairly consistent and of reasonable magnitude. Assuming spherical particles the data we have obtained for sodium cholate and sodium desoxycholate give a micelle radius of about 20 Å (Fig. 6). Combined with the molecular volume of sodium cholate, 0.81 l/mole (from viscosity data), this value implies that the micelles contain about twenty molecules in the concentration range from 0.06 to 0.25 molal. The radii of the micelles of sodium salts of conjugated bile acids (with taurine or glycine) seems to be somewhat lower.

The experimental intensity curves of soap solutions should be examined by radial distribution analysis. Such analyses have been carried out in a few cases by Brady [2] and by Andersen and Carpenter [1]. The result is a curve (Fig. 7) giving the probable distribution of distances in the examined system and, assuming the presence of micelles, these distance are those between micelle centres. Andersen and Carpenter concluded that the micelles, assumed spherical, in aqueous potassium laurate solutions are in a cubic close-packed arrangement with each micelle surrounded by twelve neighbours. The radius of the micelles is 27 Å which would imply that each micelle contains about 60 molecules [1]. Other shapes of the micelles cannot, however, be completely excluded.

We have carried out radial distribution analyses of the intensity curves of aqueous sodium caprylate solutions. As the distribution curve in Fig. 8 shows, the result is much the same as in the preceding case. The distance between micelle centres is about 34 Å and the radius of the micelle, assumed spherical, about 20 Å. The number of molecules in a micelle is hence about 70, which is rather high for spherical micelles of a soap like sodium caprylate. Studies of viscosities, conductance anisotropy, etc. [4,5] carried out by our group show that the micelles are rodlike in form in the concentration range in question (30—40 %). In this case, it is difficult to deduce by radial distribution analysis the nature of the packing because different arrangements give nearly the same distribution curve as a first approximation.

We may summarize the above by saying that the mesomorphous phases in systems containing association colloids often give rise to "crystalline" X-ray diffraction patterns which permit an elucidation of the structures of the phases. The diffuse small angle scattering of X-rays by isotropic colloid solutions is more difficult to interpret. Qualitatively the occurrence of such scattering points to the presence of colloidal particles in the system but the Bragg equation cannot be applied in the interpretation. When the intensity curve falls off monotonically with increasing scattering angle it is permissable to attempt a "slope analysis" of the curve, but in other cases radial distribution analysis must be applied. In these ways information can be derived about distances within a system which, together with experimental data obtained by other methods (partial molar volume, viscosity, conductance anisotropy, osmotic properties), can be of value in the clarification of the structures of systems containing association colloids.

## References

1. *Andersen, D. E.* and *Carpenter, G. B.* J. Am. Chem. Soc. **75** (1953) 850.
2. *Brady, C. W.*, J. Chem. Phys. **19** (1951) 1547.
3. *Corrin, M. L.*, J. Chem. Phys. **16** (1948) 844.
4. *Danielsson, I.*, Scandinavian Symposium in Surface Activity, Åbo 1962, This volume, p. 108.
5. *Ekwall, P.*, Scandinavian Symposium in Surface Activity, Åbo 1962, This volume, p. 59.
6. *Ekwall, P.*, and *co-workers*, Unpublished results.
7. *Ekwall, P.* and *Fontell, K.*, Acta Chem. Scand. **10** (1956) 327.
8. *Ekwall, P.* and *Fontell, K.*, Acta Chem. Scand. **11** (1957) 568.
9. *Ekwall, P.*, *Fontell, K.* and *Norman, A.*, Acta Chem. Scand. **11** (1957) 190.
10. *Ekwall, P.*, *Fontell, K.* and *Sten, A.*, Second Intern. Congr. Surface Activity, London 1957, Vol. I, p. 357.
11. *Guinier, A.*, Radiocrystallographie, Paris 1945, chapter 12.
12. *Guinier, A.* and *Fournet, G.*, Small Angle scattering of X-rays, New York 1955.
13. *Hosemann, R.*, Ergebn. exakt. Naturwiss. **24** (1951) 142.
14. *Hughes, E. W.*, Nature **165** (1950) 1017.
15. *Husson, F.*, *Mustacchi, H.* and *Luzzati, V.*, Acta Cryst. **13** (1960) 668.
16. *Kratky, O.*, Österreichische Chemiker-Zeitung **54** (1955) 193.
17. *Luzzati, V.*, *Mustacchi, H.* and *Skoulios, A.*, Nature **180** (1957) 600.
18. *Luzzati, V.*, *Mustacchi, H.* and *Skoulios, A.*, Discussions Faraday Soc. **25** (1958) 43.
19. *Luzzati, V.*, *Mustacchi, H.*, *Skoulios, A.* and *Husson, F.*, Acta Cryst. **13** (1960) 660.
20. *Mandell, L.*, Scandinavian Symposium in Surface Activity, Åbo 1962, This volume, p. 49.
21. *McBain, J. W.* and *Hoffman, O. A.*, J. Phys. & Colloid Chem. **53** (1949) 39.
22. *McBain-Laing, M. E.* and *Hutschinson, E.*, Solubilization and Related Phenomena, New York 1955, chapter 5.

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# Conductance Anisotropy in Solutions of Association Colloids

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Despite the associated difficulties of interpretation, it is primarily studies of the scattering of X-rays and light that have provided information about the sizes of micelles during the past two decades [1]. Our views on these problems are largely based on comparisons between crystalline systems and micellar solutions. Attempts have been made to obtain information on the dimensions of the micelles by means of viscosity measurements, but the situation is complicated by the fact that association colloid solutions are not always Newtonian liquids [2,3]. That orientation occurs in flowing association colloid solutions has been long known. Some of the first work on the diffraction of X-rays was done on flowing systems and in the forties the optical anisotropy of flowing solutions of a number of association colloids was studied [4,5]. A few years ago Heckmann and co-workers developed a method for the measurement of the anisotropy in the conductance of flowing solutions and derived a procedure for the approximate calculation of the dimensions of micelles from these measurements [6,7,8,9,10]. The conductance anisotropy is due to the fact that an anisodimensional particle moves at different speeds in different directions relative to an imposed electric field. A sphere migrates at the same rate in all directions, but a disc moves at the lowest rate in the direction perpendicular to the surface, whereas a rod moves at the highest rate in the direction of its axis. The conductance anisotropy can be qualitatively demonstrated by measuring the conductance of a solution when it is resting and when it is flowing through a tube.

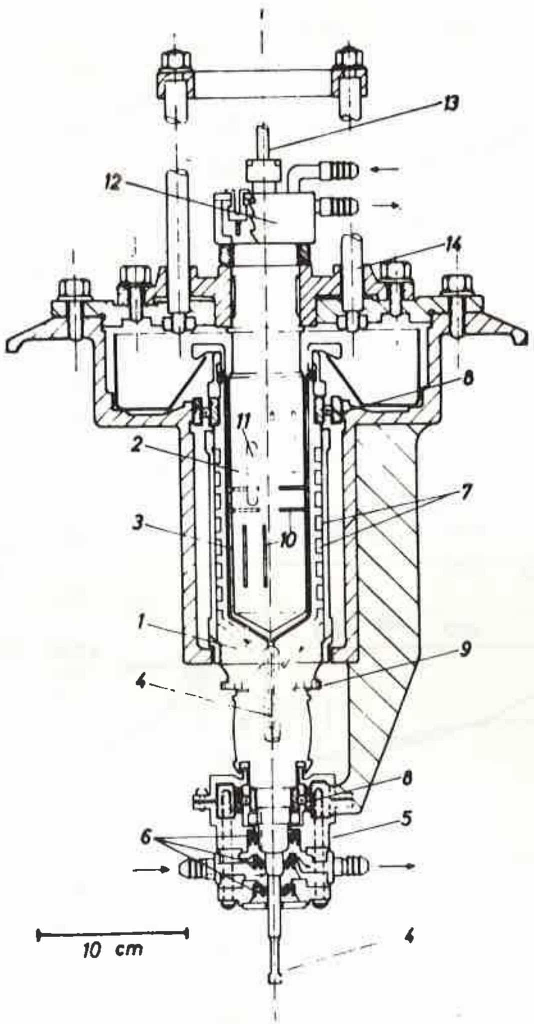

*Fig. 1.* Couette apparatus for measuring of conductance anisotropy. 1. Rotor. 2. Stator. 3. Measuring gap. 10. Electrodes.

The measurements can be made quantitatively with a Couette apparatus which consists of two concentric cylinders (Fig. 1)[10]. In Heckmann's apparatus the outer cylinder rotates at a variable speed. An electrode system on the surface of the stator makes it possible to measure the conductance of the solution between the cylinders in different directions. If platelike charged particles are present in the solution, these will orient themselve parallel with the flow direction (y) and the conductance will increase

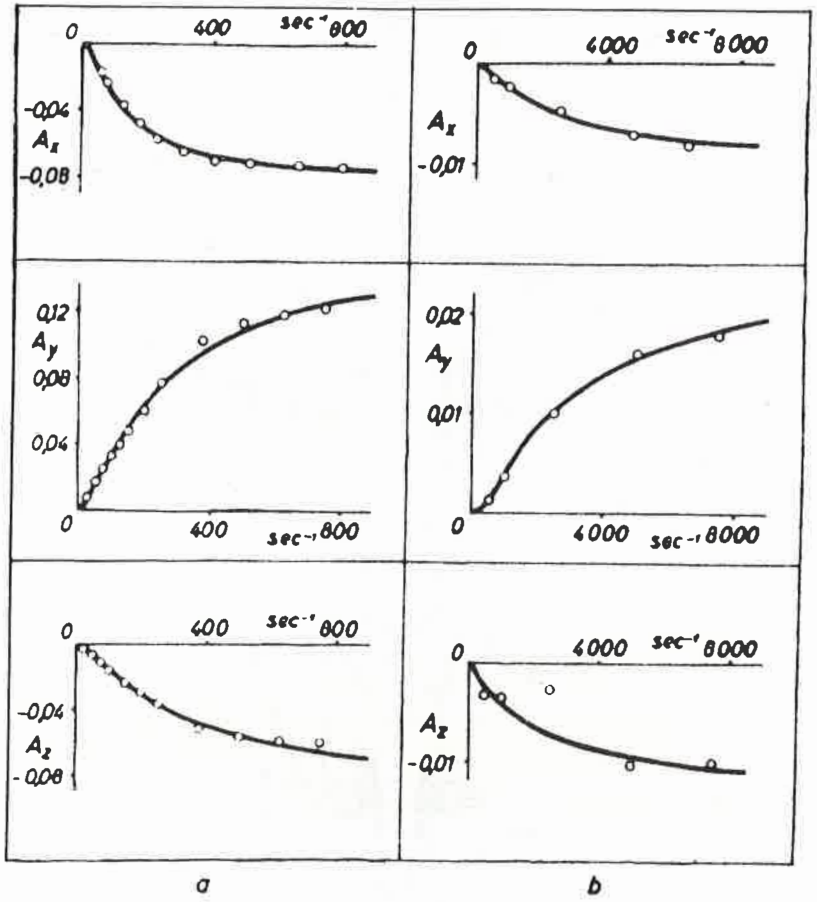

*Fig. 2.* The change in conductance $\Delta \varkappa_i$ as a function of the gradient of flow (sec$^{-1}$) and of direction (i = x, y, z). a) Aqueous solutions of sodium thymonucleinat. (0.5 %, 20°C). b) Aqueous solutions of graphitic acid (0.3 %, 25°C). The curves skow the characteristic effect of anisotropy in the case of a) rods and b) platelets.

both in the latter direction and in the direction of the axis of rotation (z), but decrease in the radial direction (x). Rodlike particles will orient themselves in the direction of flow (y), and the conductance will increase in this direction and decrease in both the axial (z) and radial directions (x). Thus we see that the change in conductance in the direction of the axis of rotation gives information about the shape of the particles; an increase in conductance implies that the particles are plates and a decrease in conductance that the particles are rod-shaped. The validity of these conclusions is shown by the curves in Fig. 2 based on

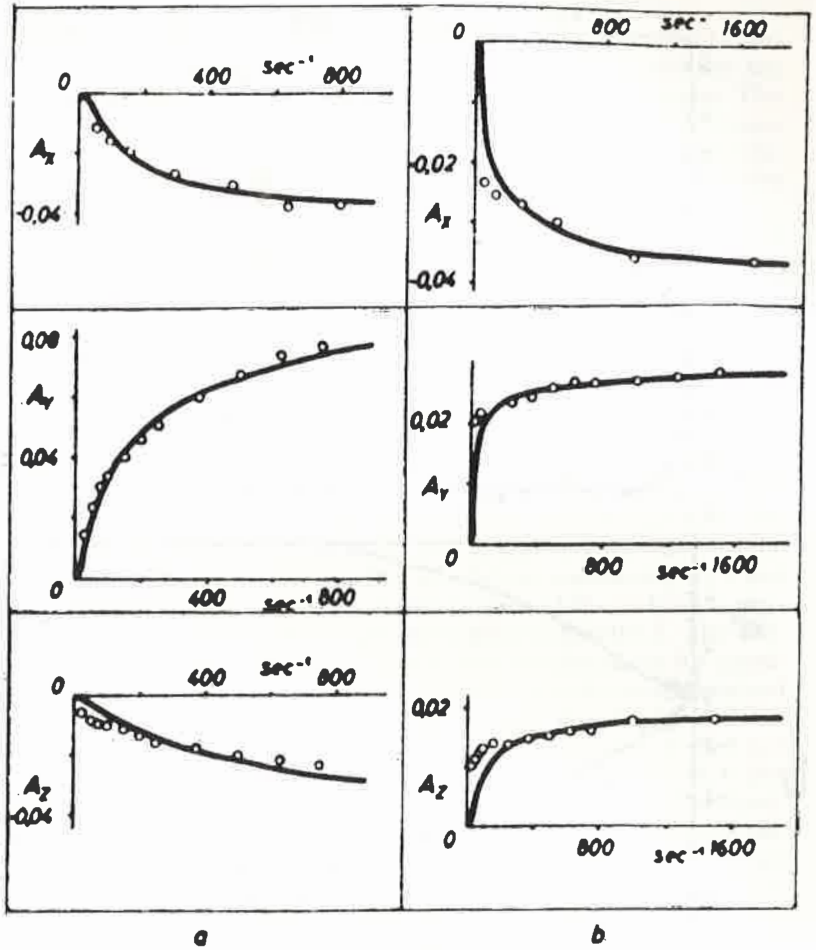

*Fig. 3.* The change in conductance $\Delta \varkappa_i$ as a function of the gradient of flow (sec$^{-1}$) and of direction (i = x, y, z). a) Cetyltrimethylammoniumbromid (19 %, 26°C). b) Sodium dihexylsulphosuccinat (32 %, 30°C). In both cases are the shape of the micelles rodlike.

data for (a) sodium thymonucleinate (rod-shaped particles) and (b) graphitic acid (plates) [10].

By following the procedure of Schwartz, Götz and Heckmann it is possible to calculate the rotary diffusion coefficient from the changes in conductance in different directions relative to the flow of the solution [7,10, 11]. It is then to draw conclusions about the dimensions of the particles possible from the value of the coefficient.

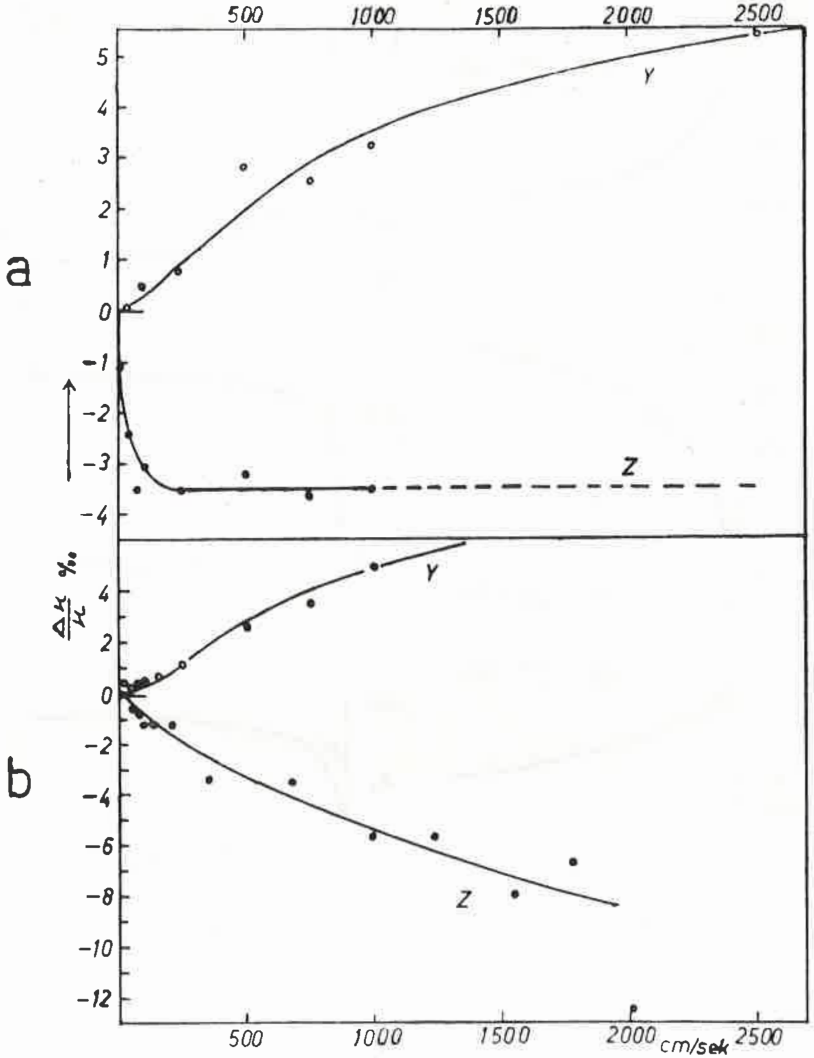

*Fig. 4.* The change in conductance $\Delta\,\varkappa_i$ as a function of the gradient of flow (sec$^{-1}$) and of direction (i = y, z). a) Aqueous solutions of sodium caprylate (40.2 %, 20°C). b) An aqueous solution containing 34.8 % sodium caprylate, and 10,8 % n-decanol (20°C): In both cases are the shape of the micelles rodlike.

With this method Heckmann and Götz found that the particles in sodium oleate, cetyltrimethylammonium bromide, and sodium dihexylsulphosuccinate solutions are rod-shaped. Data for cetyltrimethylammonium bromide solutions and sodium dihexylsulphosuccinate solutions are plotted in Fig. 3. A marked decrease in the conductance in the direction of the axis of rotation is evident [8,10]. The deduced apparent lengths of the micelles are in this case of the order of several thousands of angstroms. The dimensions are designated apparent because interactions between the charged micelles are not taken into account in the calculations. The calculated lengths of the micelles are larger than the actual lengths.

Systems containing sodium caprylate have been extensively studied at the Institute of Physical Chemistry at the Åbo Akademi. The papers read at this symposium have already revealed that these studies have led to the conclusion that the micelles in concentrated aqueous caprylate solutions are anisodimensional, probably cylindrical in form [12,13,14]. I had the opportunity of studying the forms of micelles in sodium caprylate solutions with the apparatus constructed by Heckmann and Götz at the Max Planck Institute in Göttingen. No conductance anisotropy was exhibited by solutions containing up to 35 per cent sodium caprylate, but a marked decrease in the conductance in the direction of the axis of rotation and a marked increase in the direction of flow was observed in a solution containing 40.2 per cent sodium caprylate. The apparent lengths of the sodium caprylate micelles were found to vary from 5000 to 30 000 Å. The full-drawn lines in Fig. 4 show the variation in conductance for micelles that are 30 000 angstroms long. Similar results were obtained for sodium caprylate solutions that contained solubilized decanol. The data in Fig. 4 relate to a system composed of 34.8 per cent sodium caprylate, 10.8 per cent decanol and 54.4 per cent water. Also in this system the micelles are rod-shaped. The apparent micelle lengths vary from 6000 to 12 000 angstroms.

The sodium caprylate solutions that exhibited conductance anisotropy were homogeneous, but the concentrations were close to saturation. Pure sodium caprylate solutions containing 40.5 per cent of the colloid are in equilibrium with mesomorphous soap at 20°C.

The measurement of the conductance anisotropy in concentrated soap solutions for the evaluation of the micellar dimensions is limited in the first place by the fact that the theory does not take into account the interaction between the charged aggregates. Furthermore, it is not known how the order of the highly conducting liquid between the particles arising from the orientation of the latter influences the changes in the conductance. Also the surface conductance along the highly charged oriented micelle surfaces is difficult to estimate. In the case of the highly concentrated sodium caprylate solutions, it is certainly impossible to avoid this phenomenon, but the phenomenon is less important in connection with the more dilute systems studied by Heckmann and Götz [7,8,9,10].

The application of measurements of conductance anisotropy to dilute soap solutions is limited primarily by the axis ratios of the particles, but also by the low surface tensions of these solutions, which make it impossible to use high flow rates in the Couette apparatus. It is probably difficult to detect conductance anisotropy in soap solutions where the apparent lengths of the micelles are less than 2000 angstroms.

## References

1. *Laing-McBain, E.* and *Hutchinson, E.*, Solubilization and related Phenomena. Academic Press 1955.
2. *Philippoff, W. J.*, Colloid Sci. **5** (1950) 169.
3. *Philippoff, W. J.*, Kolloid Z. **96** (1941) 255.
4. *Hess, K.* and *Gundermann, J.*, Berichte **70** (1937) 1800.
5. *Snellmann, O.*, Arkiv Kemi, mineralogi, geologi **19 B** (1944) 1.
6. *Heckmann, K.*, Naturwiss. **40** (1953) 478.
7. *Heckmann, K.* and *Götz, K. G.*, Z. Electrochem. **62** (1958) 281.
8. *Götz, K. G.* and *Heckmann, K. J.*, Colloid Sci. **13** (1958) 266.
9. *Götz, K. G.* and *Heckmann, K.*, Z. Phys. Chem. N.F. **20** (1959) 42.
10. *Götz, K. G.*, Dissertation 1961 Göttingen.
11. *Schwarz, G.* Z. Physik **145** (1956) 563.
12. *Ekwall, P.*, *Danielsson, I.*, *Fontell, K* and *Mandell, L* Finska Kemistsamfundets Medd. **70** (1961) 51.
13. *Ekwall, P.*, Scandinavian Symposium in Surface Activity, Åbo, 1962. This volume, p. 59.
14. *Fontell, K.*, Scandinavian Symposium in Surface Activity, Åbo, 1962. This volume, p. 99.

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Helsingfors 1963, Frenckellska Tryckeri Aktiebolaget