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Influence of Phase Equilibria on Properties of Emulsions

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Abstract □ An investigation was made concerning the phase equilibria in water-oil-emulsifier systems. The results have shown the presence of liquid crystalline phases and the pronounced influence of these on the properties of emulsions. The pronounced solubilizing power of emulsifier micelles in the oil phase, the changed stability due to these, and the drastic changes of volume ratios, water to oil, with increasing emulsifier concentration which this gives rise to, have been investigated.

Keyphrases □ Emulsions—phase equilibria effect □ Phase equilibria—w/o emulsions □ Stability, emulsions—emulsifier concentration □ Liquid crystalline phase—emulsions

The complicated behavior of emulsions has been treated in numerous articles and reviews, due to the importance of such systems in chemical technology and in a vast number of systems of biological origin. In his bibliography, Becher (1) dealt with the different factors that had been found responsible for the behavior of emulsions. Davies discussed the stability of emulsions based on a collision theory (2). Sherman has made important contributions concerning the general properties and rheological behavior of emulsions (3). Recently, Shinoda has introduced the PIT value (4), which denotes the phase inversion temperature. Shinoda assumes this temperature to be more useful than the well-known HLB value in the prediction of the behavior of emulsions from the properties of the emulsifiers.

The HLB value is useful to a very high degree; its success in practical emulsion preparation has shown this beyond doubt, but its shortcomings are obvious. As an example, Sherman (5) pointed out the inversion of emulsions when the amount of emulsifier is increased, and Davies (2) showed the difference in emulsion behavior when the oil phase was changed from benzene to petroleum ether. Neither of these examples can be explained by the HLB value of the emulsifier.

Preliminary results on the influence of phase equilibria on the properties of emulsions showed a sudden increase in stability in the presence of a mesomorphous phase (6). Further investigations (7) showed a pro-

nounced change in phase equilibria when the aromatic *p*-xylene in the oil phase was replaced by hexadecane. These results gave a tentative explanation to the problem stated by Davies (2). The rather complicated rheological behavior of emulsions when the emulsifier concentration was changed could also be satisfactorily explained by interpretation of phase equilibria (8). Since these results appeared to be promising, it was considered that further investigations of phase equilibria in the water-emulsifier-oil systems could be of general value.

Emulsions of w/o type are considerably more difficult to treat theoretically due to the low electric field strength in the continuous medium. Taking this into consideration, the authors chose a set of emulsifiers of the w/o type and determined the phase equilibria of the systems.

EXPERIMENTAL

Materials—The water was twice distilled. The nonylphenol diethyleneglycol ether was of commercial origin (Berol AB, Sweden), which was purified from polyglycols; other impurities are less than 0.01%. Other chemicals used were: octylamine (puriss. gas chromatographic >99%) and *p*-xylene (puriss. gas chromatographic >99.5%) (Fluka A.G., Switzerland); monocapryline (synthesized at the Institute of Medical Biochemistry, University of Gothenburg, Sweden); tricapryline (Eastman Distillation Products Industries); and lecithin, prepared from egg yolk according to a simplified method (9).

Phase Equilibria—The samples for investigation of the phase equilibria in the three-component systems given in Fig. 1 (A-D) were weighed directly into glass ampuls which were sealed. The samples were heated to homogeneity, slowly cooled to 20° under agitation, and allowed to stand at this temperature. The different phases were separated by ultracentrifugation and identified by visual observation under a polarizing microscope or by X-ray methods according to previous work on phase equilibria in ternary systems (10, 11).

Emulsion Preparation and Properties—The components were weighed into ampuls which were treated in an ultrasonic device at 20° for 1 min. followed by vacuum treatment to remove air. This was repeated five times.

The nature of the emulsion was determined by visual observation through a microscope of the spread of oil- or water-soluble dyes (Sudan III and Brilliant Blue F.C.F.). The emulsions with an

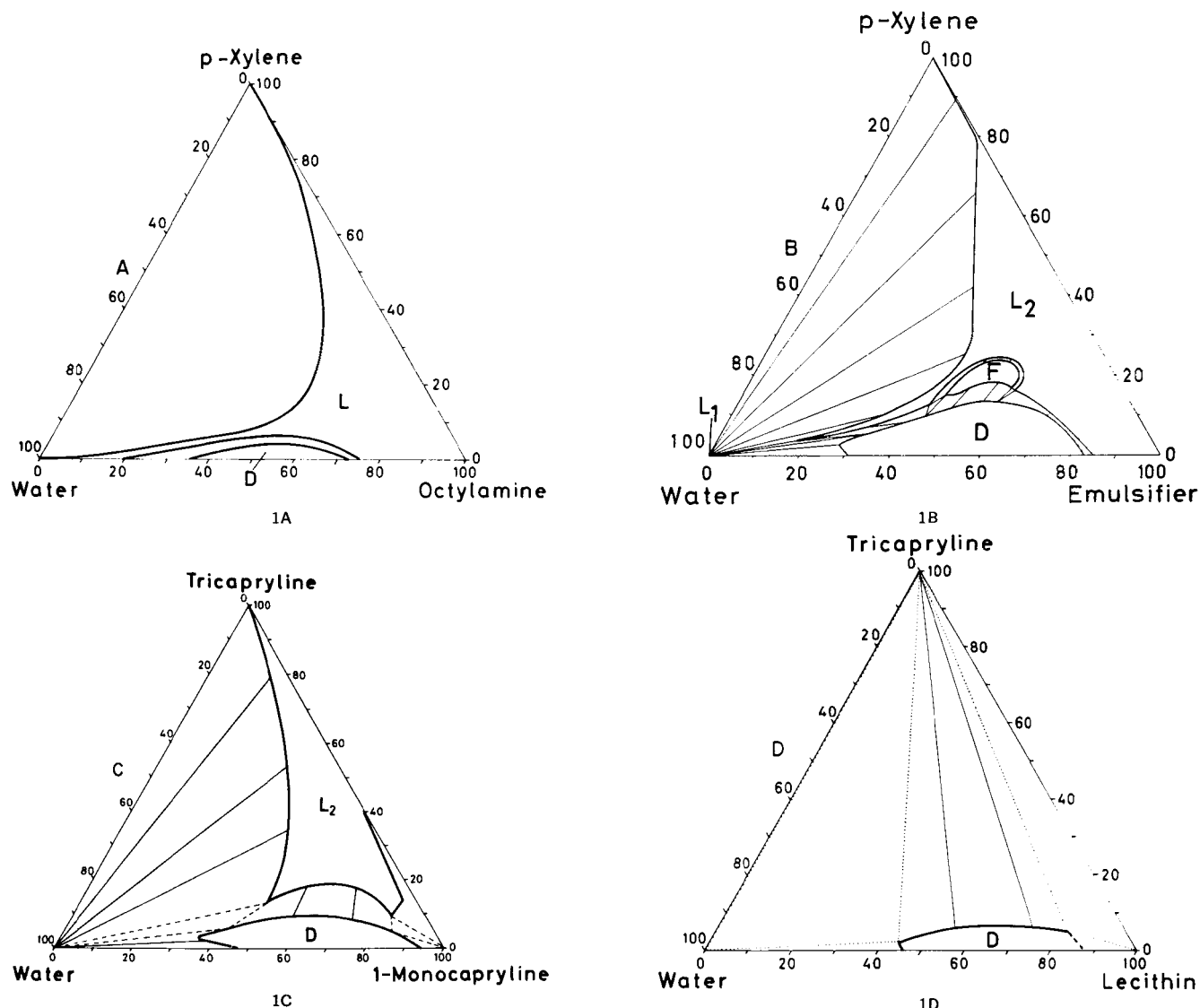


Figure 1—Phase equilibria in water–oil–emulsifier systems at 20°. Key: A, water–p-xylene–octylamine; B, water–p-xylene–nonylphenol diethyleneglycol ether; C, water–tricapryline–monocapryline; and D, water–tricapryline–egg lecithin.

amine as emulsifier were too unstable for such a procedure. In that case the emulsion was allowed to settle, and the nature of the two developing layers was determined. This eased the determination of the emulsion type when one of the layers—the emulsion—was emulsified in the other, since a change from water to oil of the continuous phase gave indications of a double emulsion, which could later be confirmed by direct observation in the microscope.

The estimation of the emulsion stability was performed in a rough way by judging the sedimentation rate from photographs. With the pronounced differences of stability characteristic of these systems, the method was considered to be satisfactory. The

emulsions containing an amine as stabilizer were too unstable to be determined in this way. In that case the time for clarification of the phases was used as a measure of the stability.

The emulsions were prepared in several series. In each series the ratio of water to oil was kept constant while the amount of emulsifier was varied. The total compositions of the emulsions are found in Tables I and II.

RESULTS

Phase Equilibria—Figures 1A–D contain diagrams of the phase equilibria in the four systems of this investigation. The conditions in the tentative three-phase areas to the right in the diagram (Fig. 1D) have not been examined in detail, since they are of no value to the present investigation.

The diagrams (Figs. 1A–C) are all of the same general shape with a pronounced solution area where the oil and the emulsifier solubilize water. Xylene and octylamine solubilize water to such a high extent that a continuous solubility area connecting all three components is formed. The solubilizing power decreases in the order A to C in the diagrams; in the water–tricapryline–egg lecithin system, too little mutual solubility is found to be observable in the diagram. The solubilization only takes place in the form of a liquid crystalline phase with a layer structure (denoted D in the figure). This phase is also found in all other diagrams and is always formed by water and the emulsifier with the oil solubilized to a few percent.

Table I—Total Composition of Water–Tricapryline Emulsions with Monocapryline as Emulsifier

Series	Ratio, % Water % Tri- capryline	—Monocapryline Sample No.—			
		1	2	3	4
I	95/5	9.5	19.2	32.1	
II	90/10	9.1	18.9	31.0	
III	80/20	8.2	16.7	28.7	
IV	60/40	6.3	13.1	23.1	36.6
V	40/60	4.2	16.8	27.9	40.5
VI	20/80	2.3	9.1	16.2	25.5

Emulsion Type—Figure 2 shows the emulsion type in the different parts of the region containing two liquid phases in the equilibrium. The system containing lecithin has not been included, since the corresponding two-phase area of that system is too small to be investigated conveniently.

The octylamine gives o/w emulsions in the water-rich part. In the remaining part of the two-phase area, it forms emulsions of the o/w/o type, which, however, are unstable and separate into two emulsions within a short time (Fig. 2A). Diglycol ether forms w/o emulsions when the emulsifier is associated in micelles in the *p*-xylene phase and when the ratio of *p*-xylene to water exceeds 0.70–0.75 (Fig. 2B). Monocapryline forms w/o emulsions in the whole area except where the water–tricapryline ratio is too high to permit the formation of a w/o emulsion (Fig. 2C).

Emulsion Stability—The stability of the system with diethylene-glycol ether as an emulsifier has previously been investigated and reported (12), and the system containing egg lecithin will not be treated here, since the solution areas of this are too small to be investigated conveniently.

The emulsions containing octylamine are considerably less stable than the other emulsions (Table II). The comparison between the stability of different emulsions in this system was consequently not done by means of photographing the emulsions, but it was made by measuring the time required for the upper phase to form a clear solution.

The upper layer is oil-continuous, and it is striking to compare (Table II) how the time for the clarification of this layer is reduced when the amount of emulsifier is increased. This tendency is most pronounced when the emulsion contains high amounts of *p*-xylene. On the other hand, the emulsions formed by the liquid crystalline phase and the solution were stable to a very high degree.

The emulsions containing water and tricapryline and with monocapryline as an emulsifier show two distinct regions of different behavior. At first, Series I and II contain the liquid crystalline phase in Sample 3 (Table I and Fig. 1C). This emulsion is by far the most stable that can be observed in Fig. 3. Only Series II is shown for spatial reasons. Sample 2, containing more emulsifier than Sample 1, is less stable.

This phenomenon of decreasing stability with increasing emulsifier concentration can be observed in all the emulsions belonging to the second region, the large two-phase area, in Fig. 1C. Only Series V is shown here as an example because of space limitations.

These results imply an optimum addition of monocapryline to obtain maximal stability. This has, however, not been investigated at present.

DISCUSSION

The results have shown two factors governing the stability of emulsions. The first one is the presence of a liquid crystalline phase

Table II—Stability of Water-*p*-Xylene Emulsions, with Octylamine as Emulsifier

Ratio, % Water % <i>p</i> -Xylene	Octylamine	Time Required for Formation of a Clear Top Layer, min.	Time Required for Clarification of the Whole Sample, min.
20/80	8.0	120	170
20/80	17.0	19	35
20/80	35.0	4.5	8
40/60	6.0	120	325
40/60	13.0	55	220
40/60	29.0	3	220
40/60	47.0	3.5	220
60/40	4.5	140	200
60/40	9.5	37	200
60/40	22.0	3	200
60/40	38.0	3	200
80/20	5.0	90	190
80/20	13.5	175	190
80/20	24.0	54	190
80/20	40.0	5	190
90/10	2.0	160	
90/10	8.5	160	1100
90/10	14.5	160	
90/10	26.0	145	1100

of the layer type which will increase the stability of the emulsion. This is well shown by Series II in Fig. 3 where Sample 3 contains the liquid crystalline phase. The same trend has been shown for other systems (6, 12). The two-phase area between water and the liquid crystalline phase containing only mono-glyceride and water was treated by Larsson (13), who also gave suggestions for the structure of such a dispersion in water.

The second factor is the presence of micelles. From the present investigations and from earlier studies (12), it appears that the emulsion will have a reduced stability when the concentration of the emulsifier is in excess of the critical micelle concentration. This is especially pronounced in the case of octylamine, *p*-xylene, and water where the increased emulsifier concentration gives a reduction of emulsion stability (Table II). The reason for this is not completely clear at present but the following explanation may serve as a hypothesis.

When two emulsified drops approach each other, a temporary oversaturation will be established in the region between the surfaces of the drops owing to the adsorbed emulsifier. This temporarily increased concentration may give rise to the formation of

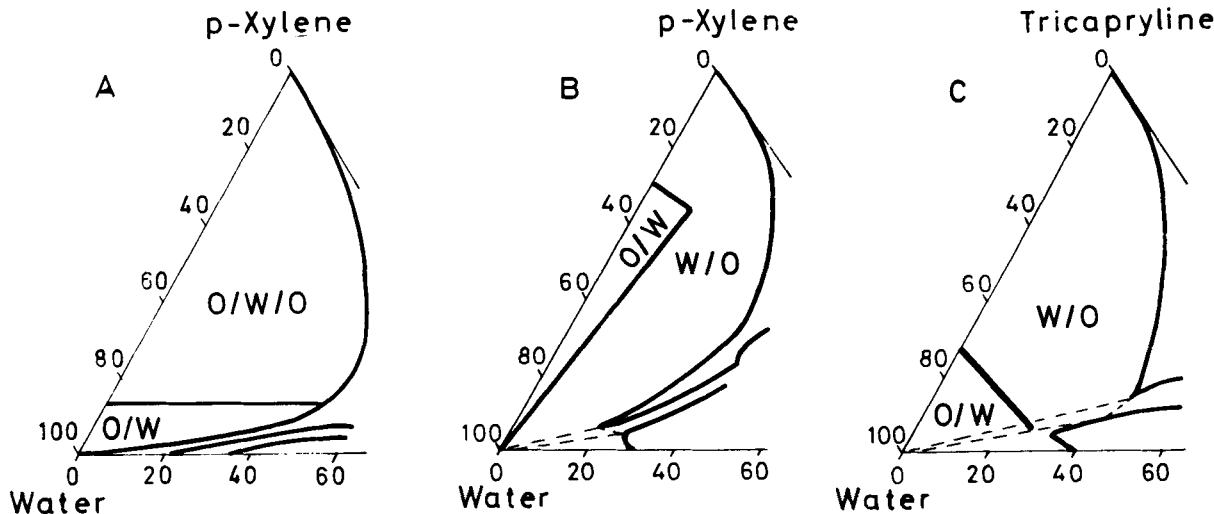


Figure 2—Emulsion type in different parts of the two-phase areas. Key: A, water-*p*-xylene-octylamine; B, water-*p*-xylene-nonylphenol diethylene-glycol ether; and C, water-tricapryline-monocapryline.

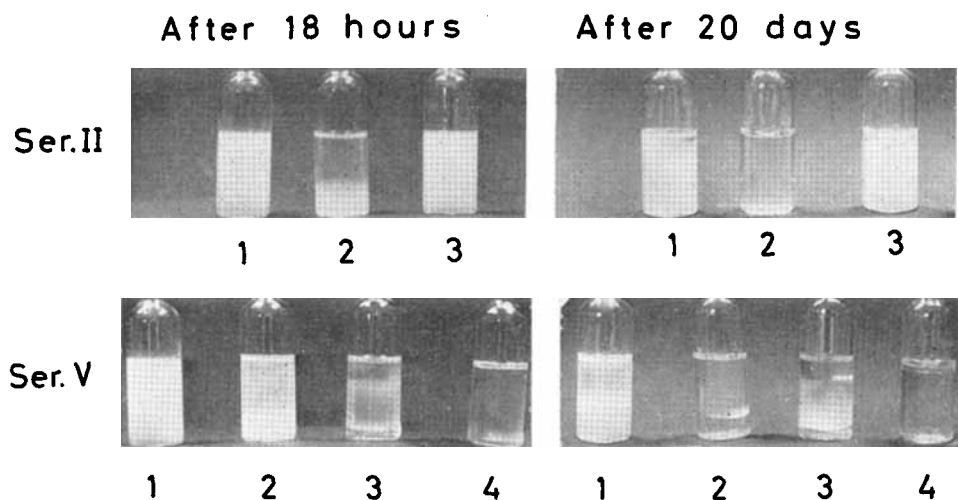


Figure 3—The behavior of emulsions in series where the ratios of water to tricapryline are constant and the amount of monocapryline is increased. The composition of the samples is given in Table I.

micelles in the continuous phase, or micelle formation also can take place in the dispersed phase in some cases. It appears likely that the formation of micelles will mean a source of decreased order between the surfaces and, consequently, the resistance to coalescence will be reduced. If the increased concentration, on the other hand, gives rise to an ordered layer structure of the liquid crystalline type, the temporary overconcentration between the surfaces will not imply a disorder phenomenon. On the contrary, a several layer structure can be formed containing more ordered structures.

This hypothesis is not contradicted by any of the results—they all support it. The water-amine-*p*-xylene system, which can form micelles both in the aqueous and *p*-xylene phase, gives rise to a very unstable emulsion when the concentration of emulsifier is increased. At high amine to *p*-xylene ratios, where the solution changes from *p*-xylene to water continuous, the stability of the emulsion is very low. For the same ratio of *p*-xylene to amine but with the water content reduced to such a degree that the liquid crystalline phase is present, the stability is increased in the most pronounced way.

The marked increase of the water-solubilizing power of the oil phase at certain ratios (oil-emulsifier), which can be observed in Figs. 1A-C, is also an important factor. The solubilizing implies that the volume ratio, water to oil, can be most drastically changed when the concentration of emulsifier is increased. This means that the changed concentration of emulsifier—in some cases due to the evaporation of the solvents—can cause an inversion of the emulsion due to volume changes under certain conditions.

CONCLUSIONS

The investigations have shown how the properties of emulsions can be related to the phase equilibria in water-oil-emulsifier systems. They have confirmed the hypothesis about the pronounced influence of the liquid crystalline phases present on the properties of the emulsion but have also pointed to the influence of micelles in the systems. Both of these factors have been neglected in earlier studies of the behavior of emulsions except one preliminary study (14).

The results have also made evident the pronounced solubilization of water in the oil phase and shown how this fact can cause drastic changes in the volume ratios of the two liquid phases.

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