

## The effect of change of solvent on the critical micelle concentration of a non-ionic surfactant

Little attention has been devoted to the physical properties of non-ionic surfactants in either non-aqueous solvents, or in mixed solvents in which water is a component. In mixed solvent systems the critical micelle concentration (CMC), of the surfactant usually varies with solvent composition. It would be useful to be able to predict, accurately, the CMC of a surfactant in any solvent, or mixture of solvents, from a knowledge of some property of the solute or solvent. This is unlikely. However, for certain systems, it should be possible to derive an approximate relation between the CMC of a surfactant and some property of a mixed solvent, such that, if two different solvent systems have the same value for this property, the CMC of a surfactant might be expected to be the same in both solvents.

To illustrate this, the CMC values of a non-ionic surfactant, dodecyl hexaoxyethylene glycol monoether ( $C_{12}E_6$ ), have been measured, or interpolated from plots of CMC against temperature, at 25°, in water, formamide and mixtures of water and formamide, water and *N*-methylformamide (NMF) and water and dimethylformamide (DMF). The CMC values, which were measured by the drop-volume surface tension method, are shown in Table 1. All the CMC values increase with increase in the concentrations of amides in the solvents. In relating these increases in CMC to changes in solvent composition, two factors are considered.

The first factor is the effect of solvent dielectric constant on CMC values. For example, the dielectric constants of water and formamide at 25° are 78.5 and 109.5 respectively. As the amounts of formamide in the solvent mixtures increase the dielectric constant will also increase towards that of formamide. Conversely, in  $H_2O$ -DMF mixtures the dielectric constant will decrease as the concentration of DMF increases, as the dielectric constant of DMF at 25° is 36.7. Table 1 shows that it would be possible for  $C_{12}E_6$  to have the same CMC in  $H_2O$ -formamide and  $H_2O$ -DMF mixtures that would have widely differing dielectric constants. The same conclusion is reached if micellization in  $H_2O$ -NMF mixtures is compared with micellization in the  $H_2O$ -formamide and  $H_2O$ -DMF mixtures. Therefore, for the systems discussed, solvent dielectric constants are of little importance in predicting CMC values and this agrees with previous findings (Schick & Gilbert, 1965).

The second factor which may be considered is the effect of solvent solubility parameters ( $\delta$ ) on CMC values (Eqn 1) (Hildebrand & Scott, 1964a),

$$\delta = \left( \frac{\Delta H - RT}{V} \right)^{\frac{1}{2}} \quad \dots \quad (1)$$

where  $\Delta H$  = heat of vapourization of liquid,  $V$  = molar volume of liquid. The solubility parameter of a liquid measures the amount of energy required to vapourize one cc of liquid, and is an indication of the forces holding the molecules of liquid together. In the derivation of  $\delta$  no assumptions are made about polarity, association,

Table 1. *Critical micelle concentrations of  $C_{12}E_6$  in various solvents (all w/w) at 25°*

Solvent	CMC (mol fraction)	Solvent	CMC (mol fraction)	Solvent	CMC (mol fraction)
$H_2O$	$1.58 \times 10^{-6}$	25% NMF	$1.81 \times 10^{-5}$	30% DMF	$2.63 \times 10^{-5}$
25% Formamide	$1.07 \times 10^{-5}$	50% NMF	$2.29 \times 10^{-4}$	44% DMF	$1.03 \times 10^{-4}$
42% Formamide	$2.49 \times 10^{-5}$	76% NMF	$1.72 \times 10^{-3}$	59% DMF	$3.54 \times 10^{-4}$
55% Formamide	$3.83 \times 10^{-5}$			65% DMF	$6.87 \times 10^{-4}$
90% Formamide	$3.46 \times 10^{-4}$			75% DMF	$2.20 \times 10^{-3}$
Formamide	$1.24 \times 10^{-3}$				

aggregation or solvation. This may seem to preclude the estimation of solubility parameters of polar liquids, such as are used here. However, if the parameters are used with discretion they provide useful, if approximate, guides to the solvent properties of polar liquids. The apparent solubility parameters of water, formamide, NMF and DMF are 23.4, 19.4, 16.1 and 12.2 respectively (Walker, 1952; Bauder & Gunthard, 1958; Hildebrand & Scott, 1964b). Several equations have been used to calculate solubility parameters of mixed solvents (Burrell, 1955), none of which is completely satisfactory. In the present work, since CMC values are quoted as mol fractions, the apparent solubility parameters of the solvents are calculated in terms of mol fractions of solvent constituents (Eqn 2)

$$\delta_{12} = \delta_1 X_1 + \delta_2 X_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

where  $\delta_1$ ,  $\delta_2$  and  $X_1$ ,  $X_2$  are solubility parameters and mol fractions of constituents 1 and 2 respectively. A plot of the logarithms of CMC values against apparent solubility parameters of the solvents is shown in Fig. 1. In systems in which the CMC values are low and the aggregation numbers are high, the logs of the CMC values are directly proportional to the free energies of micellization ( $\Delta G^\circ$ ). Since no aggregation numbers are available, for the present systems, it can be said only that there may be a simple relation between the logs of the CMC and  $\Delta G^\circ$  values, and

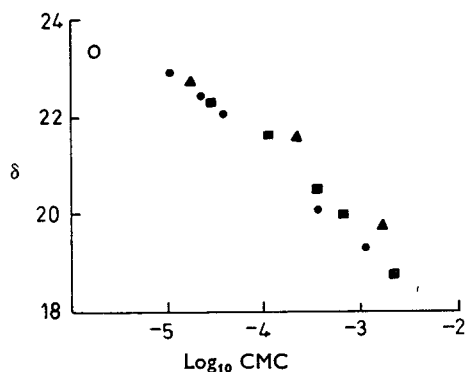


FIG. 1. Plot of logs of CMC values of  $C_{12}E_6$  in various solvents against apparent solubility parameters ( $\delta$ ) of solvents.

(○  $H_2O$ . ●  $H_2O$ -formamide. ▲  $H_2O$ -NMF. ■  $H_2O$ -DMF).

hence a relation between free energy of micellization of a surfactant and the solubility parameter of the solvent. It can be seen that, allowing for errors in the values of the solubility parameters, it would be possible to estimate the CMC of  $C_{12}E_6$  in any of the systems studied from a knowledge of the solubility parameter of the solvent.

Too few CMC measurements, in too few solvent systems are presented to allow the assumption that a general relation exists between CMC and the solubility parameter of any solvent. Also, such factors as interactions between surfactant and amides and water and amides are ignored in the present treatment and may be important (Emmerson & Holtzer, 1967).

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## The estimation of aqueous solutions of $\omega$ -diazacetophenones by polarography

The involvement of the diazo group in the inhibition of purine synthesis has been demonstrated by Levenberg, Melnick & Buchanan (1957), thus making the study of this group important in biological systems. We have investigated the effects of a group of  $\omega$ -diazacetophenones, on several biological systems both *in vivo* and *in vitro*. During the course of this work we have found that existing methods of estimating these compounds in aqueous buffers, and in solutions containing organic material, are inadequate.

$\omega$ -Diazacetophenones have characteristic absorption bands in the ultraviolet region of the spectrum (Leveson & Thomas, 1966), and this property has been used to determine the concentration of these compounds. For instance, Aziz & Tillet (1968) studied the rate of hydrolysis of diazoketones by following spectrophotometrically the decrease in their characteristic absorbances. In solutions containing protein this method is unsatisfactory, due to interference in the absorption at about 280 nm.

We have found a convenient way of assaying  $\omega$ -diazacetophenones is by polarography. The DC polarographic behaviour of  $\omega$ -diazacetophenone has been

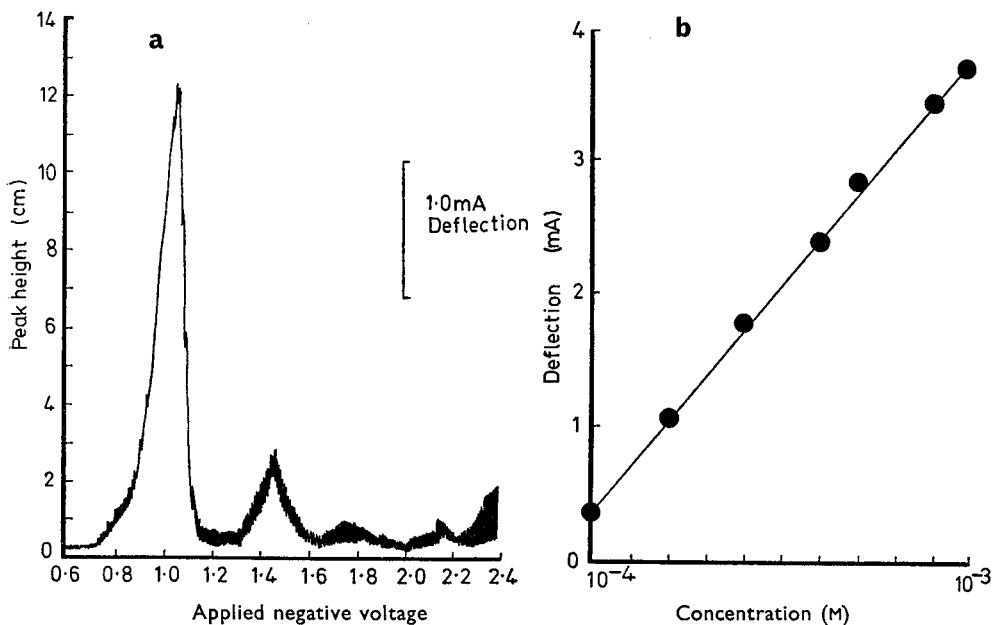


FIG. 1. a. AC polarogram of  $10^{-3}$ M  $\omega$ -diazacetophenone in 0.2M phosphate buffer at pH 6.7. The height of the primary peak is dependent on the concentration of the  $\omega$ -diazacetophenone. Substituted  $\omega$ -diazacetophenones ( $10^{-4}$ - $10^{-3}$ M) give similar traces under the same conditions.

b. The calibration curve of  $\omega$ -diazacetophenone in 0.2M phosphate buffer, pH 6.7, at 25°, using AC polarography.