

## The Properties and Structures of Aqueous Sodium Caprylate Solutions

### III. The Viscosities at Temperatures between 20° and 40°C

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The viscosities of sodium caprylate solutions have been measured with capillary viscometers at 20°, 25°, 30°, 35°, and 40°C. From the temperature dependence of the relative viscosity and the magnitude of the activation energy for viscous flow it is evident that sodium caprylate behaves like a spherocolloid up to the 3rd CMC, but no longer above the latter concentration. Over the concentration range from the CMC to the 3rd CMC, the concentration dependence of the viscosity can be expressed by the equation  $\log \eta_{\text{rel}} = A_3 C / (1 - Q' C)$ , but this range is divided into two sections with different values of the constants  $A_3$  and  $Q'$ , one between the CMC and the 2nd CMC and the other between the 2nd and 3rd CMC. The molar volume of the caprylate of the micelles increases at the 2nd CMC. This change is connected with an increased binding of water by the micelles, which in turn seems to be due to an increased degree of the counterion binding. The changes that occur at the 2nd CMC became more pronounced at higher temperatures.

From viscosity and other measurements we have concluded that changes occur in the structures of sodium caprylate solutions in the concentration range above the CMC.<sup>1,2</sup> In order to determine to what extent these structural changes depend on temperature we have measured the viscosities of sodium caprylate solutions at several temperatures between 20° and 40°C. We have also wished to determine if these structural changes are revealed by the temperature dependence of the viscosity.

The soap was prepared and the measurements were carried out as described previously.<sup>1,2</sup> The solutions were sealed in ampoules, which were stored at 20°C until they were transferred to thermostats. The ampoules were kept in the thermostats for at least 2 h before they were opened to permit transfer of the solutions to capillary viscometers. Thus, the temperature of the solutions usually was increased from 20°C to a higher value, but in several cases the

solutions were first kept for some time at a higher temperature before they were cooled to the temperature where the measurements were performed. These variations in the treatment of the solutions did not affect the results. The densities of the solutions were measured with Ostwald-Sprengel pycnometers at every temperature where the viscosity measurements were carried out. The accuracy of the results was somewhat lower ( $\pm 5$  in the fifth decimal place) than that of our previous results at 20°C. The determined densities and viscosities are collected in Table 1.

#### THE TEMPERATURE DEPENDENCE OF THE VISCOSITY AND THE ACTIVATION ENERGY OF VISCOUS FLOW

The relative viscosities of spherocolloids vary as a rule only slightly with temperature; even at high colloid concentrations the decrease in viscosity with increasing temperature is relatively small. In the case of colloids that form anisometric particles, however, an increase in temperature leads to a marked lowering of the relative viscosity, especially when the concentrations are high.

The data in Table 1 reveal that the temperature dependence of the viscosity of sodium caprylate solutions differs greatly in different concentration ranges. At concentrations up to 29 % the relative viscosity decreases only slightly with increasing temperature; the relative viscosities at 40°C are only 2–4 %

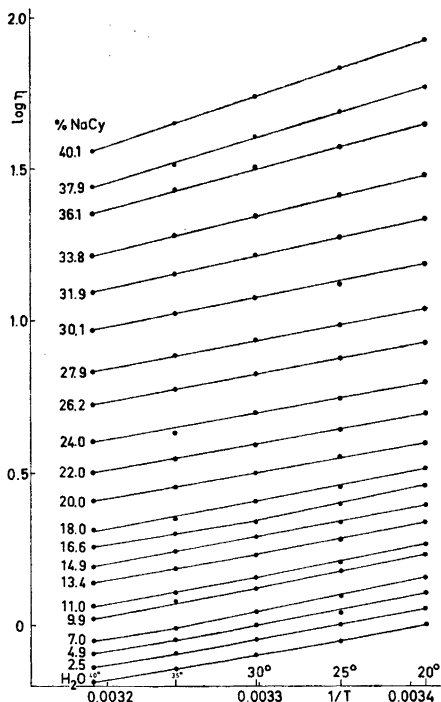


Fig. 1. The temperature dependence of the viscosities of sodium caprylate solutions between 20° and 40°C.

Table 1. The densities and viscosities of sodium caprylate solutions at temperatures between 20° and 40°C.

Weight per cent %	20°C			25°C			30°C			35°C			40°C		
	Mo-larity moles/litre	Density g/ml	Dy-namic viscosity cP	Mo-larity moles/litre	Density g/ml	Dy-namic viscosity cP	Mo-larity moles/litre	Density g/ml	Dy-namic viscosity cP	Mo-larity moles/litre	Density g/ml	Dy-namic viscosity cP	Mo-larity moles/litre	Density g/ml	Dy-namic viscosity cP
Aqua		0.99823	1.002	0.99707	0.8903	0.7975	0.99568	0.99406	0.7194	0.99224	0.6511				
2.504	0.1509	1.0013	1.139	1.0009	1.005	0.9002	1.0002	0.9988	0.8082	0.9964	0.7272				
4.887	0.2960	1.0066	1.282	1.0059	1.128	1.002	1.0049	1.0032	0.8975	1.0008	0.8072				
7.031	0.4276	1.0107	1.434	1.0097	1.255	1.110	1.0085	1.0068	0.9977	0.4249	0.8943				
7.608	0.4631	1.0117	1.480	1.0108	1.293	1.154	1.0095	1.0077	1.032	0.4602	0.9376				
8.741	0.5330	1.0135	1.589	1.0124	1.386	1.261	1.0110	1.0092	1.103	0.5296	0.9914				
9.954	0.6080	1.0152	1.713	1.0140	1.503	1.325	1.0129	1.0085	1.197	0.6041	1.073				
11.03	0.6750	1.0171	1.844	1.0159	1.615	1.440	1.0145	1.0125	1.286	0.6704	1.0101				
13.37	0.8211	1.0207	2.184	1.0193	1.915	1.709	1.0178	1.0156	1.531	0.8151	1.0132				
14.92	0.9181	1.0231	2.483	1.0218	2.183	1.953	1.0200	1.0177	1.746	0.9110	1.0151				
16.63	1.0261	1.0255	2.890	1.0240	2.511	2.239	1.0223	1.0206	2.004	1.0180	1.0174				
18.04	1.1156	1.0278	3.293	1.1136	2.863	2.557	1.0244	1.1093	2.292	1.1065	1.0194				
20.00	1.2403	1.0306	3.975	1.2380	3.583	3.175	1.0267	1.2326	2.850	1.2295	1.0216				
22.01	1.3687	1.0336	4.974	1.3662	4.404	3.934	1.0295	1.3599	3.535	1.3565	1.0244				
23.97	1.4946	1.0363	6.285	1.4919	5.569	4.888	1.0323	1.4852	4.286	1.4809	1.0268				
26.187	1.6380	1.0396	8.475	1.6344	7.514	6.710	1.0350	1.6264	5.969	1.6220	1.0294				
27.910	1.7500	1.0421	10.93	1.7461	9.625	8.649	1.0374	1.7374	7.683	1.7322	1.0315				
30.066	1.8906	1.0451	15.34	1.8863	13.49	11.97	1.0401	1.8765	10.35	1.8709	1.0342				
31.959	2.0143	1.0475	21.55	2.0091	18.78	16.38	1.0421	1.9981	14.25	1.9925	1.0362				
33.836	2.1379	1.0501	29.91	2.1322	25.68	21.97	1.0444	2.1201	18.90	2.1138	1.0383				
36.145	2.3009	1.0530	43.86	2.2831	36.90	31.80	1.0466	2.2500	26.80	2.2629	1.0405				
37.904	2.4063	1.0551	58.39	2.3985	48.07	39.81	1.0485	2.3839	33.12	2.3771	1.0423				
40.063	2.5487	1.0573	82.65	2.5408	66.48	54.09	1.0507	2.5248	44.23	2.5178	1.0445				

lower than the relative viscosities at 20°C. This weak temperature dependence shows that we here have to do with a spherocolloidal system. When the concentration exceeds about 29 %, the temperature dependence increases rapidly to a tenfold value for the 40 % solution. This indicates that the micellar structure has undergone a change and the behaviour is no longer that of a colloid that forms spherical particles. The increasingly greater dependence of the viscosity on temperature implies an increasing degree of anisometry of the micelles.

The greater part of our experimental data is presented in Fig. 1 in the form of plots of the logarithm of the dynamic viscosity ( $\log \eta$ ) against reciprocal absolute temperature since the viscosities of many liquid systems decrease logarithmically as the temperature is raised in accordance with eqn. (1)

$$\eta = B \times \exp(E/RT) \quad (1)$$

In this equation  $\eta$  is the dynamic viscosity,  $E$  the activation energy of viscous flow,  $R$  the gas constant and  $T$  the absolute temperature. The data for the sodium caprylate solutions give plots that are approximately linear, especially at the higher concentrations. The slopes of the plots are rather small at low concentrations, but increase considerably at sodium caprylate concentrations above 30 %.

The slopes and thus the values of the activation energy of viscous flow,  $E$ , can be taken as measures of the temperature dependence of the viscosity. Fig. 2 shows that the activation energy increases slowly with increasing caprylate concentration from a value of 3970 cal/mole for water to a value of about 4200 cal/mole for the 7 % solution (0.42  $C$ ), but then remains constant up to a caprylate concentration of 29–30 % (1.8–1.9  $C$ ). Above the latter concentration the activation energy increases rapidly to the value 7670 cal/mole for the 40 % solution (2.5  $C$ ).

The activation energy is hence constant from the CMC (0.35  $C$ ) to the 3rd CMC (1.8–2.0  $C$ ). Our viscosity data at 20°C demonstrated that the micelles are spherical in form from a concentration immediately above the CMC up to a concentration of about 1.3  $C$ , *i.e.* above the 2nd CMC, and that larger deviations from the spherical form hardly occur before the concentration exceeds the 3rd CMC.<sup>2</sup> This view is strongly supported by the present data

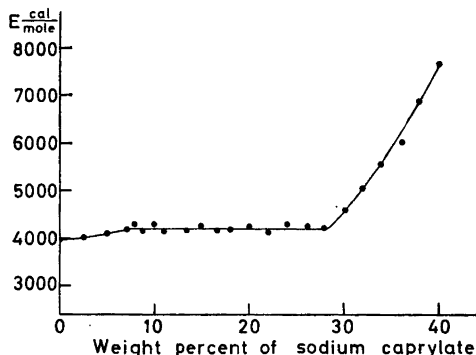


Fig. 2. The activation energy of viscous flow in sodium caprylate solutions. 20°–40°C.

on the temperature dependence of the relative viscosity and the fact that the activation energy does not change in the range between 0.42 and 1.8–1.9  $C$ . The resistance offered by the micelles to the flow of the solvent hence changes in a similar way with increasing temperature over this range. The marked change in the temperature dependence of the viscosity as revealed by the rapid increase in the activation energy above the 3rd CMC is a sign that the resistance to flow offered by the micelles is of another type than at lower concentrations and is evidently due to a change in the structure of the micelles. These new observations are in agreement with our previous conclusion that the spherical micelles change into cylindrical micelles above the 3rd CMC. It is unknown whether the marked decrease in viscosity noted with increasing temperature is due to a decrease in the micelle length or to some other cause.

The determination of the temperature dependence of the relative viscosity and of the magnitude of the activation energy thus offers a sensitive method for the detection in association colloid systems of deviations from the spherical form of the micelles.

In the following we shall examine the experimental data mainly to elucidate how an increase in temperature alters the structure of caprylate solutions in the concentration range below the 3rd CMC, where the micelles are spherical.

#### THE VARIATION OF THE CMC WITH TEMPERATURE AND THE HEAT OF MICELLE FORMATION

Previously we have found that when values of  $\eta_{sp}/C$  for sodium caprylate solutions are plotted against the molar concentration  $C$ , the critical concentration is revealed by a point of intersection of two linear parts of the viscosity curve.<sup>2</sup> The height above the axis of the lower, almost horizontal part of the curve below the CMC is given by the value of the constant  $A_2$  in eqn (2).

$$\eta_{sp}/C = (A_1/\sqrt{C}) + A_2 \quad (2)$$

The linear rising part of the curve immediately above the CMC can be represented by an equation of the type

$$\eta_{sp}/C = a_1' + a_2'C \quad (3)$$

where  $a_1'$  and  $a_2'$  are constants.

The viscosity curves have the same form also at higher temperatures. The height of the section below the CMC decreases somewhat with increasing temperature, the values of the constant  $A_2$  are 0.94, 0.90, 0.87, 0.84, and 0.82 at 20°, 25°, 30°, 35°, and 40°C. The slope of the linear part above the CMC remains unchanged and the value of the CMC increases from about 0.35  $C$  at 20° to about 0.38 at 40°C. The plot of  $\log$  CMC *versus*  $1/T$  is shown in Fig. 3.

We have estimated the heat of micelle formation  $\Delta H_m$  from the equation proposed by Stainsby and Alexander<sup>3</sup>

$$\Delta H_m = -RT^2 (\partial \ln \text{CMC} / \partial T)_p \quad (4)$$

The value of  $\Delta H_m$  increases slightly with temperature from  $-0.57$  at 20° to  $-0.96$  kcal/mole at 40°C, with a mean value of  $-0.76$  kcal/mole.

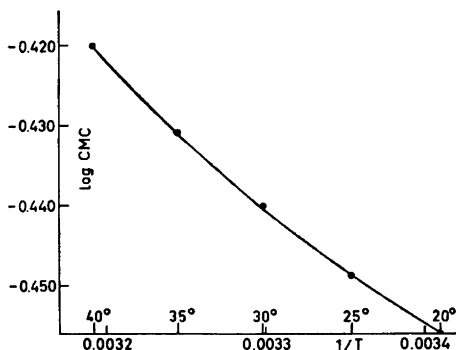


Fig. 3. The temperature dependence of CMC in sodium caprylate solutions.

#### THE INTRINSIC VISCOSITY OF THE MICELLAR SUBSTANCE

The intrinsic viscosity of the micellar substance  $[\eta_1]$  can be calculated from the data on the linear section of the plot of  $\eta_{sp\ m}/C_m$  against  $C_m$  in the range immediately above the CMC.

$$(\eta_{rel\ m} - 1)/C_m = \eta_{sp\ m}/C_m = [\eta_1] + a_2' C_m \quad (5)$$

$C_m$  ( $= C_{tot} - \text{CMC}$ ) is the concentration of micellar substance and  $\eta_{rel\ m}$  ( $= \eta_{exp}/\eta_{CMC}$ ) its relative viscosity, and  $a_2'$  is a constant. Extrapolation to the value  $C_m = 0$  gives for  $[\eta_1]$  values between 0.78 and 0.84 litres/mole, which are of the same magnitude as the value 0.83 litre/mole previously found at 20°C.<sup>2</sup> No trend with temperature is evident in these values.

The value of the shape factor, the constant  $a_1$  in the general expression (6),

$$\eta_{rel} = 1 + a_1 \Phi + a_2 \Phi^2 + \dots \quad (6)$$

can be derived from the value of the intrinsic viscosity with the aid of eqn. (7).

$$[\eta_1] = a_1 \bar{V} \quad (7)$$

In expression (6)  $\Phi$  is the volume fraction occupied by particles,  $a_1 = 2.5$  for systems containing spherical particles and  $a_2 = k_1 a_1$ .<sup>2</sup> In eqn. (7)  $\bar{V}$  is the molar volume of the hydrated micelle substance.

In the calculation of  $[\eta_1]$  we have taken into account the contributions of the micelles and their bound and free counterions upon the viscosity. The values of  $\bar{V}$  should therefore also include the volume of these counterions. By our previous calculations at 20°C we have used the value  $\bar{V} = 0.33$  litre/mole, the mole volume of micellar substance with a total counterion binding. As we shall see below this value does not vary significantly in the temperature range from 20° to 40°C. Using  $\bar{V} = 0.33$  litre/mole for all temperatures we get for the constant  $a_1$  values between 2.55 and 2.37 which show that the micelles in the concentration and temperature ranges in question are spherical or almost spherical in form.

The same result is, of course, obtained if one calculates the volume fraction of the micellar substance  $\Phi_m$  using the above mentioned value of  $\bar{V}$  and then plots the  $\log(\eta_{sp\ m}/\Phi_m)$  against  $\Phi_m$ . These curves are at higher temperatures, as at 20°C, linear up to a concentration of about 1 C, *i.e.* almost up to the 2nd CMC, and the value of  $a_1$ , derived by extrapolation to  $\Phi_m = 0$ , is that characteristic for spherical micelles.

THE VOLUME OCCUPIED BY THE MICELLAR SUBSTANCE

We have found previously that the variation of the viscosity of sodium caprylate solutions with concentration at 20°C from the CMC to rather high concentrations can be represented by eqn. (8)<sup>2</sup> which is valid for suspensions of spherical particles

$$\log \eta_{rel}/C = A_3 + Q' \log \eta_{rel} \tag{8}$$

In this equation  $A_3$  and  $Q'$  are constants.  $A_3 = 2.5 \bar{V}/2.303$  litre/mole where  $\bar{V} = \Phi/C$  litre/mole is the rigid volume of the solute including any water of hydration which is held too firmly to participate in the viscous shearing process.  $\Phi$  is the volume fraction of hydrated substance.  $Q' = Q\bar{V}$ , where

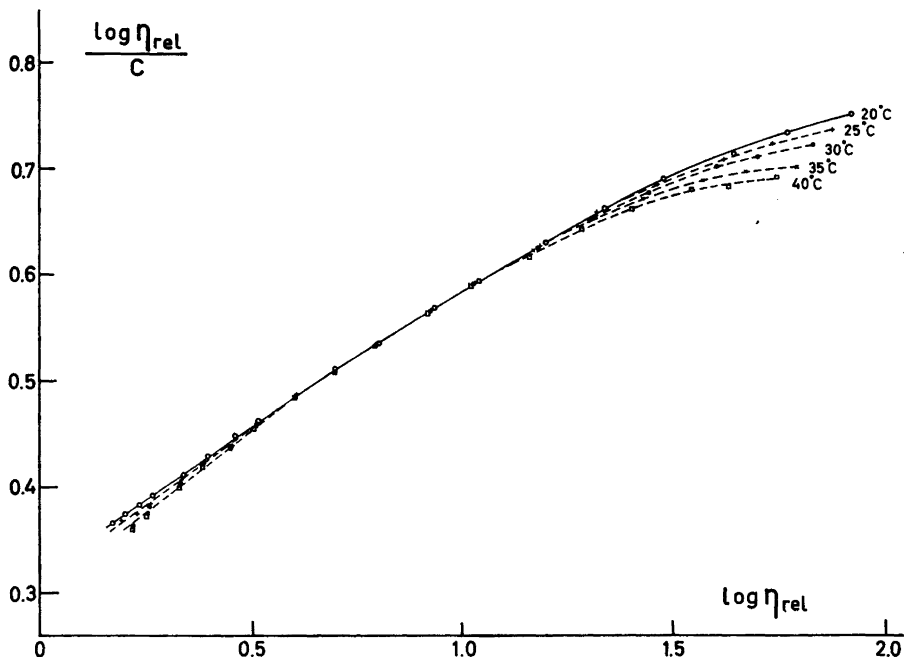


Fig. 4. Plot of  $\log \eta_{rel}/C$  versus  $\log \eta_{rel}$  of sodium caprylate solutions above the CMC at temperatures between 20° and 40°C. The full drawn curve gives previous results at 20°C (Ref. 2). New measurements: 20°C O; 25°C +; 30°C ●; 35°C ×; 40°C □.

$Q$  is an interaction parameter dealing with neutral interferences between spheres and their Brownian motion.<sup>4,5</sup> We obtained constant values of  $A_3$  and  $Q'$  from 0.45  $C$  (slightly above the CMC) up to about 1.3  $C$  at 20°C. Above the latter concentration the values of the constants changed slightly but then remained practically unaltered up to about 1.8–1.9  $C$  where their values changed greatly.<sup>2</sup>

Although our density and viscosity data at higher temperatures are not so accurate as those at 20°C, we have attempted to determine the validity of eqn. (8) at higher temperatures. Our complete set of viscosity data are presented from this point of view in Fig. 4. The previous data at 20°C are plotted as a continuous line.<sup>2</sup> The new data are marked by symbols, one for each temperature. The new experimental values at 20°C fall close to the continuous line. The points are seen to shift toward the horizontal axis with increasing temperature. This shift is smallest in the range between about 1.2 and 1.8  $C$  where the values from the different temperatures lie so close to each other that all could be taken to lie on the same curve. Above 1.8  $C$  the values for the different temperatures follow different courses and the distances between the curves increase rapidly with rising concentration. Below 1.2  $C$  the order is similar but the spread of the values is much smaller.

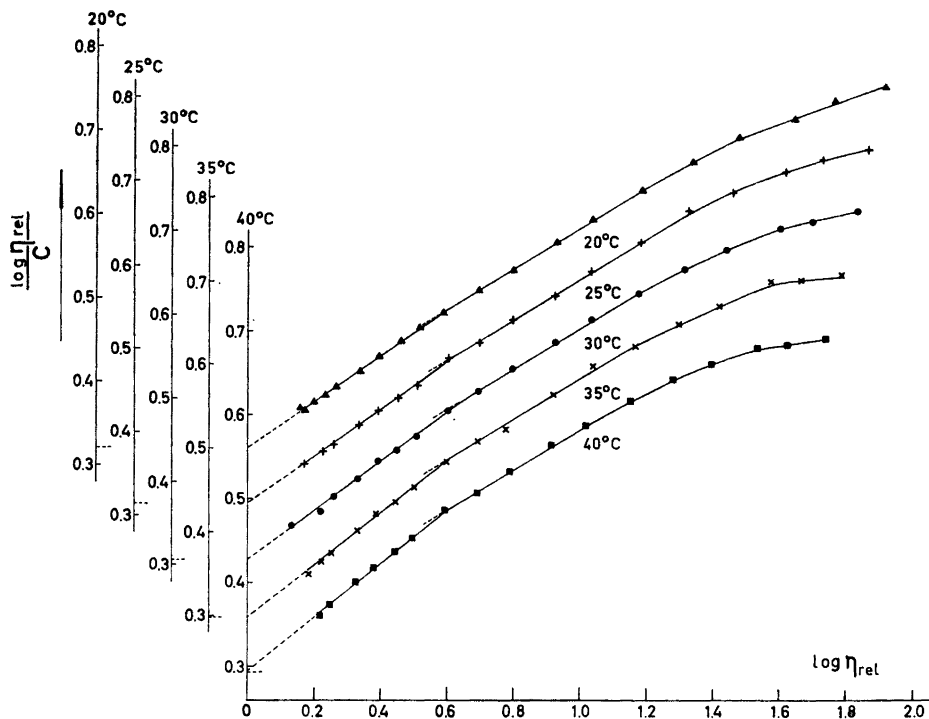


Fig. 5. Examination of the validity of equation  $\log \eta_{rel}/C = A_3 + Q' \log \eta_{rel}$  in sodium caprylate solutions above the CMC at different temperatures.



Plots of  $\log \eta_{rel}/C$  against  $\log \eta_{rel}$  at the different temperatures are drawn in Fig. 5. The plots for all temperatures are practically linear with the same slope  $Q'$  and the same intercept  $A_3$  in the intermediate range between about 1.2 and 1.8  $C$ . The lower limit of this range shifts to lower concentrations with increasing temperature from about 1.3  $C$  at 20° to about 1.1  $C$  at 40°C. The plots have approximately linear sections also below these limits which extend to a concentration slightly above the CMC, to about 0.45  $C$  at 20° and about 0.57  $C$  at 40°C. The slopes  $Q'$  of these sections increase slightly with temperature, whereas the values of the constant  $A_3$  diminish somewhat. The values of the constants are given in Table 2.

Thus, the study shows that eqn. (8) represents the concentration dependence of the viscosity at all temperatures up to a concentration of about 1.8  $C$ , the 3rd CMC, *i.e.* in that concentration range where the micelles are spherical or closely so. The range where the equation is valid is divided into two parts with a boundary at 1.1–1.3  $C$ , the 2nd CMC; this boundary is more marked at higher temperatures. The value of the constant  $A_3$  is independent of temperature above the 2nd CMC, but diminishes with rising temperature below this concentration.

Table 2. Values of the parameters  $A_3$  and  $Q'$  in different concentration ranges at different temperatures.

Temp. °C	0.5–1.1 $C$		1.2–1.8 $C$	
	$A_3$	$Q'$	$A_3$	$Q'$
20	0.321	0.274	0.344	0.241
25	0.314	0.279	0.343	0.242
30	0.306	0.290	0.341	0.243
35	0.298	0.310	0.342	0.242
40	0.294	0.318	0.343	0.240

The spherocolloidal nature of sodium caprylate in both the mentioned concentration ranges makes it justified to calculate the molar volume  $\bar{V}$  of the micellar substance with the aid of the relation  $\bar{V} = 2.303 A_3/2.5$ . The data in the range between the 2nd and the 3rd CMC yield the value  $\bar{V} = 0.316$  litre/mole at all temperatures, but the data below the 2nd CMC yield values that decrease with rising temperature:  $\bar{V}_{20} = 0.295$ ,  $\bar{V}_{25} = 0.288$ ,  $\bar{V}_{30} = 0.282$ ,  $\bar{V}_{35} = 0.275$ , and  $\bar{V}_{40} = 0.271$  litre/mole.

#### HYDRATION OF MICELLES

The preceding mole volumes apply to the hydrated micellar substance. The fact that the mole volume remains constant but has a different value in the two concentration ranges is an indication that the binding of water

to the micelles is constant within both ranges but changes by passing from the one range to the other, that is at the 2nd CMC. The variation of the molar volume with temperature in the lower concentration range suggests that the binding of water varies also with temperature in this range.

The evaluation of the hydration number, the number of water molecules bound by one mole of micellar caprylate, is somewhat uncertain, because we did not know with certainty the mole volume of caprylate in unhydrated state in the micelles, and because we are not certain that the difference between volumes of hydrated and unhydrated caprylate is fully occupied by water molecules.

In our previous calculations for the mole volume of unhydrated micellar caprylate we used the value  $V_{o \text{ liq}} = 0.137$  litre/mole estimated for sodium caprylate with hydrocarbon chain in liquid state and the values of the partial molal volume of caprylate determined by density measurements.<sup>2</sup> On the assumption that the volume difference is fully taken up by water molecules we get a hydration number between 8.9 and 8.5 moles of water per mole of micellar caprylate between CMC and the 2nd CMC at 20°C.<sup>2</sup>

When the molar volume of unhydrated sodium caprylate is taken to be  $V_{o \text{ liq}} = 0.137$  litre/mole the hydration number is found to be about 10 in the range between the 2nd and 3rd CMC, where the molar volume of the hydrated caprylate is 0.316 litre/mole irrespective of the temperature. If the volume of unhydrated caprylate is taken to be equal to the partial molal volume in this range, the hydration number is slightly lower and decreases with rising temperature from 9.55 at 20° to 9.35 at 40°C. (The partial specific volumes are 0.872 at 20°, 0.878 at 25°, 0.882 at 30°, 0.889 at 35°, and 0.893 ml/g at 40°C.)

The following hydration numbers are computed for the range between the CMC and the 2nd CMC:  $h = 8.9-8.5$  at 20°,  $8.4-8.0$  at 25°,  $8.1-7.6$  at 30°,  $7.7-7.2$  at 35°, and  $7.5-6.9$  at 40°C. (The higher values were computed using  $V_{o \text{ liq}} = 0.137$  litre/mole, the lower values using the following experimentally determined values of the partial specific volumes: 0.856 at 20°, 0.871 at 25°, 0.874 at 30°, 0.881 at 35°, and 0.887 g/ml at 40°C). An increase of temperature from 20° to 40°, thus, seems to cause a decrease of the water binding of about 1.5 moles of water per mole of micellar caprylate. This implies that the change in the water binding of micelles at the 2nd CMC becomes greater with rising temperature.

The reason for the increase in the binding of water that occurs at all temperatures at the 2nd CMC we have previously ascribed to an increased counterion binding by the micelles.<sup>2</sup> As a consequence the observed decrease in the water binding with rising temperature should also be ascribed to changes in the counterion binding; one must not, however, disregard the possibility that the ions that compose the micelles may be less hydrated and that the water of hydration of the micelles may be less strongly bound at higher temperatures. These factors together may well explain the observed changes in the hydration number with rising temperature.

The preceding discussion has been related to the binding of water by micelles in concentration ranges where the counterion binding by the latter is far from complete. We have previously estimated the degree of water

binding when the counterion binding is complete from the water contents of concentrated sodium caprylate solutions and the mesomorphous middle soap in equilibrium with the latter at 20°C. We have now determined these same water contents at 30° and 40°C. The water content of saturated sodium caprylate solution and mesophase in equilibrium with one another remain practically unaltered by rising temperature. We have found 13.6 % water in the former and 10.8 % water in the latter phase. This gives as the most probable value a volume of 0.33 litre/mole for hydrated sodium caprylate with complete counterion binding in the temperature range in question.

*Acknowledgements.* The experimental measurements described in this paper were performed at the Institute of Physical Chemistry of Åbo Akademi in 1963. The results were reported briefly at the 4th International Congress on Surface-Active Substances, Brussels 1964 (Ref. 6).

#### REFERENCES

1. Ekwall, P., Eikrem, H. and Mandell, L. *Acta Chem. Scand.* **17** (1963) 111.
2. Ekwall, P. and Holmberg, P. *Acta Chem. Scand.* **19** (1965) 455.
3. Stainsby, G. and Alexander, A. E. *Trans. Faraday Soc.* **46** (1950) 587.
4. Vand, V. *J. Phys. Chem.* **52** (1948) 277.
5. Robinson, R. A. and Stokes, R. H. *Electrolyte solutions*, 2nd Ed. Butterworths, London 1959, pp. 305–307.
6. Ekwall, P. *4th Intern. Congr. Surface-Active Substances*, Brussels 1964. Preprint No. BIV/5.

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