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.

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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

Table 1. Minimum water content for the existence of the solution L_2 and the mesophases type F and type K.

System	Molar ratio water/soap	
	Solution L_2	Mesophase type F
Na-caprylate-decanol-water	5.0–5.6	5.4
» nonanol »	4.9–5.2	5.0
» octanol »	4.9–5.3	–
» heptanol »	5.2–5.7	–
» hexanol »	5.5–5.9	–
» pentanol »	5.7–6.2	–
» butanol »	5.9–6.6	–
» propanol »	6.0–6.6	–
» ethanol »	6.0–6.8	–
Na-caprate- decanol-water	6.0–6.6	–
Na-nonylate- » »	5.9–6.4	5.9
Na-heptylate- » »	5.2–5.4	–
K-oleate- decanol-water	2.5–3.1	3.6–3.9
K-caprate- octanol »	2.7–3.1	3.3 *
K-caprylate- decanol »	2.2–2.9	3.1
Li-caprylate- decanol »	7.0–8.0	7.6

* Mesophase type K.

thus obvious that the minimum water content needed for the formation of the micellar systems in question is determined by the hydrophilic groups of the amphiphiles, *i.e.* by the sodium ion-carboxylate group of the soap and/or the hydroxyl group of the alcohol.

Similar conditions prevail in systems of a potassium soap, an alkanol, and water; here, too, the micellar solution in region L_2 forms only in the presence of water; the requisite amount of water, however, is in this case smaller, only 2–3 moles per mole of potassium soap (Table 1, Fig. 2). It is thus evident that it is not the hydroxyl group of the alcohol but the alkali ion-carboxylate group that is the critical factor.

This conclusion is confirmed by a comparison of the border of the region of the

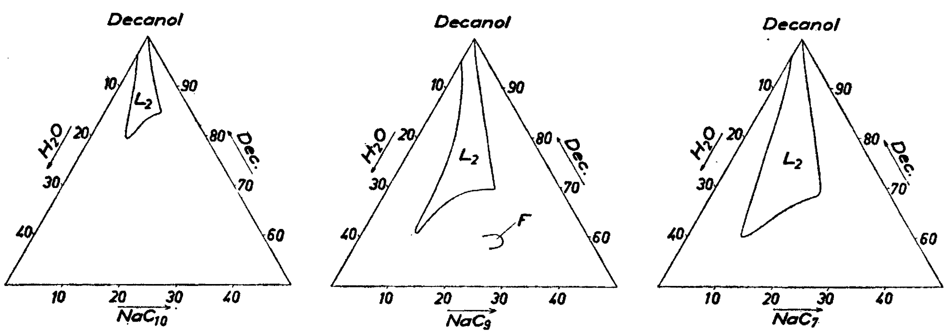

Fig. 1. Phase diagrams showing the extension of solution region L_2 and mesophase F in some sodium soap-alcohol-water systems.

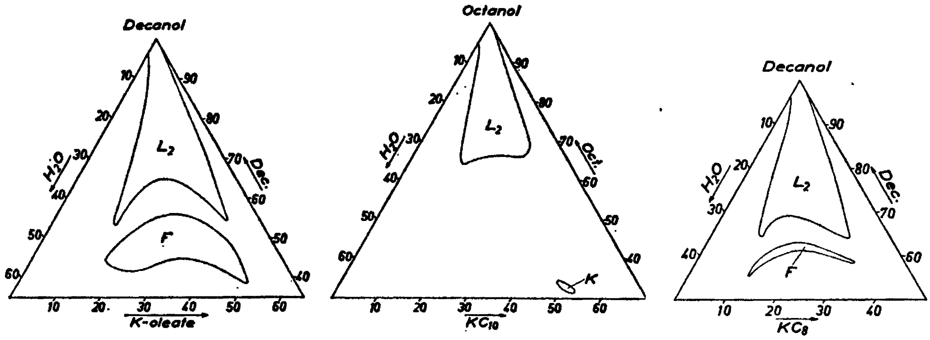

Fig. 2. Phase diagrams showing the extension of solution region L_2 and mesophases F and K in some potassium soap-alcohol-water systems.

micellar solution in systems containing the same alcohol and the lithium, sodium, or potassium soaps of one and the same fatty acid [2,3] (Table 1, Fig. 3). In the lithium soap system, too, a minimum content of water is required for the solution in question to be formed, but the minimum in this case is higher than in the previous cases, namely 7−8 moles of water per mole of lithium soap.

A characteristic feature of all these systems is thus that the micellar solutions in question do not form in the absence of water, and that the requisite amount of water varies with the nature of alkali ion, increasing from 2−3, 5−6, to 7−8 moles of water per mole of soap, when the alkali ion of the soap changes from potassium through sodium to lithium. The water-to-soap ratio thus rises with the hydration requirement of the alkali ion. This indicates that the phenomenon in question is associated with the hydration of the alkali ion and that the solution phase L_2 with its micelles of the reversed type can form only in the presence of enough water to ensure more or less complete hydration of its alkali ions. In this connection the question is left open whether at the relevant water contents there is in the core of the micelles formed a water lattice the hollows of which contain the alkali ions, or whether the alkali ions are partly, if not entirely, surrounded by water molecules in some different array.

About the same minimum water contents have been found in the mesomorphous phases with a reversed particle structure with which the micellar solutions in the L_2 regions are in equilibrium. In most cases these phases have a reversed two-dimensional hexagonal structure (type F) and they are thus composed of long parallel hexagonally arranged rodshaped aggregates; the water nuclei of the aggregates are surrounded by soap and alcohol molecules oriented with the hydrophilic groups facing inwards and hydrocarbon chains outwards. It is evident from the data in Table 1, that the existence of these mesophases, too, presupposes a minimum water content approximately covering the hydration

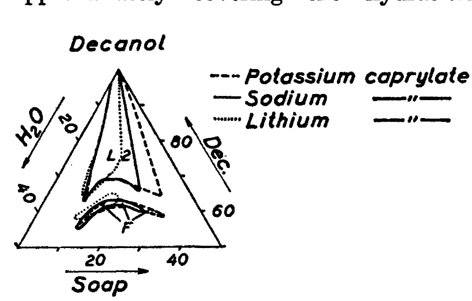

Fig. 3. Phase diagram showing the shift of the borders for the region L_2 and the mesophase F, when the potassium caprylate of the system potassium caprylate-decanol-water is replaced by sodium or lithium caprylate.

requirements of the alkali ions. This seems to apply also to the mesophase with a reversed two-dimensional tetragonal structure observed in the potassium caprate-octanol-water system (type K), where the parallel water rods with their surrounding amphiphile molecules are tetragonally arranged,[7] (Table 1, Fig. 2).

The experimental material as a whole thus provides convincing evidence that it is the alkali ion-carboxylate group that determines the minimum water content in the phases of the soap-alcohol-water systems with reversed micellar and mesomorphous structures and indicates that these structures can form only when the water content covers the hydration requirements of the alkali ions.

It is thus possible to displace the regions of existence of the reversed micellar and mesomorphous structures in alkali soap-alcohol-water systems towards a lower water content by replacing in turn the lithium ions with sodium and potassium ions. This fact and the knowledge of the minimum water content that can be achieved in the various cases, might well be of interest in technical contexts where structures of this type are concerned. The fact that the stability of the reversed micellar and mesomorphous structures of amphiphilic systems of the type in question changes when one alkali ion is replaced by another — for instance potassium by sodium ion — would suggest a mechanism that may be of significance in biologic lipid systems.

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Some Remarks on a Recent Paper by J. Almy, R. T. Uyeda and D. J. Cram on the 1,3-Proton Transfer in an Indene System

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In a recent paper,[1] Almy, Uyeda and Cram report some elegant studies which make considerable contributions to our knowledge of the 1,3-asymmetric induction in the proton transfer in the indene system, a phenomenon discovered by Bergson and Weidler.[2] In their discussion of our work,[3] however, Cram *et al.* make some serious mistakes which are of such a kind that they ought to be clarified.

The studies by Cram *et al.* of the isomerization of 1-methyl-3-*tert*-butylindene confirm our conclusions that the proton transfer in 1,3-dialkylsubstituted indenes is highly stereospecific in certain cases. Regarding our deduction,[3] however, Cram and his co-workers make the following statement: "Their earlier conclusion of *high* 1,3-asymmetric induction rested on unsupported assumptions".[4]

Let us consider the isomerization of 1-methyl-3-isopropylindene (I) to 1-isopropyl-3-methylindene (II), which was the first reaction of this kind studied.[2,3] In this system we found an equilibrium constant $K = [II]/[I]$ of about 4 from direct NMR observations. Even if Cram *et al.*, using quite different methods,[1] have found an equilibrium constant different from ours in the system 1-methyl-3-*tert*-butylindene$\rightleftharpoons$1-*tert*-butyl-3-methylindene, there is no doubt about the fact that a considerable amount of (I) is present at equilibrium in the system I$\rightleftharpoons$II. The rate constants, as specified in our papers, for the isomerization were also determined from direct NMR studies. Furthermore, we studied the optical rotation of the reaction mixture as a function of time and found a change, for example[2] from $-1.60°$ to $+1.35°$, at a rate comparable with the isomerization rate.

The crucial point is, however, what happens to the optical rotation when the state of isomerization equilibrium has been reached (practically). If the rotation then is independent of time, or more exactly, if