

## Two Types of Neat Soap in Ternary Systems

PER EKWALL, LEO MANDELL and KRISTER FONTELL

*Laboratory for Surface Chemistry (Ytkemiska Laboratoriet), the Royal Swedish Academy of Engineering Sciences, Stockholm, Sweden*

In ternary systems of water and two amphiphilic compounds two types of mesomorphous neat soap occur, which differ in respect of water uptake, a "constant expanding" type and a "variably expanding" type. So far, the first mentioned type has been observed chiefly in aqueous systems with two non-ionic amphiphilic substances, while the second type has been found in aqueous systems where one of the amphiphilic substances is of the ionic type. When in the latter systems the ratio between the non-ionic and the ionic component increases above a certain value the neat soap changes to a constant expanding one. At the same time, however, the capacity of the mesophase to incorporate water increases considerably.

It has been proposed by McBain *et al.*<sup>2</sup> and confirmed by Luzzati *et al.*<sup>8</sup> that the liquid crystalline neat soap that occurs in most *binary* systems of alkali soaps and water at fairly high soap concentrations within a wide range of temperature has a lamellar structure in which amphiphile and water layer alternate. The former are composed of double layers of ionized soap molecules oriented with the hydrophilic groups facing outwards towards the water and the paraffin hydrocarbon chains facing inwards; the interior of the double layers is in a semi-liquid state. A lamellar structure of this type is found in the corresponding mesophase in binary systems of water and many other soap-like substances of anion-active, cation-active, and non-ionic types. It also occurs in many *ternary* systems which contain, in addition to water and the soap-like amphiphile, another amphiphilic substance — for instance, a fatty acid, alcohol, aldehyde, or ester — and often extend over large concentration ranges up to high water contents. This is particularly the case when the added amphiphile is an alkanol or a fatty acid, with a long enough hydrocarbon chain. For instance, the addition of decanol displaces the formation of mesomorphous neat soap from a water content of 30 % in the binary potassium-oleate system to about 87 % in the ternary potassium oleate-decanol-water system (Fig. 1 a), and from about 33 % in the binary octylammonium chloride-water system to about 83 % in the ternary octylammonium chloride-decanol-water system (Fig. 1 b). In many cases in which the neat soap

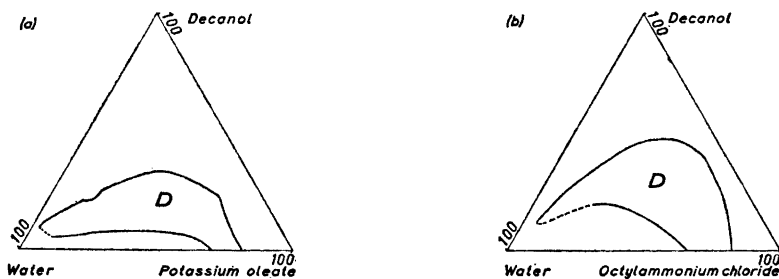


Fig. 1. Phase diagrams showing the location of the region D with lamellar mesophase of the neat soap type in ternary systems.

- (a) Potassium oleate—decanol—water 20°C.  
 (b) Octylammoniumchloride—decanol—water 20°C.

structure at the temperature in question does not occur in the binary system it does so in the three-component systems — that is to say, in the presence of an added foreign amphiphilic substance (Figs. 2 a—f and 3 a). There are

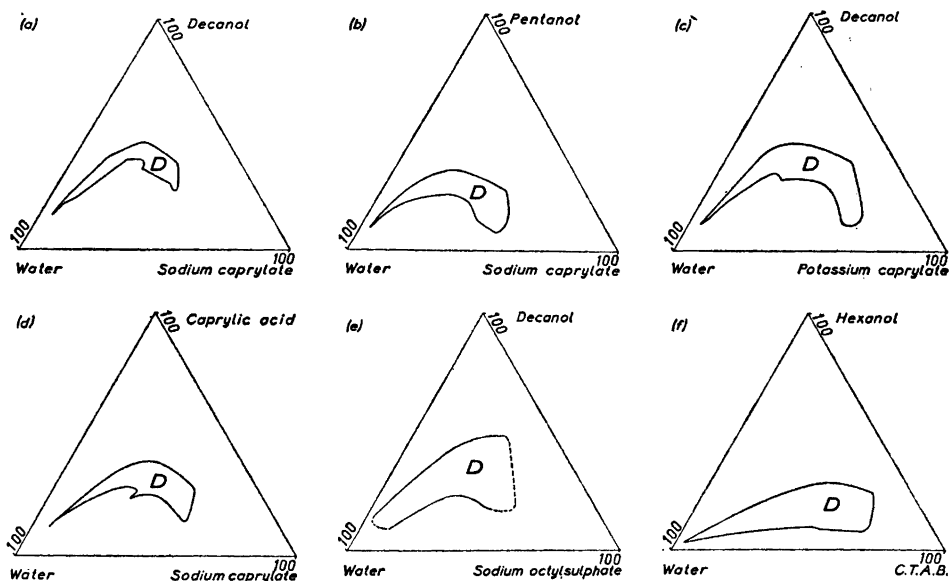


Fig. 2. Phase diagrams showing the location of the region D with lamellar mesophase of the neat soap type in ternary systems.

- (a) Sodium caprylate—decanol—water 20°C.  
 (b) Sodium caprylate—pentanol—water 20°C.  
 (c) Potassium caprylate—decanol—water 20°C.  
 (d) Sodium caprylate—caprylic acid—water 20°C.  
 (e) Sodium octylsulphate—decanol—water 20°C.  
 (f) Cetyl trimethylammonium bromide—hexanol—water 25°C.

also cases in which the added amphiphile does not appreciably influence the extent of the neat soap region in the direction of a higher water content (Figs. 3 b, c). (In all these triangular diagrams only the region of existence of the neat soap phase, denoted D, is given; complete phase equilibria diagrams have been or will be published elsewhere.)

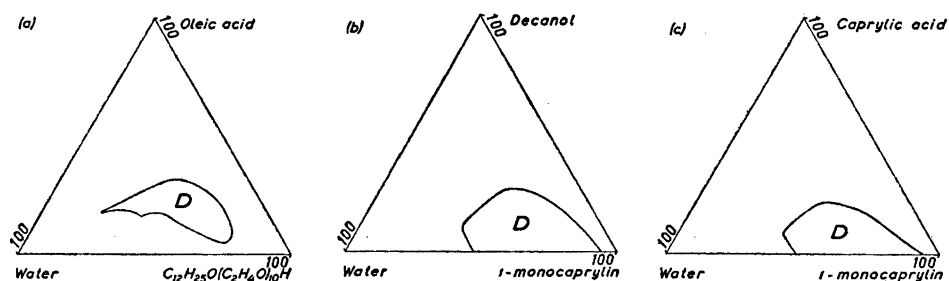


Fig. 3. Phase diagrams showing the location of the region D with lamellar mesophase of the neat soap type in ternary systems.

- (a) Lauryl deca-ethylene glycol ether—oleic acid—water 20°C.  
 (b) 1-monocaprylin—decanol—water 20°C.  
 (c) 1-monocaprylin—caprylic acid—water 20°C.

In all the cases considered the mesophase in question is characterized by a Bragg spacing ratio of 1:1/2:1/3, as is seen from the X-ray diffraction findings in Table 1, which also includes the thickness of the amphiphilic and water layers and the area per hydrophilic group at the boundary between these layers; the calculations performed on the assumption of coherent amphiphilic layers show that in all cases these consist of double molecular layers. The diffuse reflection in the wide-angle region corresponding to a Bragg spacing of about 4.5 Å is indicative of a semi-liquid state of the interior of the amphiphile layers. We thus have the consistent occurrence of a lamellar structure similar to that in neat soap. Moreover all these lamellar mesophases display the same typical, mosaic texture — No. 122.1 in Rosevear's system.<sup>1</sup>

Closer examination, however, discloses in the ternary systems two types of neat soap, which differ in respect of water uptake. In some systems the Bragg spacing increases with water content at different rates in different parts of its region of existence, whereas in other systems the rate of growth is constant throughout the region. In the binary potassium oleate—water system, for instance, (Fig. 1a) the curve  $\log d$  versus  $\log (1/v_a)$ , where  $d$  is the Bragg spacing and  $v_a$  the volume fraction of amphiphilic substance, has the slope zero, but when decanol is added the slope increases and approaches 1 when the decanol to oleate ratio exceeds a value of about 2. In the monocaprylin—decanol—water system, on the other hand, (Fig. 3b) the curve has a constant slope of about 1 throughout the whole region of existence of the neat soap.

A different behaviour of neat soap in respect of water uptake was observed in the binary systems by McBain, who noted the existence of an "expanding"

Table 1. X-Ray diffraction data of the lamellar mesophase in some binary and ternary systems.

Soap	Composition (%)		Molar ratio: Add. amphiphile/soap	Bragg spacing Å			Volume fraction of amphiphile $v_a$	Dimensions of the amphiphile layers			Slope of the curve $\log d$ vs. $\log(1/v_a)$
	Added amphiphile	Water		$d_1$	$d_2$	$d_3$		$d_a$ (Å)	$d_w$ (Å)	$S$ (Å)	
System potassium caprylate—decanol—water. 20°C.											
55.76	23.89	20.35	0.493	27.5	13.8	9.1	0.795	21.8	5.7	25.9	}0.21
51.26	21.95	26.79	0.493	28.0	14.0	—	0.730	20.4	7.6	27.6	
44.69	36.58	18.73	0.942	29.5	14.8	9.8	0.815	25.0	4.5	22.9	}0.49
39.75	32.54	27.71	0.943	30.9	15.4	—	0.726	22.4	8.5	25.5	
37.02	30.30	32.68	0.943	32.4	—	—	0.676	21.9	10.5	26.2	}1.04
18.80	43.86	37.34	2.69	37.0	18.6	—	0.646	23.9	13.1	24.9	
13.53	31.56	54.91	2.69	51.5	25.7	—	0.472	24.3	27.2	24.5	}1.04
6.02	14.08	79.90	2.69	124	—	—	0.214	26.5	97.5	22.4	
System potassium caprate—octanol—water. 20°C.											
64.27	7.74	28.59	0.180	28.8	14.4	—	0.721	20.8	8.0	30.6	}0.22
62.10	6.90	31.00	0.180	29.0	14.5	9.7	0.697	20.2	8.8	31.5	
59.12	14.78	26.10	0.404	29.7	14.8	—	0.740	21.9	7.7	27.7	}0.29
52.28	13.08	34.63	0.404	30.7	—	—	9.655	22.1	10.6	30.3	
53.84	23.07	23.09	0.692	30.4	15.2	10.1	0.769	23.4	7.0	25.0	}0.43
45.15	19.64	34.61	0.693	32.5	16.3	8.1	0.654	21.3	11.2	27.7	
41.35	17.71	40.94	0.692	34.0	16.9	—	0.591	20.1	13.9	29.1	}0.86
42.84	28.56	28.60	1.077	31.3	—	10.4	0.718	22.5	8.8	25.3	
29.09	19.46	51.45	1.080	43.5	21.7	—	0.490	21.3	22.2	26.7	}1.00
25.00	37.49	37.51	2.42	33.7	16.7	—	0.640	21.6	12.2	25.2	
20.72	31.08	48.20	2.42	40.1	20.1	—	0.534	21.4	18.7	25.5	}1.00
15.42	23.14	61.44	2.42	53.1	26.5	—	0.401	21.3	31.8	25.6	
8.60	12.90	78.50	2.42	94.6	46.7	—	0.226	21.4	73.2	25.5	}1.00
System potassium oleate—decanol—water. 20°C.											
81.0	—	19.0	—	38.1	—	—	0.810	30.9	7.3	34.1	}0
74.9	—	25.1	—	38.0	18.9	12.5	0.749	28.5	9.5	36.9	
75.0	—	25.0	—	37.8	—	—	0.750	28.3	9.5	37.2	
74.0	—	26.0	—	38.2	—	—	0.740	28.3	9.9	37.2	
71.5	—	28.5	—	37.6	—	—	0.715	26.9	10.7	39.2	
69.20	7.77	23.3	0.228	38.8	19.3	12.9	0.773	30.0	8.8	32.4	}0.44
60.16	6.68	33.16	0.225	41.4	20.6	13.8	0.672	27.8	13.6	35.0	
56.81	24.31	18.88	0.867	39.8	19.9	13.1	0.817	32.5	7.3	26.1	}0.93
52.00	22.30	25.70	0.867	40.4	20.0	13.4	0.751	30.0	10.4	28.2	
41.19	17.68	41.13	0.869	49.0	24.5	16.2	0.598	29.3	19.7	28.9	
28.17	12.06	59.77	0.867	69.4	34.5	23.3	0.412	28.6	40.8	29.6	
32.01	31.97	36.02	2.02	44.1	22.0	—	0.657	29.0	15.1	26.2	}0.98
30.00	30.00	40.00	2.03	46.8	23.5	—	0.617	28.9	17.9	26.1	
25.00	25.00	50.00	2.03	54.5	27.2	—	0.518	28.2	26.3	26.8	
23.09	23.09	53.86	2.02	59.8	29.9	—	0.480	28.7	31.1	26.4	
14.40	14.34	71.26	2.02	93.5	46.8	31.2	0.302	28.2	65.3	26.8	

Table 1. Continued.

System sodium caprylate—pentanol—water. 20°C											
48.90	18.19	32.91	0.701	24.6	12.2	8.0	0.666	16.5	8.3	26.4	}0.27
45.19	16.81	38.00	0.701	25.4	12.8	—	0.615	15.1	9.5	28.8	
40.82	15.18	44.00	0.701	25.8	12.9	—	0.554	14.3	11.5	30.4	
29.89	31.11	39.00	1.963	24.8	12.4	—	0.622	15.4	9.4	25.9	}0.90
25.48	26.52	48.00	1.963	28.9	14.4	—	0.533	15.4	13.5	25.9	
23.52	24.48	52.00	1.963	29.8	14.9	—	0.493	14.7	15.1	27.2	
System sodium caprylate—caprylic acid—water. 20°C.											
50.18	22.54	27.28	0.518	26.6	—	—	0.720	19.2	7.4	25.3	}0.38
47.64	21.49	30.25	0.518	27.0	13.5	—	0.690	18.6	8.4	27.4	
46.78	20.93	32.49	0.518	27.4	13.6	—	0.677	18.5	8.9	27.6	
38.16	35.22	26.62	1.064	27.0	13.3	—	0.739	20.0	7.0	25.8	}0.75
37.48	34.61	27.91	1.064	27.4	13.7	—	0.723	19.8	7.6	25.7	
35.20	32.49	32.31	1.064	28.3	14.1	—	0.676	19.1	9.2	26.4	
32.90	30.37	36.73	1.064	29.7	14.9	—	0.630	18.7	11.0	27.0	
31.50	29.07	39.43	1.064	31.1	15.6	—	0.605	18.8	12.3	27.4	
30.70	28.25	40.95	1.064	32.2	16.1	—	0.591	19.0	13.2	26.6	
20.87	35.84	43.29	1.98	34.4	17.2	—	0.571	19.6	14.8	25.9	}1.0
17.84	30.64	51.52	1.98	40.3	20.0	—	0.487	19.6	20.7	25.8	
15.97	27.43	56.60	1.98	44.5	22.2	—	0.434	19.3	25.2	26.1	
13.27	22.78	63.95	1.98	55.1	27.6	—	0.363	20.0	25.1	25.3	
System sodium octylsulphate—decanol—water. 20°C.											
44.40	29.60	26.00	0.977	32.6	16.2	—	—	24.2	8.4	26.2	}0.52
36.00	24.00	40.00	0.977	36.3	18.0	—	—	21.8	14.5	29.8	
20.00	33.30	46.70	2.44	47.4	23.6	—	—	25.2	22.2	23.7	}0.92
13.10	21.92	64.98	2.45	71.7	35.8	24.0	—	25.1	51.6	23.8	
8.70	13.00	78.30	2.19	108.7	53.5	—	—	23.6	85.1	25.5	
System octylammonium chloride—decanol—water. 20°C.											
81.78	—	18.22	—	23.1	—	—	0.832	19.2	3.9	30.9	}0.40
74.90	—	25.10	—	24.0	—	—	0.766	18.4	5.6	32.3	
68.11	—	31.89	—	24.8	—	—	0.701	17.4	7.4	34.1	
66.97	21.06	11.97	0.329	24.6	—	—	0.890	21.9	2.7	27.4	}0.69
61.84	19.47	18.69	0.330	25.6	—	—	0.829	21.2	4.4	28.3	
50.00	15.72	34.28	0.329	29.6	—	—	0.681	20.2	9.4	29.7	
34.40	45.60	20.00	1.388	28.8	—	—	0.821	23.7	5.1	25.8	}1.06
27.80	36.83	35.37	1.387	34.9	—	—	0.676	23.6	11.3	25.9	
19.19	25.45	55.36	1.388	50.2	25.1	—	0.478	24.1	26.1	25.4	
12.97	17.18	69.85	1.386	76.2	38.6	—	0.329	25.1	51.5	24.4	
System cetyltrimethylammonium bromide—hexanol—water. 25°C.											
92	—	8	—	36	—	—	—	33	3	40	}0
86	—	14	—	36	—	—	—	32	4	43	
65.83	12.56	21.60	0.681	38.4	19.3	13.0	0.788	30.3	8.1	29.0	}0.80
59.50	11.34	29.16	0.680	41.5	20.7	13.7	0.714	29.6	11.9	29.7	
53.15	10.08	36.77	0.677	45.4	22.7	—	0.637	28.9	16.5	30.5	
59.24	17.94	22.82	1.08	37.0	18.5	12.4	0.778	28.8	8.2	27.5	}1.03
48.01	14.57	37.42	1.08	45.4	22.7	—	0.635	28.8	16.6	27.4	
33.38	10.11	56.51	1.08	66.0	32.8	—	0.444	29.5	36.5	26.7	
39.71	26.48	33.81	2.38	38.1	19.1	—	0.678	25.8	12.3	25.1	
29.58	19.72	50.70	2.38	51.0	25.6	—	0.512	26.2	24.8	24.7	}1.05
18.37	12.25	69.38	2.38	84.6	42.4	—	0.322	27.3	57.3	23.8	

Table 1. Continued.

System monocaprylin—decanol—water. 20°C.											
90.00	—	10.00		25.6	12.8	—	0.897	23.0	2.6	29.7	} 1.00
80.00	—	20.00		29.0	14.4	—	0.795	23.1	5.9	30.5	
65.00	—	35.00		35.6	17.8	—	0.643	22.9	12.7	30.8	
50.00	—	50.00		47.5	23.7	—	0.492	23.4	24.1	30.1	
68.00	17.00	15.00	0.345	28.6	14.2	—	0.851	24.3	4.3	27.7	} 1.00
52.00	13.00	35.00	0.345	36.8	18.4	—	0.652	24.0	12.8	28.1	
44.00	11.00	45.00	0.345	44.4	22.1	—	0.553	24.4	19.7	27.7	
System monocaprylin—caprylic acid—water. 20°C.											
65.60	14.40	20.00	0.332	29.2	14.6	—	0.797	23.3	5.9	27.9	} 0.91
59.04	12.96	28.00	0.332	32.2	16.0	—	0.716	23.0	9.2	28.3	
52.48	11.52	36.00	0.332	36.4	18.2	—	0.635	23.1	13.3	28.3	
45.10	9.90	45.00	0.332	40.9	20.3	—	0.545	22.3	18.6	29.2	
System lauryl deca-ethyleneglycol ether—oleic acid—water. 20°C.											
71.86	10.55	17.59	0.326	47.1	23.6	—	0.829	39.0	8.1	45.9	} 0.80
69.39	10.08	20.53	0.322	47.6	23.7	—	0.800	38.1	9.5	47.0	
66.68	9.69	23.63	0.322	49.4	24.7	—	0.770	38.0	11.4	47.1	
64.60	9.39	26.01	0.322	50.6	25.2	—	0.746	37.7	12.9	47.5	
66.12	16.87	17.01	0.656	47.1	23.6	—	0.833	39.2	7.9	42.6	} 0.92
62.82	15.90	21.28	0.562	50.1	25.0	—	0.791	39.6	10.5	42.2	
56.55	14.31	29.14	0.561	55.1	27.1	—	0.713	39.3	15.8	42.6	
56.12	24.05	19.83	0.952	49.4	24.7	—	0.805	39.8	9.6	38.7	} 0.89
49.95	21.40	28.65	0.951	55.6	27.7	—	0.714	39.7	15.9	38.9	
43.45	18.62	51.93	0.951	61.7	30.7	—	0.626	38.6	23.1	39.9	
45.05	30.13	24.82	1.485	53.0	26.5	—	0.754	40.0	13.0	35.5	} 0.92
39.00	26.08	34.92	1.485	61.6	30.8	—	0.653	40.2	21.4	35.3	
33.01	22.07	44.92	1.486	70.3	34.7	23.3	0.554	39.0	31.3	36.4	
29.96	20.04	50.00	1.484	77.6	38.8	—	0.507	39.3	38.3	36.0	

and a “non-expanding” type.<sup>2,3</sup> Our investigations show that McBain’s “non-expanding” neat soap of the binary systems changes to a “variably expanding” neat soap when an amphiphilic compound such as an alkanol or fatty acid is added.

We have encountered neat soap of the variably expanding type in ternary systems containing a fatty acid potassium or sodium soap, sodium octyl sulphate, octylammonium chloride or cetyltrimethylammonium-bromide (Figs. 1 a, b; 2 a—f)—that is to say in systems of anionic and cationic association colloids. We have so far encountered neat soap of the constant expanding type in the monocaprylin and lauryl deca-ethyleneglycol ether systems, *i.e.* systems with a non-ionic amphiphilic substance. It thus seems as if the presence of an ionic association colloid would be a necessary condition for the formation of the variably expanding neat soap type. Support for this view is found in the literature concerning binary systems, for most systems of amphiphiles with an ionized hydrophilic group appear to give a non-expanding neat soap or at any rate one with a slope much less than 1 for the log-log curve;<sup>2,4-9</sup> most binary systems of non-ionic amphiphiles and water on the other hand, seem to give neat soap of the expanding type with a slope of about 1 for

the log-log curve (e.g. monolaurin, diethyleneglycol monolaurate, hexanolamine oleate and triethanolamine laurate),<sup>5-7</sup> The only exception we have found is ionized dihexylsulfosuccinate (Aerosol MA) with the slope 0.9 and unionized *p*-nonylphenolpolyethyleneglycol ether (Arkopal 9) with a slope of about 0.6.<sup>8,9</sup> The experimental material, however, is not large enough to resolve this point conclusively.

Within the range of variable expansion in systems of ionic amphiphiles the thickness of the amphiphile layer decreases and the area per hydrophilic group increases slightly with the water content. While these variations indicate that the water penetrates the amphiphile layers, they do not explain the small slope of the log-log curves. Much of the water seems to be incorporated in the space between the hydrophilic groups. Only in the range with the slope 1 does the uptake of water result in typical one-dimensional swelling, according to the expression  $d = d_a/v_a$  or  $\log d = \log d_a + \log (1/v_a)$ , where  $d_a$  is the constant thickness of the amphiphile layer; here all the water thus seems to be incorporated in the water layers, which alternate with the amphiphile layers. In systems of most non-ionic amphiphiles the neat soap shows a real one-dimensional swelling throughout the region of its existence.

In the systems of ionic amphiphiles the deviations from the constant expanding type thus disappear when enough non-ionized amphiphilic substance has been incorporated in the amphiphile layers between the ionized molecules. However, there is at the same time a pronounced increase in the capacity of the neat soap of many of these systems to incorporate water. This is shown by the curves for the sodium caprylate—decanol—water system (Fig. 4). Curve *a* shows how the slope of the curve  $\log d$  versus  $\log (1/v_a)$  changes with the molar ratio of decanol to caprylate, approaching unity. Curve *b* shows how the capacity of the mesophase for incorporating water increases at the above molar ratio and then rises above the maximum water content that can be bound to the hydrophilic groups.<sup>10,11</sup> It would seem that in the increasing

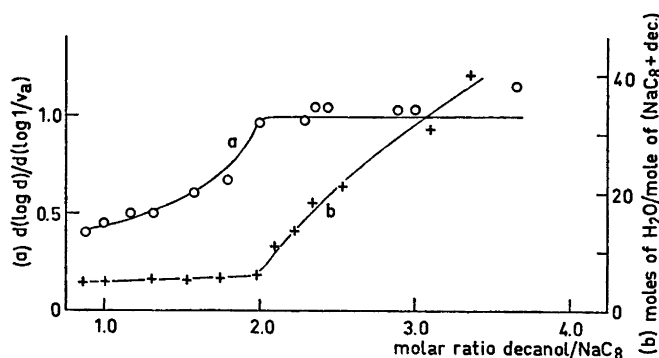


Fig. 4. Some properties of the mesophase in region D of the sodium caprylate—decanol—water system at various decanol-to-caprylate molar ratios.

- (a) Slope of the curve  $\log d$  vs.  $\log (1/v_a)$ .  
 (b) The maximum water content of the mesophase.

tendency for liberation of sodium ions of caprylate from the amphiphile layer — thereby permitting uptake of water through a Donnan distribution — we have the explanation of the increasing capacity of the neat soap phase to incorporate water in excess of the amount that can be bound by the hydrophilic groups.<sup>11</sup> Whether there is an analogous phenomenon in the case of neat soap of non-ionic amphiphiles is difficult to decide on the basis of the present experimental material; in any case there is no such phenomenon in the monocaprylin systems.

The two types of neat soap thus display considerable differences; they might be appropriately called the “variably expanding type” and the “constant expanding type”.

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