

Fig. 2A. Ordinary light. 200 \times .



Crossed Nicols. 200 \times .

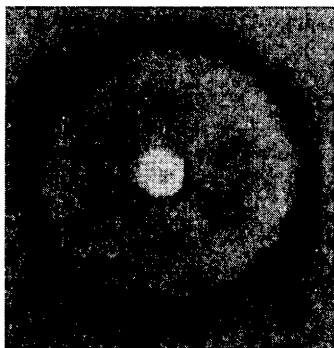


Fig. 2B.

for the water content) by dissolving the residue in glacial acetic acid and titrating it with perchloric acid employing crystal violet as indicator, and the water content either by evaporating the sample to dryness or by the Karl Fischer method. The mesomorphous phases were in addition examined with the microscope and with a X-ray diffraction camera. The X-ray photographs were taken with a Philips Norelco unit employing a copper target and Ni-filtered radiation. A small angle vacuum camera with pinhole collimators (Kiessig) and a sample to film distance of 212 mm

were employed. The X-ray room was maintained at a temperature of 20°C.

Fig. 1 shows a part of the triangular diagram for the investigated three-component system. The region of homogeneous, isotropic aqueous solutions containing caprylate and solubilised cholesterol is marked I. This region naturally starts at zero caprylate concentration, but up to a caprylate concentration of about 16 % the solubility of cholesterol is so low that the isotropic region can be indicated only by a thick line lying against the caprylate axis. When the concentration of a pure sodium caprylate solution rises to 40.5 % (the "middle soap separation concentration", MSSC) the system becomes heterogeneous owing to the separation of mesomorphous middle soap. This mesophase can take up small amounts of cholesterol. The homogeneous middle soap range is marked II. The region ABCD between the homogeneous phases I and II represents a two-phase region in which the system is divided into an isotropic caprylate solution with the composition indicated by line AB and a middle soap with the composition indicated by line CD. The division is indicated by the tie lines. The appearance (focal conic texture) of the cholesterol-containing mesomorphous phase II in a microscope in ordinary light and between crossed nicols is seen in Fig. 2A. Fig. 2B shows the X-ray diagram for the same phase. The region

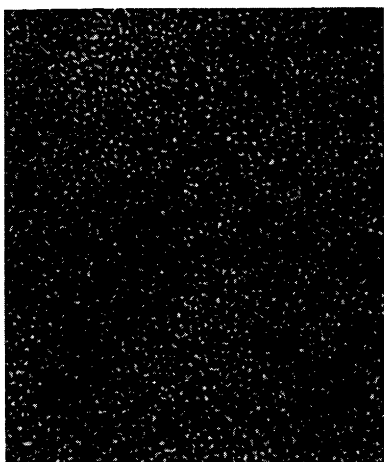
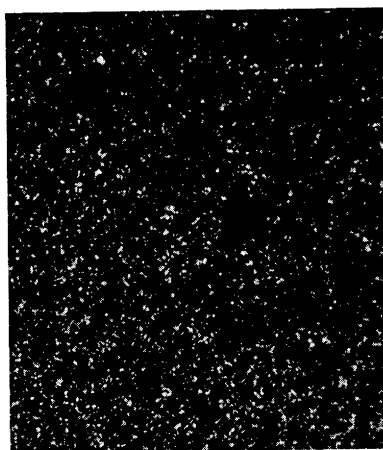
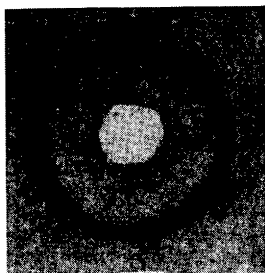
Fig. 3A. Ordinary light. 200 \times .Crossed Nicols. 200 \times .

Fig. 3B.

BEFG represents another two-phase region in which the system is divided into an isotropic caprylate solution (I) with the composition given by the line BG and a mesomorphous phase with the composition given by line EF. Line EF thus represents the lower limit of the region where the homogeneous mesophase III of high cholesterol content exists. At point E this phase is composed of 30 % cholesterol, 36 % sodium caprylate, and 34 % water and at point F of 38 % cholesterol, 27 % sodium caprylate and 35 % water. The appearance (mosaic texture) of this mesomorphous phase in a microscope is shown in Fig. 3A and its X-ray diagram in Fig. 3B. In the region GHJK there is a third two-phase

region in which the system is divided into an isotropic caprylate solution (I) with the composition given by line GK and a mesomorphous phase with the composition given by line HJ. The latter line represents the lower boundary of the region where a homogeneous mesophase IV of relatively high cholesterol content exists. The composition of this phase at point H is 17 % cholesterol, 28 % sodium caprylate and 55 % water, and at point I 23.5 % cholesterol, 8 % sodium caprylate and 68.5 % water. In a microscope this mesomorphous phase has the appearance shown in Fig. 4A. This phase exists as spool-shaped liquid crystals. This is the phase described previously (part III of this series; Fig. 2) which is stable only up to 34–38°C. Fig. 4B shows the X-ray diagram for this phase. A further two-phase region lies to the left of the line KM. The two phases are a dilute, isotropic sodium caprylate solution or water saturated with cholesterol and solid, crystalline cholesterol.

The triangles, α, β, γ , drawn with broken lines represent regions where three different phases coexist; their compositions are given by the points at the corners of the triangles. In the three-phase triangle α a 6 % (0.38 M) sodium caprylate solution, solid cholesterol and the mesomorphous phase IV are in equilibrium; in the triangle β an about 32 % sodium caprylate solution containing 1.7 % cholesterol and the meso-

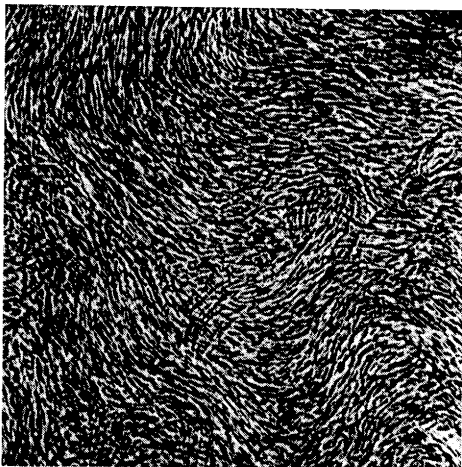
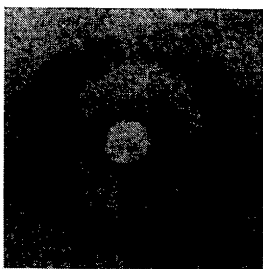
Fig. 4A. Ordinary light. 200 \times .Crossed Nicols. 200 \times .

Fig. 4B.

phases IV and III are in equilibrium, and in triangle γ an about 45 % sodium caprylate solution containing about 6 % cholesterol and the mesophases III and II are in equilibrium.

Our studies thus reveal that there exists at 20°C three different mesomorphous phases composed of water, cholesterol and sodium caprylate which differ in composition and properties and in the conditions under which they are formed. It is of parti-

cular interest that each phase is in equilibrium with only a limited range of caprylate solutions and that there hence exists a relationship between the structures of the caprylate solutions and those of the mesomorphous phases. We have previously established that a similar relationship exists also between the structures of isotropic association colloid solutions and the water-containing mesomorphous phases that these solutions form by interaction with paraffin-chain alcohols or fatty acids ².

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2. Ekwall, P., Danielsson, I. and Mandell, L. *Kolloid-Z.* **169** (1960) 113; *Proc. 3rd Intern. Congr. Surface Activity*, Cologne 1960, Vol. I, Section A, 193, 189.

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