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Preliminary IR and NMR Investigations on the Alkali Soap-Carboxylic Acid-Water Systems

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The system sodium caprylate-caprylic acid-water was investigated by Ekwall and co-workers,¹⁻⁶ who gave evidence for the presence of a crystalline acid soap $2\text{NaC}_8\text{HC}_8$, of several mesomorphous phases and of two homogeneous isotropic solution phases (L_1 and L_2) (Fig. 1).

Since molecular spectroscopy has not previously been used on systems like this with the exception of the IR investigation on solid acid soaps by Goddard⁷ and Dunken⁸ an investigation of the chemical bonds and molecular arrangements in the sodium caprylate-caprylic acid-water sys-

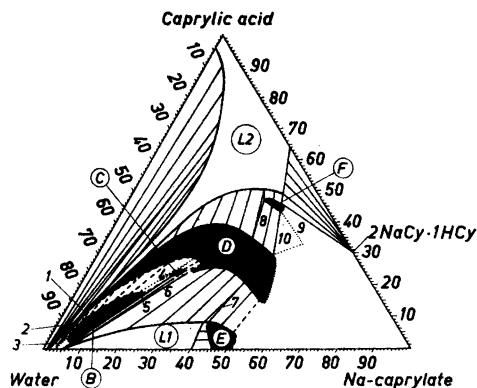


Fig. 1. The three component system water-sodium caprylate-caprylic acid.

tem by means of IR and NMR spectroscopy was thought to be of value. The present investigation has been limited to the region L_2 with a homogeneous isotropic solution. Considering the various acid salts and acid soaps which have been reported by Ekwall,^{9,10} McBain,¹¹ and Dunken^{8,12} the detection of complexes between acid and soap in the L_2 -solution would be of highest interest.

The investigations were carried out by means of an infrared spectrophotometer Perkin Elmer 221 and a high resolution nuclear magnetic spectrometer Varian A 60A.

Infrared spectra of caprylic acid solutions of sodium caprylate are given in Fig. 2. Addition of the soap to the acid decreases the frequency of the absorption of the OH stretching vibration in the region $2500-3300\text{ cm}^{-1}$ and at the same time a new absorption at 1900 cm^{-1} grows.

The absorption of the carbonyl group at 1710 cm^{-1} does not change appreciably while the frequency of the absorption of the antisymmetric vibration of the ionized carboxyl group at 1540 cm^{-1} is increased somewhat when soap is added. The absorption of the out-of-plane bending vibration of the OH groups of the carboxylic acid at 930 cm^{-1} decreases linearly with the soap content and reaches zero when the ratio acid to soap is 2:1. NMR measurements of the hydroxylic proton of the acid showed a down-field shift of the signal frequency of about 100 cps which varied linearly with added soap.

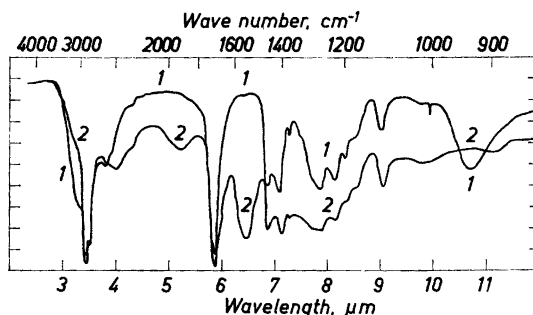


Fig. 2. Infrared spectra of solutions of sodium caprylate in caprylic acid.

No.	Weight % Acid	Soap
1	100	0
2	64.9	35.1

These results together with the information from the phase diagram (Fig. 1) give a very strong support to the hypothesis that the water-free L_2 solutions consist of definite complexes $\text{NaC}_8\cdot 2\text{HC}_8$ in equilibrium with caprylic acid. The hydrogen bonds in these complexes are stronger than those in the caprylic acid, which is shown by the down-field shift of the OH signal and by the changes of the absorption of the valence vibration in the infrared spectra. Increased amount of soap increases the line width of the signal of the carboxylic proton which shows that the proton exchange rate is lower. This gives also some indication of a stronger hydrogen bond. These results fit well into the structure (a) in Fig. 3. The structure (b) appears less likely since a coordination bond from the hydroxylic oxygen would imply a change of the carbonyl stretching frequency of the carboxylic acid.

Infrared spectra at different temperatures verify that the acid salt $2\text{NaC}_8\cdot 1\text{HC}_8$ is decomposed at about 80°C and that the decomposition products seem to contain solution L_2 .⁶ (Fig. 4). This is in complete accordance with the early results by Ekwall concerning the crystalline acid salts of other soaps.^{9,10}

NMR investigations of L_2 -solutions in the parts of the region containing water show that the coalesced signals frequency of the OH protons from the water, the carboxylic acid and the soap:carboxylic acid complexes shows an up-field shift when

the water content is increased up to about 40 %, after which the resonance position is fairly constant. This is the composition at which the tie-lines shrink to a point in the two-phase region where L_2 -solutions with a high caprylic acid and low water content and L_2 -solutions with a low caprylic acid and high water content are in equilibrium with each other. It appears highly probable that this point implies a change from carboxylic acid to aqueous solutions which has been proposed by Ekwall and co-workers on the basis of other investigations.⁵

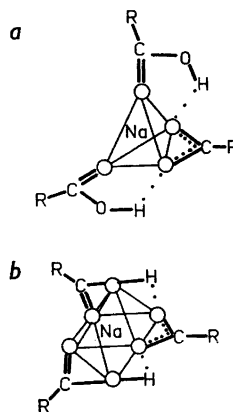


Fig. 3. Structure proposals for the compound $2\text{HC}_8\cdot \text{NaC}_8$.

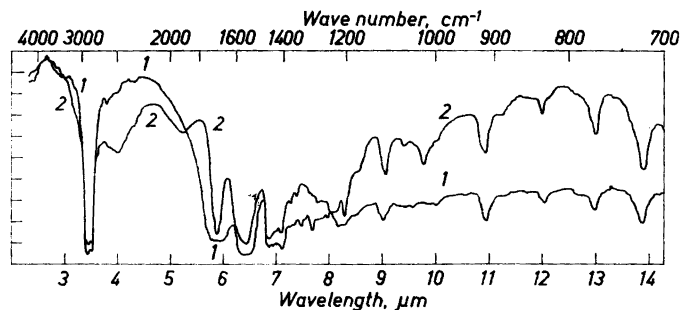


Fig. 4. Infrared spectra of the compound $2\text{NaC}_8\cdot\text{HC}_8$ at different temperatures. 1. 25°C. 2. 80°C.

Information on research devices and a more comprehensive treatise of the results will be given later.

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“Solvent Peak Subtraction”. Gas Chromatographic Determination of Low-Boiling Compounds in the Presence of an Interfering Solvent

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In some cases one has to make a gas chromatogram of a mixture of low- and high-boiling compounds in a low-boiling solvent. The choice of solvent may be limited, or perhaps only one solvent is possible. To achieve good resolution of the high-boiling component peaks, perhaps only one column can be used. In such case it may be very difficult to separate the peak or peaks of the lowest boiling components from that of the solvent, even at low temperatures. It is, however, possible to improve the situation by what we call “solvent peak subtraction”.

In principle it would be possible to eliminate the solvent peak totally, leaving the low-boiling component peaks free. This could be achieved with a double-column system with parallel, identical

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