Lyotropic Mesophases with "Normal" and "Reversed" Two-dimensional Tetragonal Structure

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It has been demonstrated that there occurs in the sodium caprylate-decanol-water system at 20°C a mesophase with linear symmetry (referred to as type C) that differs in various respects from the lamellar mesophase with a neat-soap structure (type D).[1,2] In the former type the uptake of water is accompanied by marked two-dimensional swelling — that is to say, the increase in the Bragg spacing conforms to the expressions

$$d = d_0/\sqrt{v_a}; \; \log d = \log d_0 + \tfrac{1}{2} \log (1/v_a)$$

where d is the Bragg spacing in Ångström units, d_0 is the constant thickness of the amphiphilic aggregates, and v_a the volume fraction of amphiphilic substance. Analysis of the experimental findings brought to light a structure composed of long, parallel, rod-shaped particles in tetragonal array, completely surrounded by water layers of equal thickness; in cross-section the rods appeared to be more or less square, and they were apparently composed of alternating double groups of amphiphile molecules with the molecules in one group intersecting those of the adjacent group at right angles; all the molecules were oriented with the hydrophilic groups facing towards the water.[3-5]

Later on the presence of a mesophase with similar properties and structure was found in several other ternary systems.[6-9] It appears to be particularly common in sodium soap—alkanol—water systems; besides in the above mentioned decanol system it has been encountered also in sodium caprylate—water systems containing nonanol, octanol, heptanol and hexanol. It has also been found in the potassium caprylate—water, sodium caprylate—capryclic acid—water, octylammonium chloride—decanol—water, and lauryldecaethyleneglycolether—oleic acid—water systems. The position of the region of the existence of the phase (denoted C)
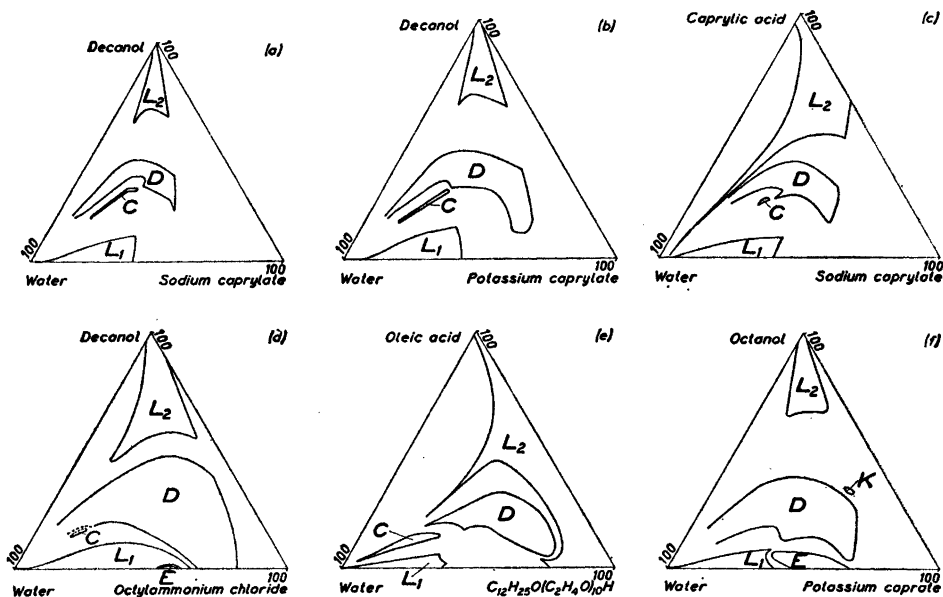

Fig. 1 a—f. Phase diagrams showing the location of regions C and K with two-dimensional tetragonal mesophases in various ternary systems.

Table 1. X-ray findings for mesophases type C and type K.

Meso-phase	Composition			Molar ratio Add.amphiphile/Soap	Volume fraction of amphiph. v_a	Bragg spacing (Å)				Dimensions of the aggregates			Slope of the curve log d vs. log $1/v_a$
	Soap	Added amphiphile	Water			d_1	d_2	d_3	d_4	d_o (Å)	$d_{w,a}$ (Å)	S (Å²)	
	System sodium caprylate- decanol-water. 20°C d_w												
C	22.1	32.9	45.0	1.57	0.566	38.4	19.2			27.6	10.8	41.5	0.56
	21.6	32.2	46.2	1.57	0.555	38.6	19.2				11.0	41.5	
	21.0	31.3	47.7	1.57	0.529	38.6	19.3				11.0	41.5	
	20.0	29.9	50.1	1.57	0.515	40.1					12.5	41.7	
	18.0	26.9	55.1	1.57	0.465	42.0					14.4	41.5	
	15.8	23.6	60.6	1.57	0.410	45.7	22.8				18.1	41.5	
	16.2	22.7	62.1	1.57	1.394						19.2	41.4	
	System potassium caprylate- decanol-water. 20°C.												
C	22.8	27.6	49.6	1.40	0.513	41.5	20.7			29.7	11.8	38.4	0.67
	20.5	24.8	54.7	1.40	0.464	44.5	22.2			30.3	14.2	37.9	
	18.1	22.0	60.0	1.40	0.410	49.0	24.4			31.3	17.7	35.8	
	System sodium caprylate- caprylic-acid-water. 20°C.												
C	26.1	24.1	49.8	1.06	0.497	38.5	19.2			27.1	11.4	37.6	0.4
	25.6	23.6	50.8	1.06	0.488	38.9	19.2			27.2	11.7	36.4	
	25.0	23.0	52.0	1.06	0.478	39.3	19.2			27.5	11.8	37.4	
	24.3	22.4	53.3	1.06	0.468	39.2	19.2			26.8	12.4	38.4	
	System lauryldecaethylene glycolether- oleic acid-water. 20°C.												
C	11.7	8.5	79.8	1.61	0.202	87.2	43.6			39.3	47.9	70.0	
	System potassium caprate - octanol-water. 20°C. d_a												
K	50.3	33.5	16.2	1.08	0.841	29.3	14.6	9.8	7.4	17.6	11.7	18.4	
	49.9	33.2	16.9	1.08	0.834	29.3	14.6	9.4		17.4	11.9	19.0	
	49.5	33.0	17.5	1.08	0.828	29.0	14.5	9.6	7.2	17.0	12.0	19.7	

in some of these systems is shown in Figs. 1 (a) — (e). The X-ray diffraction data for these systems show that the ratio between the Bragg spacings is 1:1/2:1/3, *i.e.* the mesophase displays linear symmetry (Table 1). (Data for the sodium caprylate — decanol — water system have been published earlier.[5]) Where there has been enough information the slope of the curve of log d *versus* log $(1/v_a)$ has been less than 1 — about 0.5, — which indicates that the uptake of water by the mesophase is accompanied by two-dimensional swelling. This is consistent with the supposed behaviour of a two-dimensional tetragonal structure composed of long parallel rods; this structure could also be considered as a layered one in which the amphiphilic layers are divided in long baton-like aggregates of amphiphile molecules entirely surrounded by water. The derived dimensions of these rods and the cross sectional area of a hydrophilic group in the surface layer of the rods are also given in the table.

This mesophase (region C) invariably lies between the area with lamellar mesophase of the neat soap type (region D) and the micellar aqueous solution (region L_1). The region C is usually of small extent, often a long salient extending down towards the water corner of the system. The above structure thus appears to be possible only

within narrow limits of the molar ratio between the two amphiphilic substances, while the water content can often vary over quite a wide range. In all sodium soap — alcohol — water systems the molar ratio of alcohol to soap is about 3:2.[9] This mesophase is in equilibrium *via* a two-phase zone with the solution region L_1 at concentrations from the c.m.c. up to approximately the second critical concentration; within this zone the mesomorphous substance separates spontaneously from the solution as an opaque white, flocculent substance, which rises to the surface of the solution. It is optically anisotropic, and in all systems studied has a similar microscopic texture with a more or less streaky appearance.

In another part of the system a mesophase reminiscent in some respects of that described above was encountered in one case (the potassium caprate — octanol — water system at 25°C) (region K in Fig. 1 (f) and Table 1). This is optically aniso-tropic with a microscopical texture which differs from that of the lamellar neat soap, type D. The X-ray pinhole patterns exhibit a spotty appearance and indicate thus the existence of large particles. The ratio between the Bragg spacings is 1:1/2:1/3:1/4. Owing to the small extent of the area it was difficult to obtain a clear impression of the

variation in Bragg spacing with water content. The Bragg spacings for various specimens were practically equal and the slope of the curve of log d versus log($1/v_w$) will therefore be considerably less than 1 (v_w is the volume fraction of water in the mesophase). The findings are suggestive of a structure of long parallel rods in tetragonal array, consisting of a water core surrounded by amphiphile molecules, oriented with the hydrophilic groups facing the water and the hydrocarbon chains outwards. The lattice dimensions show that the hydrocarbon portions of the various rod-like aggregates merge to form a continuous layer of paraffin chains in a semi-liquid state between the rod aggregates. It would thus seem that there is a reversed mesomorphous particle structure with two-dimensional tetragonal symmetry. The molar ratio between alcohol and caprate in this mesophase is 1.03−1.17:1; this suggests that it can exist only at a molar ratio of about 1 between the amphiphilic components. The water content lies between 3.4 and 4.3 moles of water per mole of potassium caprate.

The mesophase in question is in equilibrium via two- and three-phase zones with the lamellar mesophase of the neat soap type (region D), and with the micellar octanolic solution (region L_2). The latter contains micelles of the reversed type with a water core, and the amphiphilic layer of the micelles in that part of the solution region which is in equilibrium with mesophase K is composed of octanol and caprate in a molar ratio of 1:1 (viscosity measurements).[9]

It may be noted that the two-dimensional tetragonal mesophases C and K occur on each side of the concentration region where the lamellar mesophase of the neat soap, type D, exists. It would seem to be appropriate to call the first particle structure the "normal, two-dimensional tetragonal structure", type C, and the latter the "reversed two-dimensional tetragonal structure", type K.

1. Ekwall, P., Danielsson, I. and Mandell, L. *Kolloid-Z.* **169** (1960) 113.
2. Ekwall, P., Danielsson, I. and Mandell, L. *Proc. 3rd Intern. Congr. Surface Active Substances, Cologne 1960*, Vol. I, 193.
3. Mandell, L., Fontell, K. and Ekwall, P. "Ordered Fluids and Liquid Crystals" *Adv. Chem. Series* No. **63** (1967) 89.
4. Mandell, L. and Ekwall, P. *Acta Polytech. Scand.* Ch. 74, I (1968).
5. Fontell, K., Mandell, L., Lehtinen, H. and Ekwall, P. *Acta Polytech. Scand.* Ch. 74, III (1968).
6. Mandell, L. *Finska Kemistsamfundets Medd.* **72** (1963) 49.
7. Ekwall, P. *Wiss. Z. Friedrich-Schiller-Univ. Jena, Math.-Naturwiss. Reihe* **14** (1965) 181.
8. Mandell, L. and Ekwall, P. *Proc. 4th Intern. Congr. Surface Active Substances, Brussels 1964*, Vol. II, p. 659.
9. *Unpublished observations.*

Minimum Water Content of a Number of "Reversed" Micellar and Mesomorphous Structures

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Attention has previously been attracted to the fact that solutions with so-called "reversed" micellar structure in systems of a fatty acid soap, an alcohol, and water are formed only at a certain minimum water content.[1-5]

In the micellar decanolic solutions (region L_2) of the sodium caprylate-decanol-water system the micelles consist of a water core surrounded by a layer of amphiphilic molecules with a decanol-to-caprylate molar ratio of 2−4:1, and oriented with the hydrocarbon chains facing outwards. The region of existence for these solution extends down to a water content of 5−6 moles of water per mole of sodium caprylate. This limit for the region of existence is hardly at all displaced when the decanol of the system is replaced by an alkanol with a shorter hydrocarbon chain[6] (Table 1). Nor does the variation in the chain length of the fatty acid of the sodium soap involve any noteworthy displacement of this boundary (Table 1, Fig. 1). It is