REFRACTOMETRIC DETERMINATION OF THE CRITICAL MICELLE CONCENTRATION OF NON-IONIC SURFACE-ACTIVE AGENTS

By M. Donbrow and Z. A. Jan

From the School of Pharmacy, Chelsea College of Science and Technology, London, S.W.3

The critical micelle concentrations (CMC) values of some non-ionic surfactants have been determined by refraction and are compared with the results reported earlier by other methods. The slope values have been calculated below and above the CMC and an equation developed to predict the slope below the CMC for any member of the homologous series. The values appear to conform with those expected theoretically from atomic refraction data.
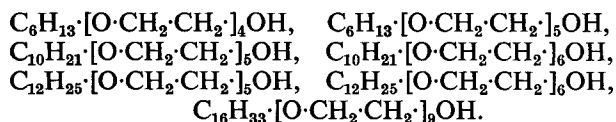
A number of methods have been employed to determine the critical micelle concentration (CMC) of non-ionic surfactants. The most widely used involve the addition of external substances such as iodine or dyes which may influence micelle formation or micelle properties (Ross and Olivier, 1959), whilst others involve measurement of properties such as surface tension or viscosity by dynamic methods, which are liable to disequilibrate the system. Refractive index, however, measures a bulk property under static conditions and should therefore be independent of external influences.

The validity of refraction measurements for the determination of CMC has already been established for ionic surfactants by Klevens (1947), who studied a number of anionic and cationic detergents and soaps. The method has not, however, been applied to non-ionic surfactants and since it appears to offer some important advantages, it is here applied to a number of pure compounds on which data have been reported by other methods.

EXPERIMENTAL

A Hilger Rayleigh Interference Refractometer for liquids (Model M154) was used. It was fitted with a constant temperature water jacket; a tungsten lamp was the light source. Cells had path lengths of 1 and 10 cm.

Chemicals. The following polyethylene oxide alkyl ethers were given by Dr. B. A. Mulley. The preparation and purity of these compounds have been previously described (Mulley, 1958, Mulley and Metcalf, 1960; Carless, Challis and Mulley, 1963).

$$C_6H_{13} \cdot [O \cdot CH_2 \cdot CH_2 \cdot]_4OH, \quad C_6H_{13} \cdot [O \cdot CH_2 \cdot CH_2 \cdot]_5OH,$$
$$C_{10}H_{21} \cdot [O \cdot CH_2 \cdot CH_2 \cdot]_5OH, \quad C_{10}H_{21} \cdot [O \cdot CH_2 \cdot CH_2 \cdot]_6OH,$$
$$C_{12}H_{25} \cdot [O \cdot CH_2 \cdot CH_2 \cdot]_5OH, \quad C_{12}H_{25} \cdot [O \cdot CH_2 \cdot CH_2 \cdot]_6OH,$$
$$C_{16}H_{33} \cdot [O \cdot CH_2 \cdot CH_2 \cdot]_9OH.$$

Method. All solutions were prepared using triple-distilled water. A series of dilutions of appropriate concentrations of surfactants were

prepared from filtered stock solutions. Refractive index increments between serial pairs of solutions were measured in terms of instrument scale division differences (ΔR), calculated using the formula:

$$\Delta R = R' - R_0$$

where R' = Instrument scale reading

R_0 = Instrument zero obtained by filling both sides of the cell with the same solution.

All readings were duplicated and an average of three to four readings was taken in every case. ΔR values were summated in the construction of the graphs. Where 1 cm. cells were employed ΔR values were recalculated for a 10 cm. path length.

The instrument was calibrated with standard sodium chloride solutions and the ΔR values were converted into absolute refractive index differences to give Δn values. In some cases in which the refractive index differences was very small, distilled water was used as a reference solution throughout the experiment.

In the course of the work it was found that the longer-chain surfactants were adsorbed at the surface of the cell, thereby altering the zero and introducing errors into the readings. The adsorbed layer could not be entirely removed by repeated washings and the cell required immersion in water overnight to restore the instrument zero to its normal position.

RESULTS AND DISCUSSION

The CMC values obtained are listed in Table I and the refractive index-concentration curves are shown in Fig. 1. The CMC values are indicated by the intersection of two straight lines which govern the slopes below and above the CMC. The values so obtained are compared in Table I

TABLE I
CMC AND SLOPE VALUES FOR POLYETHYLENE OXIDE ALKYL ETHERS

Compounds	CMC (moles/litre at 20° C)			$\Delta(\Delta n)/\Delta c$ litres/mole × 10⁴ (Slope × 10⁴)	
	Refraction	Surface tension	Iodine solubilisation	Below CMC	Above CMC
$C_6H_{13}\cdot(O\cdot CH_2\cdot CH_2\cdot)_4OH$	$9\cdot0 \times 10^{-2}$	$9\cdot0 \times 10^{-2}$	$9\cdot0 \times 10^{-2}$	326	308
$C_8H_{13}\cdot(O\cdot CH_2\cdot CH_2\cdot)_5OH$	$9\cdot25 \times 10^{-2}$	$9\cdot0 \times 10^{-2}$		373	356
$C_{10}H_{21}\cdot(O\cdot CH_2\cdot CH_2\cdot)_5OH$	$7\cdot8 \times 10^{-4}$	$8\cdot6 \times 10^{-4}$	$9\cdot5 \times 10^{-4}$	471	365
$C_{10}H_{21}\cdot(O\cdot CH_2\cdot CH_2\cdot)_6OH$	$9\cdot6 \times 10^{-4}$	$9\cdot2 \times 10^{-4}$	$9\cdot5 \times 10^{-4}$	520	442
$C_{12}H_{25}\cdot(O\cdot CH_2\cdot CH_2\cdot)_5OH$	$5\cdot00 \times 10^{-5}$	$4\cdot0 \times 10^{-5}$	$3\cdot5 \times 10^{-5}$	380	492
$C_{12}H_{25}\cdot(O\cdot CH_2\cdot CH_2\cdot)_6OH$	$10\cdot00 \times 10^{-5}$	$8\cdot2 \times 10^{-5}$	$7\cdot8 \times 10^{-5}$	570	418
$C_{16}H_{33}\cdot(O\cdot CH_2\cdot CH_2\cdot)_9OH$	—	$3\cdot6 \times 10^{-5}$	$3\cdot9 \times 10^{-5}$	—	760*

* Lowest concentration measured 1 × 10⁻⁵M (against water)

with those previously reported for the same compounds by Mulley and Metcalf (1962) and Carless and others (1963) who used the surface tension and iodine solubilisation methods. Agreement is reasonable, though the C_{12} compounds give slightly higher values by the refraction method.

The slopes of the lines have been calculated below and above the CMC and are given in Table I as $\Delta(\Delta n)/\Delta c$ values, where Δn is the

refractive-index difference between two solutions having a concentration difference of Δc. The C_{12} compound with five ethylene oxide groups is anomalous both in its slope values and their ratios, and although duplicate estimations on the same sample gave concordant values, the
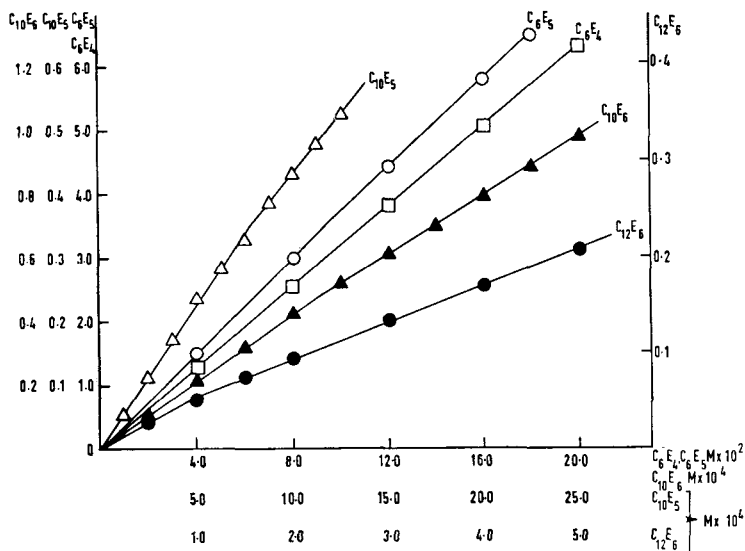
FIG. 1. Variation in refractive indices with concentration.
Ordinates: $\Delta n \times 10^4$. Abscissa: concentration (molar)

compound must nevertheless be considered doubtful. Some comparable $\Delta(\Delta n)/\Delta c$ values for sodium alkyl sulphonates taken from the data of Kleven (1947) and some values for long chain alkyl betaines are included

TABLE II
$\Delta(\Delta n)/\Delta c$ VALUES LITRE/MOLE $\times 10^4$ (SLOPE $\times 10^4$)

		Non-ionic surfactants		Sodium alkyl sulphonates		Betaines	
		Below CMC	Above CMC	Below CMC	Above CMC	Below CMC	Above CMC
C_6	E_4	326	308				
	E_5	373	356				
C_8				303	284		
C_{10}	E_5	471	365	343	327	350	293
	E_6	520	442				
C_{11}						380	251
C_{12}	E_5	380	492	379	367	403	353
	E_6	570	418				
C_{14}				424	397	532	304
C_{16}	E_9	—	760	461	438	760	—

in Table II. The values for the betaines have been calculated from the empirical results of Beckett and Woodward (1963), who used the identical instrument and method as a result of this work, and have not previously

been reported. The slope values obtained for the non-ionic surfactants are higher than those for the alkyl sulphonates and betaines, as would be expected if the contribution of the ethylene oxide groups to the molar refractions of the respective systems were greater than those of the polar heads of the ionic surfactants. The change of slope per CH_2 group between members of a homologous series is fairly constant below the CMC though greater in the non-ionic surfactants and betaines (24 $\times$ 10^{-4} approx.) than in the alkyl sulphonates (20 $\times$ 10^{-4} approx.). These slope increments are plotted as a function of the number of CH_2 groups in Fig. 2. The betaine series show a striking anomaly: while the lower members have about the same values as the non-ionic surfactants, the longer chain compounds showed an unexpected break in the slope and much larger slope increments.
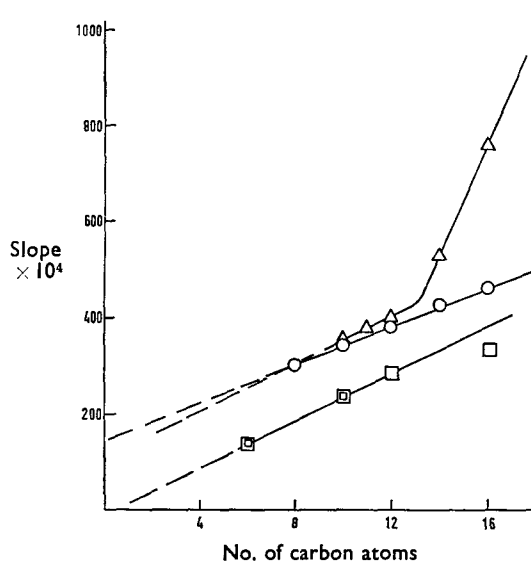

FIG. 2. Refractive index slopes of various types of surfactants as a function of the number of CH_2 groups. $\triangle$, Betaines. $\bigcirc$, Sodium alkyl sulphonates. $\square$, Polyethylene oxide alkyl ethers. Polyethylene oxide alkyl ethers have been corrected for ethylene oxide groups on the basis of the equation in the text.

Below the CMC, the slope values $\Delta(\Delta n)/\Delta c$ of the non-ionic series would appear to be an additive function of the number of hydrophobic and hydrophilic groups of the compounds and may be predicted for any member of the series having the general formula of $C_nH_{2n+1}[\cdot O \cdot CH_2 \cdot CH_2 \cdot]_m OH$, with fair accuracy, on the basis of the following equation:

$$\Delta(\Delta n)/\Delta c = 1[\Delta(\Delta n)/\Delta c]_C + m[\Delta(\Delta n)/\Delta c]_E$$

where $[\Delta(\Delta n)/\Delta c]_C = 22 \cdot 8 \times 10^{-4}$

$[\Delta(\Delta n)/\Delta c]_E = 47 \cdot 5 \times 10^{-4}$

1 = number of C groups (C = alkyl)

m = ,, ,, E groups (E = ethylene oxide)

Group slope increments for C and E groups were estimated from the average differences in the values listed in Table I (excluding $C_{12}E_5$). The slopes of various compounds studied were calculated theoretically on the basis of the above equation and are compared in Table III. From this Table it is apparent that the experimental and theoretical values are in good agreement with the exception of $C_{12}E_5$. The experimental slope value obtained for $C_{16}E_9$ was considered to be that above the CMC and has been included in Table III and plotted in Fig. 2 for comparison with the theoretical value below the CMC; it would appear to be of the correct order. Percentage refractive-index increments per CH_2 and ethylene oxide group were also calculated using atomic refraction data (Bauer and Fajan, 1949). The molar refraction for a CH_2 group is 4·62 and for a $(O\cdot CH_2\cdot CH_2\cdot)$ group, 10·88. For a unit containing one of each of these groups, the percentage increase in molar refraction on the addition of a further CH_2 is 29·8 while the percentage increase in slope increment calculated from the experimental group increment is 32·4. The corresponding percentage increases per ethylene oxide group are 70·2 from the molar refraction data and 67·5 from the group increments. This is an

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL SLOPE VALUES

Compounds	$\Delta(\Delta n)/\Delta c$ litres/mole $\times 10^4$ (Slope $\times 10^4$)		Deviation per cent
	Experimental	Theoretical	
C_8E_4	326	327	0·30
C_8E_5	373	374	0·26
$C_{10}E_5$	471	466	1·07
$C_{10}E_6$	520	513	1·36
$C_{12}E_5$	380	510	25·49
$C_{12}E_6$	570	560	1·78
$C_{16}E_9$	760*	790	3·79

* Value above CMC used in this case.

indication that below the CMC the additivity in refraction properties corresponds approximately to that expected theoretically.

Nash (1958, 1959), Becher and Clifton (1959) and Taubman and Nikitina (1960) have observed changes in foam viscosity, fluorescence, light scattering, surface tension and dye titration properties indicative of the existence of non-equilibrium states in micellar solutions, CMC values being obtained over a finite range of concentration determined by kinetic factors. However, the refraction method used here gave single CMC values with abrupt slope changes, readings remaining constant, within experimental limits, for several hours after preparation of the dilutions. Carless and others (1963) obtained evidence of ageing by surface tension measurements with the same $C_{16}E_9$ compound used in this study. The $\Delta(\Delta n)/\Delta c$ values observed for this compound were unchanged, within the limits of experimental error, over a 24 hr. period, but since the CMC was uncertain and the ageing is usually observed below the CMC no clear inference can be drawn.

As the CMC values of non-ionic surfactants are generally much lower than those of ionic surfactants, the concentration range available for plotting the slope below the CMC is somewhat restricted, particularly for the long chain compounds, in which the differences measured approach the order of the accuracy of the instrument. The CMC value obtained is then determined mainly by the accuracy of the backward extrapolation from points near to but above the CMC. In the present work, discrepancies observed in repeated experiments on the C_{16} compound were attributed to adsorption on the cell walls from the very dilute solutions required, and a greater path length or instrument sensitivity is needed to deal with this compound.

REFERENCES

Bauer, N. and Fajan, K. (1949). *Physical Methods of Organic Chemistry*, Editor, Weissberger. Vol. 1, Part II, 1163. New York: Interscience.
Becher, P. and Clifton, N. K. (1959). *J. Colloid Sci.*, **14**, 519–523.
Beckett, A. H. and Woodward, R. J. (1963). *J. Pharm. Pharmacol.*, **15**, 422–431.
Carless, J. E., Challis, R. A. and Mulley, B. A. (1963). *J. Colloid. Sci.*, in the press.
Klevens, H. B. (1947). *J. Chem. Phys.*, **51**, 130–148.
Mulley, B. A. (1958). *J. Chem. Soc.*, **423**, 2065–2066.
Mulley, B. A. and Metcalf, A. D. (1960). *Proc. 3rd Intern. Congr. Surface Activity*, Cologne, Section A, No. 4.
Mulley, B. A. and Metcalf, A. D. (1962). *J. Colloid Sci.*, **17**, 523–530.
Nash, T. (1958a). *J. appl. Chem.*, **8**, 440–444.
Nash, T. (1958b). *Nature, Lond.*, **182**, 1536.
Nash, T. (1959). *J. Colloid Sci.*, **14**, 59–73.
Ross, S. and Olivier, J. P. (1959). *J. Phys. Chem.*, **63**, 1671–1674.
Taubman, A. B. and Nikitina, S. A. (1960). *Doklady Akademii Nauk, S.S.S.R.*, **135**, 1169–1172.