Lyotropic Mesophases with 'Normal' and 'Reversed' Two-dimensional Hexagonal Structure

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Besides the neat soap the middle soap is the commonest lyotropic mesomorphous phase in binary alkali soap—water systems. This mesophase occurs also in numerous systems where the fatty acid soap is replaced by another association colloid of the anionic, cationic, or non-ionic types. As Luzzati and his co-workers have shown middle soap has a two-dimensional hexagonal structure, with long, parallel, hexagonally disposed rod-shaped aggregates consisting of amphiphile molecules oriented with the hydrocarbon parts facing towards the centre and the hydrophilic groups

towards the surface.[1,2] The state in the rod score which consists of hydrocarbon chain, may be described as semi-liquid. The water of the mesophase is considered to form a coherent layer between the amphiphile aggregates.

This structure is also encountered in a large number of ternary systems that, apart from the soap-like amphiphilic substance and water, also contain an amphiphilic or lipophilic component such as a fatty acid, alcohol, aldehyde, ester, nitrile, or hydrocarbon.[3-7] In these cases, however, the middle soap also contains the foreign component; in most systems it is incorporated — together with the association colloid — in the amphiphile aggregates sometimes in large amounts.

The binary systems middle soap occurs in the concentration region between the micellar aqueous solution and the mesomorphous neat soap. In the ternary systems the region of existence of this mesophase extends from the mentioned region on the soap—water axis to a more or less high concentration of the foreign component. If this consist of a markedly lipophilic substance, a hydrocarbon or chlorinated hydrocarbon, it usually does not exceed a
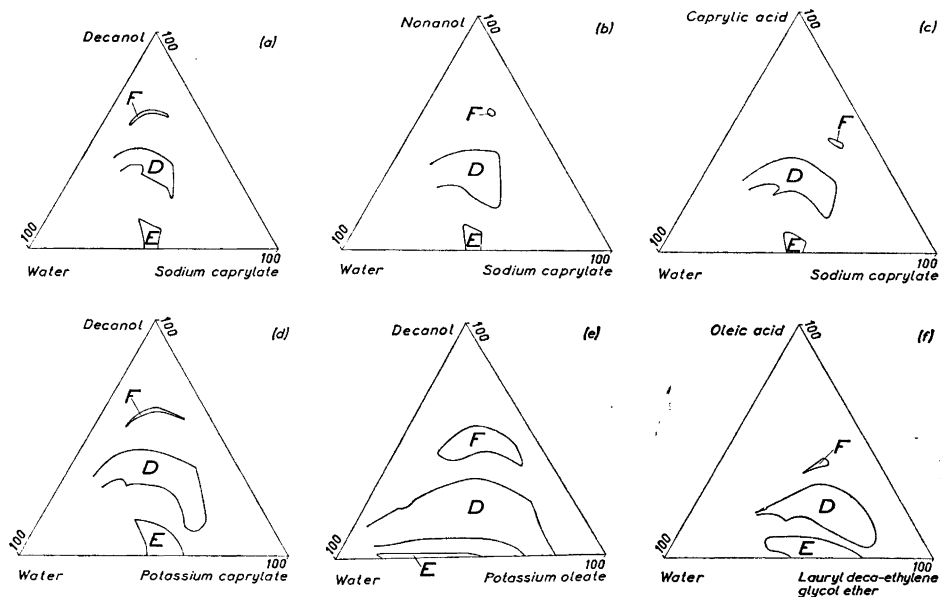

Fig. 1. a—f. Phase diagrams showing the location of the regions E and F with two-dimensional hexagonal mesophases in various ternary systems.

Table 1. X-Ray findings for two-dimensional hexagonal mesophases type E and F.

Meso-phase	Composition (%) Added Soap amphiphile Water			Molar ratio Add. amphiphile / Soap	Volume fraction of amphiph. v_a	Bragg specing Å d_1	d_2	d_3	Lattice parameter d_p	Dimensions of the aggregates d_c (Å)	$d_{w,a}$ (Å)	S (Å²)
	System potassium caprylate-decanol-water. 20°C.									d_w		
E	57.01	—	42.99	—	0.550	25.0	14.5	12.7	28.9	22.5	6.4	47.7
	53.50	—	46.50	—	0.515	25.7	—	—	29.7	22.4	7.3	48.1
	49.24	—	50.76	—	0.472	26.2	15.1	13.1	30.3	21.8	8.5	49.2
	52.53	7.85	39.62	0.172	0.588	29.4	—	14.7	34.0	27.3	6.7	39.8
	49.53	7.41	43.06	0.172	0.552	29.4	—	14.5	34.0	26.5	7.5	41.0
	45.85	6.86	47.29	0.172	0.510	29.7	17.1	14.8	34.3	25.7	8.6	42.2
										d_a		
F	19.99	62.46	17.55	3.60	0.839	29.4	—	—	34.0	14.3	19.7	25
	13.88	60.35	25.77	5.01	0.765	35.3	20.0	18.0	40.8	20.8	20.0	29
	System potassium oleate-decanol-water. 20°C									d_w		
E	50.10	—	49.90	—	0.501	48.8	28.2	24.6	56.4	41.7	14.7	51.0
	40.10	—	59.90	—	0.401	53.0	30.8	—	61.2	40.7	20.5	52.2
	30.00	—	70.00	—	0.300	61.1	35.3	30.7	70.6	40.6	30.0	52.4
	20.00	—	80.00	—	0.200	74.5	43.5	37.3	85.5	40.4	45.1	52.6
										d_a		
F	44.72	44.73	10.55	2.03	0.904	30.8	17 9	—	35.6	11.6	24.0	21
	42.96	42.97	14.07	2.03	0.872	33.0	19.7	—	38.1	14.3	23.8	22
	28.76	53.44	17.80	3.76	0.843	33.2	—	16.7	38.3	16.0	22.3	29
	23.85	44.31	31.84	3.76	0.713	44.4	25.7	22.3	51.3	28.8	22.5	27
	System sodium caprylate-caprylic acid-water. 20°C.									d_w		
E	49.54	2.61	47.85	0.061	0.506	26.7	15.4	13.3	30.8	23.0	7.8	43.4
	47.56	2.50	49.94	0.061	0.486	26.8	—	—	31.0	22.6	8.3	44.4
	44.92	2.35	52.73	0.060	0.458	26.3	15.0	—	30.3	21.5	8.8	46.5
	48.18	5.35	46.47	0.128	0.522	27.9	16.2	14.0	32.2	24.5	7.8	41.0
	46.26	5.14	48.60	0.128	0.501	27.8	16.0	—	32.1	23.8	8.2	42.1
	43.75	4.89	51.36	0.129	0.474	28.6	—	—	33.0	23.9	9.1	42.1
										d_a		
F	41.65	46.04	12.31	1.27	0.894	23.3	13.5	11.6	26.9	9.3	17.6	20
	41.23	45.56	13.21	1.27	0.884	23.7	13.7	—	27.4	9.8	17.6	21
	40.86	45.17	13.97	1.27	0.877	22.6	13.1	11.2	26.1	9.6	16.5	23
	System lauryldecaethylene glycolether-oleic acid-water. 20°C.									d_w		
E	71.01	—	28.99	—	0.704	46.8	26.8	—	54.1	47.6	6.4	83.8
	62.52	—	37.48	—	0.619	49.0	28.1	—	56.6	46.8	9.8	85.8
	55.30	—	44.70	—	0.547	50.6	29.1	24.7	58.4	45.3	13.1	88.5
	48.99	—	51.01	—	0.484	51.4	30.1	25.7	59.4	43.4	16.0	92.8
	50.39	8.90	40.71	0.39	0.591	56.9	32.8	29.0	65.7	53.0	12.7	66.1
	45.10	7.96	46.94	0.39	0.529	57.7	33.4	29.7	66.6	50.9	15.7	69.0
	38.31	6.77	54.92	0.39	0.449	61.7	35.3	30.6	71.3	50.1	21.2	77.0
										d_a		
F	36.48	40.00	23.52	2.43	0.780	58.7	33.5	29.2	67.8	33.4	34.4	39
	34.93	38.30	26.77	2.43	0.749	60.5	34.5	30.0	69.9	36.8	33.1	42

few per cent of the middle phase, while in the case of amphiphilic compounds the content may rise to quite a high level; the highest contents found so far (20—40 %) have been for amphiphilic substances with quite weak hydrophilic groups, e.g. a nitrile or ester group.

A mesophase with a two-dimensional hexagonal structure has, however, been observed also in a part of ternary systems quite different from that where the ordinary middle soap structure occurs. The first system in which it was found was probably sodium caprylate—decanol—water at 20°C (1959).[3,4] The experimental findings consistently indicated a reversed hexagonal structure with long, parallel, rod-shaped aggregates in hexagonal array, and consisting of a water core surrounded by a layer of amphiphile molecules oriented with the hydrophilic groups facing the water and the hydrocarbon chains facing outwards. Between the rod-shaped aggregates there is thus a continuous layer of hydrocarbon chains in semi-liquid state.[4,6,7] Later on this structure has been found in quite a large number of aqueous ternary systems containing an association colloid of the anionic or non-ionic type, and another amphiphilic component of the alcohol or fatty acid type.[5,6] The X-ray diffraction findings given in Table 1 for a number of ternary systems where both these mesophases occur, confirm the two-dimensional hexagonal symmetry; on the basis of these data the values for the "normal" and the "reversed" structures have been calculated.

The regions of existence of the two two-dimensional hexagonal mesophases in a number of systems are shown in Fig. 1a—f (besides the here represented systems the "reversed" hexagonal structure was observed also in the sodium caprate and sodium nonylate systems with decanol and water). The regions for the ordinary middle soap structure are labelled E, and those for the reversed hexagonal structure, F. In all cases these regions are distinguished by

an area with a homogeneous lamellar mesophase (labelled D), as well as by the two- and three-phase zones. (Complete phase equilibria diagrams have been or will be published in another connection.) The water content of the reversed hexagonal mesophases is lower than that for the lamellar phases. In most systems studied so far the regions for the reversed structure are of quite small extent — less than those for ordinary middle soap. It would seem as if the existence of the reversed structure is limited to certain molar ratios between the components, especially that between water and the amphiphilic substance. The temperature stability too, differs distinctly for the two hexagonal mesophase types; while the normal middle-soap structure can exist to quite high temperatures, the reversed structure breaks down already at 30—60°C in the systems studied so far.

It would seem appropriate to reserve the term "middle soap structure" for the normal hexagonal rod structure (type E) and to call the other one the "reversed hexagonal structure" (type F).

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