A phase-rule study of multiple-phase formation in a model emulsion system containing water, n-octanol, n-dodecane and a non-ionic surface-active agent at 10 and 25°

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A four-component emulsion system containing the non-ionic surfactant $C_8H_{17}(O \cdot CH_2 \cdot CH_2)_6OH$ has been investigated, particularly in regions in which liquid crystal or more than two condensed phases are formed. Liquid crystal does not exist in the binary surfactant–water system at 25° but extensive regions form when the organic liquids octanol and dodecane are present, although these are not joined to the main two-liquid regions of the emulsion system. The surfactant is almost completely dissolved in the aqueous phase in water-dodecane mixtures but when substantial amounts of octanol are also present the partition coefficient is reversed in favour of the organic phase. At certain intermediate compositions three liquid phases are present. The significance of these results to the system as an emulsion are briefly discussed.

Although emulsions are treated by many workers as two-phase systems, there is increasing realization that more than two phases are frequently present, particularly in dispersions containing synthetic surfactants. The solubility of many surfactants in water is low, and in some instances limited not by the separation of a solid phase, but by liquid crystal (McBain, 1950). The situation is more complex in systems containing three components, which correspond to the simplest emulsions, and the phases present depend markedly on the nature of the third component, as well as on the properties of the surfactant (Lawrence, 1958; Mulley & Metcalfe, 1964; Mandell & Ekwall, 1968). It seems likely that some of the most important features of emulsions, for example emulsion-type, stability and viscosity, may in certain instances be explained by phase-rule studies (Salisbury, Leuallen & Chavkin, 1954; James & Goldemberg, 1960; Mulley, 1961; Burt, 1965; Lachampt & Vila, 1967; Friberg, Mandell & Larsson, 1969). A number of other workers in the emulsion field have referred to the multiphase character of their systems (Barry & Shotton, 1967; Talman, Davies & Rowan, 1967; Talman & Rowan, 1970). In practice, many emulsions have more than three components, although these are often not part of the emulsifying system; but a basic formula may commonly be considered to consist of four components, two being immiscible liquids and the others the emulsifying agent and the stabilizer. The properties of the system are often adjusted by varying the relative proportions of the two latter components.

The present paper describes a phase-rule study of such a model four component emulsion system containing an homogeneous non-ionic surfactant, a fatty alcohol as stabilizer, and a saturated hydrocarbon as the oil phase, with the object of finding

those regions of the system which form more than two condensed phases, as a pre-
liminary to a study of the relation between the nature of the phases present and the
properties of the system as an emulsion. A preliminary report describing a region where
three liquid phases were found in this system, resulting in the formation of multiple-
drop emulsions, was recently published (Mulley & Marland, 1970).

<div align="center">MATERIALS AND METHODS</div>

Materials

n-Octanol (M.A. grade, Mann Research Laboratories Inc.) and an 'oil' phase of
n-dodecane (BDH Ltd., 99% plus by g.l.c.) were used. The surfactant was 3,6,9,-
12,15,18-hexaoxahexacosan-1-ol, $[C_8H_{17}.(OCH_2.CH_2)_6OH]$ or C_8E_6 (Mulley, 1967). A
pure sample was obtained by the following method. Sodium (5·3 g) was dissolved in
triethylene glycol (137 g) and then heated with C_8E_3 Cl [prepared by treating C_8E_3 with
a chlorinating mixture of thionyl chloride and pyridine (Mulley, 1958); 64 g, b.p. 109
to 110°/0·1 mm, m.p. −23·1°, n^{20} 1·4466]. Water (900 ml) was added and the product
extracted with light petroleum (b.p. 100 to 120°, 600 ml, and 2 × 50 ml), at 70°. The
organic phase was dried (MgSO$_4$) and fractionally distilled to give C_8E_6 (26%, b.p. 184
to 186°/0·1 mm, m.p. 7:5°, n_D^{20} 1·4528). Gingras & Bayley (1958) prepared C_8E_6 by a
one-stage Williamson ether synthesis, while Corkill, Goodman & Ottewill (1961) used
a two-stage process. The physical data recorded by these workers for their samples
are (b.p. 180°/0·07 mm; n_D^{20} 1·4499 and b.p. 205°/0·0001 mm, f.p. 9·0, n_D^{40} 1·4463)
respectively. The infrared spectrum measured with a Unicam S.P. 200 spectrophoto-
meter confirmed the structure, but revealed traces of carbonyl and unsaturated im-
purity (Corkill & others, 1961). The compound was also assessed by g.l.c. (Mulley &
Winfield, 1970). The results showed the compound to have a purity of at least 98 to
99%.

Phase-rule measurements

The binary, ternary and quaternary systems were investigated by a combination of
synthetic (Mader, Vold & Vold, 1959), and analytical methods at 25°. The C_8E_6–water
binary system was studied between 2 and 90°, and the ternary and quaternary systems
at 10°, though less comprehensively than at 25°, and only by the synthetic method.

(a) Synthetic method

The quaternary system was systematically investigated by preparing ternary
mixtures of composition suitable for studying the various phase boundaries, but all
lying in one of several triangular sections through the tetrahedral model. The trian-
gular planes begin as lines in the C_8E_6–water–dodecane face, which run from the
C_8E_6 apex, and cut the water–dodecane axis at fixed ratios. Addition of octanol to a
three-component mixture on one of the lines in the C_8E_6–water–dodecane face, alters
the composition along a straight line drawn from the initial composition to the
octanol apex, and maintain the ratios of the first three components.

The mixtures were prepared in glass ampoules sealed with rubber teats; additions to
the ampoules were made using a micro-syringe. They were equilibrated for periods
ranging from 5 min to 7 days before visual, and in some instances microscopical
examination. Problems of equilibration were found, particularly in regions where

two-liquid plus liquid crystal regions were thought to exist. Gel-like regions were viewed in polarized light, any sample showing birefringence, and marked viscosity was taken to be liquid crystal.

(b) *Analytical method*

Mixtures of known composition were equilibrated for periods of not less than seven days in ampoules sealed by glass fusion and immersed in a water bath at 25°. The phases into which the solutions divided were separated by microsyringe, and analysed for three of the four components, the other being obtained by difference. Octanol, dodecane and C_8E_6 were determined by g.l.c. (Mulley & Winfield, 1970); the water content was measured by the Karl Fischer method.

(c) *Construction of the tetrahedral model*

The data obtained by the above methods were used to construct a three dimensional (Petrucci, 1965) tetrahedral model, using the geometric properties of this solid to represent the four-component system (Ricci, 1951). The faces (50 cm, sides) were made from 1/16 inch Perspex with chamfered edges for an accurate fit. Each hetero-geneous region was built up from balsa wood, metal sheet and cellulose filler suitably painted, and could be dismantled to show the relation between the various regions.

RESULTS

The terms 1L, 2L, 1L + LC, 2L + LC and 3L represent one liquid, two-liquid, one liquid plus liquid crystal, two-liquid plus liquid crystal, and three-liquid, phases respectively. All composition data are given as percentage (w/w) of surface-active agent, octanol, water and dodecane in that order. Where uncertainty exists about the precise nature of phase equilibria within certain regions of the diagram e.g. in the case of the transition from 1L + LC to LC and vice versa, this is indicated by broken lines.

Binary and ternary systems

Fig. 1 shows a projection prepared by a method described by Woodman (1946) consisting of the four "peeled" ternary faces of the tetrahedron at 25°. A general view of the tetrahedral model is shown in Fig. 2. The system at 25° comprises two pairs of immiscible liquids (n-octanol–water, dodecane–water), the remaining four binary systems being completely miscible at this temperature. The binary surfactant–water system is shown in Fig. 3. Points A and D (Fig. 1) represent the solubility of octanol and dodecane in water, which have been reported as 0·03 at 20° (Marsden & Mann, 1963), and $8·9 \times 10^{-10}$ mol fraction at 25° (Franks, 1966) respectively. Points C and F represent the solubility of water in octanol and dodecane; the former was found to be 3·52 at 25°, but the latter was not measured.

Phase analysis of conjugate layers in the main three component 2L areas (ABC, DEF, and ACFD Fig. 1) gave the direction of the tie-lines. These indicate that the plait points for the binodal curves ABC and DEF lie very close to the water and dodecane corners respectively. The results were also plotted as conjugation curves (Coolidge, 1926) and the surfactant content at the plait points was found in both cases to be below 1%. A further 2L region LMN exists at both 10 and 25°. Analytical investigation of its boundaries was made by preparing starting mixtures R and T and separating and analysing the phases, which then fixed the points R° and T° (Fig. 4).
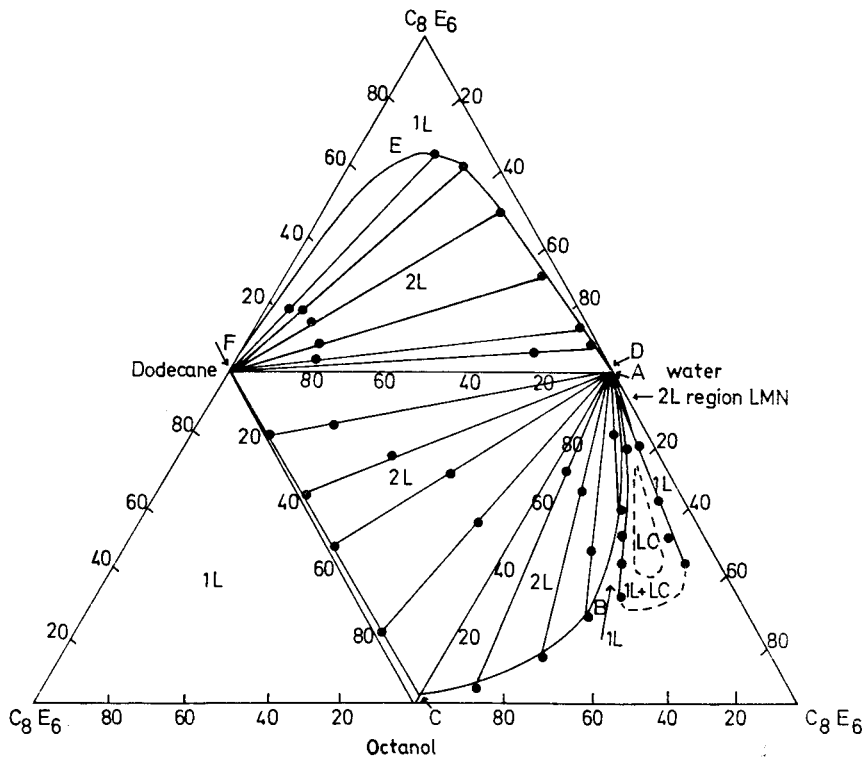
FIG. 1. Phase diagram of the four ternary faces of the tetrahedral model representing the system C$_8$E$_6$–water–octanol–dodecane at 25° plotted by Woodman's method (Woodman, 1946).
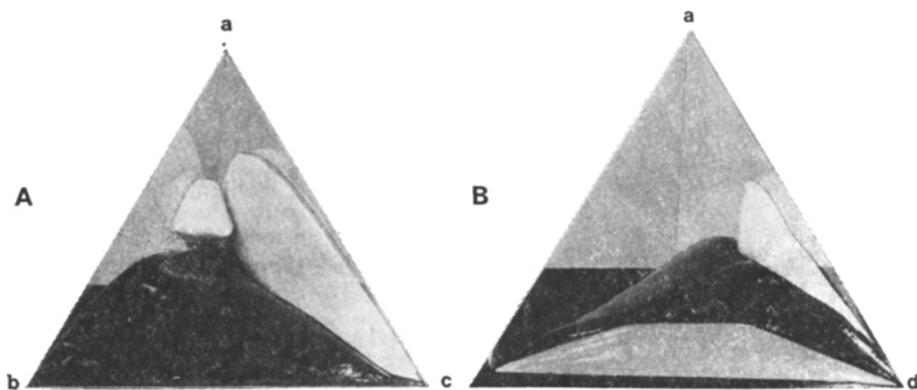

FIG. 2, A. Tetrahedral model of the system at 25° looking towards the C$_8$E$_6$–octanol–dodecane face. The 3L region may just be seen as a line between the black and the white 2L regions. The small light coloured volume extending from the octanol–water–C$_8$E$_6$ face is a liquid plus liquid crystal region.

B. Tetrahedral model looking towards the C$_8$E$_6$–dodecane–water face. The 2L volume extending from this face (the white region in Fig. 2A) has been removed to show the light coloured 3L region between this and the other 2L volume coming from the C$_8$E$_6$–octanol–water face. a, C$_8$E$_6$; b, octanol; c, dodecane; d, water.
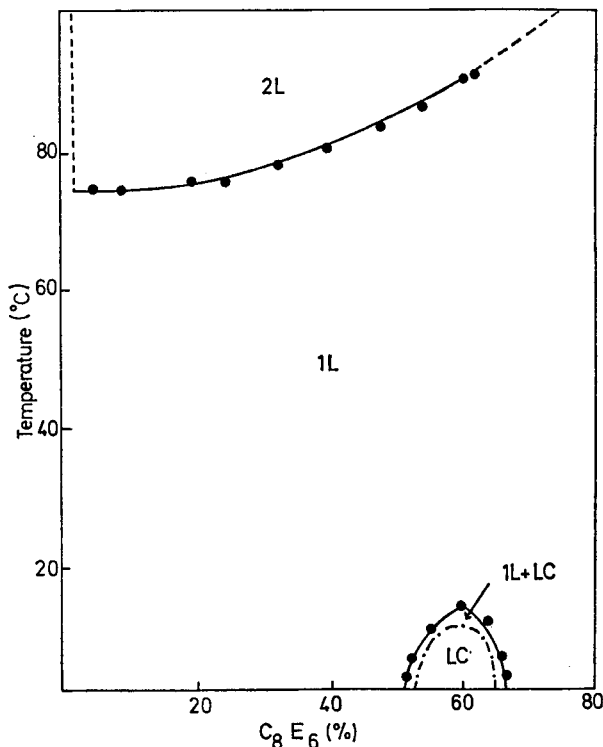
FIG. 3. Phase diagram for the system C_8E_6–water.

The area between the two 2L regions ABC and LMN was difficult to investigate mainly because small changes in composition markedly affected the observed phase situation. Difficulty was also experienced in equilibrating the systems. For example one mixture in this region (S, Fig. 4), after careful mixing and equilibration, separated into two liquids plus a liquid crystal phase, but after 14 days changed so that only one liquid and one liquid crystal phase were present. This was assumed to be the true situation, but the phase pattern within the region is shown by broken lines.

Quaternary system

Analytical data obtained in the 2L extension from the C_8E_6–octanol–water ternary face into the tetrahedron are given in Table 1, No. 3–23. The upper phase always contained most of the organic components including the surfactant, but the lower was almost entirely water, and contained so little of the other components that accurate analytical results were not obtained. In the 2L extension from the C_8E_6–water–dodecane ternary face, as in the ternary system, almost the exact reverse is the case; the lower aqueous phases are rich in surfactant and in equilibrium with upper ones containing very little. However, when the C_8E_6 content of the overall mixture is reduced, and substantial amounts of octanol are present, the composition of the upper phase begins to move away from the dodecane apex, and contains progressively more C_8E_6 and octanol (e.g. Table 1, No. 24 and 30). The tie-lines appear to 'swing over' without crossing. A similar situation must exist near the water axis for the other two-liquid region, but this was found impossible to demonstrate experimentally.

Table 1. *Tie line data in the two-liquid quaternary regions at 25°.*   Results 1 and 2 lie in the volume extending from the ternary LMN region; 3–23 and 24–44 in the volumes extending from ABC and DEF respectively.   A-(C_8E_6), B-(octanol), C-(dodecane).   The water compositions may be obtained by difference.

No	Total composition A	B	C	Upper phase A	B	C	Lower phase A	B	C
1	6·8	1·8	1·2	14	5	3·5			
2	4·55	1·5	1·7	15·5	4	5			
3	5·4	1·8	3·8	14·5	7	14			
4	10·1	2·9	1·7	17	4·5	2·5			
5	12·3	6·6	2·1	22	13·5	4·5			
6	6·35	3·4	2·65	25·5	14	11			
7	8·4	5·1	2·4	29	15·5	7·5	The lower phase		
8	6·2	3·2	0·8	13	6	1·5	was chiefly water		
9	4·9	14·9	47·5	7	22·5	69·5	and contained		
10	5·0	13·9	32·2	9	25	60	less than 0·5,		
11	5·15	31·5	19·1	9	51·5	35	0·2 and 0·3% of		
12	5·1	44·15	5·7	9	75	11·5	C_8E_6, octanol		
13	9·6	22·9	23·9	13	36·5	40	and dodecane		
14	9·6	13·5	36·9	14	21	53	respectively.		
15	16·7	26·3	17·2	20·5	36·5	24·5			
16	19·6	16·1	16·5	25·5	22	23			
17	20·1	22·5	7·0	27	33·5	9·5			
18	10·0	9·3	39·7	14	13·5	59			
19	11·7	12·2	69·3	14·5	14·5	53			
20	8·1	8·1	23·2	15	16	44·5			
21	7·4	8·75	42·3	12	14	64·5			
22	6·5	6·9	42·0	9	10	64·5			
23	9·35	8·7	40·8	11·5	13·5	66·5			
24	7·0	4·5	77·5	0·5	3·0	92·5	24·5	6	18·5
25	12·0	5·5	67·0	0·5	3·5	96	24·5	7	23
26	18·5	1·9	11·7	0·5	—	99·5	20	2	4
27	7·3	1·7	11·1	0·5	5·5	90	9	1	1·5
28	11·45	1·9	8·0	—	—	—	11·5	2·5	7
29	17·4	1·8	11·6	—	—	96·5	20	1·5	4·5
30	11·3	5·2	44·2	0·5	5	94	21	5·5	17·5
31	21·2	6·1	47·7	0·5	2·5	96	31	8	28·2
32	26·1	5·2	46·2	0·5	1·5	97	39	7	24·5
33	29·4	5·6	44·2	0·5	1·5	98	37	7	28
34	36·1	5·1	45·4	0·5	0·5	97	36·5	5	15
35	35·25	2·2	40·4	0·5	0·5	98·5	48	4	16·5
36	15·5	4·1	48·65	—	—	96	25·5	6	16
37	24·5	4·8	47·9	0·5	1	95·5	39·5	6	21·5
38	34·9	3·8	39·3	—	1	98·5	46	6	20·5
39	14·75	3·1	50·5	—	1	97·5	24	5·5	13
40	3	1·2	48·1	0·5	2	94·5	4·5	0·5	1·5
41	14·9	1·4	80·7	—	0·5	96	58	4	28
42	8·1	4·9	43·3	0·5	5·5	92	10·5	4·5	14·5
43	9·0	6·2	45·9	0·5	5·5	91·5	14·5	5	20·5
44	24·4	3·2	44·7	0·5	0·5	97	36·5	5	15

(—) results not obtained.

Tie-lines just interior to the ternary 2L region LMN of Fig. 4 follow the same pattern as in the extension of the 2L region ABC into the quaternary figure.   Whether the two regions eventually join is difficult to say, but the main 2L region takes on a "humped" appearance in the vicinity of the water corner, which could be due to their amalgamation.
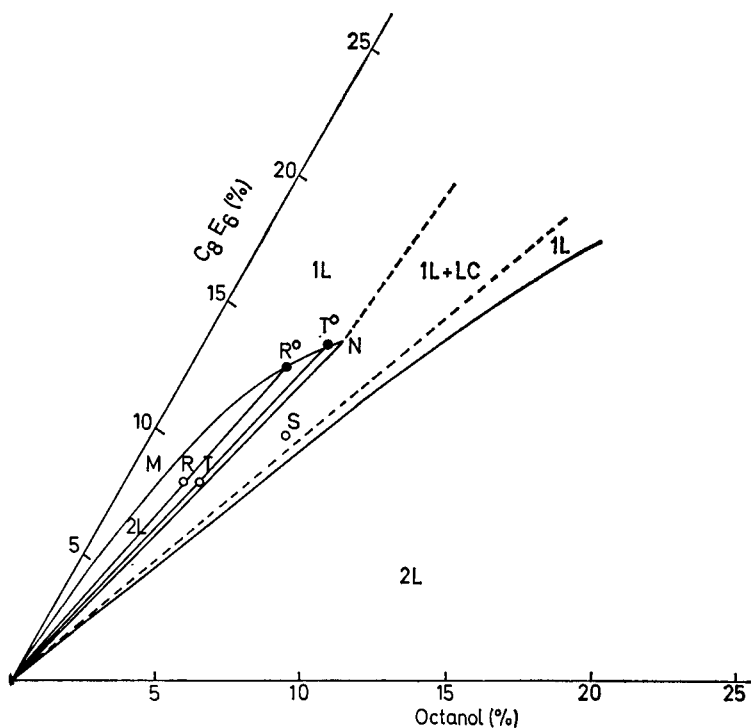
FIG. 4. The water-rich corner of the C_8E_6–octanol–water system at 25°.

3L region in the quaternary system

The position of this region is shown in Fig. 2B. In a quaternary system such a three-phase region has one degree of variance, unlike its counterpart in a three-component system. A composition in the three-phase region can be represented by a point in a triangular plane, the apices of which define the composition of each phase. The boundaries of the 3L region are defined by an infinite number of these planes. Lines joining their apices form edges to the region, and represent changes in the composition of the three phases concerned. The sides of the triangles form tie-lines in the surface between the 3L and 2L regions. Each set of data in Table 2 defines a triangular plane, and the projection drawn from these results (Fig. 5) gives an idea of the shape and size of the 3L region. The middle phase of the three contains a high percentage of non-ionic surfactant compared with the other two, and is also more variable in composition. The lower phase is essentially water, and experimental evidence for the changes in its composition, which must occur (see below), was not obtained. The upper phase consists of dodecane with small proportions of C_8E_6 and octanol; change in the composition of this phase, observed experimentally, is intermediate between that of the other two. The tie-line OP (Fig. 5) which represents the extremity of the 3L region in contact with the 2L volume above ACED, shows that the three liquid phases originate from the aqueous phase containing very small amounts of the other components (point O), and an oil phase, which is mainly dodecane (point P). As the overall amount of surfactant and octanol increases, the aqueous, oil, and third phase change in composition along the lines OX, PX, and OSX, and presumably end in a three-phase four-component plait point at X. The results define

Table 2.   *Tie-line data in the three-liquid region at 25°.   A-(C$_8$E$_6$), B-(octanol), C-(dodecane).   The water compositions may be obtained by difference.*

Total composition			Upper phase			Middle phase		
A	B	C	A	B	C	A	B	C
5·9	6·55	44·8	2	8·5	88·5	13	13	49·5
9·1	6·5	43·6	2	8·5	88	15	6·5	25
3·3	4·3	45·9	2	8	88·5	5·5	2·5	9·5
4·75	4·9	47·4	2	7·5	89	7·5	3	11·5
8·6	6·3	42·1	—	7·5	88	15·5	6·5	26
7·9	6·6	42·6	—	—	—	13	10·5	46·5
5·5	6·1	45·1	2	9	88·5	14	8·5	31·5
9·7	6·5	43·4	—	7·5	92·5	13·5	8	30
9·2	9·1	60·9	4·5	9·5	72·5	13	10	55·5

(—) results not obtained.   The third and lower phase was chiefly water and contained less than 0·5, 1·0 and 1·0% of C$_8$E$_6$, octanol and dodecane respectively.
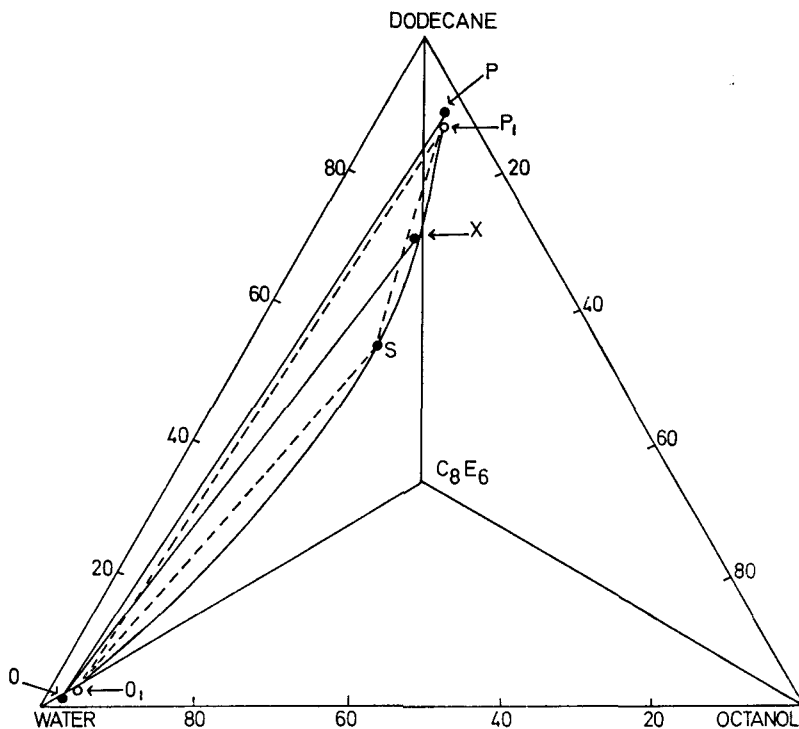

FIG. 5.   Triangular-orthogonal projection of the three liquid region on the octanol–water–dodecane face.   OX, PX and OSX represent the change in composition of the water, oil and surfactant phases respectively, OP being the last tie-line of the 3L region.   O$_1$P$_1$S (broken lines) is a projection of plane 1, Table 2 (the position of points O, O$_1$ and P$_1$ are not shown to scale for clarity).

OSX and PX quite well, but as in the ternary system, the composition of the aqueous phase is very sensitive to changes in overall composition, which only occur in the immediate proximity of the line OX, and therefore, no data along OX were obtained.

Effect of temperature on the equilibria

The main difference between the ternary system C_8E_6–water–octanol at 10°, and the results at 25°, was a small increase in the 1L + LC region allied to a slight reduction in the area under the main 2L binodal curve. The liquid crystal region at both 10° and 25° extends from the vicinity of the water apex to concentrations of surfactant between 30 and 40%, but in the former instance the region appears to be rather wider. A further gel-like region appears on the ternary face C_8E_6–water–dodecane at 10°. This region, whilst not possessing any marked birefringence, had an appreciable viscosity, and, although not investigated thoroughly, appeared to form most readily at concentrations of surfactant and dodecane between 30 to 35% and 10 to 20% respectively. At 25°, it was only a little more viscous than a normal 1L phase, and it has therefore not been shown as a separate area in Fig. 1. In addition to the main gel or liquid crystal regions so far referred to, another smaller region extending from the water/C_8E_6 axis exists at 10°, which is presumably an extension of the liquid crystal region observed in the binary system at this temperature (Fig. 3).

In the quaternary system, results at 10° compared with those at 25°, revealed that the main liquid crystal region was more extensive at the former temperature. This was accompanied by a reduction in the 2L volume extending from the octanol–water–C_8E_6 face, and to a lesser extent in the 2L volume based on DEF (Fig. 1).

The synthetic data also showed the presence of a gel-like region at 10°, extending into the tetrahedron from the dodecane–water–C_8E_6 face, and lying very close to the 2L binodal curve. The gel was clear, and had a marked viscosity, but in most cases examined did not exhibit birefringence. Although the exact form of the diagram at 10° is uncertain, it seems unlikely that the gel merges with the main liquid crystal region. The area between the gel and the 2L region extending from the C_8E_6–water–dodecane face consisted of a white, opaque gel-like mass, which was obviously heterogeneous. Great difficulty was encountered in equilibrating the phases within this region, and no visible separation had occurred after seven days. Microscopy revealed the presence of two liquid phases, and it is probable that at least two liquids plus a liquid crystal phase are present.

DISCUSSION

Only a few quaternary systems have been investigated fully by phase-rule methods (Francis, 1963), and most of these were studied in connection with solvent extraction. A quaternary system derived from six pairs of liquids, four miscible and two immiscible, which also form a three-liquid phase region, does not appear to have been reported. In the present case the 3L region occurs near the ternary face which contains the two pairs of partial miscibility. It produces at first a single pair in the ternary and quaternary systems, but three phases occur when greater amounts of the fourth component are present. The nearest system we can find is that studied by Hartwig, Hood & Maycock (1955), which has three immiscible liquid pairs. Phase-rule studies on binary, ternary and a few quaternary systems containing surfactants have been made, mostly where the surfactant is ionic (McBain, 1950; Dervichian, 1957; Ekwall, Danielson & Mandell, 1960; Lawrence & Pearson, 1964), but a few on binary

and ternary systems containing non-ionic surfactants have also appeared (Marsden and McBain, 1948; Nakagawa & Tori, 1960; Mulley & Metcalfe, 1964; Shinoda, 1967; Corkill & Goodman, 1969; Friberg, Mandell & Fontell, 1969). These surfactant systems exhibit many differences from solvent mixtures, in particular the formation of liquid crystal phases.

From the former studies in surfactant systems it appears that the 1L phase near the C_8E_6–water axis, which extends over the 2L and 3L regions to the narrow single-phase organic solution bounded by CF and the octanol and dodecane apices (Figs 1 and 2), is a micellar solution of the two water-insoluble liquids, octanol and dodecane. The structure of organic solutions containing non-ionic surfactants has been less widely studied, but may contain micelles of the inverse type (Hartley, 1955). Solutions above CF may be like this. Solubility in the aqueous micellar solutions is limited in quaternary regions tending towards the C_8E_6–water–dodecane face, by separation of excess organic liquid (mainly dodecane), when more of the organic components are present than the micelles can hold. The tie-lines show the distribution of the surfactant between the phases to be unusual in comparison with that of other solutes in systems where the solute is miscible with both solvents. In most systems of the latter type the distribution is usually fairly even. This abnormality is repeated, although the distribution is reversed in the other main 2L region containing large amounts of octanol. Here the general form of the phase diagram is similar to the ternary system containing a phenol studied by Mulley & Metcalfe (1964), although in the present case a 1L "channel" (Palit, Moghe & Biswas, 1959) appears to separate the 2L region LMN and the liquid crystal area from the binodal curve ABC. The transition across the 1L/2L phase boundary ABC and its extension into the quaternary system, leads to an aqueous phase containing so little surfactant that micelles are probably not present, and the molecules are monomolecularly dispersed (Mulley & Metcalfe, 1964). Tie-line distributions of this type fit the theoretical considerations discussed by Mertslin & Nikurashina (1960) concerning 2L volumes surrounding three-phase regions in quaternary systems.

Formation of the 3L region between the two two-liquid volumes entering the tetrahedron from ABC and DEF, is the result of the different distribution of components within each, as shown by the two sets of tie-lines. Increasing the amounts of dodecane and water in the organic phase of the region extending from ABC, reduces the solubility of C_8E_6 so that eventually the phase divides into two: one rich in surfactant and containing some water forms, its composition given by a point on OSX; and the other containing an increasing amount of dodecane (composition along XP) (Fig. 5). The solution structure of 3L phases in such systems has been discussed earlier (Mulley & Metcalf, 1964). Further addition of dodecane–water moves the composition of the surfactant phase along XSO until eventually so little octanol is present that the surfactant and water phases merge at O, and the dodecane phase reaches P. Beyond this the characteristic distribution in the 2L volume extending from FED supervenes.

Difficulties found in measuring changes in composition of the aqueous phase were mentioned in the results section. Similar problems occur in other areas for the same reason. Included in these are the narrow channel region, and the phases situated in the surface near it, where the junction of the 3L and 2L phase regions are found. The latter are not separated in the base of the quaternary region, but it seems probable that a narrow 2L volume exists between and above the lines OSX and OX, although this was not confirmed experimentally.

The drop in temperature from 25 to 10° caused a reduction in volume of the main two- and three-liquid regions, although the general form of the diagrams is almost identical. This result is probably explained by a decrease in the hydrophilic nature of the surfactant at the higher temperature. The surfactant properties of the non-ionic class are almost destroyed above the cloud point. Rising temperature usually reduces liquid crystal formation by surfactants (McBain, 1950; Winfield, 1968), and this is the case in the present four-component system.

It is clear from this study that the surfactant, although miscible with water, octanol and dodecane, is distributed completely differently in the two pairs, water–octanol and water–dodecane, and that this will have important effects on the nature of emulsions formed within the two regions. The presence of three-liquid phases in some regions also means that the dispersions produced will be more complex than in two-phase emulsions. Liquid crystal, which is likely to be crucial in emulsion stability, does not invade the liquid phase regions in this surfactant system, but seems likely to do so with compounds containing longer alkyl chains.

Acknowledgement

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