

Effect of micelle formation and the nature of the oil-phase on the distribution of a non-ionic surfactant in three- and four-component emulsions

J. S. MARLAND AND B. A. MULLEY

Postgraduate School of Studies in Pharmacy, University of Bradford, Bradford, BD7 1DP, U.K.

As part of an investigation into the mechanisms responsible for the formation and stability of emulsions, the partition of the homogeneous non-ionic surfactant $C_8H_{17} [O \cdot CH_2 \cdot CH_2]_6 OH$ or C_8E_6 (E = ethoxy) in the main two-liquid (2L) regions of the three-component systems C_8E_6 -water-dodecane, C_8E_6 -octanol-water and the four-component system C_8E_6 octanol-water-dodecane has been determined. Cmc and aggregation numbers have been obtained for the surfactant in the different phase regions. The relation of these results to emulsification in the systems is discussed.

Although it has been shown on several occasions that the partition of the surfactant between the oil and water phases of an emulsion is a type-determining factor (Bancroft, 1912; Woodman, 1946; Wellman & Tartar, 1930; Davies, 1957) its role in so far as stability is concerned is less clear. It is generally accepted that an appreciable surfactant solubility in the continuous phase is necessary for stability (Bancroft, 1912) although Greenwald, Kice & others (1961) have suggested that if the distribution is too much in favour of this phase much surfactant may be wasted.

Previously Marland & Mulley (1971) noted that the surfactant (3,6,9,12,15,18-hexa-oxahexacosan-1-ol; $C_{18}H_{34} [O \cdot CH_2 \cdot CH_2]_6 OH$) was dissolved mainly in the water in water-dodecane mixtures but in the 'oily' phase when octanol was substituted for dodecane. The plait points in both cases were very close to one apex of the triangles used to represent the systems in that phase-rule study. We now report more comprehensive measurements of the distribution of the surfactant in the same three- and four-component systems, especially in relation to the micellar properties of the surfactant in the various phases present.

THEORY

The effect of association on the distribution law is well documented and theoretical treatments of various kinds have been developed by which the nature of the associated species, especially the aggregation number and the dissociation constant, may be obtained (Davies & Hallam, 1956). All methods for determining molecular association require extremely accurate data but this is particularly true of some of the more complicated treatments (Kreuzer, 1943). Most of the theoretical work has been developed in systems with low aggregation numbers. Little appears to have been done on the distribution of surfactants where micelles are the associated species. Micelles usually have high aggregation numbers and in view of this and the degree

of accuracy with which the surfactant could be analysed, two relatively simple treatments have been employed.

The distribution coefficient of a substance is defined as C_s/C_w where C_w is the concentration of solute in the aqueous phase and c_s the corresponding concentration in the organic phase. Gross & Schwarz (1930) described a method of evaluating association equilibria assuming that aggregation was confined to one of the phases. They obtained the relation:

$$\log (K_d - K_{d_1}) = (n - 1) \log C_s + \text{constant} \quad \dots \quad (1)$$

where K_d is the apparent distribution coefficient, K_{d_1} is the distribution coefficient for monomers, n the aggregation number of the associated species and C_s the concentration of surfactant in the organic phase (phase in which association is occurring). K_{d_1} is obtained by extrapolating a plot of K_d versus C_s to zero concentration. A plot of $\log (K_d - K_{d_1})$ against $\log C_s$ will have a slope of $(n - 1)$.

Elworthy & Florence (1967), assuming association of the surfactant occurs in both phases above the cmc, derived the equation:

$$\log C_s = \frac{1 + n_2}{1 + n_1} \log C_w + \text{constant} \dots \dots \dots (2)$$

where n_1 is the number of monomers per micelle in the aqueous phase and n_2 the corresponding value for the organic phase.

In the present systems at low concentrations of the surfactant, that is below the cmc, dimerization occurred in the organic phase when this consisted substantially of dodecane. Above the cmc, larger aggregates were formed in the aqueous phase. The slope of plots of $\log C_s$ against $\log C_w$ enabled n_1 to be calculated if n_2 was assumed to remain as 2.

The distribution law only strictly holds when (a) concentrations are expressed in mol fractions (although for solutions of one molar or less the errors are negligible) and (b) the solvents are completely immiscible (Davies & Hallam, 1956). The latter is never so and for surfactants some increase in miscibility of the aqueous and organic components usually takes place by micellar solubilization. Both assumptions are inherent in the above treatments.

MATERIALS AND METHODS

The preparation and purity of the components have been described previously (Marland & Mulley, 1971).

Distribution measurements

Mixtures of octanol-water and dodecane-water (1:1 by weight) were prepared and varying concentrations of surfactant added. The mixtures were equilibrated at $25^\circ \pm 0.5^\circ$ for periods of 1-6 weeks. Similar results were obtained in four-component systems in which the ratio of three of the four components (water, octanol and dodecane) were almost constant (water, 56.0-58.6%; octanol, 3.0-4.2%; dodecane, 36.2-38.1%).

The surfactant concentration in each phase was measured by g.l.c. A Varian series 712 gas chromatograph fitted with a flame-ionization detector and capable of being temperature programmed was employed. A copper column 4 ft \times $\frac{3}{8}$ in internal diameter was used, packed with 20% SE52 on 45/60 acid-washed silanized Chromasorb W. Oven temperature was programmed from 220-320° at 20°/min.

Nitrogen and hydrogen flow rates were 60 and 30 ml/min respectively and the injector-detector port was maintained at 400°.

The phases were separated by removing the upper phase as completely as possible using a microsyringe, before sampling the lower phase. This technique kept contamination to a minimum. At very low surfactant concentrations in the aqueous phase it was impossible to detect the surfactant because the water dampened the response of the flame ionization detector. These solutions were concentrated using a controlled evaporation procedure. The dilute surfactant solution (1–2 ml) was distilled with a mixture of benzene and ethanol (1:2, 10 to 20 ml) under vacuum. The residue was taken up in a small amount of isopropanol and analysed. It was found from test experiments that this procedure also removed on average 10% of the surfactant, and consequently all results were adjusted to allow for this.

RESULTS AND DISCUSSION

Fig. 1 illustrates a plot of $\log C_s/\log C_w$ for the systems C_8E_6 -octanol-water (A),

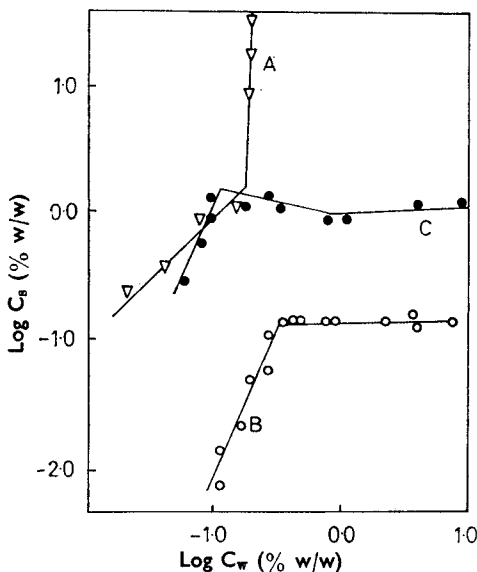


FIG. 1. Plot of $\log C_s/\log C_w$ for the systems C_8E_6 -octanol-water (A), C_8E_6 -water-dodecane (B) and C_8E_6 -octanol-water-dodecane (C).

C_8E_6 -dodecane-water (B), C_8E_6 -octanol-dodecane-water (C). The plots are of the form described by Greenwald & others (1961) with the exception that system (C) apparently had two inflection points.

Aggregation numbers above and below the cmc for system (A) have been obtained using the Gross-Schwarz (1930) method. Above the cmc in systems (B) and (C) where both phases appear to be aggregated, association numbers have been obtained using the Elworthy-Florence (1967) treatment assuming that dimerization occurred in the dodecane systems. Table 1 summarizes the results; cmc and aggregation numbers have been recorded in that phase in which the major association appeared to occur.

Table 1 reveals that for systems (B) and (C) the cmc values quoted in the aqueous phase are reduced in comparison with that recorded for the binary system C_8E_6 -water (Corkill, Goodman & Ottewill, 1961), particularly so for system (C). It appears that the presence of octanol as a fourth component in the aqueous phase enables micelle formation to occur at a much lower concentration. This effect has also been reported in single-phase systems containing octanol (Lawrence & Stenson, 1957). The two phases in equilibrium are composed of relatively immiscible solvents whose small intersolubilities produce a situation which is not dissimilar to that in which a third and possibly even a fourth component is added to single-phase surfactant-water mixtures. The effect of traces of other components in the major solvent is determined by the amounts present. Where the components comprising the two phases are almost immiscible, the situation is not too far removed from the binary system, and consequently association numbers and cmc are likely to be similar in the single-phase and two-phase systems. If the miscibility is pronounced, however, the effect will be more noticeable.

The system C_8E_6 -octanol-water on the other hand does not exhibit a cmc in the aqueous phase (Table 1), but an inflection point corresponding to 1.5% w/w was

Table 1. *Cmc and association number for C_8E_6 in various systems at 25°. Corkill & others (1961) obtained a cmc of 0.39% w/w and an aggregation number of 32 for the binary C_8E_6 -water system at 25°.*

System	cmc % w/w		Association numbers (below cmc)		Association numbers (above cmc)	
	Aqueous phase	Organic phase	Aqueous phase	Organic phase	Aqueous phase	Organic phase
(A) C_8E_6 -octanol-water	—	1.5	1	1	1	20
(B) C_8E_6 -dodecane-water	0.34	—	1	2	66	2
(C) C_8E_6 -octanol-dodecane-water	0.11	—	1	2	60	2

obtained for the surfactant in the organic phase. This points to a greater affinity between octanol and surfactant than between surfactant and water, due possibly to their similar chemical configurations.

The distribution below the cmc was not constant in systems (B) and (C). By application of the Gross-Schwarz treatment, an aggregation number of two was found in both systems. The formation of dimers and trimers by alcohols and acids in non-polar solvents is quite common (Mukerjee, Mysels & Dulin, 1958) and usually thought to be due to hydrogen bonding between the terminal hydroxyl groups. A similar situation may be responsible for the present results reinforced by polar attractions between the polyether portions of the surfactant molecules. In contrast the polar character of the octanol militates against dimer formation in this solvent.

Greenwald & others (1961) obtained a constant distribution below the cmc contrary to the present results. This is surprising since iso-octane is a saturated hydrocarbon similar to dodecane rather than to octanol. Two points at the end of their partition isotherm do, however, suggest that dimerization may occur below the cmc.

An aggregation number of 20 was calculated for the surfactant in the organic phase of the two-liquid region forming in the system C_8E_6 -octanol-water. The factors controlling micelle formation and aggregation number in organic solutions have not

been as widely investigated as their aqueous counterparts. The differences presumably mean that the polar/non-polar solvent affinities of the surfactant are more easily accommodated in octanol than in water. The high cmc in octanol (Table 1) supports this view and since the surfactant concentration in the aqueous phase never apparently exceeds the cmc, oil solubilization and o/w emulsification would be expected to be very limited in this system. The aggregation numbers in the aqueous phases above the cmc in the systems C_8E_6 -water-dodecane and C_8E_6 -octanol-dodecane-water were 66 and 60 respectively. These results are based on the assumption that the organic phase contained surfactant distributed as dimers. The values are much higher than the figure obtained by Corkill & others (1961) in aqueous solution but are nearer the figure ($n = 51$) obtained by Balmbra, Clunie & others (1964) for the binary systems at 50°. The dodecane content of the aqueous phase of system (B) (solubilized dodecane) changes from well under 0.1% below the cmc, to approximately 1.4% where the surfactant concentration is 18.6% (Marland, 1970). The dodecane content of the aqueous phase of system (C) is even higher. Nakagawa (1967) has shown by light scattering that addition of decane to the surfactant solution increases the micellar aggregation number and that decanol can have an even greater effect. Since the aqueous phase is saturated with the organic phase in all the present systems the results agree with Nakagawa's experiments although the aggregation numbers of systems (B) and (C) are possibly the reverse of what would be expected. Since the partition method was originally used for determining low association numbers, and the inherent inaccuracies are large when the treatment is applied to higher association numbers, the apparent anomaly cannot be regarded as proven.

In the quaternary system the distribution of surfactant is initially in favour of the organic phase, but on further addition a point is reached where the concentration in the two phases becomes equal, after which the aqueous rather than the organic phase contains most surfactant. Several explanations concerning the two inflection points are possible. The most likely is that the first inflection point marks the cmc in the aqueous phase. Because of this the organic phase, which still contains most surfactant, is partially stripped of C_8E_6 by micellization, so that there is a fall in the concentration in this phase even though the overall concentration of the surfactant is increasing. As the concentration of C_8E_6 is increased further, so the surfactant content of the aqueous phase rises until eventually the surfactant activity begins to rise in both phases. The observations are reminiscent of the dips found in surface-tension curves of surfactants, which were traced to the presence of third components such as alcohols.

The assumption that all the tie lines in this region lie in triangular planes having the water- C_8E_6 axis of the model tetrahedron used to represent the system (Marland & Mulley, 1971) as a common side, is only approximately true (Marland, 1970). Furthermore, practical difficulties made it impossible to maintain exactly the same ratios of water, octanol and dodecane, which may have led to some variation in the composition of the phases and therefore to the partition of surfactant. Another possibility is that the triangular plane selected (see variation in ratios recorded in the experimental section) may have infringed the boundaries of the three-liquid region (Marland & Mulley, 1971) with which it closely borders. (During equilibration several mixtures appeared to consist initially of three phases before eventually changing to form two phases.)

The completely different distributions in the ternary systems C_8E_6 -octanol-water

and C_8E_6 -dodecane-water are due to the high surfactant aggregation numbers which occur in the organic and aqueous phases respectively of the two-liquid regions forming in these systems. The high association numbers mean that practically all the surfactant goes into the phase in which aggregation occurs which accounts for the distribution being heavily biased in favour of one phase. It seems likely that homogeneous surfactants will show similar patterns in many systems but for impure surfactants the distribution selectivity may be less clearly defined. This is most interesting phenomenon as far as emulsification is concerned. Cockbain & McRoberts (1953) suggested that if the interfacial film is readily displaced in favour of the disperse phase then the stability of the emulsion will be reduced. This is unlikely in systems where the distribution is markedly in favour of one phase.

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