

## The Properties and Structures of Aqueous Sodium Caprylate Solutions

### II. The Viscosities of Sodium Caprylate Solutions at 20°C Measured with Capillary Viscometers

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The viscosities of homogeneous 0–40.5 % (0–2.55  $C^*$ ) sodium caprylate solutions at 20°C have been measured with capillary viscometers. Below the CMC (0.356  $C$ ) of sodium caprylate, the viscosities of the solutions vary like those of solutions of uni-univalent electrolytes. In the concentration range from 0.09 to 0.35  $C$  the dependence of viscosity on concentration is given by the equation  $\eta_{rel} = 1 + A_1\sqrt{C} + A_2C$  where  $A_1 = 0.0050$  and  $A_2 = 0.940$ . Above the CMC the relationship between viscosity and concentration can be expressed by means of the equation  $\log \eta_{rel} = A_3C/(1 - Q'C)$  (originally derived by Vand for suspensions containing spherical particles) when  $A_3 = 0.321$  litre/mole and  $Q' = 0.274$  up to the concentration 1.2  $C$ . The intrinsic viscosity  $[\eta_i]$  of the micelles above the CMC has been determined to 0.83 litre/mole, which gives the value 2.55 for the shape factor  $a_1$ . This shows that the micelles are spherical in form. To judge from the viscosity data, no greater changes from the spherical form occur before the concentration exceeds 1.8  $C$ , but marked changes do occur in the range above this concentration. In the latter range, the viscosity increases with concentration in accordance with the equation  $\log(\eta_{sp m}/C_m) = k_1' + k_2'(C - 1.8)$ , where  $k_1' = 0.74$  and  $k_2' = 0.95$ .

The molar volume of the hydrated sodium caprylate, incorporated in the micelles in the range where the latter are spherical in form, we have found to be  $\bar{V} = 2.303 A_3/2.5 = 0.295$  litre/mole. This corresponds to a hydration number  $h$  of 8.5–8.9 moles of water per mole of caprylate in these micelles with a degree of counterion binding of about 60 %. The maximum number of water molecules bound per mole of caprylate when the counterion binding is 100 % is estimated at about 11.

The viscosity data indicate that the concentration range from 1.0–1.2  $C$  to 1.8–1.9  $C$ , *i.e.* between the 2nd CMC and 3rd CMC, is a transition range between the small micelle range with its spherical micelles and the concentrated solutions where the micelles are cylindrical in form. The increase in viscosity observed in this range may be at least partly ascribed to a greater binding of counterions and an associated increase in hydration and micelle volume.

\*  $C$  denotes the concentration in moles per litre.

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

Caprylate content		Dynamic viscosity cP	Caprylate content		Dynamic viscosity cP	Caprylate content		Dynamic viscosity cP
Weight %	Molarity <i>C</i>		Weight %	Molarity <i>C</i>		Weight %	Molarity <i>C</i>	
0	0	1.002	9.008	0.5503	1.640	21.00	1.305	4.485
0.2503	0.01504	1.0296	9.429	0.5764	1.659	22.09	1.375	4.989
0.3869	0.02325	1.0368	10.02	0.6131	1.720	22.90	1.427	5.544
0.5016	0.03016	1.0407	10.54	0.6455	1.787	22.90	1.427	5.582
0.5455	0.03276	1.0463	11.00	0.6741	1.848	24.13	1.506	6.555
0.7426	0.04467	1.0540	11.48	0.7040	1.899	25.10	1.569	7.402
0.9880	0.05946	1.0682	12.06	0.7502	2.020	26.10	1.634	8.465
1.005	0.06048	1.0683	12.50	0.7678	2.040	26.10	1.634	8.525
1.242	0.07479	1.0769	13.00	0.7990	2.137	26.83	1.685	9.435
1.508	0.09086	1.0865	13.00	0.7990	2.147	28.00	1.757	11.28
1.743	0.1051	1.102	13.55	0.8336	2.216	28.00	1.757	11.31
1.980	0.1194	1.112	13.97	0.8599	2.288	28.92	1.817	12.97
1.986	0.1198	1.118	14.54	0.8957	2.401	30.00	1.886	15.22
2.476	0.1495	1.139	14.90	0.9185	2.482	31.05	1.956	18.33
3.000	0.1813	1.171	14.90	0.9185	2.490	31.98	2.017	21.50
3.468	0.2099	1.200	15.49	0.9556	2.605	32.94	2.080	25.46
4.000	0.2422	1.234	16.07	0.9922	2.742	33.99	2.149	30.58
4.490	0.2722	1.254	16.45	1.016	2.874	35.00	2.215	36.81
4.980	0.3021	1.293	17.00	1.051	2.979	35.79	2.266	40.75
5.475	0.3325	1.321	17.00	1.051	2.982	35.84	2.270	40.81
6.024	0.3662	1.358	17.58	1.088	3.159	36.53	2.315	46.40
6.370	0.3874	1.389	17.92	1.109	3.256	37.01	2.347	50.86
7.020	0.4275	1.448	18.49	1.145	3.457	37.95	2.408	58.68
7.460	0.4547	1.474	19.00	1.178	3.618	37.95	2.408	58.76
7.662	0.4671	1.491	19.00	1.178	3.622	37.95	2.408	58.90
8.270	0.5046	1.549	19.58	1.215	3.833	38.50	2.445	63.88
8.270	0.5046	1.554	19.88	1.234	3.983	39.15	2.488	71.09
8.783	0.5364	1.596	21.00	1.305	4.445	39.60	2.518	75.70
						39.85	2.534	78.56
						40.00	2.543	83.65
						40.08	2.549	83.17
						40.09	2.550	83.19

## EXPERIMENTAL METHODS AND RESULTS

The viscosities of sodium caprylate solutions containing up to 40 % of the soap have been measured at 20°C. The sodium caprylate was prepared as described previously.<sup>1</sup> The equivalent weights of the different preparations were  $166.2 \pm 0.4$ . The water employed in the preparation of the solutions had been twice distilled and had a specific conductance of  $0.6 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>. The solutions were kept in sealed ampoules or glass-stoppered Pyrex flasks in a 20-degree thermostat for at least 24 h before their viscosities were measured.

Capillary viscometers of the Ubbelohde type were employed. The viscometers were carefully cleaned, rinsed with distilled water and alcohol and dried before they were filled and immersed in the thermostat. The solutions were filtered before they were introduced into the viscometers to remove dust etc. After 25 min the solutions were sucked up through the capillary and allowed to flow down once before the actual measurements. At least four flow times were measured with a stop watch to the nearest hundredth of a

second. No time correction due to the retardation of the stop watch was found necessary. The Hagenbach-Couette corrections were applied. The values of the kinematic viscosity in centistokes were obtained by multiplying the corrected flow times by viscometer constants. Density values determined by Ekwall, Eikrem and Mandell<sup>1</sup> were employed to convert the kinematic viscosities to dynamic viscosities.

The reproducibility of the viscosity values of the solutions varied from  $\pm 0.1\%$  at the low to  $\pm 0.15\%$  at the highest concentrations. Even with the most concentrated solutions no changes in flow time were observed when the solutions were sucked up and allowed to flow through the capillary several times (up to 10 times). Viscometers with capillaries of varying width gave practically identical viscosity values.

The viscosity values in centipoises are collected in Table 1.

THE RELATIONSHIP BETWEEN VISCOSITY AND CONCENTRATION

The dependence of viscosity on concentration for electrolytes at high dilutions is expressed by

$$\eta_{rel} = \eta/\eta_0 = 1 + A_1\sqrt{C} \tag{1}$$

where  $A_1$  is a constant whose value is determined by the properties of the solvent, the ionic charges, ion mobilities and temperature. The values of  $A_1$  for uni-univalent electrolytes in water at 20° is 0.0050.<sup>2a</sup> Our measurements were not extended to solutions as dilute as those for which this equation is valid.

For more concentrated solutions, a third term must be introduced into the equation.

$$\eta_{rel} = 1 + A_1\sqrt{C} + A_2C \tag{2}$$

where  $A_2$  is a cumulative sum of contributions of the individual ions present. Its value is very specific and, depending on the nature of the interactions of ions and solvent, may have either a negative or a positive value. The values are large and positive for solutions containing highly hydrated ions (the value for the sodium ion in water at 20° is + 0.086).<sup>2b</sup> The same is true for solutions of non-electrolytes like glycerol and sugar with large molecules.

The value of  $A_2$  derived from our viscosity data for sodium caprylate solutions between 0.09 and 0.35 molar, *i.e.* below the critical micelle concentration (0.356  $C$  accordingly to our density measurements<sup>1</sup>), is 0.940 when the value taken for  $A_1$  is the theoretical one, 0.0050. The contribution of the caprylate

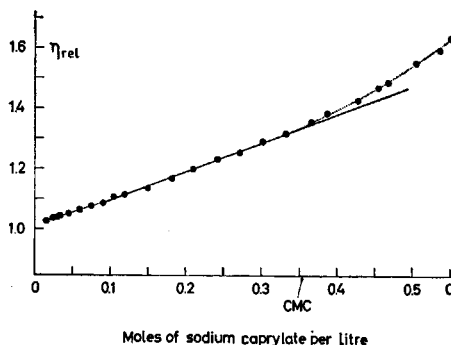


Fig. 1. The concentration dependence of the relative viscosity,  $\eta_{rel}$ , in diluted sodium caprylate solutions at 20°C. The full drawn part of the curve plots the equation  $\eta_{rel} = 1 + A_1\sqrt{C} + A_2C$ ;  $A_1 = 0.0050$ ,  $A_2 = 0.940$ .

ion to the value of  $A_2$  is hence rather high, 0.854. In Fig. 1 the experimental values are marked with dots; the continuous curve plots eqn. (2) when the constants  $A_1$  and  $A_2$  have the above values. Small deviations from this curve occur below 0.09  $C$ . When the caprylate concentration exceeds 0.35  $C$ , that is the CMC, the calculated value of  $A_2$  is not constant but rapidly increases with concentration (Fig. 1); thus above the mentioned limit eqn. (2) is no longer valid.

The increase of the viscosity with the concentration in solutions containing relatively large spherical particles is expressed by the Einstein equation

$$\eta_{\text{rel}} = 1 + 2.5 \Phi \quad (3)$$

where  $\Phi$  is the volume fraction taken up by the particles.

This equation is valid only for very low concentrations. At somewhat higher concentrations the dependence of viscosity on the concentration can be represented as a power series of the type

$$\eta_{\text{rel}} = 1 + a_1\Phi + a_2\Phi^2 + \dots \quad (4)$$

where  $a_1, a_2$  are constants. The constant  $a_1$  is a measure of the disturbance of the flow of the solvent due to the presence of the solute particles at infinite solutions,  $a_2$  measures the disturbance of the flow caused by hydrodynamic interactions when the particles are at infinite distances from each other. For systems with spherical particles  $a_1 = 2.5$  and has higher values when the form of the particles is non-spherical.

By introducing a factor  $Q$ , an interaction parameter taking into account interference between neutral spheres, and their Brownian motion, Vand has derived an expression valid for suspensions of spherical particles up to rather high concentrations.<sup>3</sup>

$$\ln \eta_{\text{rel}} = 2.5 \Phi / (1 - Q\Phi) \quad (5)$$

This equation can be modified to

$$\log \eta_{\text{rel}} = A_3 C / (1 - Q' C) \quad (6)$$

where  $A_3 = 2.5 \bar{V} / 2.303$  and  $Q' = Q\bar{V}$ ;  $\bar{V} = \Phi / C$  is the rigid volume of the solute ("the molar volume of the solute including any water of hydration which is held too firmly to participate in the viscous shearing process").<sup>2c</sup>

Eqn. (6) has been found valid for both solutions of highly hydrated electrolytes and solutions of non-electrolytes with viscosities up to 5–10 times as high as the viscosity of water. However, the equation describes the concentration dependence of the viscosity of very dilute solutions less exact than by eqn. (2) as it does not include the square root of the concentration.<sup>2c</sup>

Above the CMC (0.356  $C$ ) the sodium caprylate solutions are assumed to contain micelles more or less spherical in form. The viscosity of these solutions exceeds five times the viscosity of water only when the soap concentration exceeds 1.4  $C$  and ten times the viscosity of water when the concentration exceeds 1.7  $C$ . Thus, in the concentration range above the CMC, the conditions for the validity of equation 6 seem to be fulfilled.

The equation may be written

$$\log \eta_{\text{rel}} / C = A_3 + Q' \log \eta_{\text{rel}} \quad (6a)$$

Fig. 2 shows that the plot of  $\log \eta_{rel}/C$  against  $\log \eta_{rel}$  is linear above the CMC when the sodium caprylate concentration increases from 0.45 to 1.2  $C$  as required by eqn. 6a. The value of the constant  $A_3$  is 0.321 litre/mole and that of  $Q' = 0.274$ . The fact that the dependence of viscosity on concentration can be expressed by means of eqn. (6) which is valid for suspensions containing spherical particles supports the view that the sodium caprylate micelles are spherical in the concentration range above the CMC. As will be shown below a closer examination of the viscosity data confirms this conclusion.

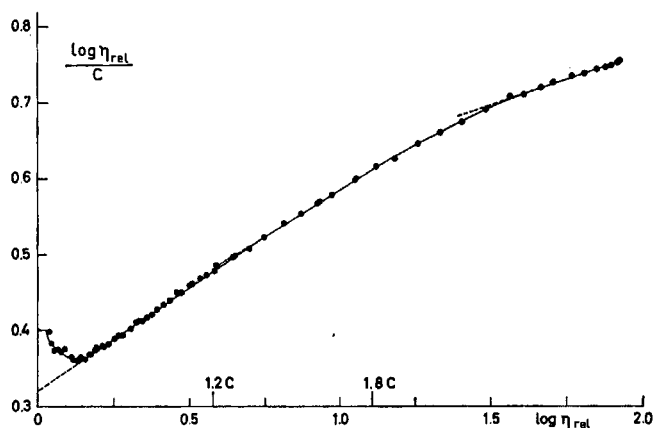


Fig. 2. Examination of the validity of the equation  $\log \eta_{rel}/C = A_3 + Q' \log \eta_{rel}$  in sodium caprylate solutions above the CMC at 20°C. The constants  $A_3$  and  $Q'$  have the following values: between 0.45  $C$  and 1.3  $C$ ,  $A_3 = 0.321$  litre/mole and  $Q' = 0.274$ ; between 1.5  $C$  and 1.8  $C$ ,  $A_3 = 0.345$  litre/mole and  $Q' = 0.241$ ; above 2.3  $C$ ,  $A_3 = 0.498$  litre/mole and  $Q' = 0.138$ .

The curve in Fig. 2 undergoes a slight, but definite change in slope over a short range of concentrations near 1.3  $C$  and then runs approximately linear up to a concentration of about 1.9  $C$ . The latter linear section is represented by eqn. (6) when  $A_3 = 0.345$  litre/mole and  $Q' = 0.241$ . Between the concentration 1.9 and 2.3  $C$  the slope of the curve changes again but now more rapidly to resume a relatively linear course which yields  $A_3 = 0.489$  litre/mole and  $Q' = 0.138$ . The presented data do not provide any direct explanation for these deviations from the initial linear course. The question arises to what extent the application of eqn. (6) is justified at the higher concentrations. One reason to the deviations may be that the viscosity already in the range above 1.3  $C$  increases from 4.5 to 15 times the viscosity of water and then in the range above 1.9  $C$  to up to 80 times the viscosity of water. Another may be that the size and form of the micelles change. The first deviation from the initial course is, however, so insignificant that it can hardly be attributed to any greater change in the form of the micelles from the spherical, but the much more marked change in slope between 1.9 and 2.3  $C$  may well be a sign of such a change. If this is the case, the tendency of the curve to assume a linear course

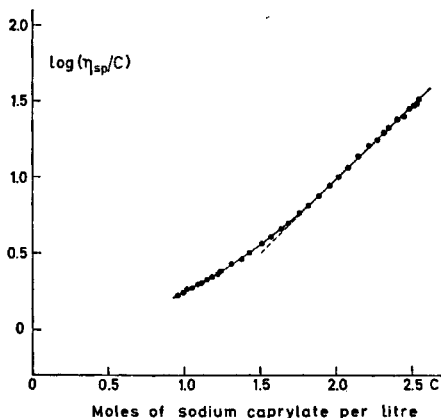


Fig. 3. Curve plotting the values of  $\log(\eta_{sp}/C)$  versus  $C$  in sodium caprylate solutions at 20°C. Note the linear part of the curve above 1.8  $C$ . This part of the curve plots the equation  $\log(\eta_{sp}/C) = k_1 + k_2C$ ;  $k_1 = 0.795$ ;  $k_2 = 0.955$ .

at the highest concentrations shows that, in this concentration range, again there must exist a simple relationship between the viscosity and the volume fraction of the micellar substance even if the micellar structure of the solutions differs from that in the range immediately above the CMC. The changes in the micellar structure that begin already at the concentration 1.3  $C$  and continue from the concentration of 1.9  $C$  upwards, thus, seems to diminish above the concentration of 2.3  $C$ .

At high concentrations, in the range above 1.8–1.9  $C$  the value of the logarithm of the reduced viscosity increases linearly with the concentration, as shown in Fig. 3. Thus, the dependence of the viscosity on the concentration here can be expressed by an equation of the type (7).

$$\log [(\eta_{rel}-1)/C] = \log(\eta_{sp}/C) = k_1 + k_2C \quad (7)$$

where  $k_1$  and  $k_2$  are constants ( $k_1 = 0.795$ , the value at 1.80  $C$ ,  $k_2 = 0.955$ ). This relationship points to a uniform micellar structure in this concentration range. It may be pointed out that we have previously found that the partial specific volume of sodium caprylate, after undergoing changes in an intermediate range, remains constant up to high concentration (above 2.1  $C$ )<sup>1</sup> Also these observations suggest that, at these high concentrations, there is a uniform micellar structure.

The examination of the experimental data reveals thus that the dependence of the viscosity on the concentration must be expressed by three different expressions, each of them valid in a certain concentration range. Below the CMC the dependence on concentration can be expressed by eqn. (2) derived for typical uni-valent electrolytes. Over a wide concentration range above the CMC the dependence can be expressed by eqn. (6), which presumes the existence of large spherical particles. At higher concentrations, where the viscosity increases very rapidly with concentration, the dependence can be expressed by an equation of the form of eqn. (7).

## THE INFLUENCE OF THE AGGREGATION ON THE VISCOSITY AND THE INTRINSIC VISCOSITY OF THE MICELLES

According to the Einstein equation, (3), only the total volume of the solute and not the size of solute aggregates determines the viscosity. We have nevertheless seen that not only the association of free ions to micelles at the CMC becomes evident in the viscosity curve, but that changes occur in the concentration dependence of the viscosity also at higher concentrations, that could be a result of changes in aggregation. A closer study of the connection between the association process and the viscosity may therefore be justified.

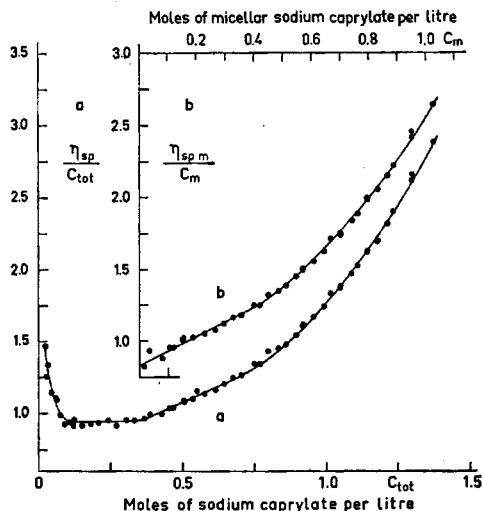
Hess, Philippoff and Kiessig<sup>10</sup> and Wright and Tartar<sup>11</sup> were the first to observe that micelle formation alters the viscosity of an association colloid solution. A change in slope was observed at the CMC in the plot of  $\eta_{rel}$  against concentration; the viscosity increases more rapidly with increasing concentration above than below the CMC. Tyuzyo and co-workers confirmed this by re-examining previously published viscosity data and by carrying out measurements of the viscosities of solutions of a large number of association colloids of different types.<sup>12</sup> They claimed that a plot of the reduced viscosity,  $\eta_{sp}/C$ , against the molar concentration  $C$  has a minimum at the CMC in most cases and that the CMC can be more accurately determined from this plot than from the plot of  $\eta_{rel}$  against  $C$ . They were inclined to attribute the occurrence of the minimum to an adsorption of free ions to the walls of the viscometer.<sup>9</sup>

Fig. 4a shows that the curve plotting our values of  $\eta_{sp}/C$  against  $C$  for sodium caprylate has a large negative slope at low concentrations, but runs almost parallel to the concentration axis ( $\eta_{sp}/C = 0.94$ ) in the range from 0.09 to 0.35  $C$ . Above 0.35  $C$ , thus from the CMC upwards, the value of  $\eta_{sp}/C$  increases. Micelle formation is hence clearly revealed by a change in the course of this curve. The almost horizontal course of the curve over a fairly wide range below the CMC is in complete accordance with the theory for dilute

Fig. 4. Curves plotting the values of  $\eta_{sp}/C$  versus  $C$  in sodium caprylate solutions at 20°C.

4a.  $\eta_{sp}/C_{tot}$  versus  $C_{tot}$ ; the abscissa at the bottom. Note the almost horizontal part of the curve below the CMC between 0.09  $C$  and 0.35  $C$ .

4b. The inserted figure:  $\eta_{sp m}/C_m$  versus  $C_m$ ; the abscissa at the top.  $C_m = C_{tot} - \text{CMC}$  = the molarity of the micellar substance. CMC = 0.35  $C$ .  $\eta_{sp m} = (\eta_{exp}/\eta_{CMC}) - 1$ . Note: Immediately above the CMC a linear part of the curve, intersecting the ordinate at 0.83 when  $C_m = 0$ .



electrolyte solutions as expressed by eqn. (2) ( $A_1 = 0.005$ ,  $A_2 = 0.940$ ) and this minimum needs no other explanation.

In view of the linear course of the curve in Fig. 4a above the CMC, it should be easy to determine the intrinsic viscosity of the micelles. In this evaluation one should not, as both Kushner<sup>14,15</sup> and Tyuzyo<sup>9,12,13</sup> have pointed out, start from the total association colloid concentration, but from the concentrations  $C_m (= C_{\text{tot}} - C_{\text{cmc}})$  of micellar matter and the relative viscosity  $\eta_{\text{rel } m}$  of the latter; this relative viscosity is the ratio of the viscosity at the concentration in question to the viscosity at the CMC ( $\eta_{\text{rel } m} = \eta_{\text{exp}}/\eta_{\text{cmc}}$ ). The reduced viscosity calculated in this manner  $\eta_{\text{sp } m}/C_m$  is plotted against  $C_m$  in Fig. 4b. Also this plot is linear above the CMC. We may hence write:

$$(\eta_{\text{rel } m} - 1)/C_m = \eta_{\text{sp } m}/C_m = [\eta_1] + a_2' C_m \quad (8)$$

where  $[\eta_1]$  and  $a_2'$  are constants. The intrinsic viscosity of the micelles is then  $[\eta_1] = \lim_{C_m \rightarrow 0} (\eta_{\text{sp } m}/C_m) = (\eta_{\text{sp } m}/C_m)_{\text{cmc}} = 0.83$  litre/mole and  $a_2' = 1.18$ .

As the concentration is here expressed in mole/litre, the relationship between  $[\eta_1]$  and the shape factor  $a_1$  in eqn. 4 is

$$[\eta_1] = a_1 M/1000d = a_1 \bar{V} \quad (9)$$

where  $M$  is the gram-molecular weight of the micelle-forming compound,  $d$  the density of the micellar matter and  $\bar{V}$  its molar volume. The micellar substance is hydrated, and therefore we must calculate with the  $M$ -,  $d$ - and  $\bar{V}$ -values for hydrated sodium caprylate. As will be shown below, we have found the molar volume of hydrated micellar sodium caprylate to have the value 0.33 litre/mole.\* When this value is substituted in eqn. (9), the value of  $a_1$  is found to be 2.55, which is in good agreement with the value (2.5) expected for spherical micelles. The ionic strength is rather high in the micellar caprylate solutions, the CMC of which is 0.35  $C$ . Because of that the viscosity of these solutions does not seem to be influenced by any electroviscous effect.

According to the theory and confirmed by experiments the following connection exist between the values of the constants  $a_1$  and  $a_2$  of eqn. (4) and between the values of  $[\eta_1]$  and  $a_2'$  of eqn. (8)

$$a_2 = k_1 a_1^2 \quad (10)$$

In our case, using the experimental values  $a_2' = 1.18$  and  $[\eta_1] = 0.83$ , we find  $k_1 = 1.72$ .

Kushner<sup>14,15</sup> has measured the viscosities of some association colloids (sodium dodecylsulfate and three cation active substances) with much lower CMC:s than that of the caprylate. Their intrinsic viscosities were determined in solutions containing increasing amounts of sodium chloride; the electroviscous effect seemed to be neutralized already in solutions of a ionic strength of about 0.1  $C$ . Whether the hydration or the size and shape of the micelles

\* The values of the viscosity which have been used for the calculation of  $[\eta]$  include not only the influence upon the viscosity of the micelles themselves but also the influence of their free counterions. We have therefore used a value of  $\bar{V}$  referring to the micellar matter inclusive equivalent amount of counterions.



also was affected by the addition of salt seems not to be clear. Using the theoretical molecular weights and assuming the density of the micellar substance to be 0.75 (nearly that of liquid hydrocarbons above their melting points), Kushner from the found intrinsic viscosity values came to the conclusion that the micelles are spherical in these solutions in the concentration range above the CMC. Tyuzyo<sup>12,13,9</sup> computed the intrinsic viscosities of a large number of association colloids and reported for sodium caprylate the value 0.65 which is lower than the value we have computed.

Our previously published density measurements have shown that the partial specific volume of sodium caprylate changes at 1.0 *C* (1.1 molal) and between 1.85 and 2.0 *C* (2.4–3.1 molal).<sup>1</sup> We have attributed these changes to changes in the micellar structure of the solution (2nd CMC and 3rd CMC). Some information is already available about the nature of the latter of these changes. Rotational viscosity measurements<sup>16,17</sup> (the data will be presented in another paper of this series) point to the existence of anisodimensional micelles above a concentration of about 1.9 *C*, that is above the 3rd CMC. Studies of the equilibrium between the 40.5 % isotropic caprylate solution and the mesomorphous middle soap has led us to conclude that the micelles in the mentioned solution are long rodshaped cylinders;<sup>8</sup> investigation of the conductance anisotropy of the solutions has confirmed that this is the case.<sup>18</sup> Studies of the X-ray diffraction by sodium caprylate solutions have led to the conclusion that cylindrical micelles of decreasing length exist in caprylate solutions down to about 2 *C*, *i.e.* down to the 3rd CMC.<sup>8,16</sup>

We have seen above that the dependence of the viscosity on concentration can be represented by the expression (6) in the concentration range from 0.45 to 1.9 *C*, that is from about the CMC up to the 3rd CMC. At 1.3 *C*, that is somewhat above the 2nd CMC, the values of the two constants  $A_3$  and  $Q'$ , however, are changed. From about 1.8–1.9 *C* upwards, that is above the 3rd CMC, the value of the logarithm of the reduced viscosity increases linearly with the concentration (Fig. 3; eqn. 7). The same is the case also if we take into account only the influence of the micellar matter on the viscosity. Eqn. (7) may in this case be rewritten

$$\log (\eta_{sp\ m}/C_m) = k_1' + k_2'(C-1.8) \quad (7a)$$

$k_1' = 0.74$ , the logarithm of the reduced viscosity at the 3rd CMC, and  $k_2' = 0.95$ , the slope of the curve above this concentration.

The rapid increase of the viscosity above the 3rd CMC points as such to the appearance of non-spherical particles. A similar linear dependence of the viscosity on concentration as in eqns. (7) and (7a) has been found in some colloidal systems with rigid rod or long flexible particles.<sup>19–21</sup> The extrapolation to the concentration zero gives according to Martin in these cases the logarithm of the intrinsic viscosity of these colloids<sup>19</sup> (the constant  $k_1 = \log [\eta]$ ; the slope of the curve  $k_2 = k_1 [\eta]$ ). The systems contained in the mentioned cases particles of constant length and the increase of the viscosity was caused by the increasing amount of these particles. Whether that is the case also in sodium caprylate solutions above the 3rd CMC is not certain. In these solutions we have not only an increase of the amount of micellar substance but may be also an increase of the length of the micelles. We do not attempt to estimate

the intrinsic viscosities of the micelles in the mentioned concentration range until this question has been cleared up. However, it may be underlined, that the values of the intrinsic viscosity for these solutions considerably deviate from those for spherical micelles, irrespective of how they are calculated.

It may finally be pointed out that also Tyuzyo has reported that in the range above the CMC a change of the micellar structure is indicated by the course of the viscosity curve. According to Tyuzyo there occurs a second micelle formation concentration in concentrated solutions of many association colloids revealed by a sharp break in the curve plotting  $\eta_{sp,m}/C_m$  against  $C_m$ ; the viscosity curve rises steeply above this break point.<sup>12,13,9</sup> Owing possibly to the relatively short hydrocarbon chain in sodium caprylate we have not observed a break of this kind in the corresponding plot for this soap. As we have seen, the reduced viscosity increases very rapidly above the 3rd CMC and the dependence of the viscosity on concentration is of another type above than below this concentration, but any break-point does not appear in the curve. On the basis of present experimental data it is therefore difficult to decide whether the break points in the curves for association colloids with long chains, observed by Tyuzyo, actually give the 2nd CMC's or give the concentrations we have termed the 3rd CMC's.

#### VISCOSITY AND HYDRATION

The fact that the constant  $A_3$  of eqn. (6) has one value, 0.321 litre/mole, over the sodium caprylate concentration range from 0.45  $C$  to 1.3  $C$  shows that the molar volume of hydrated sodium caprylate does not change in this concentration range. This molar volume  $\bar{V}$  is  $2.303 A_3/2.5 = 0.295$  litre/mole and includes any water of hydration which is held to firmly to participate in the viscous shearing process. Given this value, it is possible to estimate the degree of hydration, *i.e.* the number of bound water molecules per mole of micellar substance,<sup>2b</sup> although this requires a number of assumptions.

The mole volume  $V_{o,cr}$  of sodium caprylate in the crystalline state is estimated at 0.122 litre/mole.<sup>4</sup> If we assume that the difference in the molar volumes of hydrated and crystalline sodium caprylate is fully occupied by water molecules, we may deduce the maximum number, 9.6, of water molecules bound by one mole of hydrated micellar sodium caprylate. It may be noted, however, that the hydrocarbon cores of the micelles are not crystalline but most probably liquid. On melting, the molar volume of crystalline heptane increases 12.6 %.<sup>5</sup> If we take the mole volume to increase 12.6 % when crystalline sodium caprylate changes into caprylate with a liquid hydrocarbon chain, the mole volume of the latter will be  $V_{o,liq} = 0.137$  litre/mole and the hydration number 8.9.

$$h = (\bar{V} - V_{o,liq}/0.018) = (0.295 - 0.137)/0.018 = 8.9 \quad (11)$$

A slightly lower value, 8.5 litre/mole, results if the mole volume  $V_o$  is taken to be the partial molal volume, 0.1414 litre/mole, of sodium caprylate in its solutions above the CMC.<sup>1</sup>

Another uncertainty is due to the fact that the binding of counterions by the micelles is not complete. By Corrin's method we have found the pro-

portion of bound counterions to be 60 % in the vicinity of the CMC. The value of the mole volume of the micellar substance that we derived from the viscosity data applies to one mole of caprylate ion and 0.6 mole of sodium ion. The values of  $V_0$  employed above refer to sodium caprylate containing equivalent amounts of sodium and caprylate ions. The contributions of sodium ions to the mole volume of crystalline and liquid sodium caprylate is, however, very small (of the order of less than 1 %) and hence the error arising from this source is relatively small.

The hydration number of micellar caprylate in the concentration range above the CMC can hence be expected to lie between 8.5 and 8.9. It is of interest to compare this hydration number derived from the viscosity data with other available data.

In a previous investigation we have established that a mesomorphous middle soap separates from sodium caprylate solutions when the soap concentration exceeds 40.5 % or when the water content falls below 13.6 moles per mole of sodium caprylate.<sup>6</sup> The hydration number of sodium caprylate hence cannot be higher than 13.6 in these concentrated solutions. The mesophase, on the other hand, contains 10.8 moles of water per mole of sodium caprylate.<sup>6</sup> We have come to the conclusion that the micelles are transferred rather unchanged with their water of hydration from the concentrated solutions to the more ordered state of the mesophase.<sup>6-8</sup> A highly probable hydration number for micellar sodium caprylate in the most concentrated solutions is hence 10.8 assuming equivalent amounts of sodium and caprylate ions.

An estimate of the maximal number of firmly bound water molecules can be arrived at by a rough calculation based on the assumption that the maximal hydration number of the sodium ions is 4-6 and that each of the free electron pairs on the oxygen atoms of the carboxyl group of the caprylate ion binds a water molecule by hydrogen bonding, or 5 water molecules in all. The maximal number of water molecules bound by one mole of sodium caprylate should hence be 9-11.

If we take the maximal hydration number of sodium caprylate to be 11 and the mole volume of the unhydrated salt to be 0.137, a mole volume of 0.335 litre/mole is obtained for micellar sodium caprylate with total counterion binding. For micellar caprylate with 60 % counterion binding, the hydration number can be estimated as 8.6, which is equal to the number deduced from the viscosity data.

It is necessary to distinguish between the total number of water molecules bound by one mole of sodium caprylate and the number of water molecules actually bound by the micelles. The first number may be assumed to remain practically constant throughout the micellar range and equal to the sum of the maximal numbers of water molecules bound by the sodium and caprylate ions. The second number is a function of the degree of counterion binding by the micelles and increases with the latter.

The viscosity data show directly that the degree of hydration of the micelles remains constant from 0.45 *C* to 1.2-1.3 *C* and hence that the degree of counterion binding also remains constant (at about 60 %) within this concentration range. The slight increase in the value of the constant  $A_3$ , and the value of the molar volume, that occurs between the concentrations 1.3 and 1.9 *C* may be

attributed to an increased hydration of the micelles resulting from an enhanced counterion binding. (In this range the molar volume  $\bar{V} = 0.317$  litre/mole and this value together with the value of  $V_{o, \text{liq}}$  given above lead to hydration number 10. If we in the calculation make use of the values of the partial molal volume of the micellar substance in this range, 0.1433–0.1441 litre/mole, the hydration number will be somewhat lower, about 9.6. An increase in the counterion binding to 76–77 % would be sufficient to explain the observed increase in the molar volume between 1.3 and 1.9  $C$ ).

The value 0.498 litre/mole found for constant  $A_3$  from the data for the highest concentration range above 2.3  $C$  and the value 0.459 litre/mole computed for  $\bar{V}$  on the assumption that the micelles are still spherical lead to a very high hydration number (17–19) which greatly exceeds the number possible with complete counterion binding. This seems to confirm our conclusion that at these high concentrations the micelles are of another type than the spherical micelles below the 3rd CMC.

#### THE VISCOSITY AND THE VOLUME FRACTION OF THE MICELLAR SUBSTANCE

The above mentioned results render it possible to connect the viscosity with the volume fraction of the micelles, as the theory requires, instead of connecting it with the molar concentration, as we have done hitherto. We have calculated the volume fraction of hydrated micellar substance,  $\Phi_m$ , from the molar volume of this substance. The above calculated  $\eta_{sp, m}$ -values are valid for the micelles and their free counterions; in calculating the values of  $\Phi_m$  we therefore used the value  $\bar{V} = 0.33$  litre per mole of sodium caprylate disregarding any possible changes in the counterion binding by the micelles. As a first approximation we have started from the assumption that the total amount of non-micellar sodium caprylate remains unaltered (= 0.35 mole/litre) in the whole concentration range above the CMC.

Fig. 5a shows the plot of  $\log(\eta_{sp, m}/\Phi_m)$  as a function of  $\Phi_m$ . This plot is seen to be linear above the CMC. When the plot is extrapolated to the value  $\Phi_m = 0$  the intercept on the vertical axis is 0.40, which yields

$$\lim_{\Phi_m \rightarrow 0} (\eta_{sp, m}/\Phi_m) = 2.5 \text{ in accordance with the theory for spherical particles.}$$

The linear section of the plot in Fig. 5a extends to the value  $\Phi_m = 0.21$ , corresponding to 0.99  $C$ , which is close to the 2nd CMC. At the 2nd CMC, thus, between a fifth and a fourth of the volume of the system consists of micelles. The slope of the plot is 1.38. Above the value  $\Phi_m = 0.49$ , between 1.8 and 2.55  $C$ , *i.e.* above the 3rd CMC, the plot in Fig. 5a is again linear. The slope of the plot, 2.87, gives the variation of the viscosity with the volume fraction of the micellar substance in the concentration range in question. This slope is 2.1 times the slope of the plot between the 1st and 2nd CMC.

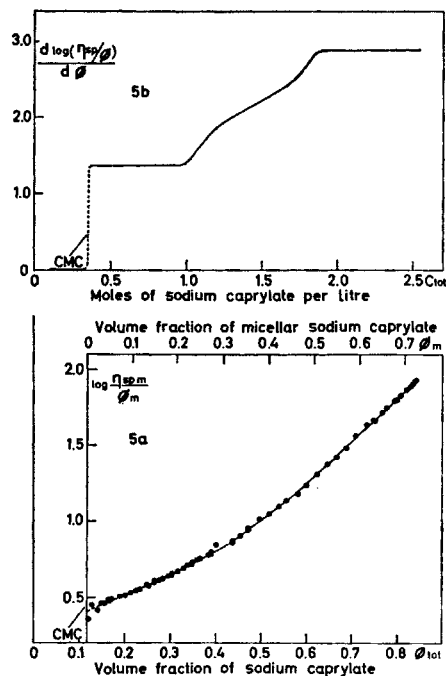
For the purpose of facilitating the comparison of the structural changes shown by the partial specific volume and the viscosity, we have connected the slope of the viscosity curve in Fig. 5a with the molar concentration (Fig.

Fig. 5. Curves showing the connection between the viscosity and the volume fraction of dissolved substance in sodium caprylate solutions at 20°C.

a.  $\log(\eta_{sp m}/\Phi_m)$  versus  $\Phi_m$ \*

$\Phi_m = \Phi_{tot} - \Phi_{CMC}$  = the volume fraction of micellar substance.  $\Phi_{CMC} = 0.115$ .  $\eta_{sp m} = (\eta_{exp}/\eta_{CMC}) - 1$ . The abscissa at the top gives the  $\Phi_m$ . At  $\Phi_m = 0$  the lower linear part of the curve intersects the ordinate at 0.40. The abscissa at the bottom gives the  $\Phi_{tot}$ .

b. The slope of the curve in Fig. 5a versus the total molar concentration of the caprylate solution. Two regions with constant slope: between CMC and about 1.0 C and above about 1.8 C up to the highest concentrations. Between them a region with increasing slope. Below the CMC the curve  $\log(\eta_{sp tot}/\Phi_{tot})$  versus  $\Phi_{tot}$  is almost horizontal.



5b). In this presentation the two sections with a constant slope, that between the 1st and the 2nd CMC, and that above the 3rd CMC, occurs as horizontal parts of the curve. In the range between the 2nd and 3rd CMC the slope increases gradually in value. From the point of the above presented viscosity data, this middle range thus appears as a transition range between the small micelle range with its increasing number of spherical micelles of constant size and the most concentrated solutions with their asymmetric, probably cylindrical micelles. This view is in agreement with the results of the density measurements, which also suggest that changes occur in the properties of the micelles between the 2nd and 3rd critical concentrations.<sup>11,16</sup>

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