Stabilization of oil-in-water emulsions by non-ionic detergents: properties of synthetic detergents at anisole- and chlorobenzene-water surfaces

P. H. ELWORTHY AND A. T. FLORENCE

From Department of Pharmaceutical Technology, University of Strathclyde, Glasgow, C.1, Scotland

As part of an investigation into the mechanisms of stabilization of emulsions, the interfacial activity of three synthetic non-ionic detergents, $CH_2 \cdot [CH_2]_{15} \cdot [O \cdot CH_2 \cdot CH_2 \cdot]_x OH$, with x = 3, 6 and 9, at the anisole-water and chlorobenzene-water interface has been determined by measurement of interfacial tension. Surface pressure (π)-area (A) relations have been derived. The films are more expanded than at the air-water interface and an equation of the form $(\pi - \pi_x)A = xkT$ fits the results. It is suggested tentatively that π_R, which is in most cases positive, and which increases with polyoxyethylene chain length, arises from the interaction between the ethylene oxide chains as they approach closely. The apparent critical micelle concentrations determined from the interfacial tension-concentration curves are higher than the true critical micelle concentrations obtained at the air-water interface.

Although a knowledge of the behaviour of detergents at oil-water interfaces is of importance in any investigation of their mode of action as stabilizers of emulsions, few investigations of this nature have been made with synthetic non-ionic detergents. Becher's recent review (1967) on emulsification with non-ionic detergents mentions the only comprehensive study (Crook, Fordyce & Trebbi, 1963) with synthetic polyoxyethylene octylphenyl ethers at the water-iso-octane interface. Wrigley, Smith & Stirton (1957) and Becher (1963) have studied the interfacial tension lowering properties of a number of commercial non-ionic detergents at various oil interfaces.

The lowering of interfacial energy by adsorption of surface-active species is important in the process of emulsification, but its role in maintaining stability once the emulsion has been formed is not clear. In a previous paper (Elworthy & Florence, 1967), the stability of emulsions of anisole and chlorobenzene in the presence of the commercial non-ionic detergent, cetomacrogol 1000, was discussed. It was concluded that the main source of stability was the steric or hydrational repulsive force which arose from the interaction of the long polyoxyethylene chains. It appeared that the zeta potential of the oil globules play a secondary role in stabilization, as an increase of cetomacrogol concentration above the critical micelle concentration (CMC) decreased the zeta potential significantly yet resulted in only a small reduction in stability.

In the present paper this work is extended to include the effects of synthetic detergents with the structure $C_{16}H_{33}[O \cdot CH_2 \cdot CH_2 \cdot]_x OH$ with x = 3, 6 and 9, on the interfacial tension at anisole-water and chlorobenzene-water interfaces, in order to determine the effect of polyoxyethylene chain length.

<center>EXPERIMENTAL</center>

Apparatus and Methods

Interfacial tensions were measured using a pendant drop apparatus based on the design of Andreas, Hauser & Tucker (1938) as previously described by Elworthy & Florence (1967). At 20° ± 0·01° a value for the surface tension of water of 72·68 dynes cm^{-1} was obtained (72·79 dynes cm^{-1}) [literature values in brackets] for hexane-water interfacial tension, 51·03 dynes cm^{-1} (51·1 dynes cm^{-1}), and for carbon tetrachloride-water 44·85 dynes cm^{-1} (45·05 dynes cm^{-1}). Measurements were made at intervals to determine ageing in the systems. Chlorobenzene and anisole were fractionally distilled, and water was distilled from potassium permanganate. The detergents were synthesized using methods described previously (Elworthy & Macfarlane, 1962a, b; 1963) and were chromatographed on alumina and recrystallized before use. The Williamson ether method was used to prepare Me[CH$_2$]$_{15}$ [O·CH$_2$· CH$_2$]$_3$·OH. Redistilled hexadecyl bromide (Eastman Kodak), 1 mole, was condensed with monosodium trioxyethylene glycol, prepared by reaction of sodium (1 mole) with redistilled trioxyethylene glycol (BDH) (4 mole). The detergent was separated from the reaction mixture, from which the sodium bromide had been removed, with a light petroleum–ether mixture, the residue after evaporation fractionally distilled, redistilled and then purified as described above. All compounds had the same melting points as described (Elworthy & Macfarlane, 1962a, b; 1963) and assays for ethylene oxide content gave the theoretical amount (±0·2%).

<center>RESULTS AND DISCUSSION</center>

The equilibrium interfacial tensions of the detergents, C$_{16}$H$_{33}$·[O·CH$_2$·CH$_2$]$_x$OH with x = 3, 6 and 9 (abbreviated to C$_{16}$n$_3$, C$_{16}$n$_6$, C$_{16}$n$_9$) were determined as a function of concentration at 20° ± 0·01°. Some results are shown in Fig. 1.

Interfacial tension

For trioxyethylene and the hexaoxyethylene ethers, the detergents were dissolved in the oil phase and the interfacial tension measured against pure water. The nonaoxyethylene compound was also studied in this way but, in addition, the detergent was placed in the aqueous phase and equilibrated with pure oil. Table 1 summarizes the results, showing the apparent CMC's of the detergents and the interfacial tension at this concentration and areas/molecule in the immediate pre-CMC region, calculated on the assumption that the Gibbs' adsorption equation holds for the present systems. (Table 1). Gibbs' adsorption equation was used in its simple form,

$$\Gamma_2 = - \frac{1}{RT} \frac{d\,\aleph}{d\ln c}$$

where Γ_2 AN = 10^{16}, N being Avogadro's number and A the area/molecule (Å^2), neglecting solute activities. This was considered to be admissible because of the low concentrations of surfactant involved in the pre-CMC region. Errors occur in the estimation of areas/molecule using the equation in this form only when the mole fraction of solute, N$_2$, is large (greater than 0·01) (Hutchinson, 1949). N$_2$ of the surfactants in the regions in which the areas/molecule were calculated was in all cases less than 4 × 10^{-4}. At the air-water interface, only when the concentration of similar non-ionic surfactants approached 30% (N$_2$ ~ 10^{-2}) did appreciable errors occur in areas/molecule when the simple form of Gibbs' equation was used (Florence, 1965).
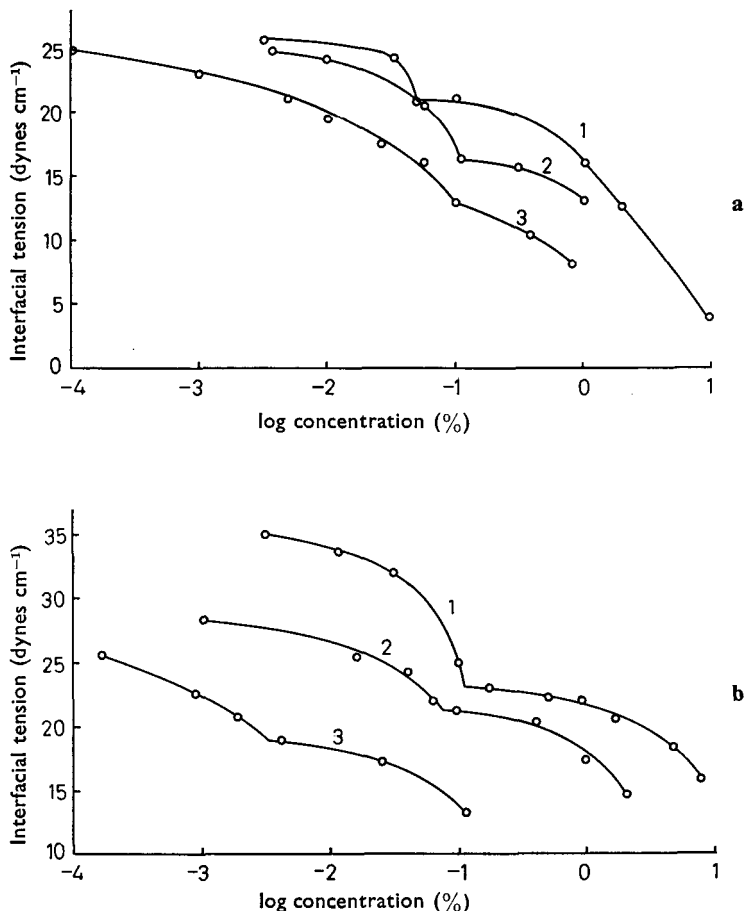
FIG. 1a. Anisole-water system. Effect of (1) $C_{16}n_3$, (2) $C_{16}n_6$, and (3) $C_{16}n_9$ on the interfacial tension. **b.** Chlorobenzene-water system. Effect of (1) $C_{16}n_3$, (2) $C_{16}n_6$, and (3) $C_{16}n_9$ on the interfacial tension.

Table 1. *Apparent critical micellar concentrations (mole litre^{-1}), areas per molecule and interfacial tensions at the* CMC

Oil phase	Compound	CMC mole litre^{-1}	Interfacial tension at CMC dynes cm^{-1}	Area/molecule Å^2	Area/molecule (Å^2) at air/water interface
Anisole	$C_{16}n_3$	1.74×10^{-2}	20·0	45	31†
	$C_{16}n_6$	6.92×10^{-3}	16·2	56	38*
	$C_{16}n_9$	1.59×10^{-3}	12·8	76	53
	$C_{16}n_{25}$‡	0.23×10^{-3}	5·2	154	120
Chlorobenzene	$C_{16}n_3$	3.17×10^{-3}	23·1	48	31†
	$C_{16}n_6$	1.55×10^{-3}	21·3	80	38*
	$C_{16}n_9$	1.05×10^{-3}	14·3	100	53
	$C_{16}n_{25}$‡	0.06×10^{-3}	7·5	184	120

† From surface pressure data using $C_{16}n_3$ spread on water

* Areas/molecule at air-water interface from Elworthy & Macfarlane (1962a) and Elworthy (1960).

‡ Cetomacrogol 1000, data from Elworthy & Florence (1967).

Greenwald, Kice & others (1961) have shown that the distribution coefficients of surfactants between oil and water show no concentration dependence below the CMC.

The areas/molecule at the oil-water interfaces so calculated are greater than those at the air-water interface; and the areas at the chlorobenzene-water are greater than at the anisole-water interface.

Interfacial tensions at the CMC fall with increasing ethylene oxide chain length, characteristic of non-ionic detergents at aromatic hydrocarbon interfaces (Becher, 1963). At aliphatic hydrocarbon-water interfaces (e.g. iso-octane) Crook & others (1963) found that the interfacial tension increased with increasing polyoxyethylene chain length, for a series of nonylphenyl polyoxyethylene ethers.

The work of adhesion of anisole to water is 81·6 dynes cm^{-1} compared with 67·9 dynes cm^{-1} for chlorobenzene suggesting that the methoxy group of the anisole is strongly oriented to the water (Adamson, 1960). This may account for the lower interfacial tensions in the anisole systems. There is also likely to be a difference in the structure of the interfacial films formed by long and short polyoxyethylene chain detergents. Becher, (1963) has suggested that some of the ethylene oxide units of short polyoxyethylene chain detergents reside in the oil phase, but as the chain length is increased the surfactant molecules become drawn more into the aqueous phase.

In contrast to the situation in some aqueous solutions the CMC in the oil-water systems studied here decreases as the polyoxyethylene chain of the detergent is lengthened. The CMC's are also many times higher in the oil-water system than the CMC's of the detergents in aqueous solution in the absence of oil. The same trends are observed in the results of Crook & others (1963) who suggest that the higher CMC's result from the preferential distribution of the detergent to the non-aqueous phase. Thus a large amount of detergent has to be present in the system before sufficient is present in the aqueous phase to form micelles. Obviously this has practical consquences as the CMC of oil-soluble surfactants determined from measurements at the air-water interface thus bear little relation to the minimum concentration which can be used to prepare the emulsions. The distribution explanation seems to be correct as the discrepancy between the true and apparent CMC's decreases as the chain length increases, in accord with the decreasing partition coefficient, K_w^o, as the series is ascended. All the systems studied show a further decrease of interfacial tension above the apparent CMC, which may be due to a further change in the structure of the interfacial film.

Ageing effects

Ageing at the oil-water interface is not pronounced with these short-chain detergents, but some results are presented in Fig. 2, for surfactants dissolved in chlorobenzene compared with those disolved in pure water. Concentrated systems came to equilibrium more rapidly than dilute ones (compare B and C, D and E, in Fig. 2).

Equation of state

π (surface pressure) *vs* A (area/molecule) plots were constructed from interfacial tension data, and in Fig. 3, these results are presented as plots of πA *vs* A. It can be seen that none of the lines obey the simple relation.

$$\pi A = kT$$

but that over large portions of the lines an equation of the type

$$\pi A = mA + xkT$$

is obeyed.   Writing m = π_R we obtain

$$(\pi - \pi_R)A = xkT \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1)$$

where π_R may be considered to be a measure of the interaction between the adsorbed molecules.   The values of π_R and xkT are recorded in Table 2.
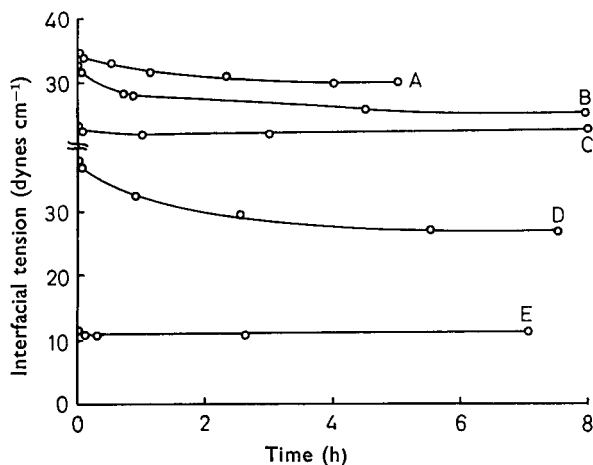

FIG. 2.   Ageing effects ot the chlorobenzene-water interface.
(A)   0·00029% $C_{16}n_3$ (B)   0·00018% $C_{16}n_6$
(C)   0·19% $C_{16}n_6$ (D)   0·0001% $C_{16}n_9$
(E)   1·018% $C_{16}n_9$

Table 2.   *Values of π_R and xkT from πA vs A plots at the oil-water interface*

Oil	Detergent	π_R dynes cm^{-1}	xkT	x
Anisole	$C_{16}n_3$	—0·6	200	0·5
	$C_{16}n_6$	+1·0	400	1·0
	$C_{16}n_9$	2·9	760	1·9
	$C_{16}n_{25}$	8·9	1340	3·4
Chlorobenzene	$C_{16}n_3$	2·8	398	1·0
	$C_{16}n_6$	10·8	400	1·0
	$C_{16}n_9$	12·5	800	2·0

NOTE: The change in sign of π_R suggests that it is made up of two components such that
$$\pi_R = \pi_{HC} + \pi_{PEG}$$
where π_{HC} is the interaction between the adsorbed hydrocarbon chains and π_{PEG} is the force between the polyoxyethylene chains.   At the air/water interface π_{HC}, which will be negative, will predominate and π_R will thus be negative as indeed was found: π_R for $C_{16}n_3$ at the air-water interface = —14·7 dynes cm^{-1}.

Two factors are usually considered to cause the product πA to deviate from kT; molecular attraction between the adsorbed surfactant (causing it to decrease below kT) and the finite size of the molecules (causing it to increase above kT).   At the non-polar oil-water interface lateral intermolecular attractions are so slight that an equation

$$\pi(A - A_0) = kT \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad (2)$$

has been found to hold for some surfactants, e.g. an equimolecular film of $C_{18}H_{37}\overset{+}{N}Me_3$ and $C_{22}H_{45}SO_4^-$ gives results obeying the equation $\pi(A - 20) = kT$ (Davies & Rideal, 1963).   For equation (2) to hold, (a) there must be no electrical repulsive forces operating, (b) there must be no cohesive forces between the hydrocarbon chains, and, (c) there must be no repulsive forces of other origin.   It is likely that conditions
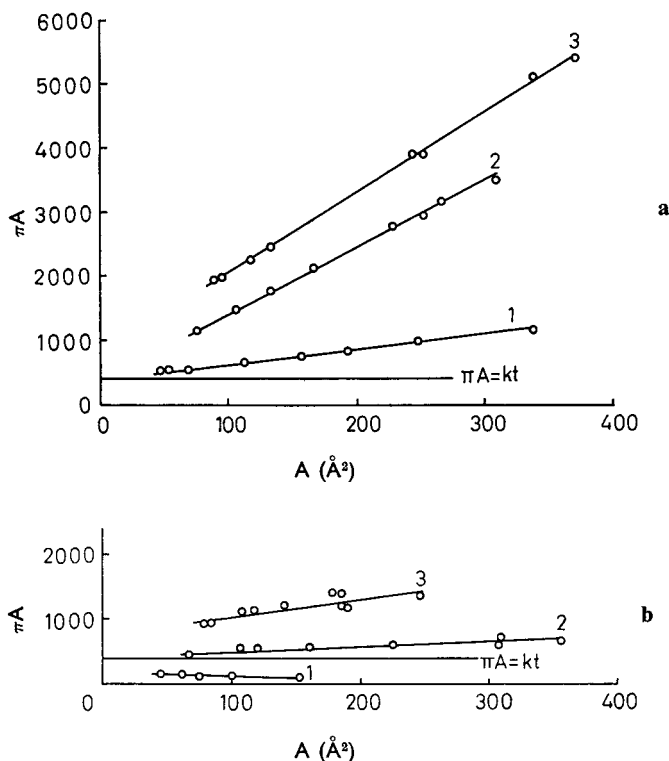
FIG. 3a. πA-A plots for (1) $C_{16}n_3$, (2) $C_{16}n_6$, and (3) $C_{16}n_9$ at the anisole-water interface. b. πA-A plots for (1) $C_{16}n_3$, (2) $C_{16}n_6$ and (3) $C_{16}n_9$ at the chlorobenzene-water interface.

(*a*) and (*b*) hold for non-ionic films, the latter because the polyoxyethylene chains are the determinants of closest approach.   For the compounds studied here equation (2) does not hold, indicating that some repulsive force is in operation.   This repulsion seems likely to arise from steric interactions of the ethylene oxide chains.

The fact that π_R increases with ethylene oxide chain length would imply that this interaction plays some part in the determination of the character of the πA *vs* A plot, as a positive value of π_R indicates the operation of repulsive forces.   The small negative value obtained for $C_{16}n_3$ in anisole may be partially due to experimental error, and partially to the possibility that only a small part of the polyoxyethylene chain of this molecule resides in the aqueous phase.

The increase of π_R with chain length is probably due to an entropic effect arising from the penetration of adjacent polyoxyethylene chains into one another's available space.   From the theory of Mackor (1957), this will give an increased free energy in the system.   Such effects are also important in the interpretation of stability data on emulsions, and preliminary work has shown that the stability increases with increasing polyoxyethylene chain length.

REFERENCES

ADAMSON, W. A. (1960). *Physical Chemistry of Surfaces*, p. 71, Interscience, New York.

ANDREAS, J. M., HAUSER, E. A. & TUCKER, W. B. (1938). *J. phys. Chem., Ithaca*, **42**, 1001–1091.

BECHER, P. (1963). *J. Colloid Sci.*, **18**, 665–673.

BECHER, P. (1967). in *Nonionic Surfactants*, pp. 604–626, Editor: Schick, M., New York: Marcel Dekker.

CROOK, E. H., FORDYCE, D. B. & TREBBI, G. F. (1963). *J. phys. Chem., Ithaca*, **67**, 1987–1994.

DAVIES, J. T. & RIDEAL, E. K. (1963). *Interfacial Phenomena*, 2nd edn, pp. 228–229. New York: Academic Press.

ELWORTHY, P. H. (1960). *J. Pharm. Pharmac.*, **12**, 293–299.

ELWORTHY, P. H. & FLORENCE, A. T. (1967). *J. Pharm. Pharmac.*, **19**, *Suppl.*, 140S-154S.

ELWORTHY, P. H. & MACFARLANE, C. B. (1962a). *J. chem. Soc.*, 537–541.

ELWORTHY, P. H. & MACFARLANE, C. B. (1962b). *J. Pharm. Pharmac.*, **14**, *Suppl.* 100T-102T.

ELWORTHY, P. H. & MACFARLANE, C. B. (1963). *J. chem. Soc.*, 907–914.

FLORENCE, A. T. (1965). Ph.D. Thesis, University of Glasgow, p. 101.

GREENWALD, H. L., KICE, E. B., KENLY, M. & KELLY, J. (1961). *Analyt. Chem.*, **33**, 465–468.

HUTCHINSON, E. (1949). *J. Colloid Sci.*, **3**, 219–234.

MACKOR, E. L. (1957). *Ibid.*, **6**, 492–495.

WRIGLEY, A. N., SMITH, F. D. & STIRTON, A. J. (1957). *J. Am. Oil Chem. Soc.*, **34**, 39–43.