

The Properties and Structures of Aqueous Sodium Caprylate Solutions

I. The Densities and Partial Specific Volumes

PER EKWALL, HENRIK EIKREM and LEO MANDELL

Institute of Physical Chemistry, Åbo Akademi, Åbo, Finland

The densities of homogeneous sodium caprylate solutions have been determined at 20°C. In the concentration ranges from 0 to 6 %, from 8 to 16 %, and from 34 to 40.5%, the variation of the density (d) with concentration (x) can be expressed by formulae of the type

$$d = d_0 + k_1x + k_2x^{3/2}$$

The value of the constant k_2 is, however, in all cases so small that the last term in the equation can be disregarded and the plot is practically linear in each of the above concentration ranges. In the intermediate concentration ranges the density curve bends toward the concentration axis. The partial specific volumes of water and caprylate change abruptly in the concentration ranges 6–8 % (0.38–0.52 M), 16–19 % (1.15–1.41 M) and 29–34 % (2.4–3.1 M). The first abrupt change takes place at the CMC where micelle formation begins. The partial specific volume is constant within the small micelle range which extends from the CMC to a well-defined narrow concentration range where the partial specific volume again changes abruptly (2nd CMC). In the following, extended concentration range the partial specific volume increases which implies that the properties of the micellar substance change continuously. After the third abrupt change (3rd CMC) the partial specific volume again remains constant with increasing concentration.

We believed that interesting information could be obtained by studying, using different methods, the properties of aqueous solutions of one and the same association colloid over the whole concentration range from zero up to the concentration where the system becomes heterogeneous as a result of the separation of mesomorphous middle soap. Such a series of studies, which would reveal how the properties of the colloid solutions vary with concentration in different ranges, would, it seemed to us, clarify yet unknown aspects of the internal structures of the solutions below and above the critical micelle concentration and provide a clearer picture of the whole association process than

has been attained hitherto. We were particularly interested in collecting new experimental data which would reveal whether changes in structure other than those accompanying micelle formation at the critical concentration take place at other concentrations and whether these are so pronounced that it is permissible to speak of other concentration limits besides the critical concentration.

The association colloid whose behaviour we chose to study was sodium caprylate and the temperature where the experiments were carried out was 20°C. We are at that temperature above the Krafft point of sodium caprylate and the solutions are homogeneous and isotropic up to the concentration of 40.5 %, where middle soap begins to separate.

The various methods we have employed in our studies of the solutions comprised measurements of density, viscosity, vapour pressure, conductance, diffraction of X-rays, protolytic equilibria and the ability of the colloid to solubilise hydrocarbons and amphiphilic compounds.

In this paper, which is the first of a series, we report the results of the density measurements.

MATERIAL AND METHODS

Sodium caprylate was prepared by neutralising caprylic acid (Eastman grade) in absolute ethanol with the equivalent amount of sodium ethylate. The sodium caprylate that precipitated was isolated by filtration and dried. The equivalent weight of the salt was found to be 166.2 ± 0.3 .

The solutions were prepared by weighing sodium caprylate and twice-distilled, air-free water ($\kappa = 0.6 \times 10^{-6} \text{ ohm}^{-1}$) directly into glass ampoules. The sodium caprylate was brought into solution by heating the sealed ampoules in a water bath. The ampoules were then cooled to 20°C, and subjected to centrifugation. After the centrifugation, the ampoules were kept in a thermostat at 20°C for at least 24 h. The densities of most of the solutions were measured using Ostwald-Sprengel pyknometers with capacities of 7–8 ml. These measurements were performed with the greatest care at a temperature of $20^\circ \pm 0.02^\circ$. The weighings took place in a room with a constant temperature of 20°C. The usual corrections for air buoyancy were applied. As a rule, two or three independent determinations were carried out on each solution. The reproducibility of the measured density values was somewhat poorer for the more concentrated than for the more dilute solutions: the standard deviations were 1.1×10^{-5} for the 0–15 % caprylate solutions, 1.8×10^{-5} for the 15–30 % solutions, and 2.6×10^{-5} for the 30–40 % solutions. The densities of some preparations of mesomorphous middle soap were also determined in this investigation. The latter measurements were performed using a pyknometer of the bottle type and in these cases the standard deviation was 2.6×10^{-4} .

THE DENSITIES OF THE SOLUTIONS

The densities of the sodium caprylate solutions are collected in Table 1, which includes also the value of the density of the mesomorphous middle soap in equilibrium with the isotropic solution.

The slopes of the plots of density against concentration for aqueous solutions of inorganic electrolytes increase slightly as a rule with increasing concentration¹. To judge from data reported in the literature, the same applies also to solutions of the alkali metal salts of the lower fatty acids (to, for example, 0–60 % potassium acetate solutions, 0–38 % potassium propionate

Table 1. The densities of sodium caprylate solutions at 20°C.

Caprylate content %	Density d_4^{20}	Caprylate content %	Density d_4^{20}
Isotropic solutions			
0			1.03273
1.006	0.998234	21.114	1.03330
1.968	1.00030	21.500	1.03404
2.991	1.00232	22.911	1.03604
4.023	1.00435	22.940	1.03595
5.166	1.00650	23.720	1.03722
6.000	1.00887	24.159	1.03762
6.770	1.01057	25.412	1.03941
7.732	1.01191	26.154	1.04021
8.928	1.01351	26.784	1.04123
10.000	1.01539	27.649	1.04245
11.008	1.01709	28.230	1.04320
12.001	1.01854	29.400	1.04459
12.064	1.02003	30.002	1.04538
13.103	1.02005	31.104	1.04678
13.481	1.02171	31.433	1.04724
13.560	1.02223	32.121	1.04794
14.000	1.02261	32.819	1.04891
14.981	1.02308	33.883	1.05027
15.801	1.02458	34.426	1.05088
16.562	1.02592	36.301	1.05291
17.610	1.02681	36.539	1.05322
18.376	1.02848	37.838	1.05481
18.823	1.02945	38.231	1.05512
19.383	1.03032	39.649	1.05688
20.493	1.03098	39.851	1.05695

Mesomorphous middle soap.

46.00 $1.06342 \pm 6 \times 10^{-5}$

solutions, 0–10 % sodium butyrate solutions and 0–12 % sodium isovalerate solutions)². In contrast to this, the data of Davies and Bury show that the densities of potassium caprylate solutions rise less rapidly with concentration at high than at low concentrations³. We have found this to be true also in the case of sodium caprylate solutions; the resulting plot of density against concentration, which is not reproduced here, is hence concave toward the concentration axis for this salt. The slope of the plot furthermore differs greatly in different concentration ranges; a slight curvature or linearity in certain concentration ranges alternates with a marked curvature in other ranges. A statistical evaluation of the numerical data confirmed this.

The variation of the density with concentration in the sodium caprylate concentration range from 0 to 6 % (concentration range 1) can be expressed, as Root *et al.* have shown for a number of common electrolytes, by the equation

$$d = d_0 + k_1 x + k_2 x^{3/2}$$

where d and d_0 are the densities of the solution and water, respectively, x is the concentration in parts per hundred by weight (or the molarity), and k_1 and k_2 are constants⁴. Our measurements give (for x in %)

$$d = 0.998239 + 2.05018 \times 10^{-3} x + 2.24 \times 10^{-6} x^{3/2}$$

The value of the constant k_2 derived from our data is so low (2×10^{-6}) that the plot in the range in question is satisfactorily expressed by a straight line

$$d = a + bx$$

where a ($=d_0$) has the value 0.998235 and the constant b the value 0.0020559 ± 0.0000071 (95 % confidence limits). The sums of the squares of the deviations of the values from the plots of the two equations are practically equal ($\Sigma(\Delta d)^2 = 25.84 \times 10^{-10}$ and 26.29×10^{-10}). The experimental values deviate significantly from the straight line when the concentration exceeds 6 %. Above this latter concentration to a concentration of 8 % the points can be fitted by the second-order equation

$$d = a + bx - cx^2$$

where a , b and c are constants. From the concentration of 8 % and upwards to 16 % the values can, however, again be expressed by an equation of the

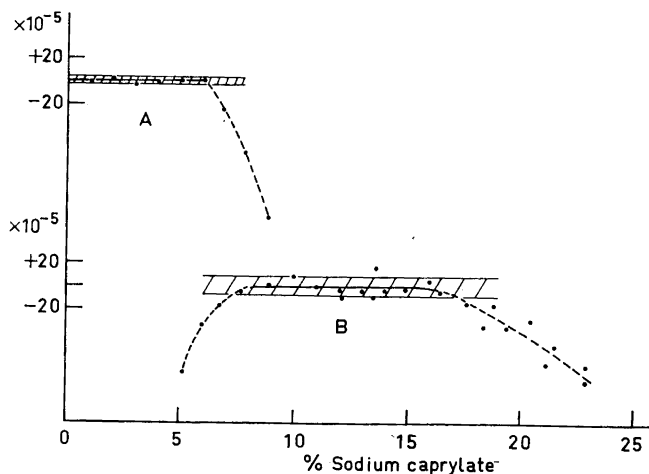


Fig. 1. Experimental and calculated densities in the ranges 1 and 2. The value of the density computed from the equation $d = a + bx$, where d is the density, x the concentration in weight per cent, and a and b are constants, are given by the full-drawn horizontal line. The experimental density values are marked by points. The units on the y axis are the deviations of d from the horizontal line. In the region where the experimental values deviate clearly from the calculated plot, a broken curve passes through the experimental values. The 95 % confidence limits are indicated by the shaded area.

A. Concentration range 1. The values of the density were calculated from the equation $d = 0.998235 + 2.0559 \times 10^{-3} x$. The deviations are significant at concentrations exceeding 6 %.

B. Concentration range 2. The values of the density calculated from the equation $d = 1.001733 + 1.527 \times 10^{-3} x$. The deviations are significant at concentrations below 8 % and above 19 %.

type proposed by Root *et al.*, but as the value of the constant k_2 is of the order of 10^{-8} , they can equally well be expressed by a straight line $d = a + bx$, where $a = 1.001733$, $b = 0.001527 \pm 0.000006$ (95 % C.L.) ($\Sigma(\Delta d)^2 = 641.0 \times 10^{-10}$ and 647.0×10^{-10}). Deviations from the latter plot are shown by the experimental values for concentrations exceeding 16 %, where the curve again slopes downwards; above 18–19 % the deviations are significant. The results of the statistical analysis of the data are shown in Figs. 1 A and 1 B.

Owing to the greater scatter of the experimental values for concentrations exceeding 17 %, it was more difficult to determine the dependence of the density on concentration in this range. The curve for the most part has a downward curvature. Overlooking some interesting details, the values of the density for concentrations from 17 to 40 % could be roughly expressed by the second order equation $d = 0.9998 + 1.7719 \times 10^{-3} x - 8.47 \times 10^{-6} x^2$. However, the curvature is definitely smaller in the concentration range from about 19 to 28 % where the data could be expressed better by the same equation with the constants $a = 1.0032$, $b = 1.4917 \times 10^{-3}$ and $c = 2.63 \times 10^{-6}$. Furthermore, the curve exhibits a definitely larger curvature in the range from about 29 to 34 %, whereas in the range from 34 to 40 % the curve again conforms to an equation of the Root type (with k_2 = about 10^{-6}) or to the linear equation $d = a + bx$, where $a = 1.0118$, $b = 1.1365 \times 10^{-3} \pm 0.024 \times 10^{-3}$ (95 % C.L.) (Figs. 2 A and 2 B).

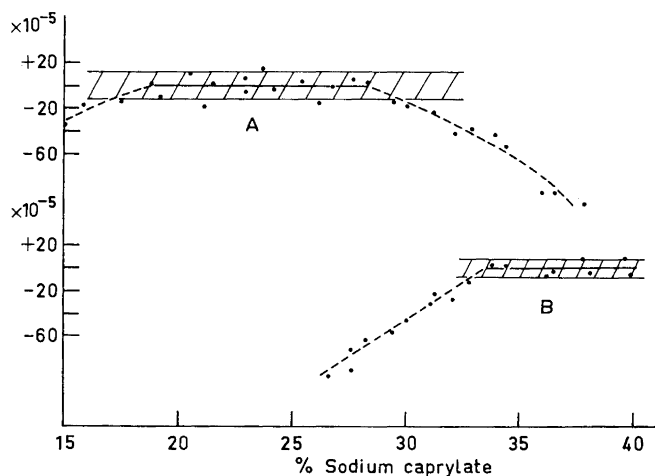


Fig. 2. Experimental and calculated densities in the ranges 3 and 4. The density values computed from equations of the form $d = a + bx - cx^2$ (range 3) and $d = a + bx$ (range 4) lie on the full-drawn horizontal lines. The experimental density values are marked by points. The units on the y axis are the deviations of d from the horizontal line. In the range where the latter deviations from the calculated plot are significant, a broken curve passes through the experimental points. The 95 % confidence limits are indicated by the shaded area.

A. Concentration range 3. The density values were computed from the equation $d = 1.00317 + 1.4917 \times 10^{-3} x - 2.63 \times 10^{-6} x^2$. The deviations are significant at concentrations below 17 % and above 31 %.

B. Concentration range 4. The density values were computed from the equation $d = 1.01179 + 1.1365 \times 10^{-3} x$. The deviations are significant at concentrations below 33 %.

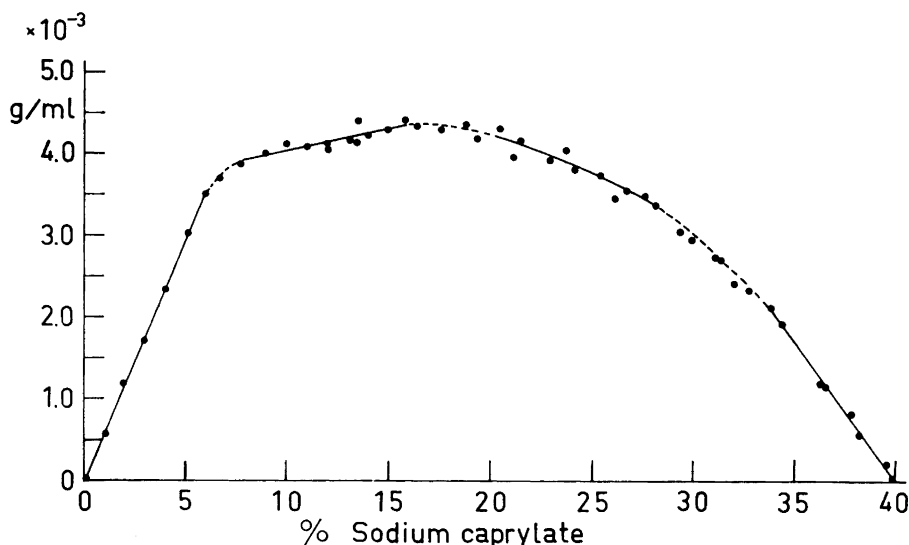


Fig. 3. The location of the various concentration ranges. The x axis gives the concentration in weight per cent. The y axis gives the excess of the density over the straight line drawn through the densities of the 0 % and 40 % solutions.

$$y = d_{\text{sol}} - [d_0 + x(d_{40} - d_0)/40]$$

The experimental values are marked by dots. The full-drawn curve sections within different concentration ranges plot the equations derived for these ranges (see text and Figs. 1 and 2).

The results thus show that the plot of density against concentration for sodium caprylate solutions is linear or slopes slightly upwards in the concentration ranges 0–6 %, 8–16 % and 34–40 % and slopes slightly downwards in the range 19–28 %. Between these ranges, *i.e.* in the ranges 6–8 %, 17–19 % and 29–34 %, the plot is pronouncedly concave toward the concentration axis.

In three different concentration ranges (1, 2 and 4), the density thus varies with concentration in a similar manner for sodium caprylate solutions as for common electrolytes. That this is the case for the dilute caprylate solutions below the critical concentration is quite natural, because caprylate behaves here also in other respects like a typical electrolyte. A closer examination reveals that the variation with concentration in range 1 is approximately that which would be expected for a fatty acid salt with eight carbon atoms. It is, however, interesting to find that the concentration dependence of the density is similar (in accordance with the Root equation or the simpler linear equation) also above the CMC in the concentration range 2 where the added caprylate forms micelles, even though the density here increases less rapidly than in the range 1. A further point of interest is that in the range 4 the increase in density with increasing content of micellar matter is similar

Table 2. Partial specific volumes of water and sodium caprylate.

Concentration weight per cent	Moles/ 1000 g H ₂ O	Partial specific volume Water ml/g	Sodium caprylate ml/g
0	0	1.0018	0.798
1.0	0.067	1.0018	0.798
2.0	0.123	1.0018	0.798
3.0	0.186	1.0018	0.798
4.0	0.251	1.0018	0.798
5.0	0.317	1.0018	0.798
6.0	0.384	1.0018	0.798
6.5	0.418	1.0011	0.818
7.0	0.453	0.9991	0.843
7.5	0.489	0.9978	0.848
8.0	0.523	0.9980	0.851
9.0	0.595	0.9980	0.851
10.0	0.669	0.9980	0.851
11.0	0.744	0.9980	0.851
12.0	0.820	0.9980	0.851
13.0	0.899	0.9980	0.851
14.0	0.979	0.9980	0.851
15.0	1.062	0.9980	0.851
16.0	1.145	0.9978	0.851
17.0	1.232	0.9972	0.855
18.0	1.320	0.9965	0.860
19.0	1.410	0.9957	0.862
20.0	1.504	0.9953	0.864
21.0	1.599	0.9951	0.865
22.0	1.696	0.9947	0.866
23.0	1.796	0.9946	0.867
24.0	1.900	0.9944	0.867
25.0	2.005	0.9941	0.868
26.0	2.111	0.9939	0.869
27.0	2.225	0.9938	0.869
28.0	2.340	0.9935	0.870
29.0	2.457	0.9931	0.870
30.0	2.578	0.9925	0.872
31.0	2.703	0.9920	0.874
32.0	2.831	0.9916	0.875
33.0	2.963	0.9901	0.878
33.5	3.031	0.9883	0.880
34.0	3.099	0.9868	0.885
35.0	3.240	0.9868	0.885
36.0	3.384	0.9868	0.885
37.0	3.533	0.9868	0.885
38.0	3.689	0.9868	0.885
39.0	3.847	0.9868	0.885
40.0	4.011	0.9868	0.885
40.5—46.0	4.1—5.1	0.986	0.886

as in the ranges 1 and 2, after having deviated from the latter type in a wide intermediate concentration range between 17 and 34 %.

The relationships between the densities in these different concentration ranges are illustrated in Fig. 3, where the ordinate gives not the density itself,

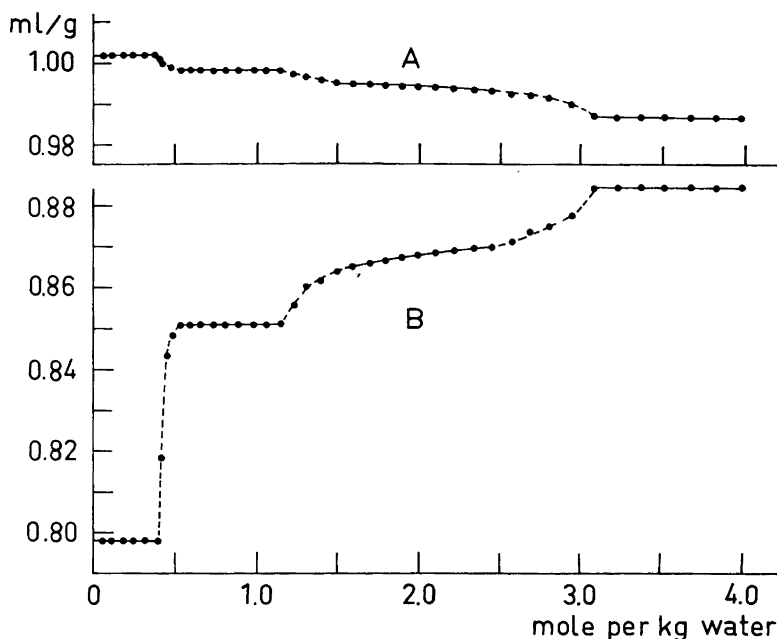


Fig. 4. Partial specific volumes of water and sodium caprylate at different caprylate concentrations (in moles per 1000 g of water). The values given in Table 2 are marked by dots. The full-drawn lines plot the equations given in the text and in Figs. 1 and 2.

but the excess of the density over the values given by the straight line drawn through the points for pure water and the 40 % sodium caprylate solution. The experimental values are marked with dots and the full-drawn curves plot the equations fitted to the values in the different concentration ranges.

THE PARTIAL SPECIFIC VOLUMES

We have calculated the partial specific volumes of sodium caprylate from the experimental density values by the method of intercepts. The partial specific volumes at regularly spaced points (intervals of 0.5 and 1 %) are shown in Table 2. Figs. 4 A and 4 B show the variation of the partial specific volumes with concentration (in molality). The values given in Table 2 are marked in the figures with dots; the fully drawn lines plot the equations given above.

It is natural that the changes in slope of the density curve should be apparent in the partial volume-concentration curves. The partial specific volume of water diminishes with increasing caprylate concentration. Fig. 4 A shows that the decrease is pronounced in the three concentration ranges 0.38–0.52 M, (6–8 %), 1.15–1.41 M (16–19 %), and 2.4–3.1 M (29–34 %). It is seen from Fig. 4 B that the partial specific volume of sodium caprylate increases with increasing caprylate concentration. After remaining at a practically constant value in the low concentration range, it increases very rapidly

between the concentrations 0.38 M and 0.52 M, then remains practically constant again over a wide concentration range, and rises rapidly in the range between about 1.15 M and 1.41 M. Above the latter concentration the specific volume increases less rapidly in the beginning but then more rapidly in the concentration range between about 2.4 M to 3.1 M. At the highest concentrations the partial specific volume again tends to assume a constant value. A value that differs only slightly from the latter value is obtained for the mesomorphic phase containing 46 % (5.12 M) sodium caprylate. This concentration is the upper limit of the two-phase range between 40.5 % and 46 % (*ca.* 4.1–5.1 M) caprylate where the mesomorphic middle soap is in equilibrium with the isotropic solution.

In his classical study Bury determined the partial specific volume of potassium caprylate at 25°C up to a caprylate concentration of 2.2 moles per 1000 g of water³. A comparison of his and our data in this range reveals a good agreement. The exceptionally marked change in partial volume of caprylate at the critical concentration (at about 0.47 M according to Bury and at 0.38 M in our experiments) is clearly seen in both series of measurements. A slight indication of a horizontal course of the curve that we have noted between 0.6 and 1.1 M can be seen also in Bury's curve. The few values of the partial volume measured by Bury in the concentration range above 1 M are compatible with our observation that the partial volume increases above this concentration.

The occurrence of pronounced steps in the curve plotting partial volume against concentration in addition to that at the critical concentration (0.38 M) implies that fairly marked changes occur in the structures of the solutions at definite concentrations above the CMC. The jump in the curve at 1.15–1.4 M is smaller than at the CMC, but it is nevertheless so marked that it seems necessary, also in this case, to speak about a concentration limit above which the structure of the solution changes. This view is supported by the observation that also many other properties of both pure caprylate solutions and caprylate solutions containing solubilised compounds undergo change in the same concentration range (1.15–1.41 M) where the rapid increase in the partial volume of caprylate is observed (these observations will be described in later publications of this series). The stepwise change in the partial volume curve between 2.4 and 3.2 M is less pronounced, but may also be taken to imply a change in solution structure. It may be appropriate to speak about a concentration limit in this case too. For brevity, these concentration limits may be called the second and third critical concentrations (2nd CMC, 3rd CMC).

The marked increase in the partial volume of sodium caprylate at the CMC is known to be a consequence of the aggregation of simple ions to micelles and has been considered to be primarily due to the greater space taken up by the caprylate ions when they are incorporated in micelles than when they are free in the solution. After the narrow transition range at the CMC is passed, however, the partial volume of caprylate remains constant over a wide concentration range from 0.5 to 1.1 M (range 2). This implies that the properties of the micellar substance remain constant and hence that the micelle structure, and evidently also the micelle size, does not change. The range in question is the so-called small micelle range in which, as has been found

for other association colloids, the properties of the micelles are constant. Our studies show that this range has a well-defined upper limit at the caprylate concentration of about 1.2 M, the 2nd CMC.

It seems natural to assume that the cause of the increase in the partial volume observed at the 2nd CMC is similar to that responsible for the increase at the CMC. This means that here again the process is a change in the aggregation, either a change in the type of aggregation or an increase in the size of the micelles as a result of an increase in the aggregation number or the number of bound counter ions or water molecules, or a combination of these processes. A noteworthy observation is that the partial volume of caprylate increases continuously from the 2nd CMC up to a concentration of about 2.4 M, although this increase gradually slows down with increasing caprylate concentration. We consider this to indicate that the factors which begin to exert their effect at the 2nd CMC alter the properties of the micellar substance and the structure and size of the micelles over the whole range in question. A marked difference hence exists in the behaviour in this range (the range 3) and in the range where the small micelles with constant properties occur (the range 2). Constant conditions are not attained at these higher concentrations until a new rather rapid change in the properties of the micellar substance has taken place. Also this latter change that takes place in the concentration range 2.4–3.1 M, the 3rd CMC, is probably connected with a variation in the size and structure of the micelles. It is worth noting that above the 3rd CMC the partial volume of the caprylate tends to remain constant, thus indicating that micelles with constant properties are formed.

Of considerable interest is finally the observation that the partial volume of the caprylate in the mesomorphous middle soap in equilibrium with isotropic solutions is approximately equal to the partial volume of the micellar caprylate in the most concentrated homogeneous solutions. This shows that the type of aggregation is the same for the micelles in the most concentrated solutions as for the caprylate units in the mesomorphous phase, that is to say, the micelles pass practically unchanged from the saturated, isotropic caprylate solutions to the mesomorphous phase.

THE SECOND CRITICAL CONCENTRATION

Although the opinion is prevalent that there is no other concentration limit than the CMC in association colloid solutions, there is a small number of investigators who claim to have observed a second "critical concentration" where the structure of the micellar association colloid solutions undergoes a change. McBain already took the observed variation of the equivalent conductance and the osmotic activity to be a sign of a change in structure at high colloid concentrations⁵. The first indication that there exists a more or less well defined concentration limit above which a change in properties reflects a change in structure was noted in connection with X-ray diffraction measurements on association colloid solutions (Hess and co-workers: the roentgenographic micelle formation concentration⁶; Stauff: the 2nd CMC⁷). The conclusiveness of these observations was, however, rendered doubtful when Harkins discovered

the so-called M band and found that this prevails down to the (first) CMC⁸ and when the manner of calculations of micellar structure based upon small-angle X-ray diffraction measurements were criticized from the theoretical point of view. At this time, however, other experimental evidence was presented that supported the existence of a 2nd critical concentration. One of us found that the ability of the micellar substance to solubilise hydrocarbons undergoes a change at a certain colloid concentration and that this concentration is in the range where the equivalent conductance passes through a minimum and where the roentgenographic micelle formation concentration was stated to lie⁹. In the fifties the results of the solubilisation studies received support from several new investigations¹⁰⁻²², at the same time as a systematic review of earlier published X-ray data and new roentgen diffraction measurements²³ seemed to reveal that the X-ray diffraction maximum that formerly was called the I band was observed down to a concentration close to that where the solubilising power of the micellar substance changed and the equivalent conductance was a minimum. Later it was found that the 2nd CMC occurs as a well-defined concentration limit in certain three-component systems comprising water, an association colloid and a amphiphilic substance of the paraffin-chain alcohol or fatty acid type from which systems a mesomorphous phase separates; the concentration limit is here observed as a limit below and above which the solutions are in equilibrium with different types of mesomorphous substances²⁴⁻²⁶. Also the viscosity variation of the solutions studied by Tyuzyo²⁷⁻²⁹ points to the existence of a 2nd CMC, and it can be concluded from the vapour pressure measurements of Robinson and coworkers³⁰ that also the osmotic activity changes at this concentration. In this connection it may be noted that Heckmann and co-workers have recently discovered a conductivity anisotropy in concentrated association colloid solutions, but that this phenomenon seems not to have been observed down to the 2nd CMC³¹⁻³⁴.

Further evidence for the existence of a 2nd critical concentration is provided by the data presented here on the variation of the density and partial specific volumes at high concentrations. Alongside the solubilisation phenomena, these new results seem to represent weighty evidence that, in addition to the change in structure at the (first) CMC, there occurs a change in structure at a much higher concentration, the 2nd CMC. Whereas the solubilisation observations were made on association colloid solutions in which the micelles contained solubilised matter in addition to the association colloid itself, the results presented here show clearly that also the micelles in pure association colloid solutions undergo a change at a certain concentration. A second critical concentration thus occurs both in solutions that contain association colloid only and in solutions that contain also solubilised compounds.

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