The effect of detergent concentration on monomer activity in a non-ionic detergent solution

C. B. MACFARLANE,* P. H. ELWORTHY† AND D. O. GYANE‡

The School of Pharmaceutical Sciences, The University of Strathclyde, Glasgow, U.K.

The mono-octyl ether of hexaoxyethylene glycol has been synthesized and carefully purified using foam fractionation in the ultimate stages of the purification. Surface tension measurements of solutions of the detergent in water using a Wilhelmy plate indicate a continuing decrease in surface tension with increasing detergent concentration above the critical micellar concentration. Vapour pressure osmometry using the Mechrolab 302 substantiated the interpretation of the results in terms of the law of mass action.

Two main theories of micellization are extant. One, the "pseudophase," treats micelle formation as the production of a separate but soluble phase commencing at the critical micellar concentration. This theory implies constant activity of the monomers at total detergent concentration values greater than the critical micellar concentration. The second theory considers micellization as the reversible formation of an aggregation of monomers with an equilibrium between the monomers and micelles that can be described by a law of mass action type equation. In this theory the activity of the monomeric species continues to change as the concentration of detergent is increased even above the critical micellar concentration.

Dialysis experiments (Harrap & O'Donnell, 1954; and Abu-Hamdiyyah, Mukerjee & Mysels, 1963) as well as surface tension measurements (Hudson & Pethica, 1964; Elworthy & Mysels, 1966) have shown that the activity of monomers continues to increase with detergent concentration. Elworthy, Gyane & Macfarlane (1969) discussed the effect of purity and contamination on the surface tension of aqueous solutions of a non-ionic detergent. We have now examined the monomer activity over a range of concentrations above and below the critical micellar concentration.

MATERIALS AND METHODS

Syntheses of glycol and detergent

3,6,9,12,15-Pentaoxaheptadecane-1,7-diol was synthesized as described by Elworthy & Macfarlane (1963).

3,6,9,12,15,18-Hexaoxahexacosane-1-ol (hexaoxyethylene glycol mono-octyl ether, C_8E_6). Sodium (0·25 mol) was dissolved in 3,6,9,12,15-pentaoxaheptadecane-1,7-diol (1 mol) under a layer of light petroleum (100–120°) (cf. Macfarlane, 1963). 1-Bromo-octane (0·25 mol) was slowly added to the solution over 4 h and the reaction mixture held at 120° for a further 4 h. C_8E_6 was extracted from the cooled reaction mixture

* Present address and to whom all communications are to be sent: Lilly Research Centre Ltd., Erl Wood Manor, Windlesham, Surrey, U.K.
† Present address: The University, Manchester, U.K.
‡ Present address: University of Science and Technology, Kumasi, Ghana.

with diethylether, which was then evaporated and the residue re-extracted with light petroleum (60–80°). The light petroleum was evaporated and the extracted material was decolourized by gently stirring at 30° in a 30% suspension of charcoal in acetone (charcoal: extract ratio 1:2, by weight). The charcoal was filtered off and the solvent evaporated. 50 ml of a 20% solution of extract in absolute ethanol was then passed down a column of 120 ml of a strong anion-exchange resin. The eluate was recycled twice then a further 100 ml of absolute ethanol passed. The solvent was evaporated from the total eluate and the residue dried under vacuum in the presence of phosphoric oxide. Infrared spectra of the residue failed to detect any carbonyl impurities.

This crude product (2 g) was then adsorbed from benzene onto a column of Mallinckrodt silicic acid (25 g) mixed with celite (5 g). The column was washed with increasing concentrations of acetone in benzene. All pre-run was removed by 25% acetone in benzene while C_8E_6 was eluted by 30% acetone in benzene. The yield of this stage was approximately 65% of the adsorbed product.

Final purification was by foam fractionation* of a 0·35% aqueous solution of the compound until the solution was reduced to 60% of its volume. The foamed solution was then freeze dried in an all glass apparatus and the remaining water removed under vacuum at 30° in the presence of phosphoric oxide. Found: C, 61·2; H, 10·6; $CH_2.CH_2.O$, 66·9. Calculated for $C_{20}H_{42}O_7$; C, 60·9; H, 10·7; $CH_2.CH_2.O$, 67·0.

Materials

All organic solvents (Analar grade) were dried and redistilled immediately before use. Chromatographic materials were soaked in and thoroughly eluted with the appropriate solvents.

Water used was from the laboratory still, redistilled from alkaline permanganate then finally distilled in a seasoned and sterilized all glass still.

All glass joints were hand ground to obviate the need for vacuum grease.

Surface tension measurements

Surface tensions were measured using a light glass Wilhelmy plate (see Elworthy & Macfarlane, 1962). The difference in weight of the plate in the air–solution interface and in air was measured using a torsion balance of sensitivity of ±0·1 mg. With the size of plates used this is equivalent to ±0·02 dynes cm^{-1}. The solution flask was immersed in a thermostat bath at 25 ± 0·02°.

A CI microbalance giving readings of better than ±0·01 mg (0·002 dynes cm^{-1}) was used in the study of the region above the cmc. The glass plate was suspended from the left arm of the balance and counterbalanced by a specially prepared counterweight and the zero adjustment circuit of the apparatus. Readings of surface tension were obtained by counterbalancing the greater part of the pull by a further set of specially prepared platinum weights to bring the force exerted by the balance within the range of the scale selected.

---

* *Foam fractionation.* The all glass apparatus consisted principally of a one litre round bottomed flask containing the solution, and a two-necked adapter that served as an inlet for the gas diffusion tube used as a bubbler, and as exit for the foam and point of attachment for a vertical Vigreux fractionating column. The column was connected through adapters to a receiver flask. (For fuller details see Gyane, 1970.)

By slow, controlled, bubbling of oxygen-free, water-saturated nitrogen into the solution, foam was formed which rose slowly up the Vigreux column. Drainage of the foam during this process effectively concentrated the more surface-active impurities which were carried over into the receiver flask. The rate of foaming was adjusted to give as dry a foam as possible (ideally black films).

By allowing the horizontal lower edge of the Wilhelmy plate to just touch the surface of the solution, buoyancy effects were minimized. To reduce evaporation and aerial contamination and to ensure a saturated atmosphere above the solution a glass cover, with only a small hole in the middle to allow passage of the suspending rod, was fitted to a flask containing the solution being measured. This flask was always cleaned with chromic acid, thoroughly rinsed with triple distilled water then rinsed with a very dilute foamed solution and drained before use. This procedure, apart from removing any undesirable substance from the glass that might affect the result, compensates for concentration errors due to adsorption of detergent onto the glass.

Vapour pressure osmometry

A range of concentrations of C_8E_6 was studied using a Mechrolab Model 302. Drop size was controlled using a telescopic measuring device (Deshmukh & Fleming, 1969). The apparatus was calibrated using sucrose and had a calibration factor of 45 over the concentration range studied.

RESULTS AND DISCUSSION

The surface tension as a function of concentration of solutions of C_8E_6 is illustrated in Fig. 1.
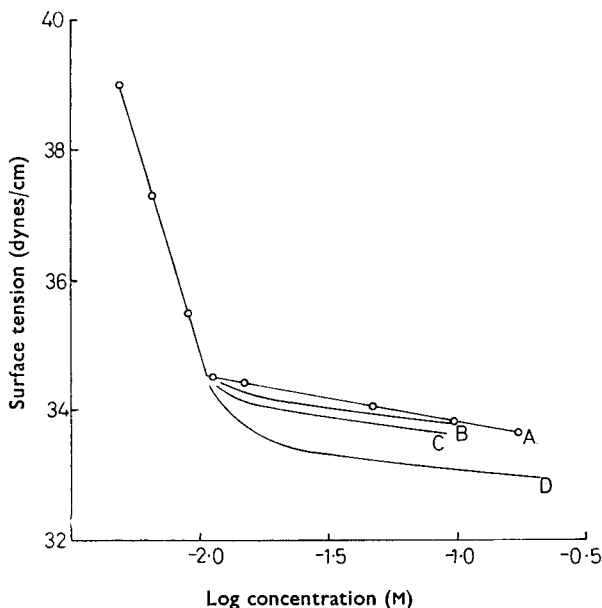

FIG. 1. Measured and theoretical values of surface tension *vs* concentration of aqueous solutions of C_8E_6. Plot A—measured; plots B, C and D were calculated from K equal to 10^{12}, 10^{11} and 10^9 respectively.

While there is the normal change of gradient attributed to the formation of micelles, the plot does not show the usual pattern of a line parallel to the abscissa above the critical micellar concentration but the continuance of a negative slope. This is not a unique effect but it can be masked by inadequate purification or by contamination.

The continuing decrease in surface tension of these solutions with increasing solute

concentration above the critical micellar concentration would therefore appear to indicate that the activity of the monomers of C_8E_6 continues to increase in this region.

Calculation of critical micellar concentration

If the micelles formed by a non-ionic detergent are in equilibrium with the monomers present, then using the law of mass action and replacing activities by concentration, the system may be described by

$$K = \frac{m}{x^n} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (1)$$

where m is the concentration of micelles; x the concentration of monomers; n the number of monomers per micelle; and K the equilibrium constant.

The total concentration of solute in the system, C, may be described by:

$$C = x + nm \qquad .. \qquad .. \qquad .. \qquad .. \qquad (2)$$

Hence knowing n and assuming arbitrary values for K, the respective values for m and C can be calculated for a range of values of x.

To obtain theoretical values that are significant the calculated cmc requires interpretation in a manner that correlates with the practical measurements. Three methods of obtaining this value have been used:

(1) It was taken as the point of intersection of straight lines drawn through the pre- and post-micellar regions of a plot of x against C. As the plot is not straight above the critical micellar region, the line chosen depends on subjective judgment and the method was used to obtain only an *approximate* value for K.

(2) On the premise of Phillips definition (Phillips, 1955) that the cmc could be described by $d^3\phi/dC^3 = 0$, where ϕ is any colligative property of the system, the value of C corresponding to the maximum change of slope of dx/dC was calculated. dx/dC was obtained by combination of equations (1) and (2) and differentiation.

(3) Mathematically, where C becomes greater than x can also be taken as the cmc. This assumes that when micelles appear they make a measureable contribution to the physical properties of the system. This method requires a decision being taken about the point at which the presence of micelles is acknowledged in the calculated results.

Using a value of 36 for n, obtained from the work of Balmbra, Clunie & others (1964) values of K were adjusted until the critical micellar concentrations obtained by the respective methods coincided with that obtained practically.

The values of K used and cmc calculated are:

Calculated cmc (%)	K	Method	Equation 3 constant
0·403	10^{12}	1	8·352
0·403	10^{11}	2	8·579
0·403	10^9	3	8·720

Plots of monomer concentration as a function of total detergent concentration are plotted in Fig. 2. This shows that for a given method increasing the value of K for a given aggregation number decreases the cmc obtained.

Calculation of surface tension was made using the integrated form of Gibb's adsorbtion equation and can be expressed as

$$\gamma = - 2 \cdot 303 \, RT\Gamma_2 \log a + \text{constant} .. \qquad .. \qquad .. \qquad (3)$$

where Γ_2 is the surface excess of solute; a the solute activity; and γ the surface tension of the solution.
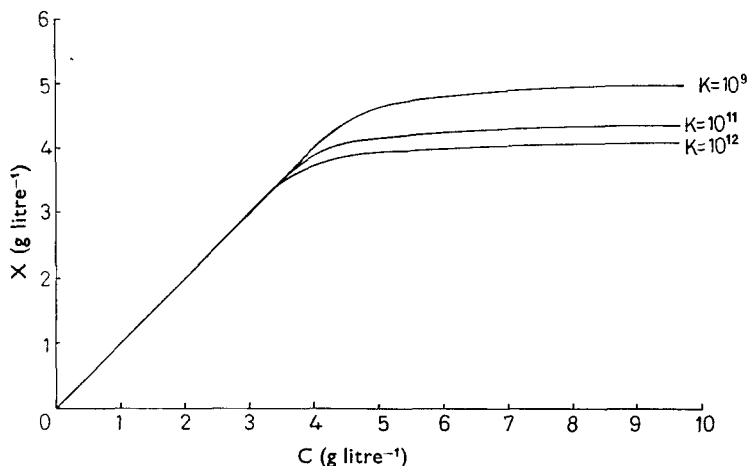
FIG. 2. Plot of C *vs* x calculated from an aggregation number of 36 and equilibrium constants of 10^9, 10^{11} and 10^{12} respectively.

Assuming an activity coefficient of 1, the surface excess was calculated from the slope of the surface tension graph just below the cmc. The calculated monomer concentration of and surface tension at the cmc was substituted with Γ_2 into equation (3) to obtain the appropriate values of the constant. These are also given in Table 1. The constants were used in equation (3) to calculate the theoretical surface tensions shown in Fig. 1.

Theoretical values obtained by methods 1 and 2 are in reasonable agreement with these obtained practically (light scattering aggregation number used in these calculations is subject to an error of around $\pm 10\%$).

The results from method (3) substantiate the inherent problem of differentiating between a theoretical and a practical critical micellar concentration.

Vapour pressure osmometry

A number of average molecular weight, M_n, can be obtained by this technique from

$$\int \frac{\Delta R}{C_{c \to 0}} = \frac{H}{M_n} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (4)$$

where ΔR is the resistance increment, and H the apparatus calibration factor.

For micellar systems this is modified to

$$\int_{C - cmc \to 0} \frac{\Delta R - \Delta R_{cmc}}{C - cmc} = \frac{H}{M_n} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (5)$$

to compensate for the effects of the monomers in the solution. Results for aqueous solutions of C_8E_6 in this form are shown in Fig. 3.

In the non-ionic detergent system studied a straight line graph would be expected if the activity of the monomer remained constant above the cmc. Results for aqueous solutions of C_6E_6 (unpublished observations) indicate that this system behaves ideally to a concentration of more than $2\cdot5\%$ of detergent. It is therefore reasonable to assume that the results obtained in a comparable concentration range with C_8E_6 are not due to non-ideality.

The detergent number average molecular weight for a system made up of monomers and micelles can be calculated from

$$M_n = \left(\frac{y + z}{ny + z}\right) Mn \quad .. \quad .. \quad .. \quad .. \quad (6)$$

where y and z are the concentrations of monomers and micelles respectively, and M is the monomer molecular weight.

Theoretical values for $\dfrac{\Delta R - \Delta R_{cmc}}{C - cmc}$ were calculated using equations (5) and (6) with the monomer and micellar concentrations previously obtained corrected for their respective cmc values. These are shown in Fig. 3.

The similar pattern between practical and theoretical results further endorses the view of a continuing increase in monomer activity above the cmc.
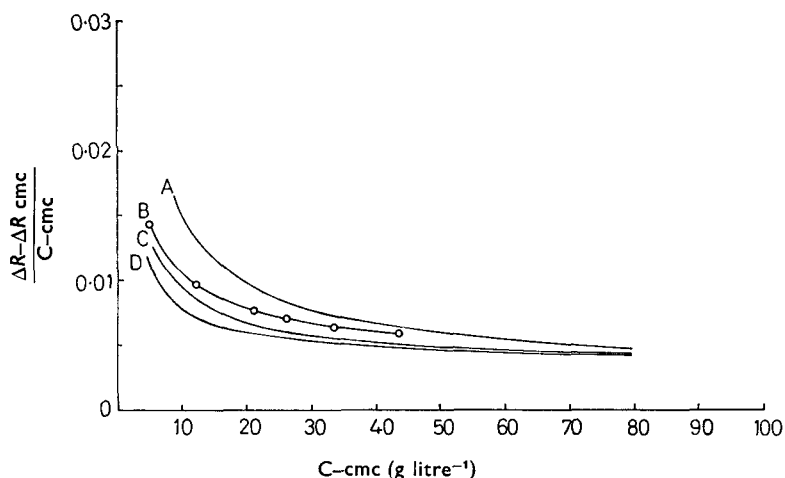

FIG. 3. Measured and calculated vapour pressure osmometry values plotted as a function of corrected concentration. B—measured; plots A, C and D were calculated from monomer and micellar concentrations corresponding to equilibrium constants of 10^9, 10^{11} and 10^{12} respectively.

REFERENCES

ABU-HAMDIYYAH, M., MUKERJEE, P. & MYSELS, K. (1963). J. phys. Chem., 67, 1943–1944.

BALMBRA, R. R., CLUNIE, J. S., CORKILL, J. M. & GOODMAN, J. F. (1964). Trans. Faraday Soc. 60, 979–985.

DESHMUKH, A. & FLEMING, R. (1969). J. Pharm. Pharmac., 21, Suppl., 91S–97S.

ELWORTHY, P. H., GYANE, D. O. & MACFARLANE, C. B. (1969). Ibid., 21, 617–619.

ELWORTHY, P. H. & MACFARLANE, C. B. (1962). Ibid., 14, Suppl., 100T–102T.

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

ELWORTHY, P. H. & MYSELS, K. J. (1966). J. Colloid Inter. Sci., 21, 331–347.

GYANE, D. O. (1970). Ph.D. Thesis, Strathclyde University.

HARRAP, B. S. & O'DONNELL, I. J. (1954). J. phys. Chem., 58, 1097–1099.

HUDSON, R. A. & PETHICA, B. A. (1964). Proceedings of the Fourth International Congress on Surface Active Substances. Gordon and Breach, New York, 2, 631–639.

MACFARLANE, C. B. (1963). Ph.D. Thesis, Glasgow University.

PHILLIPS, J. N. (1955). Trans. Faraday Soc., 51, 561–569.