permit any profound discussion of the reaction mechanism.

The conclusion that the original assumption was correct opens up an interesting and technically important field of research, including, for instance, the corrosion of high tension transmission lines and transformers. The influence of various factors has naturally to be studied, *e.g.* the difference of potential and strength of current flow, as well as the choice of metal and gas.

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# A Lamellar Mesophase with Single Amphiphile Layers

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The usual neat soap structure with double amphiphile layers occurs in, for instance, the ternary systems of an ionic association colloid, water, and an alkanol having a long enough hydrocarbon chain. A lamellar mesophase of the neat soap type also appears in these systems when the univalent alcohol is replaced by a bivalent straight chained alcohol with terminal hydroxyl groups, but in this case the structure displays a number of different features. This will be illustrated by experimental results obtained for the lamellar mesophase in the sodium caprylate—1,8-octanediol—water system.

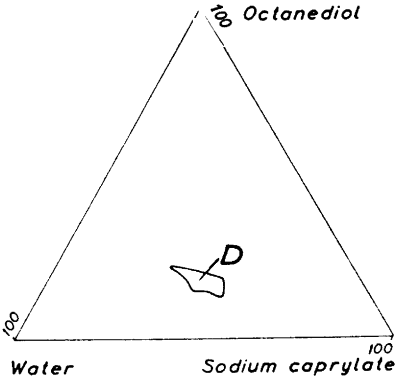

*Fig. 1.* Phase diagram showing the location of the region with lamellar mesophase in the sodium caprylate—1,8-octanediol—water system.

Here a lamellar mesophase occurs at 20°C in the region denoted D in Fig. 1. (The complete phase equilibria diagram will be published in an other connection.) This mesophase has the typical mosaic texture characteristic of the neat soap phase (No. 122.1 in the Rosevear system [1]) (Fig. 2). The Bragg spacing ratio of 1:1/2 is indicative of a lamellar structure (Table 1). Assuming that all the diol is contained in the amphiphile layers and using experimental values for the volume fraction of the amphiphilic substance, we obtain values between 13.5 and 14.7 Å for the layer thickness. These are considerably lower than those for the amphiphile layers in the corresponding mesophase in the sodium caprylate—decanol—water [2-4] and the sodium caprylate—octanol—water [5] systems, namely 22 and 20 Å. As the molecules of sodium caprylate and octanediol are about 13 and 14 Å in length the observed values would be incompatible with a double-layered structure of the amphiphile layers

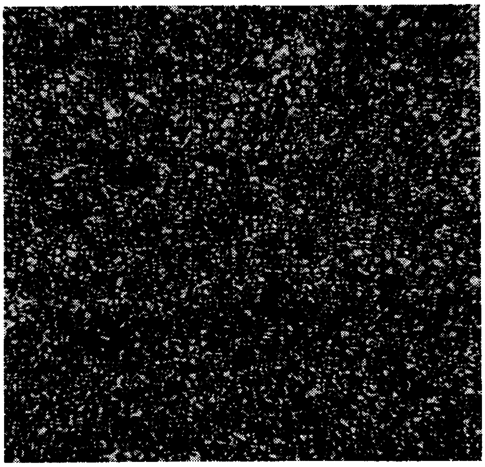

*Fig. 2.* Photomicrograph of the mesophase in region D. Crossed nicols 150 ×.

*Table 1.*

| Composition (%) | | | Molar ratio octanediol/ $NaC_8$ | Bragg spacing (Å) | | Volume fraction of amphiphile $v_a$ | Dimensions of the amphiphile layers | | |
|---|---|---|---|---|---|---|---|---|---|
| $NaC_8$ | Octanediol | $H_2O$ | | $d_1$ | $d_2$ | | $d_a$ (Å) | Area (Å$^2$) [a] | |
| | | | | | | | | $S_1$ | $S_2$ |
| 40.32 | 15.68 | 44.00 | 0.441 | 24.4 | — | 0.552 | 13.5 | 28.5 | 18.6 |
| 40.30 | 15.70 | 44.00 | 0.442 | 24.6 | — | 0.552 | 13.6 | 28.1 | 18.4 |
| 38.30 | 15.70 | 46.00 | 0.466 | 25.0 | 12.4 | 0.531 | 13.3 | 28.7 | 18.9 |
| 37.05 | 19.95 | 43.00 | 0.610 | 24.5 | 12.2 | 0.557 | 13.6 | 26.4 | 18.4 |
| 35.62 | 19.18 | 45.20 | 0.611 | 24.6 | 12.3 | 0.535 | 13.2 | 27.3 | 18.9 |

[a] $S_1$ = area/hydrophilic group,
$S_2$ = area/hydrocarbon chain.

in the system in question unless one assumes an angle of about 40° between the hydrocarbon chains and the surface of the amphiphilic layers and quite sharply bent diol molecules, or if is assumed that one of the hydroxyl groups of the diol is situated in the interior of the hydrocarbon layer. The observed Bragg spacing values thus suggest a single molecular layer, the thickness of which is determined primarily by the fact that the diol molecules are oriented with their terminal hydrophilic groups at the amphiphile/water interface.

If all the hydrophilic groups of the amphiphilic substances are in contact with water, an area of $27-30$ Å$^2$ per group is obtained. These values are slightly greater than those for the neat soap structure of systems with univalent alcohols,[3,4] as would be expected for the supposed single layered structure. On the other hand, the value of about 18.7 Å$^2$ for the cross sectional area per hydrocarbon chain in the interior of the amphiphile is indicative of extremely tight packing. This value will be somewhat higher if one supposes that the maximum possible amount of octanediol (*ca.* 1 %) is dissolved in the water layers. Furthermore one has to consider a certain uncertainty in the evaluation of the Bragg spacings. The X-ray diffraction in the wide-angle region gives a diffuse reflection corresponding to a Bragg spacing of 4.5 Å, which, however, indicates a semi-liquid state in the hydrocarbon parts of the layer.

Both the above cross sectional area values — per hydrophilic group and per hydrocarbon chain — increase slowly with the water content of the mesophase. In this respect the conditions in the lamellar phase of the diol system resemble those in the alcohol-poor parts of the corresponding phase in systems containing univalent alcohols. The slope of curves of log $d$ *versus* log $(1/v_a)$ is less than 1 and increases with the molar ratio of alcohol to soap, as in other ternary systems of ionized association colloids, alcohol and water.[3,4,6]

The structure of the amphiphile layers that would seem to be the most likely one to judge from these data, is shown in Fig. 3. The presence of the octanediol, with its two terminal alcohol groups would thus seem to lead to a lamellar structure in which the amphiphile layers, alternating with water layers, are composed of single molecular layers.

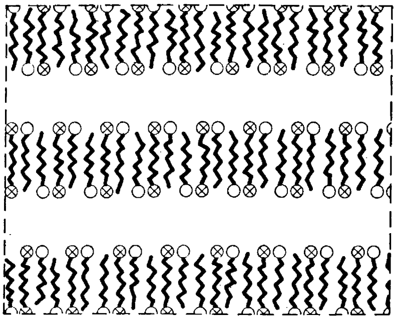

*Fig. 3.* Schematic drawing of the single layered mesomorphous structure.

It would seem justified to reserve the term "neat soap structure" for the types of lamellar mesophase composed of double amphiphilic layers, and to call the mesophase structure encountered in the sodium caprylate—octanediol—water system the "single layered lamellar type" with the designation type $D_S$.

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1. Rosevear, F. B. *J. Am. Oil Chemists' Soc.* **31** (1954) 628.
2. Fontell, K., Ekwall, P., Mandell, L. and Danielsson, I. *Acta Chem. Scand.* **16** (1962) 2294.
3. Mandell, L., Fontell, K. and Ekwall, P. *Ordered Fluids and Liquid Crystals, Advan. Chemistry Series* **63** (1967) 89.
4. Fontell, K., Mandell, L., Lehtinen, H. and Ekwall, P. *Acta Polytech. Scand.* Ch. 74, III (1968).
5. Mandell, L. *Unpublished measurements.*
6. Ekwall, P., Mandell, L. and Fontell, K. *Acta Chem. Scand.* **22** (1968). *In press.*

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# Semisynthetic Penicillins

## VIII.* The Use of Tributyltin 6-Aminopenicillanate in Penicillin Synthesis**

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In a recent paper[1] we reported the convenient preparation of pyridylmethylpenicillins by acylation of phenacyl 6-aminopenicillanates with pyridylacetic acids in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC).

During our investigations on other carboxyl protecting groups suitable in penicillin synthesis, we employed the tributyltin ester grouping which has recently been used by Frankel *et al.*[2] in the preparation of peptides. These authors prepared the triethyl- and tributyltin esters of free and N-protected amino acids. The esters were easily cleaved with acetic acid and other organic or inorganic acids or with bases such as methoxide or hydroxide. Tributyltin esters obtained from free amino acids were described as extremely sensitive to water or ethanol. Their instability made it impossible to use them in coupling reactions with DCC as the free acid present in the reaction mixture immediately cleaved the ester group.

We could prepare tributyltin 6-aminopenicillanate (I) from 6-APA and tributyltin oxide in high yield and purity by treatment of 6-APA with tributyltin oxide in boiling benzene and removal of the water formed by distillation. Partial evaporation of the remaining benzene and addition of petroleum ether precipitated the crystalline product.

The tributyltin ester of 6-APA was somewhat more stable than the α-amino acid tin esters described by Frankel *et al.* It could be stored unchanged for weeks at room temperature and in ethanolic solution it was stable for hours. The product was easily soluble in most organic solvents such as ether, ethyl acetate, benzene *etc.*

With one equivalent of potassium thiophenoxide (KSPh) in dimethylformamide (DMF), the ester was cleaved almost quantitatively within *ca.* 15 min to potassium 6-aminopenicillanate and phenyl tributyltin sulfide (II) without any appreciable destruction of the sensitive penicillin nucleus (Scheme 1).

We used the tributyltin 6-aminopenicillanate as a starting material in the synthesis of methylpenicillins carrying a nitrogen-containing heterocycle in the α-position in the manner described previously for phenacyl 6-aminopenicillanates.[1]

Tributyltin 6-aminopenicillanate was easily acylated with heterocyclic acetic acids using *N,N'*-dicyclohexylcarbodiimide (DCC) as the coupling reagent. In order to attain complete acylation of the 6-APA ester, a moderate excess of the carboxylic acid and DCC was used. The intermediate tributyltin penicillinates (III) were freed

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* Paper VII. *Acta Chem. Scand.* **21** (1967) 2210.

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