Phase Equilibria and Their Influence on the Properties of Emulsions

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Abstract

Phase diagrams water-emulsifiers-oil have been investigated. Results show that not only the association of the three compounds into liquid crystalline phases has an effect on the properties of the emulsion but also that the association into micelles of the emulsifier in the oil phase influences both the type and the stability of the emulsion.

Introduction

A recent article (1) gave a schematic view of the phase equilibria in a system water-oil-nonionic emulsifier. The authors also gave their opinion on the properties of emulsions in different parts of the two phase region constituting the emulsion. They also discussed the presence of different liquid crystalline phases.

Friberg et al. (2) accurately determined the phase regions in a system water/nonionic emulsifier/*p*-xylene, and showed how the presence of liquid crystalline phases determined the properties of the emulsions. Further, it was suggested on a theoretical basis that the presence of these phases could explain some of the hitherto unexplained behavior of the emulsions, such as sudden changes in viscosity, stability or inversion.

The present authors (3) have later determined the influence on the phase-equilibria when *p*-xylene was replaced by hexadecane as the nonpolar substance, and found that this had a remarkable effect on the regions for the different phases. The water-retaining capacity of the mesomorphous phase with layered structure (neat soap structure) is reduced to a striking degree (Region D, Fig. 1, A and C). Reduction of the hydrophilic part of the emulsifier changing it from an O/W to a W/O emulsifier completely changed the phase regions (Fig. 1, A and B).

Since it was found that the differences in emulsion behavior, when the nonpolar solvent is changed from an aromatic hydrocarbon to hexadecane, could not be explained by any other approach, continued investigations along these lines were considered to be of general value.

Phase equilibria were determined in systems of water-nonionic emulsifiers-hydrocarbons, water/1-monocaprylin/tricaprylin, water-lecithin-tricaprylin and water/octylamine/*p*-xylene. Of these, only the two first mentioned will be discussed here, while the others will be published elsewhere (Friberg and Mandell, to be published).

Experimental Procedures

Materials

Twice distilled water was used; the nonionic emulsifiers were nonylphenol polyethylene glycol ethers of commercial origin (Berol AB, Sweden) which were carefully purified from polyglycols. Other impurities were less than 0.01%. The monocaprylin was synthesized at the Institute of Medical Biochemistry at

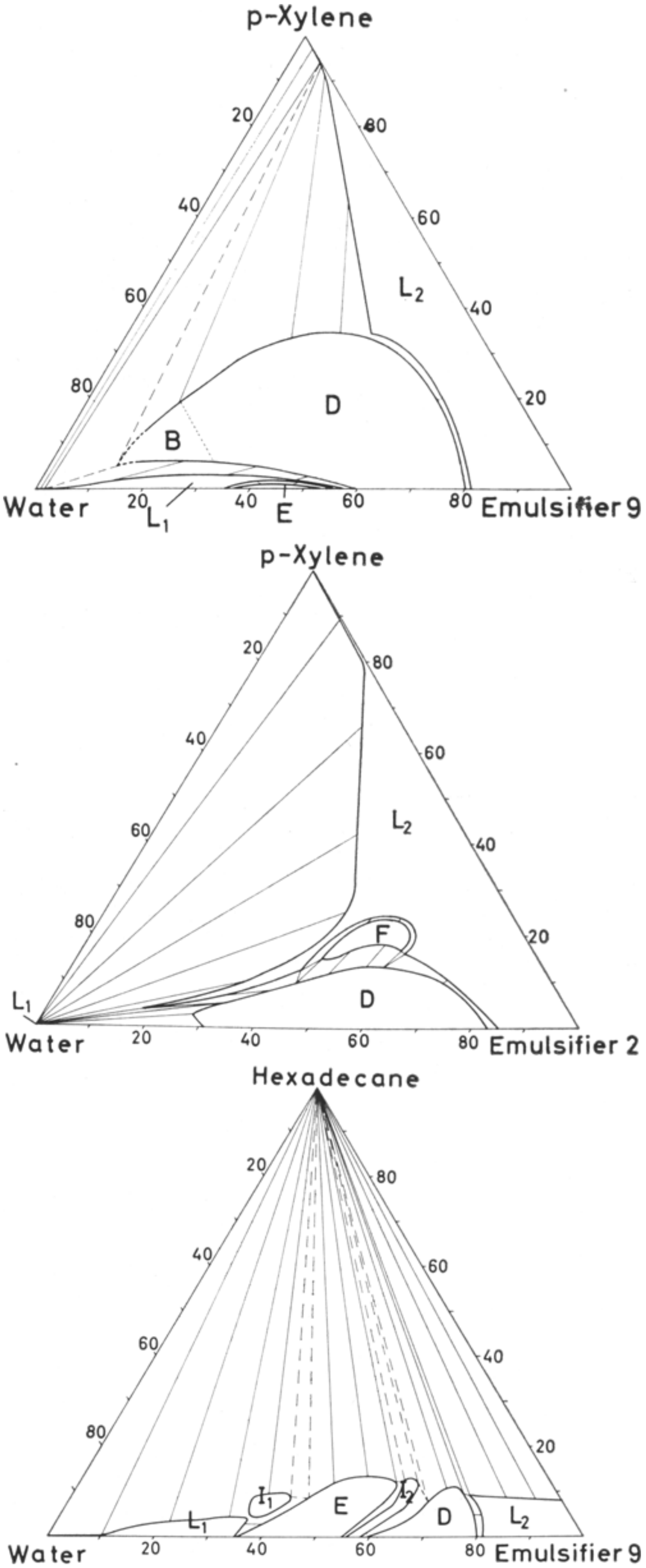


FIG. 1. Phase diagrams for the three-component systems at 20 C: A, water/nonylphenol nonaethylene glycol ether/*p*-xylene; B, water/nonylphenol diethylene glycol ether/*p*-xylene. C, water/nonylphenol nonaethylether/hexadecane. L_1, L_2 Regions with homogeneous isotropic solutions. B, D, E, F, I_1, I_2 Regions with homogeneous mesomorphous phases.

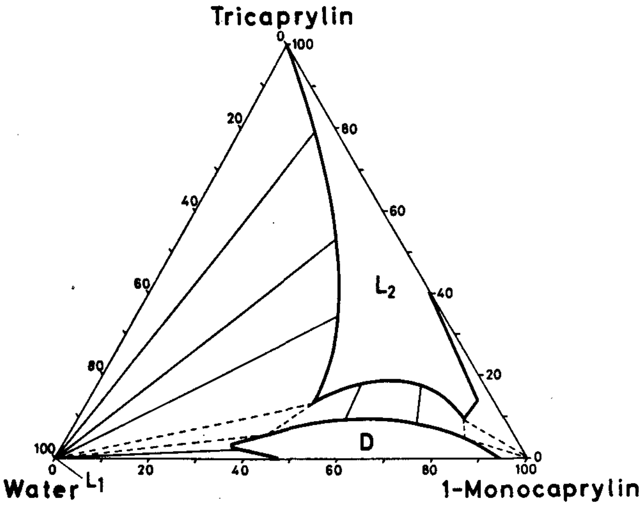


FIG. 2. Phase diagram for the three-component system: Water-monocaprylin-tricaprylin at 20 C. L_1, L_2 Regions with homogeneous isotropic solutions. D, Region with homogeneous mesomorphous phase.

the University of Gothenburg, Sweden; tricaprylin was supplied from Eastman Distillation Products Industries.

Phase Equilibria

Phase equilibria were determined by visual inspection of weighed samples in a microscope with crossed polaroids, combined with analysis of different phases in equilibrium separated by means of centrifugation (4). The different phases were also identified by means of their x-ray diffraction patterns (5).

Emulsion Behavior

The substances were weighed into ampoules which were fused. The samples were treated on a waterbath in order to dissolve the emulsifier, then thermostated at 20 C and treated by an ultrasonic device (SonBlaster, Narda Ultrasonics Corp.) for 5 min at this temperature.

The emulsions were stored at 20 C, visually observed and photographed. The emulsion type was determined by adding small amounts of water to the emulsion and visually observing the continuous phase.

Results

Phase Equilibria

The phase regions in the systems water-nonionic emulsifiers-hydrocarbons are shown in Figure 1, A to C. The changes of the phase regions when *p*-xylene is replaced by hexadecane are remarkable. The area of the neat phase (Region D) is reduced, and that of the middle soap phase (Region E) is increased. The liquid phase L_2 is reduced to a small area where the emulsifier solves small amounts of hydrocarbon and the aqueous solution area is divided into three parts, one micellar solution and two isotropic mesomorphous phases.

When the hydrophilic part of the emulsifier is reduced from a mean value of nine ethylene glycol ether groups, Figure 1 A, to the corresponding value two, Figure 1 B, the phase equilibria changes completely. Only two mesomorphous phases exist, the neat soap (D) and a reversed middle soap (F) (5). The micellar solution (L_2) forms a narrow continuous region from the complete nonaqueous part to about 78% water. The solubility of the emulsifier in water is less than 0.05%, and this solution was not investigated in detail.

The system water/monocaprylin/tricaprylin (Fig. 2) is similar to the last mentioned in its main behavior. No reversed middle soap phase exists, however, and the solutions in region L_2 solubilize only about 40% water.

Emulsion Type

The emulsion type in the two phase regions where water forms one phase is described in Figure 3. When the water content is less than 70% the tricaprylin/water emulsions are W/O emulsions. The water/*p*-xylene emulsions are O/W emulsions when the water content is more than 30% and when the emulsifier has not reached the concentration where micelles begin forming in the *p*-xylene phase, as judged from the sudden increase of the water solubility.

Emulsion Stability

Photographs of the emulsions water/tricaprylin, when stored for varying lengths of time after the preparation, are shown in Figure 4. The three emulsions with the ratio water/tricaprylin (95:5) are all considerably stable. The two samples with 19.2%

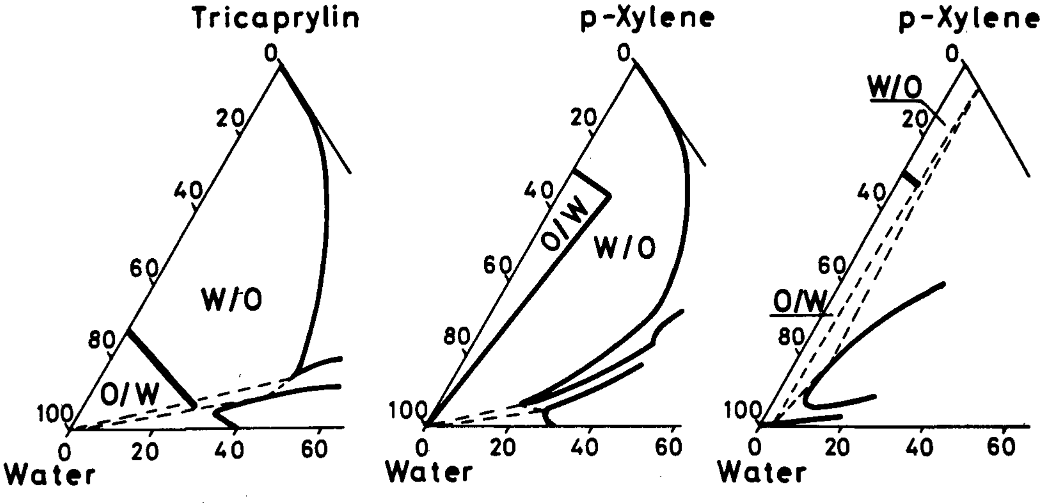


FIG. 3. Part of phase diagrams for the three-component systems: A, water/1-monocaprylin/tricaprylin; B, water/nonylphenol diethylene glycol ether/*p*-xylene; C, water/nonylphenol nonaethylene glycol ether/*p*-xylene. The diagrams show the emulsion type in the two-phase region between the aqueous solution in region L_1 and the solutions in region L_2 with a low water content.

and 32.1% emulsifier contain a mesomorphous phase and are very stable. When the W/O ratio is decreased to 9 the sample with 18.4% emulsifier is rather unstable and the others are very stable, especially the one having 46.3% emulsifier, which consists entirely of a mesomorphous phase. The same pattern of decreasing stability with an increasing amount of emulsifier is shown by the other emulsions also investigated. It is interesting to note how the stability increases in the neighborhood of the border between O/W and W/O emulsions and at low concentrations of the emulsifier. This latter condition indicates that emulsions with high ratio W/O are considerably more stable when the emulsifier concentration is increased.

The stability of emulsions water/*p*-xylene/nonylphenol diethylene glycolether follows a similar pattern (Fig. 5). Increases in the stability are found in the neighborhood of the borderline between O/W and W/O emulsions, and to a higher degree when the mesomorphous phase is present. The critical micelle concentration (CMC) of the *p*-xylene phase has a pronounced influence on the nature and properties of the emulsion.

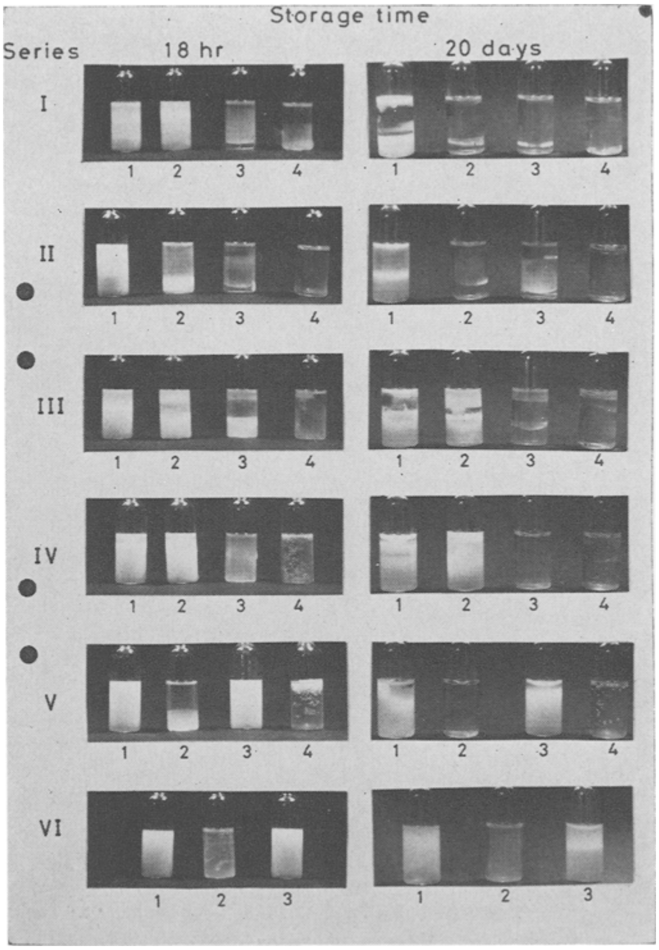
The stability of the emulsion water/*p*-xylene/nonylphenol nonaethylene glycolether is dependent on the phase distribution in a more complicated manner, and will not be discussed in detail here. The influence of the mesomorphous phase has been dealt with earlier (2).

Discussion

These preliminary investigations have shown that the behavior of emulsions is not only dependent on the properties and amounts of the two compounds which form the emulsion, but also on the properties of the emulsifier molecule, such as the HLB value and also to a very high degree on the amount of emulsifier present. This dependence has furthermore been shown to be governed by the state of the emulsifier in the phases. The emulsifier can be molecularly solved in these phases, it can exist in the form of micelles or it can, if the concentration is increased to a sufficiently high level, form liquid crystalline phases together with the other compounds.

This dependency of the properties of the emulsion on the presence of a liquid crystalline state has been shown previously for a single case (2) of an emulsifier of the O/W type. The pronounced increase of the stability of the emulsion, when this phase is present, has now been shown to exist also for several emulsifiers of the W/O type.

The present results also give a good example of how both the amounts of the solutes present and the state of the emulsifier determine the behavior of the emulsion. Nonylphenol diethylene glycolether gives emulsions of the O/W type when the amount of *p*-xylene is less than about 70–75%. This is in complete accordance with the old rule in which the volume of closely packed spheres in a liquid is considered. But this rule is only valid when the emulsifier has not reached the CMC value in the *p*-xylene phase. When the emulsifier concentration is in excess of this value, the emulsions are of the W/O type independent of the ratio of the solvents.

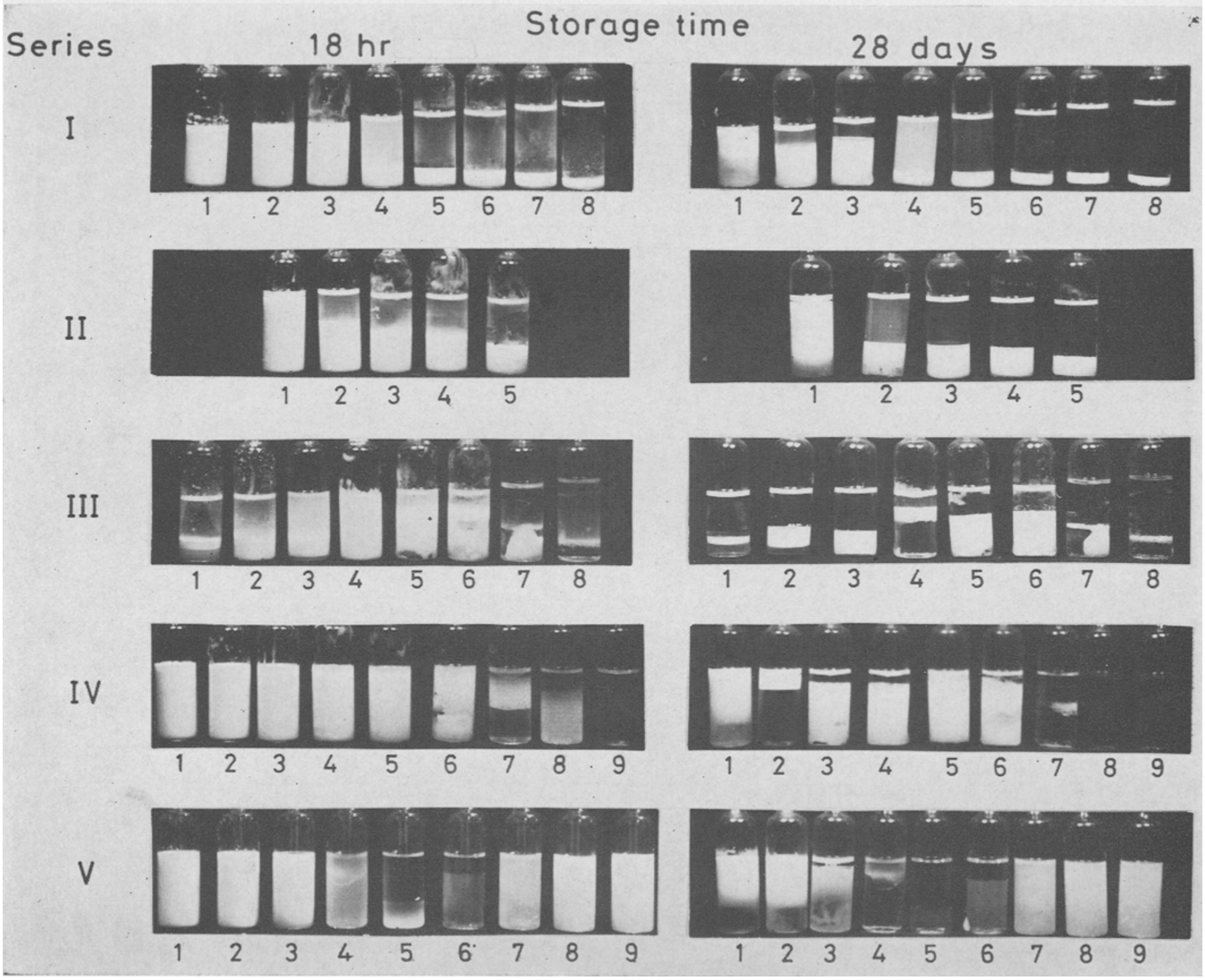


Series	Ratio water/ tricaprylin	1-monocaprylin, %			
		Sample No.			
		1	2	3	4
I	20/80	2.3	9.1	16.2	25.5
II	40/60	4.2	16.8	27.9	40.5
III	60/40	6.3	13.1	23.1	36.6
IV	80/20	8.2	16.7	28.7	43.4
V	90/10	9.1	18.4	31.0	46.3
VI	95/ 5	9.5	19.2	32.1	......

FIG. 4. The behavior of the emulsions in the system water/1-monocaprylin/tricaprylin when stored for varying lengths of time at 20 C.

When the conditions in which the presence of a liquid crystalline phase is not taken into consideration, the emulsions are most stable in the neighborhood of the CMC. An increase in the stability is to be expected when the concentration of the emulsifier is increased, since the interphase will be saturated when the concentration is in the region of the CMC. However, the decrease of the stability when the amount of emulsifier is further increased is not completely understood yet. Fundamentally, this is a question of collision rates between emulsified droplets and micelles and of the dependency of exchange rates between molecularly solved emulsifier and water molecules, the same specia in micelles and in emulsion droplets. These problems will, however, be discussed elsewhere.

The emulsion of tricaprylin-water with monocaprylin as an emulsifier shows a different behavior. The question of the existence of micelles in the nonaqueous part is equally determined, but it appears rather probable that micelles are already present at very low concentrations, since the water solubility increases rather rapidly with no definite increase



Series	Ratio water/ p-xylene	Nonylphenol diethylene glycolether, %								
		Sample No.								
		1	2	3	4	5	6	7	8	9
I	25/75	2.0	5.0	8.0	12.0	17.0	22.0	27.0	32.0	
II	50/50	5.0	10.0	15.0	20.0	25.0				
III	75/25	2.0	5.0	8.0	12.0	17.0	22.0	27.0	32.0	
IV	90/10	1.0	2.0	5.0	7.5	10.0	13.0	18.0	23.0	26.0
V	97/ 3	1.0	2.0	4.0	7.0	10.0	13.0	15.0	18.0	23.0

FIG. 5. The behavior of the emulsions in the system water/p-xylene/nonylphenol diethylene glycol ether when stored for varying lengths of time at 20 C.

as in the above mentioned case. If this is true, the behavior with decreasing stability from low concentrations of the emulsifier and very high O/W ratios before transition from W/O to O/W type of emulsion is quite in accordance with the case of water/p-xylene with nonylphenol diethylene glycol ether as emulsifier.

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