NOTES

Mesomorphous Phases, a Factor of Importance for the Properties of Emulsions

An emulsion consisting of macrodroplets of a liquid distributed in a second liquid, the latter forming a continuous phase. is not a thermo-dynamically stable system, since the interphase area has not attained a minimum value. In those cases where the interphase tension is zero, so-called microemulsions (1, 2) are formed, which cannot be considered as "true" emulsions. These are solutions with solubilized water or solubilized hydrocarbons (3).

In spite of not being stable in the sense of having attained the lowest possible energy state, emulsions of certain compositions can be stored for very long periods without measurable changes. Such a behavior implies the presence of several energy minima in the system and has its source in the energy changes when the dispersed drops approach each other, flocculate, and coalesce. The long-range repulsive forces are due to gradients of the electric potential around the droplets, whereas the short-range forces arise from changes in the concentration gradient in the vicinity of the interphase and from structural changes in the interphase layer at later stages in the demulsification process. Several attempts have been made to show that specific factors are responsible for the stability of emulsions (4-6) but they have met with only moderate success. The HLB-value, which is a measure of the solubility of the emulsifier in the two phases, can be used to predict what kind of emulsion will be formed when the concentration of emulsifier is low. At higher concentrations the emulsions can suddenly be reversed (7) - a phenomen which has not been satisfactorily explained previously. The presence of a liquid crystalline phase in the ternary systems of two nonionic emulsifiers and water with a constant amount of paraffin oil has an influence on the properties of air emulsion; this has been pointed out several times (8, 9).

We shall now show how the recent research concerning these mesomorphous phases has given results which provide the answers to several earlier unanswered questions. This liquid crystal region in ternary systems of a surface-active substance, water, and an amphiphilic substance (10) has after careful investigations (11) been shown to consist of several mesomorphous phases in equilibrium with each other and with the isotropic solutions. A part of such a system which is important for emulsion problems is presented in Fig. 1. It shows the two isotropic solutions A and B in equilibrium with each other and with the mesomorphous phase C.

The area A + B gives emulsions of the W/O type. Those emulsions become more stable with increasing concentrations of the emulsifier.
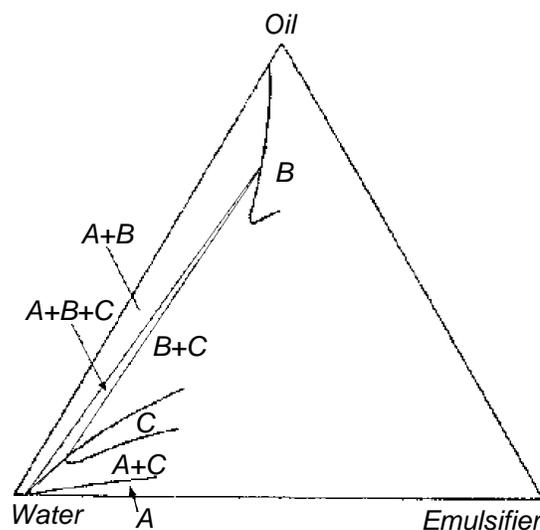

Fig. 1. The phase diagram of a system water-oil-emulsifier. A: water solution of emulsifier. B: solution of emulsifier. C: mesomorphous phase present in the system.

The explanation for this is not to be found explicitly in the diagram, and will be the subject of further investigations.

When the concentration of the emulsifier has increased to such a degree that the composition of the system passes from the two-phase area A + B to the three-phase area A + B + C, the stability of the emulsion increases suddenly and the viscosity rises. Both these changes are due to mesophase C distributed in the solution B, which is the continuous phase of the emulsion.

When the concentration of the emulsifier is further increased three alternative developments are possible.
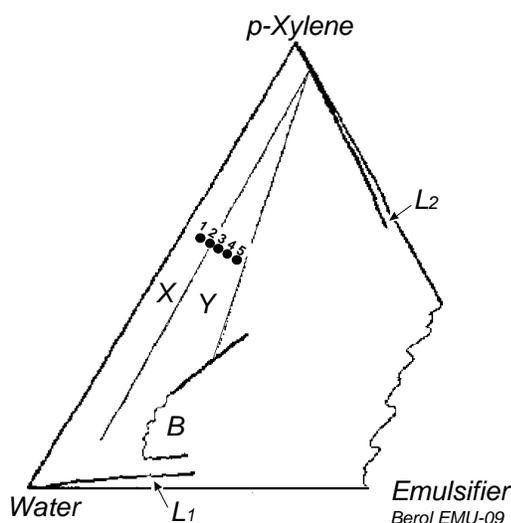
FIG. 2. Part of a phase diagram containing a commercial emulsifier. L1 and L2: Aqueous and *p*-xylene solutions at the emulsifier. B: Mesomorphous phase. X:Two-phase area L1 + L2. Y-Three-phase area L1 + L2 + B. Points 1-5: shows the total composition of the samples in Fig. 3.

If the total composition corresponds to a point in the area B + C, the "emulsion" will possibly not appear to be very different when prepared, but the viscosity will increase to a very high degree. When the total composition corresponds to a point in the mesophase area C, this phase will be formed, and a very thick gel arises. If the water content of the emulsion has a high enough value, the total composition of the emulsion will correspond to a point in the area A + C. In that case, the "emulsion" will consist of "drops" of the mesophase C distributed in the solution A and the emulsion appears to be reversed from a W/O to a O/W type when the concentration of the emulsifier is increased.

This hypothetical case shows how many hitherto unexplained properties of emulsions can find a reasonable explanation when ternary systems prepared under equilibrium conditions are used.

As an example we shall show the results of an investigation on a commercial emulsifier Berol EMU-09 in water and *p*-xylene. The phase diagram is shown in part by Fig. 2, where the border line is marked between the region X with no mesomorphous phase B, and the region Y, where this phase is present.

Emulsions were carefully prepared by treating the weighed-in samples in an ultrasonic generator for 5 minutes it a temperature of 20 °C. The emulsions were then stored at 20 °C and the rate of sedimentation was followed by photographing at 24-hour intervals.
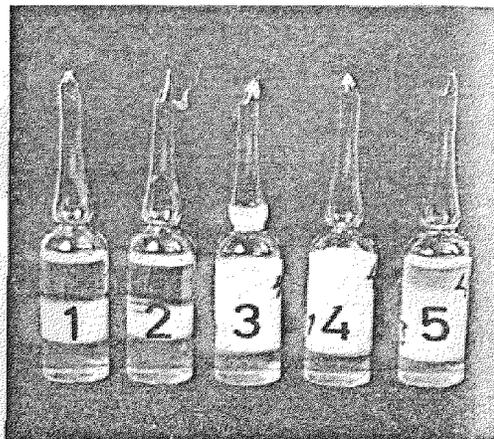

FIG. 3. Emulsions, with the composition marked in Fig. 2, after a 9-day storage.

The results (Fig. 3) give evidence of the improved stability in the samples 3, 4, and 5, where the meso morphous phase B is present.This is, however, not true for those parts of the diagram where the ratio water to *p*-xylene is very high or very low. Investigations to explain these phenomena are being continued at our laboratory.

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