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

II. Density and Viscosity of the Solutions

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The concentration dependence of partial specific volume of the sodium caprylate and water mixture dissolved in decanol and of viscosity of the solutions show that the structure of the solutions undergoes a change when the decanol content falls below 90—85 %. Combined with small-angle X-ray diffraction observations the conclusion is drawn that this change is caused by micelle formation. A rather well defined value for the c.m.c. of the solutions has been derived from viscosity findings. These findings show that the micelles possess a more or less spherical shape and that they contain besides sodium caprylate and water also decanol. Their molar composition varies from 1 sodium caprylate:1.9 decanol:6.0 water in the water-poor part to 1 sodium caprylate:3.6 decanol:23 water in the water-rich part of the solution region. The intermicellar solution consists of decanol.

EXPERIMENTAL

Data on the purity of the initial material have been given in earlier papers.[1,2] The stock solutions were prepared by heating a mixture of the three components in the required proportions until completely dissolved. Dilution series were then prepared by adding the appropriate amounts of decanol. Sealed ampoules of the solutions were stored in a thermostate at 20°C.

The density was determined in the usual way with Sprengel-Ostwald type pycnometers; the reproducibility was $\pm 7 \times 10^{-5}$ g/cm^3. The viscosity was determined with Ubbelohde viscometers; a reproducibility of ± 0.1 % was obtained. All the determinations were performed at 20 ± 0.01°C.

The results of the experiments are given in Table 1. Each experimental series contained sodium caprylate and water in a constant proportion by weight, and a range of concentrations of decanol. The positions of the examined solutions are shown in Fig. 1.

DENSITY

The density of aqueous decanol increases almost linearly with the water content up to 3 % (Fig. 2). As saturation is approached there is a slight retardation of this trend. In the linear segment the partial specific volume of

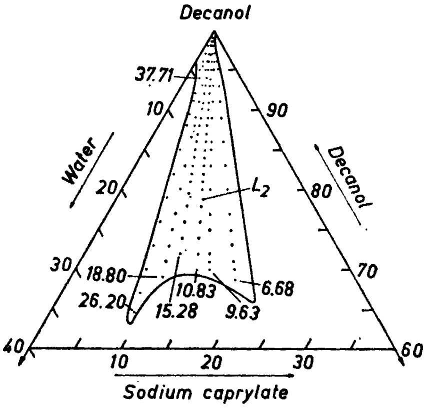

Fig. 1. The L_2-region in the three-component system sodium caprylate-decanol-water at 20°C. The numerals 6.68—37.71 indicate the molar ratio water/caprylate of a number of experimental series; the positions of the individual specimens are indicated by dots.

water is 0.988 cm^3/g; this rather low value suggests that the water may be bound to the decanol.

Even when aqueous solutions of sodium caprylate were dissolved in decanol, small additions of them give a linear increase in density with the water content (Fig. 2). When the caprylate concentration of the added solution exceeded about 25 %, the part of the L_2 region was entered in which the solubilities of the caprylate and water are mutually enhanced, and here it is most appropriate to study the dependence of the specific volume on the amount of caprylate solution added — that is to say on the decrease in the decanol content. These curves contain two linear segments with different slopes linked by an intermediate part with a slight downward curvature. In some cases a further downward curvature was observed at the largest additions of caprylate and water.

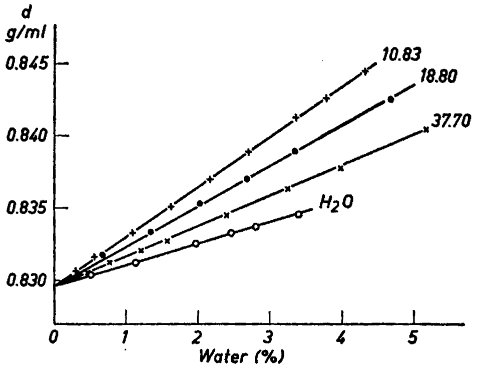

Fig. 2. The density plotted as a function of the water content.

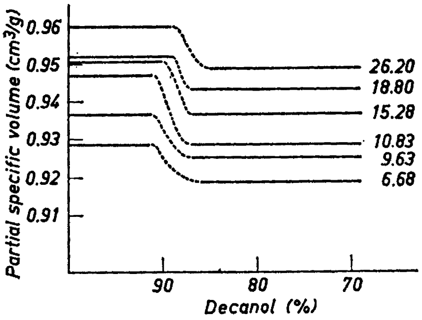

Fig. 3. The partial specific volume of sodium caprylate and water dissolved in decanol. Series with constant molar ratio water/caprylate.

Table 1. Density and viscosity values at 20°C.

Composition (%)			d	η
Decanol	Water	NaC_8	g/cm^3	cP
Series decanol-water				
100	0	—	0.82963	14.06
99.492	0.508	—	0.83039	13.81
98.863	1.137	—	0.83125	13.59
98.517	1.483	—	0.83185	13.51
98.027	1.973	—	0.83255	13.46
97.550	2.450	—	0.83333	13.46
97.192	2.802	—	0.83365	13.52
97.097	2.903	—	0.83398	13.56
96.611	3.389	—	0.83465	13.60
Series 37.71 moles H_2O/1 mole NaC_8				
99.44	0.45	0.11	0.83062	13.84
99.05	0.76	0.19	0.83123	13.82
98.51	1.20	0.29	0.83213	13.82
98.04	1.57	0.39	0.83280	13.84
97.01	2.40	0.59	0.83456	14.01
95.98	3.23	0.79	0.83630	14.40
95.06	3.97	0.97	0.83785	14.85
95.56	5.17	1.27	0.84054	15.70
Series 26.18 moles H_2O/1 mole NaC_8				
98.50	1.11	0.39	0.83306	14.21
97.00	2.21	0.79	0.83484	14.30
95.50	3.33	1.17	0.83803	14.84
94.00	4.44	1.56	0.84038	15.69
92.00	5.91	2.09	0.84423	17.24
91.00	6.65	2.35	0.84601	18.03
88.00	8.87	3.13	0.85105	21.00
85.00	11.09	3.91	0.85652	26.01
82.00	13.31	4.69	0.86245	30.95
79.00	15.52	5.48	0.86819	36.56
76.00	17.74	6.26	0.87398	46.45
73.00	19.96	7.04	0.87989	55.91
70.00	22.18	7.82	0.88573	68.85
67.00	24.40	8.60	0.89344	82.27
64.52	26.23	9.25	0.90151	101.53
Series 18.8 moles H_2O/1 mole NaC_8				
99.00	0.67	0.33	0.83179	13.93
98.00	1.34	0.66	0.83342	14.05
96.99	2.02	0.99	0.83532	14.31
96.00	2.68	1.32	0.83707	14.71
95.00	3.35	1.65	0.83896	15.24
93.04	4.67	2.29	0.84263	16.50
91.04	6.01	2.95	0.84620	18.18
89.04	7.35	3.61	0.85007	20.63
88.00	8.05	3.95	0.85198	22.07
86.68	8.93	4.39	0.85452	23.71

Table 1. Continued.

Composition (%)			d	η
Decanol	Water	NaC_8	g/cm^3	cP
83.06	11.36	5.58	0.86147	30.01
80.13	13.33	6.54	0.86719	36.72
77.16	15.32	7.52	0.87315	45.77
75.01	16.76	8.23	0.87745	52.98
73.00	18.11	8.89	0.88159	61.01
70.99	19.46	9.55	0.88552	70.64
68.99	20.80	10.21	0.89038	—
Series 15.28 moles H_2O/1 mole NaC_8				
99.58	0.29	0.18	0.83096	13.92
99.00	0.62	0.38	0.83190	13.96
98.01	1.24	0.75	0.83386	14.06
97.00	1.87	1.13	0.83545	14.32
96.01	2.49	1.50	0.83770	14.70
95.00	3.12	1.88	0.83922	15.29
94.00	3.74	2.26	0.84099	15.94
93.00	4.36	2.64	0.84279	16.65
91.99	4.99	3.02	0.84465	17.33
91.00	5.61	3.39	0.84643	18.24
90.09	6.18	3.73	0.84830	19.25
89.01	6.85	4.14	0.85026	20.19
87.99	7.49	4.52	0.85219	21.60
86.98	8.12	4.90	0.85410	22.74
86.00	8.73	5.27	0.85620	24.22
85.00	9.35	5.65	0.85798	25.86
84.05	9.94	6.01	0.85975	27.92
83.00	10.60	6.40	0.86190	30.03
82.00	11.22	6.78	0.86384	32.35
81.00	11.84	7.16	0.86560	34.07
79.61	12.71	7.68	0.86854	38.28
77.95	13.74	8.31	0.87191	43.21
76.00	14.96	9.02	0.87603	49.74
74.00	16.21	9.79	0.88023	58.27
71.99	17.46	10.55	0.88421	67.42
Series 10.83 moles H_2O/1 mole NaC_8				
99.48	0.28	0.24	0.83062	14.15
98.99	0.55	0.46	0.83138	14.17
98.00	1.08	0.92	0.83327	14.40
96.99	1.62	1.39	0.83505	14.69
96.00	2.16	1.84	0.83701	15.16
95.01	2.69	2.30	0.83897	15.76
93.79	3.35	2.86	0.84134	16.61
92.99	3.78	3.23	0.84269	17.20
92.00	4.32	3.68	0.84464	18.11
90.84	4.94	4.22	0.84670	19.10
90.00	5.40	4.60	0.84831	19.96
89.01	5.93	5.06	0.85054	21.04
88.01	6.47	5.52	0.85255	22.42
87.00	7.02	5.98	0.85457	23.87

Table 1. Continued.

Composition (%)			d	η
Decanol	Water	NaC_8	g/cm^3	cP
86.01	7.55	6.44	0.85638	25.45
85.00	8.10	6.90	0.85846	26.89
84.00	8.64	7.36	0.86065	28.88
83.00	9.17	7.83	0.86280	31.10
82.01	9.71	8.28	0.86471	33.15
81.01	10.25	8.74	0.86680	35.18
80.00	10.79	9.21	0.86890	38.07
78.00	11.87	10.13	0.87293	44.42
76.00	12.95	11.05	0.87732	52.27
74.00	14.03	11.97	0.88137	60.66
72.01	15.11	12.88	0.88603	71.52
70.00	16.19	13.81	0.89022	83.94
Series 9.63 moles H_2O/1 mole NaC_8				
99.00	0.51	0.49	0.83208	14.17
97.97	1.04	0.99	0.83392	14.39
96.95	1.56	1.49	0.83558	14.76
95.98	2.05	1.97	0.83754	15.25
94.99	2.56	2.45	0.83941	15.77
92.93	3.61	3.46	0.84348	17.26
91.04	4.58	4.38	0.84710	18.99
89.01	5.61	5.38	0.85136	21.13
85.99	7.15	6.86	0.85751	25.97
85.00	7.66	7.34	0.85967	27.70
82.99	8.68	8.33	0.86363	31.59
83.00	8.68	8.82	0.86383	31.51
80.04	10.19	9.77	0.86996	39.32
76.99	11.75	11.26	0.87607	49.69
75.07	12.73	12.20	0.88009	57.82
72.99	13.79	13.22	0.88464	68.15
70.97	14.82	14.21	0.88894	80.02
69.99	15.32	14.69	0.89133	87.87
Series 6.68 moles H_2O/1 mole NaC_8				
96.98	1.27	1.75	0.83582	—
95.92	1.71	2.37	0.83798	15.76
95.00	2.10	2.90	0.83988	16.44
92.96	2.96	4.08	0.84378	17.93
90.98	3.79	5.23	0.84774	19.73
89.00	4.62	6.38	0.85230	22.22
86.00	5.88	8.12	0.85795	26.29
83.08	7.11	9.81	0.86406	33.17
80.04	8.38	11.58	0.87059	41.77
77.08	9.62	13.30	0.87699	52.88
75.04	10.48	14.48	0.88152	62.70
73.09	11.30	15.61	0.88601	73.94
71.03	12.10	16.81	0.89050	88.09
70.10	12.56	17.34	0.89267	—
68.67	13.16	18.18	0.89580	108.31

The caprylate and water dissolved in the decanol may be regarded as an admixed substance whose composition is constant for each series; its partial specific volume can be determined from the density. In all the series the partial volume of this admixed substance falls off from its initial value at low caprylate-water contents to a lower value at higher contents. As Fig. 3 shows, this change occurs when the concentration of the admixed substance exceeds about 10—15 % — that is, in the 90—85 % decanol solutions.

It is thus evident from the density measurements that the volume of the sodium caprylate-water mixture contracts when its concentration exceeds a certain value. This is indicative of a change in structure of the decanolic solutions in the concentration range in question.

VISCOSITY

When water is dissolved in decanol the viscosity decreases, at first rapidly and then at an ever-decreasing rate, until finally, as saturation is approached, it begins to rise (Fig. 4). This drop in viscosity due to the water occurs also when very weak aqueous solutions of caprylate are dissolved in decanol. As the caprylate content of the aqueous solution increases, however, this drop gradually slows down and changes rapidly to an increase due to the caprylate. As a result the curves for the relative viscosity of the decanolic solutions *versus* the caprylate content pass through a weak minimum, or follow a more or less horizontal course for the first small additions of caprylate-water solution before rising at greater additions. As Fig. 5 shows, the former segments extend to caprylate contents of about 0.04—0.06 mole of sodium caprylate per litre of solution, after which the viscosity rises more rapidly with the soap content the higher the molar ratio of water to caprylate.

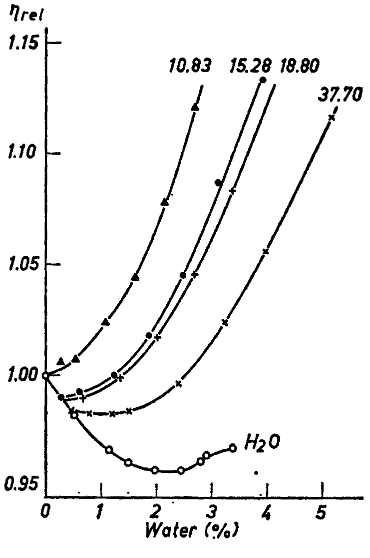

Fig. 4. The relative viscosity plotted as function of the water content. Series with constant molar ratio water/caprylate.

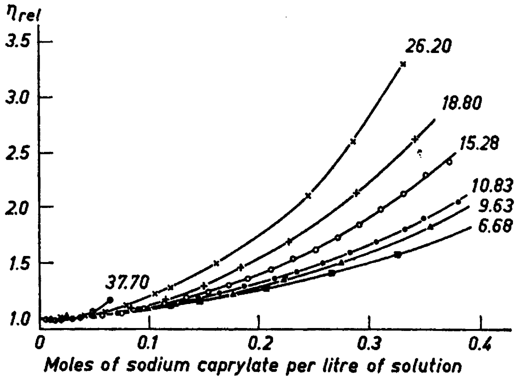

Fig. 5. The relative viscosity plotted as function of the sodium caprylate concentration. Series with constant molar ratio water/caprylate.

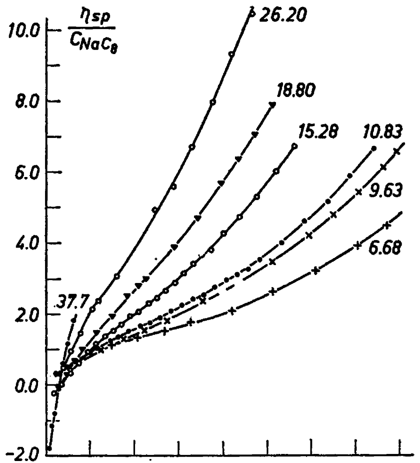

Fig. 6. The reduced viscosity plotted as a function of the sodium caprylate concentration. Series with constant molar ratio water/caprylate.

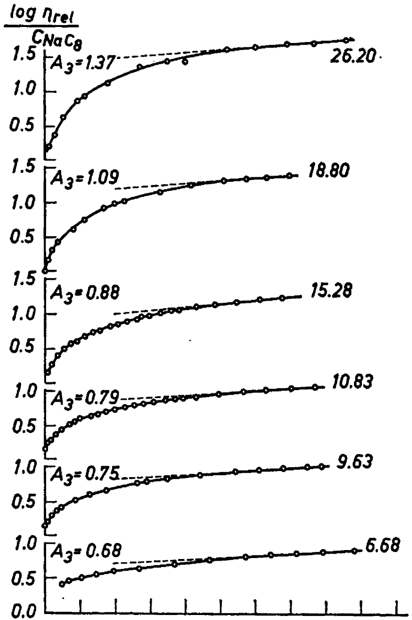

Fig. 7. Examination of the validity of the equation

$$\log \eta_{rel}/C_{NaC_8} = A_3 + Q' \log \eta_{rel}$$

in solutions of sodium caprylate and water in decanol. Series with constant molar ratio water/caprylate.

Table 2. Position of the concentration range of micelle

1	2	3	4	5
Series Molar ratio H_2O/NaC_8	Position of the range of micelle formation			
	According to		c.m.c. calculated from A_3	
	density measurements (moles of NaC_8/litre)	viscosity measurements (moles of NaC_8/litre)	(moles of NaC_8/litre)	% (NaC_8+H_2O)
6.68	0.27 – 0.45	0.19 – 0.40	0.39	13
9.63	0.22 – 0.38	0.18 – 0.38	0.35	14
10.83	0.21 – 0.35	0.13 – 0.31	0.31	13
15.28	0.15 – 0.28	0.12 – 0.30	0.23	12
18.80	0.15 – 0.25	0.11 – 0.30	0.18	11.5
26.18	0.09 – 0.20	0.11 – 0.20	0.14	11

The curves show that caprylate not only inhibits the reduction in viscosity caused by the water but that, in presence of caprylate, the water conversely promotes the increase in viscosity due to the soap. This suggests that in the presence of caprylate the eventual binding of water to the decanol observed in the decanol-water solutions is inhibited because the water is bound instead to the soap. The curves for reduced viscosity *versus* concentration, calculated with respect to the caprylate concentration of the decanolic solutions are all slightly sigmoid in form (Fig. 6); after an initial almost linear segment with a fairly rapid increase in viscosity, an intermediate range is entered in which η_{sp}/C_{NaC_8} increases more slowly with the caprylate content. Thereafter the increase is again more rapid. The intermediate range lies for the most part between about 0.10 and 0.30—0.35 moles of caprylate per litre, that is, approximately in the same range (95—83 % of decanol) for which the density measurements showed a decrease in the partial specific volume of the caprylate-water admixture. The same change in the structure that produces a reduction in the partial volume thus seems to be responsible for the retardation in the increase in viscosity.

DISCUSSION

In columns 2 and 3 in Table 2 the concentration ranges are given in which the changes in density and viscosity are indicative of a structural change. As has been mentioned previously, there is experimental evidence that these solutions give a low-angle X-ray diffraction pattern characteristic of colloidal systems, and that this occurs at and above the previously mentioned concentration range.[1,3] This would indicate that the change in structure is due to formation, and properties and composition of the micelles.

6 Uniform spherical micelles are formed above the concentration (moles of NaC_8/litre)	7 Intrinsic viscosity of micellar matter $[\eta]$ (litre/mole NaC_8)	8 Micelle volume per mole of NaC_8 (litre/mole NaC_8)	9 Approximate composition of micelles per mole of NaC_8
0.67	1.56	0.626	1 NaC_8 : 1.9 Decanol : 6.0 H_2O
0.60	1.73	0.696	1 NaC_8 : 2.0 Decanol : 8.6 H_2O
0.55	1.79	0.729	1 NaC_8 : 2.1 Decanol : 9.7 H_2O
0.42	2.00	0.814	1 NaC_8 : 2.2 Decanol : 13.8 H_2O
0.38	2.49	1.004	1 NaC_8 : 2.8 Decanol : 17.4 H_2O
0.29	3.15	1.262	1 NaC_8 : 3.5 Decanol : 24.0 H_2O

aggregation to micelles. This implies that the concentration range in question is comparable with the region of critical micelle formation in aqueous solutions of association colloids.

To calculate the intrinsic viscosity of the micellar substance $[\eta]$ it is necessary to know its concentration C_m — that is, the position of the c.m.c. This is given by the expressions

$$C_m = C_{tot} - \text{c.m.c.} \tag{1a}$$

$$\eta_{rel\ m} = \eta_{exp}/\eta_{c.m.c.} \tag{1b}$$

From this equations we have

$$(\eta_{rel\ m} - 1)/C_m = \eta_{sp\ m}/C_m = [\eta] + a_2 C_m \tag{2}$$

As the position of the c.m.c. so far is known only as a fairly wide transitional region the calculations will contain a large arbitrary factor. Another way of calculating $[\eta]$ and finding a narrower range of the c.m.c. has therefore been entered.

The intrinsic viscosity is related to the shape factor a_1 as follows:

$$[\eta] = a_1 M/1000d = a_1 \overline{V} \tag{3}$$

where M is the gramme-molecular weight of the micelle-forming substance, d is the density of the micellar matter and $\overline{V}$ its molar volume. As the micellar matter contains caprylate, water and, possibly, decanol it is necessary to take account of the relevant values of M, d, and $\overline{V}$ for this mixed matter.

On the other hand, it has been shown by one of us that the dependence of the viscosity on concentration in aqueous sodium caprylate solutions in the region above the c.m.c. where the micelles are spherical in form is represented by a formula evolved by Vand for suspensions with spherical particles,[4-6] namely

$$\log \eta_{\rm rel} = A_3/(1-Q'C) \tag{4}$$

A_3 and Q' are constants. This expression can be written

$$\log \eta_{\rm rel}/C = A_3 + Q'\log \eta_{\rm rel} \tag{5}$$

For all the series examined the curves of $\log \eta_{\rm rel}/C$ *versus* $\log \eta_{\rm rel}$ are almost linear at higher concentrations — as should be the case, if the viscosity of the L_2 solutions behaves in accordance with eqn. (4) (Fig. 7). This indicates that at fairly high caprylate concentrations the micelles of these solutions assume a uniform spherical shape. This occurs at values of $\log \eta_{\rm rel}$ above about 0.5 — that is, at caprylate concentrations above 0.29 molar in series 26.2, and 0.67 in series 6.68 (Table 2, col. 6), that is to say, above the intermediate range at which the reduced viscosity increases at a lower rate. In all the series at these caprylate concentrations the amount of caprylate and water is 21—23 %; it is thus evident that the growth and shape of the micelles is dependent on these two substances together, and not the caprylate alone.

The value of the constant A_3 was determined by extrapolation to zero concentration, where $\log \eta_{\rm rel} = 0$. A_3 has the dimension of volume, and for spherical particles it is related *via* eqn. (6) to the shape factor a_1 (2.5) and the molar volume of the micellar substance, $\overline{V}$.

$$A_3 = 2.5\ \overline{V}/2.303 \tag{6}$$

Combining eqns. (3) and (6) we have

$$[\eta] = 2.303\ A_3 \tag{7}$$

From the values of $[\eta]$ so obtained (Table 2, col. 7) and eqns. (1) and (2) more accurate values of the c.m.c. were estimated (col. 4). These values fall within the concentration ranges where the density and viscosity measurements indicate a structural change, and where micelles are supposedly formed. In respect of the sodium caprylate concentration the c.m.c. values for the various series fall with the water/caprylate ratio from 0.39 molar in series 6.68 to 0.14 in series 26.2. However, the combined amounts of caprylate and water at the c.m.c. vary only slightly from one series to another, the range being 11—14 % (Table 2, col. 5). This confirms that it is not the soap content alone that determines the micelle formation.

The volume $\overline{V}$ of sodium caprylate in eqn. (6) is the rigid volume of the micellar matter, including any water and decanol that is too firmly held to participate in the viscous shearing process. The values of $\overline{V}$ (calculated from A_3) are given in Table 2, col. 8. Provided that all the water is contained in the micelles it is possible with a knowledge of the partial specific volume of the sodium caprylate-water matter to calculate the volume of these two components in the micelles per mole of sodium caprylate. As this volume is considerably smaller than $\overline{V}$, the micelles may also contain decanol. From the partial specific volume of decanol, namely 1.207 cm^3/g, at the relevant concentrations, it is possible to estimate the maximum amount of decanol per mole of sodium caprylate that is required to account for the difference in volume. For the four series with fairly low water contents the calculation gives a decanol/caprylate ratio in the micelles of about 2 (rising from 1.90 to 2.20 with increasing water content). For the two series with most water, slightly higher decanol contents are obtained, namely 2.8 and 3.5 moles of decanol, respectively (Table 2, col. 9). In the calculation of these values the amount of water that is dissolved in the free decanol has been taken into account (about 1 mole of water to 3.1 moles of decanol).

It is thus found that the micelles contain not only caprylate and water but also decanol as in fact would be expected. The derived molar ratios would appear to be quite reasonable; in any case they provide a rough impression of the composition of the micelles in the caprylate-decanol-water solutions in question. If the composition of the micelles remains unchanged up to the lower border of region L_2, about one half of the decanol would be present there, too, in the unbound form as intermicellar solution. The measurements were not, however, extended to this border, and no conclusions regarding the composition and shape of the micelles just within the border can therefore be drawn.

To summarize, the L_2 solution in the sodium caprylate-decanol-water system resemble the L_1 solution of the system in that both form micelles and that these begin to form in a more or less well defined critical concentration range. The micelles in the decanolic solutions (L_2), as in the aqueous caprylate solutions containing decanol in solubilized form (L_1), are composed of sodium caprylate, decanol, and water. In the aqueous solutions the c.m.c. is displaced towards lower caprylate concentrations as the decanol content is increased; in the decanolic solutions it is displaced in the same direction, as the water content is increased. An interesting difference between the two types of solutions is that whereas in aqueous solutions the formation of micelles leads to a marked *increase* in the partial specific volume of the micelle-forming matter, in the decanolic solutions it leads to a *reduction*.

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