

## Review Article

### The physical chemistry of some non-ionic detergents\*

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THE physical chemistry of non-ionic detergents, in particular their surface activity and micellar properties in aqueous solution, has received much attention. In this review the physical chemistry of polyoxyethylene-ether detergents of the type  $\text{Me}\cdot[\text{CH}_2]_y\cdot[\text{OCH}_2\cdot\text{CH}_2]_x\cdot\text{OH}$  is outlined. For convenience, the formulae are abbreviated in the style thus: Dodecyl- $n_6$  for  $\text{Me}\cdot[\text{CH}_2]_{11}\cdot[\text{OCH}_2\cdot\text{CH}_2]_6\cdot\text{OH}$ ,  $n$  representing the ethylene oxide unit.

Non-ionic detergents do not ionise in aqueous solution, and thus have many advantages both in detergent properties and for chemical studies. Furthermore, a range of compounds with a constant hydrophobic portion, but a varying hydrophilic moiety, can be obtained without fundamentally altering the chemical structure of the detergent, enabling a fuller and more comprehensive study to be made than is possible in an ionic series where the hydrophilic portion can be altered only by changing the ion.

Although polymers of ethylene oxide of up to six units were first synthesised over 100 years ago, it was not until around 1930 that their commercial potential, and particularly that of their derivatives, was realised. Since then wide ranges of compounds incorporating the polyoxyethylene glycols have been produced for a multitude of purposes, ranging from aids in drilling to pharmaceutical preparations, where their wetting, foaming, dispersing, or emulsifying properties are utilised.

In the study of non-ionic detergents the most important experimental methods used have been those described below.

#### LIGHT SCATTERING

Measurement of the turbidity,  $\tau$ , as a function of concentration,  $c$ , gives the micellar weight,  $M$ , from

$$\frac{Hc}{\tau} = \frac{1}{M} + 2Bc \quad \dots \quad \dots \quad \dots \quad (1)$$

where  $H$ , is the optical constant (dependent on the wavelength of light used, the specific refractive index increment);  $c$  and  $\tau$  are previously corrected by subtraction of the appropriate values for the concentration and the turbidity of the solution at the critical micellar concentration.  $B$ , the second virial coefficient, is a function of the size and shape of the micelles.

In equation (1) it is assumed that no micellar dimension exceeds  $\lambda/20$  ( $\approx 250 \text{ \AA}$ ). For larger particles, this equation is modified to include the particle scattering factor,  $P(\theta)$ .

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\* The first of two articles discussing this topic.

## VISCOSITY

Measurement of the specific viscosity,  $\eta_{sp}$ , as a function of concentration enables the intrinsic viscosity,  $[\eta]$ , to be determined.

$$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = [\eta] = v(\bar{V}_2 + w_1 V_1^0) \quad \dots \quad (2)$$

where  $v$ , is a factor depending on the shape of the particles (Simha, 1945);  $\bar{V}_2$ , the partial specific volume of the solute;  $V_1^0$ , the specific volume of the solvent; and  $w_1$ , the solvation expressed as solvent/g solute. The measured intrinsic viscosity therefore depends on both the shape and the solvation of the micelles.

## DIFFUSION

For a spherical, unsolvated micelle the diffusion coefficient,  $D$ , after extrapolation to zero concentration, is related to the micellar weight and the viscosity of the medium,  $\eta$ , by:

$$D = \frac{RT}{6\pi\eta N \left( \frac{3M\bar{V}_2}{4\pi N} \right)^{\frac{1}{3}}} \quad \dots \quad (3)$$

where  $N$ , is Avogadro's Number;  $R$  and  $T$  have their usual significance. Corrections for deviations from a spherical shape or for the presence of solvation may be determined using viscosity or sedimentation velocity results.

The combination of diffusion, viscosity, and sedimentation data in the manner suggested by Scheraga & Mandelkern (1953), can lead to the independent determination of particle shape and hydration. The use of these relationships implies that the micelle is treated as a reasonably rigid particle.

## SEDIMENTATION VELOCITY

From the measurements of the sedimentation coefficient,  $s$ , extrapolated to zero concentration, the micellar weight can be obtained from:

$$M = \frac{RTs}{D(1 - \bar{V}_2\rho)} \quad \dots \quad (4)$$

where  $\rho$  is the density of the solvent. The micellar weight obtained from this last equation is independent of particle shape and solvation.

## Preparation of ethylene oxide adducts

Ethylene oxide is a colourless gas with an ether-like odour, prepared on a small scale by heating 2-chloroethyl acetate with potassium hydroxide and on a commercial scale by the chlorohydrin process, or by direct oxidation of ethylene. Highly inflammable, liable to undergo exothermic reaction with itself, and of a toxicity similar to carbon monoxide, it is however the fundamental unit in the production of polyoxyethylene



As a compromise, Weibull & Nycander (1954) produced a simplified formula based on the assumption that the rate of ethylene oxide additions for each step was equal, but differed from that of the initial reaction step of ethylene oxide with the parent hydrophobe.

Fractional distillation of compounds prepared by Wrigley, Howard & Stirton (1960) showed a distribution of chain lengths which agreed with Weibull & Nycander's equation, rather than with the Poisson distribution. This work, however, was limited to long chain fatty alcohol adducts. On the other hand, the Flory-Poisson distribution has been found valid for the oxyethylation of ethylene glycol (Weibull & Nycander, 1954), phenols (Miller, Bann, & Thrower, 1950; Mayhew & Hyatt, 1952), and stearic acid (Birkmeier & Brander, 1958); in the last instance presumably because of preferential combination of the parent compound with ethylene oxide before significant further reaction of the ether alcohols took place (Schechter & Wynstra, 1956; Wrigley & others, 1957).

Industrially an alkaline catalyst seems to be preferred although the reaction may also be catalysed by acid, or even proceed uncatalysed (Chitwood & Freure, 1946). Acid catalysts may be used if low temperature conditions are required (Staudinger & Schweitzer, 1929). The choice of catalyst and the purity of the starting materials have a striking effect on the end product. For obvious reasons manufacturers do not disclose their particular routes, but work by Drew & Schaeffer (1958) illustrates this point. In their experiments they found acid-catalysed reactions gave rise to byproducts, the amount of which increased with the degree of polymerisation, and the presence of traces of water (either by contamination or by formation during the reaction) resulted in the formation of glycols. The concentration and type of catalyst, and the reaction conditions affected the distribution of chain lengths (Gee, Higginson, & Merral, 1959; Tischbirek, 1960; Ginn, Church & Harris, 1961), and in practice, these factors are often varied to obtain the most suitable product for a particular purpose.

Thus there is a great variation in the possible distribution of the ethylene oxide chain lengths in a glycol or detergent; the properties identified with the various commercial products are influenced by this distribution as well as by the average molecular ratio of ethylene oxide to hydrophobe (Mayhew & Hyatt, 1952; Raphael 1958).

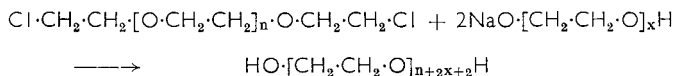
In an attempt to obtain a clearer view of the properties of this type of compound, various means have been tried to obtain a homogeneous preparation, i.e. one which did not contain a distribution of chain lengths. Fractionation of the polymerised products by distillation (Mayhew & Hyatt, 1952) and chromatography (Gallo, 1953; Kelly & Greenwald, 1958) have been tried, but as yet have only succeeded in narrowing the chain length distribution. Alternative routes of building up the chains have also been investigated. As mentioned previously, short length polyoxyethylene glycols were first described by Laurenci (1859), who prepared them by reacting ethylene glycol with either ethylene dibromide or ethylene bromohydrin, and by Wurtz (1859), who reacted ethylene oxide with ethylene glycol or by hydration of ethylene oxide, whereas

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Mohr (1866a,b) heated ethylene glycol monoacetate with the monosodium derivative of ethylene glycol.

Although certain early workers suggested a cyclic structure (Roithner, 1894) for the polyoxyethylene glycols, much of the data supporting this was of a negative nature, and the detection of hydroxyl groups was taken as evidence of an open chain (Carothers, 1931; Fordyce, Lovell & Hibbert, 1939).

The first direct method of synthesising a single polyoxyethylene glycol, devised by Perry & Hibbert (1936), used a Williamson type ether reaction of the  $\alpha,\omega$ -dichloro-derivative of a pure lower glycol with two molecules of the monosodium salt of another or the same glycol.



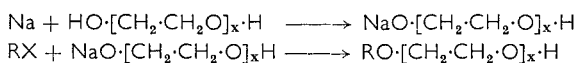
Using this procedure, Fordyce & others (1939) synthesised glycols containing up to 186 ethylene oxide units. The compounds containing up to six ethylene oxide units were distilled, but the longer ones had to be purified by extraction and crystallisation; the final purity being assessed by time/temperature cooling curves. Examination of these synthesised polyoxyethylene glycols by X-ray diffraction (Barnes & Ross, 1936) showed, that as far as could be detected by that technique, there was no essential difference between them and the products of ethylene oxide polymerisation, substantiating the claims of other workers about the identity of the two end products (Staudinger & Schweitzer, 1929; Carothers, 1931).

Synthesis of homogeneous glycol derivatives presents an even more formidable problem, particularly when a compound with a hydrophobic radical at one end only is required. Certain workers have tried to evade this problem by using a short sodium alkoxide (Nakagawa, Kuriyama & Inoue, 1960; Kuriyama, 1962a), e.g., sodium methoxide, to initiate the polymerisation reaction, obtaining a methoxypolyoxyethylene glycol, fractionating this, and converting the required fraction to its sodium salt. Thence, by the Williamson reaction with the hydrophobe halide, they obtained the desired compound. Such a compound is based on the product of the polymerisation reaction, and hence a uniform chain length is extremely difficult to obtain (Mayhew & Hyatt, 1952; Kelly & Greenwald, 1958). Moreover the compound must be used as its methoxy derivative; removal of this group without breaking the hydrophobe-glycol link is virtually impossible.

A few reports have appeared in the literature describing synthesised compounds (Turner, Saunders & Willaman, 1951; Goto, Sugano & Koizumi, 1953; Gingras & Bayley, 1957, 1958; Wrigley, Howard & Stirton, 1960), but most have contained short polyoxyethylene chains of up to six ethylene oxide units (Mulley, 1958, 1961; Corkill, Goodman & Ottewill, 1961).

For detergents, the synthetic route used has also been via Williamson ether synthesis type reactions, two ways being available :

(a) Building up the glycol by the method of Perry & Hibbert (1936) converting it to its monosodium salt, and reacting this with the hydrophobe halide, RX



(b) By preparing a detergent containing a small number of ethylene oxide units by route (a), chlorinating the terminal hydroxyl group with thionyl chloride, then reacting this compound with a monosodium derivative of a glycol.

Yields by either route are not particularly good and side reactions such as dehydrohalogenation of the chloro-compound have been reported (Corkill & others 1961). The largest homogeneous detergents reported in the literature, a range of hexadecyl monoethers containing six to twenty-one ethylene units respectively, have been successfully synthesised by these routes (Elworthy & Macfarlane, 1962a, 1963); similarly, some branched hydrocarbon chain compounds have recently been obtained by these methods (Elworthy & Florence, 1964).

Alkyl *p*-tolylsulphonates have been described as intermediates (Shirley, Zeitz, & Reedy, 1953), and the stepwise synthesis of the monodecyl ethers of mono- to tetra-oxyethylene glycols by acid-catalysed addition of ethylene oxide has been reported (Chakhovskoy, Martin & Van Nechel, 1956).

The difficulties encountered in the purification and separation of the end products from the reaction mixture have been one of the main causes of delay in the syntheses of longer chain compounds. Traces of glycols are one of the most common contaminants and crystallisation and other purification techniques are hampered by the similarity of the properties of these trace glycols to those of the adduct, particularly when the glycol chains become large. Further complications arise because of the surface-active properties of the derivatives which cause emulsion formation when partition techniques are used. To overcome this, partition between ethyl acetate and saturated sodium chloride solution (Weibull, 1960) has been used, so has heating an aqueous solution of the mixture to about 100° and separating the detergent-rich phase (Nakagawa & others, 1960); in both instances the glycol and other water soluble products of the reaction were retained in the aqueous phase. A relatively short oxyethylene chain compound, such as the monohexadecyl ether of hexaoxyethylene glycol, is about the longest which will withstand normal distillation, and, even under vacuum, the conditions required are rather rigorous for an organic compound of this nature (b.p. 235°/10<sup>-3</sup> mm). Neither do the actual distillation procedures used seem to produce an entirely satisfactory compound, as oxidised byproducts have been reported (Gingras & Bayley, 1957; Corkill & others, 1961) in the distillate, and chromatography on silica was required to remove them.

A chromatography step would appear to be all important in the purification of these compounds, as tests have shown (Macfarlane, unpublished) that experimental conditions can be adjusted so that traces of

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contaminating glycols are held very firmly on the column, while impurities (containing peaks at ca. 1740–1750  $\text{cm}^{-1}$  in their infrared spectra) are removed in the first stages of the elution. The desired detergent follows these impurities down the column. Furthermore, on an alumina column, by careful control of the elution scheme,  $\text{Me}\cdot[\text{CH}_2]_{15}\cdot[\text{O}\cdot\text{CH}_2\cdot\text{CH}_2]_9\cdot\text{Cl}$  has been separated from  $\text{Me}\cdot[\text{CH}_2]_{15}\cdot[\text{O}\cdot\text{CH}_2\cdot\text{CH}_2]_{15}\cdot\text{OH}$  in the working up of the reaction mixture in the synthesis of the latter compound. For compounds containing short hydrocarbon chains, silica gel appears to be a better agent for chromatography than alumina.

### Analysis

In estimating the purity of synthesised compounds, it has been shown that although standard analyses (percentages of C, H, and O) gave figures indicating satisfactory purity, such analyses were not sufficiently sensitive to detect in this type of compound impurities which caused minima in the surface tension/concentration curves (Corkill & others, 1961). Estimation of the hydroxyl group by acetylation or other techniques also loses its sensitivity when only small samples are available and the hydroxyl group is equivalent only to some 1–2% of the molecular weight.

Various assays have been developed to estimate the ethylene oxide content of the adducts. Most of these have been dependent on degradation of the chain, or on complex formation; the complexes being formed by reacting the ethylene oxide derivatives with heteropoly inorganic acids, such as silico-tungstic (Schaeffer & Critchfield, 1947; Wurzschnitt, 1950; Schonfeldt, 1955), or phosphomolybdic (Oliver & Preston, 1949; Stevenson, 1954) acids, or with tannins, potassium ferrocyanide or other suitable reagents (Haakh, von Candie & Mobus, 1951; McAllister & Lisk, 1951; Coppini & Cameron, 1953; Brown & Hayes, 1955). These complexes were then quantitatively estimated either by gravimetric, volumetric, or absorptiometric techniques, and a direct relationship could be established with the particular detergent being determined.

Dichromate oxidation has been advocated by Edkins, Storlazzi & Hammond (1942), Werner & Mitchell (1943) and others, but this lacks the desired specificity for ethylene oxide units. Morgan (1946), using a modified alkoxyl apparatus, decomposed the ethylene oxide residue to ethylene iodide and ethylene with constant boiling hydriodic acid. The latter method has been developed by Siggia, Starke, Garis & Stahl (1958), who refluxed the polyoxyethylene adduct with excess hydriodic acid under an atmosphere of carbon dioxide, and titrated the liberated iodine with sodium thiosulphate. This reaction has the advantage over the other chemical methods that it is an absolute method; no standard curve need be prepared.

All the above methods estimate the total amounts of ethylene oxide present, thus the presence of glycols will affect the result. Several methods of estimating the amount of glycol present have been devised

(Nakagawa & Nakata, 1956; Weibull, 1960; Ginn & others, 1961), generally these involve the separation of the glycol from the detergent, but, recently, correlation of total ethylene oxide content obtained by the hydriodic acid analysis with the percentage of hydroxyl groups found by acetylation, has been used to calculate the quantity of glycol in the adduct (Elworthy, 1963).

## Properties in aqueous solution

### FORMATION OF MICELLES

In contrast with the copious work on ionic detergents (Pethica, 1960), the number of papers on the micellar structure of non-ionic detergents in aqueous solution is relatively small. Using the Scatchard method (Scatchard, Jones & Prentice, 1932) of determining freezing-point depressions, Gonick & McBain (1947) found that results obtained for both Triton X 100, a commercial octyl-phenyl oxyethylene adduct, and a monolaurate of nonaoxyethylene glycol, in aqueous solution, bore a striking resemblance to those obtained for colloidal electrolytes. Correlating this work with previous results on solubilisation of benzene and various dyes by the lauryl adduct (Gonick, 1946), and X-ray diffraction (McBain & Marsden, 1947), they concluded that non-ionic detergents also formed micelles. This deduction has since been confirmed by other workers using X-ray and solubilisation techniques, and by viscosity and turbidimetric data (McBain & Marsden, 1948; Schulman, Matalon & Cohen, 1951; Goto, Sugano & Koizumi, 1954; Greenwald & Brown, 1954; Kushner & Hubbard, 1954; Kuroiwa, 1956).

Many theories have been put forward for the formation of detergent micelles (Pethica, 1960; Veis & Hoerr, 1960; Mukerjee, 1962; Aranow, 1963). In one of the simpler theories for an ionic detergent, Debye (1949) proposed that as the number of long chain ions aggregated to form a droplet or core of hydrophobic tails, the number of charges per aggregate increased. The charge density at the periphery rose and with it the electrostatic free energy of the growing aggregate. An equilibrium was reached when the drop in energy due to aggregation of hydrophobic groups was balanced by the rise in energy due to electrostatic repulsion. Criticism has been levelled at Debye's treatment as it was based on minimising the free energy of the micelle rather than the entire system (Oosika, 1954; Reich, 1956).

It is evident from knowledge of the non-ionic detergents that other factors must also be at work in the process of micelle formation; the necessity of looking for these additional factors which could balance the drop in energy due to aggregation of hydrophobic groups, and thus the need to look at the behaviour of all other components has been stressed by Reich (1956), who calculated the equilibrium micellar size from energy and entropy changes taking place during micelle formation. His calculation was based on a simple model of coalescence of hydrocarbon tails to a liquid droplet, and fitting the ethylene oxide chains over their surfaces. On the basis of his theory, Reich also postulated that micelle formation



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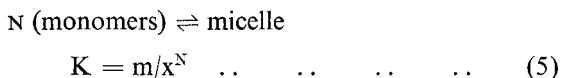
of non-ionic detergents occurred at a distinct critical micellar concentration (CMC), that the CMC decreased with increasing hydrocarbon chain length, and increased with increasing ethylene oxide chain length.

Kushner, Hubbard & Doan (1957) have pointed out that the sharpness of the micelle appearance forecast by Reich was dependent on the values assigned to the entropy and energy change associated with micelle formation; his assignment of a rather high negative value for the entropy change was probably unwarranted since it was based primarily on considerations of the heat of vaporisation of dodecane, and neglected the positive contribution to the total entropy change which results from the uncurling of the hydrocarbon portion of the molecule when it enters the micelle. Choice of a smaller value for  $\Delta S$  would have reduced the predicted sharpness of micelle formation.

Hoeve & Benson (1957), in an extensive statistical mechanical treatment, extended Reich's approach and also pointed out that dehydration phenomena had to be taken into account. The simple shielding of hydrocarbon tails from water by ethylene oxide used in Reich's calculations accounted for only "complete micelles" i.e., where the hydrocarbon core was entirely covered by ethylene oxide chains. It has also been pointed out that, unfortunately, undefined parameters in Hoeve and Benson's theory makes comparison with practical results somewhat difficult (Debye & Prins, 1958; Schick, Atlas & Eirich, 1962). Aranow (1963) has reanalysed Reich's model from the two phase approach and developed a theory of micellar statistical mechanics from the extended theory of dilute solutions (Fowler & Guggenheim, 1956), the dielectric continuum model of the solvent, and the statistical mechanical treatment of physical clusters at constant pressure (Hill, 1955). Aranow has also formulated a more general theory by elimination of the first two approaches.

A theory postulated by Nakagawa & Kuriyama (1957a), considered that the main factors preventing association are the heat of hydration and the configurational entropy terms of the flexible hydrophilic chain. It gave quantitative predictions for the CMC, micellar weight and other properties in solution, but could not reasonably explain temperature effects and clouding phenomena.

Illustrated in terms of the monomer concentration, the two main approaches to miscellisation are shown in Fig. 1. The mass action approach considers the equilibrium between monomers and micelles (molar concentrations  $x$  and  $m$  respectively), in terms of an equilibrium constant  $K$ , and an aggregation number  $N$



Concentrations have been written for activities in (5), and the activity of water entering into the equilibrium has been neglected, perhaps in an unwarranted manner for low  $N$  values, but the point at issue here (Fig. 1) is that the concentration of monomers increases above the CMC, as a

result of the mass action approach. The increase is more pronounced at low aggregation numbers than at high ones.

The pseudophase approach, which suggests that all micellised solute forms a separate but soluble phase, would give the picture shown by the broken lines in Fig. 1; as the concentration is increased above CMC, all added solute micellises, and there is no further increase in monomer concentration.

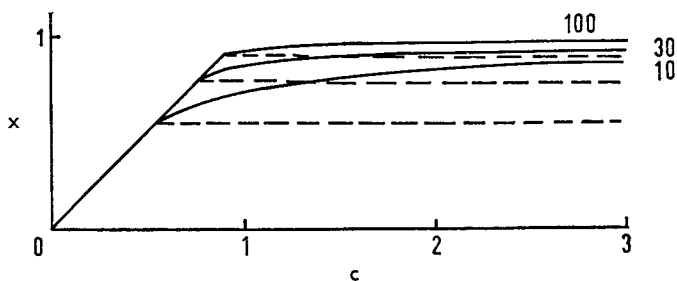


FIG. 1. Plot of concentrations of monomers,  $x$ , against total detergent concentration  $c$ , evaluated from equation (5). In all instances  $K = 1$  (unbroken lines). The broken lines indicate the monomer concentration above the CMC as expected from the pseudo-phase theory of micellisation. Figures on the curves are aggregation numbers.

Practically, if the aggregation number is greater than 20, then either model gives the same thermodynamic properties of micellisation, within experimental error. Fundamentally, it is necessary to know which approach is correct; at the present time there are several *experimental* inconsistencies.

Gibbs' equation relates the change in surface tension,  $d\gamma$ , to the surface excess,  $\Gamma_2$ , and the solute activity,  $a_2$ .

$$-d\gamma = \Gamma_2 RT d \ln a_2 \quad \dots \quad (6)$$

Provided  $\Gamma_2$  is constant, as it appears to be in the post CMC region, any change in solute activity should give rise to a change in surface tension. Using the mass-action law and Gibbs' equation, rough calculations of the surface tension variation between one and ten times the CMC can be made, giving a few tenths of a dyne/cm at an aggregation number of 100, and around 1 dyne/cm at  $N = 20$ . Examination of most surface tension-concentration curves reported in the literature shows a constant surface tension in the post CMC region (the exception are the results of Hudson & Pethica, 1964). At first sight this is support for the pseudo-phase model of micellisation, even at low micellar aggregation numbers. These results are inconsistent with vapour pressure-concentration curves of Corkill, Goodman & Harrold (1964) on  $C_8n_6$ , or Corkill, Goodman & Tate (1964) on  $C_6n_6$ , and of Elworthy & Florence (unpublished) on  $C_4n_6$  and  $Me_2CH \cdot CH_2n_6$ . The vapour pressure studies clearly show a change of solute activity above the CMC, which would be expected if the mass action approach applied to micellisation.

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These inconsistencies are within (not between) the results of two groups of workers, and it is difficult to see why they have arisen, unless the synthesised compounds are satisfactory for the study of bulk properties, but not sufficiently pure for surface chemistry. It is pertinent to report unpublished work of Mysels & Elworthy, who have found that a clear picture of the surface tension of sodium dodecyl sulphate solutions at concentrations greater than the CMC could be obtained only if the detergent was purified by foaming immediately before use, and all measurements were made in essentially a closed system. The variation of surface tension with concentration was then apparent, indicating that the mass action approach was valid for this system.

A recent paper by Mukerjee (1962) has come down heavily in favour of the mass action approach and attempted to point out some of the difficulties and inaccuracies of the two phase theory.

Some concern about the thermodynamic picture being built up may be necessary, as the CMC values from which these properties are calculated are largely determined from surface tension measurements. There is need for a second precise method of determining CMC, preferably based on bulk properties; unfortunately dye solubilisation or interferometry do not appear to be precise enough.

Using the pseudo-phase approach, the temperature dependence of the CMC can be used to evaluate the heat of micellisation,  $\Delta H_m$

$$\Delta H_m = -RT^2 \left( \frac{\partial \ln \text{CMC}}{\partial T} \right)_p \dots \dots \dots (7)$$

and the entropy of micellisation,  $\Delta S_m$

$$\Delta S_m = \Delta H_m/T \dots \dots \dots (8)$$

$\Delta S_m$  is positive for a variety of synthetic detergents, and micellisation is governed to a large extent by the gain in entropy associated with the transfer of a monomer into a micelle. This seems to be due to the loss of the "iceberg" structure of water from around the hydrocarbon chain during this step (Corkill, Goodman & Ottewill, 1961; Schick, 1963a; Elworthy & Florence 1963, 1964; Corkill, Goodman & Harrold, 1964; Corkill, Goodman & Tate, 1964). Wishnia (1963) has shown that on transferring n-butane from an aqueous solution into a hydrocarbon phase, the entropy change is 23 cal mole<sup>-1</sup> deg.<sup>-1</sup>. Similar data for the series of normal hydrocarbons usually found in non-ionic detergents would be a very useful starting point for the discussion of the thermodynamics of micellisation. Other factors pertinent to the micellisation process are configuration entropy changes of hydrocarbon and polyoxyethylene chains, and possible changes of the solvation of the polyoxyethylene chain when micellisation takes place. The useful approach of direct measurement of heats of micellisation by calorimetry has recently been made by Corkill, Goodman & Tate (1964), showing an increase in  $\Delta S_m$  with increasing hydrocarbon chain length for monoethers of hexaoxyethylene glycol.

It is somewhat of a disadvantage to know so little of the properties of monomers of non-ionic detergents in solution. However, preliminary studies of synthetic glycols and of detergents with short hydrocarbon chains indicate a fairly high degree of hydration of the polyoxyethylene chains in solution (Elworthy & Florence, unpublished).

#### CRITICAL MICELLAR CONCENTRATION

The formation of micelles causes abrupt changes in many of the physical properties of a solution of a surfactant (Grindley & Bury, 1929) provided that the aggregation number is fairly large, and measurement of the concentration at which these changes take place is generally taken as indicative of the coalescence of the monomers. Phillips (1955) has proposed that the CMC could conveniently be defined mathematically as the total concentration ( $c$ ) at which some colligative property  $\phi$  gave  $d\phi^3/dc^3 = 0$  but the choice of the colligative property for defining the CMC generally depended on factors of convenience. The exact location of the CMC is thus to some extent subjective, but can be recorded with sufficient meaning in most instances.

Due to the absence of electrostatic repulsion, non-ionic detergents tend to form micelles at much lower concentrations (Bury & Browning, 1953; Cohen, 1952) than their ionic counterparts (Nakagawa, Kuriyama, Inaba & Tori, 1956; Weil & Stirton, 1956), thus other common methods are not sufficiently sensitive. Techniques have therefore been developed in an effort to overcome these difficulties.

Ross & Olivier (1959) have reported a photometric method for the determination of the CMC of polyoxyethylene adducts in both aqueous and nonaqueous solutions, based on the formation of a molecular complex between iodine and the non-ionic micelle which showed an absorption maximum at  $360\text{ m}\mu$  and Becher (1959) has shown good agreement between the results of this method and values obtained from light scattering with a range of commercial non-ionic detergents. Elworthy (1960a) followed up this work using cetomacrogol, a commercial polyoxyethylene monocetyl ether containing an average of 22 ethylene oxide units, and obtained consistent results for three methods: the iodine method, solubilisation of a dye (dimethyl yellow), and a surface tension technique. Japanese workers (Nakagawa, Kuriyama, Inaba & Tori, 1956; Nakagawa, Kuriyama & Tori, 1956; Nakagawa & Kuriyama, 1957b), as well as using conventional surface tension and solubilisation methods, have suggested polarographic and other techniques. Surface potential measurements (Schick, 1963b), showing similar results to those obtained from surface tension (Schick, 1962), have also been described. Donbrow & Jan (1963) reported the use of interferometry for determining the CMC of some synthetic compounds.

As already mentioned, the absence of electrostatic repulsive forces results in the formation of micelles at very low concentrations, and figures down to  $10^{-6}$  molar appear in the literature (Corkill & others, 1961; Elworthy & Macfarlane, 1962b). The CMC, as might be expected, has been interpreted as a function of the hydrophobe-hydrophile balance of

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the molecule, and Reich's suggestion (Reich, 1956), that, for a given hydrophobic moiety, the CMC will increase with increasing ethylene oxide chain length, has been demonstrated by several workers (Nakagawa & Kuriyama, 1957b; Lange, 1960; Schick, 1963b). Formulae for their relationship, on lines parallel to that of Klevens (1953) for a homologous series of ionic detergents, have been published (Hsaio, Dunning & Lorenz, 1956; Becher, 1959; Elworthy & Macfarlane, 1962b) i.e.,

$$\log \text{CMC} = A + Bx$$

where A and B are constants for a given hydrophobe and x is the number of ethylene units per molecule. These equations may only hold over a limited range of ethylene oxide chain lengths (see Table 1), as a comparison of octadecyl ethers containing fourteen and one hundred ethylene oxide units per molecule respectively, have shown an unpredictably lower CMC values for the latter (Schick, 1962) while for some short hydrocarbon chain compounds, Mulley & Metcalf (1962) have claimed that increasing the glycol chain lengths had little effect on the CMC (up to six ethylene units per molecule).

As far as alteration of the hydrophobic group was concerned the number of carbon atoms, even in a saturated hydrocarbon chain, did not necessarily directly influence the hydrophobic weighting of that moiety as far as CMC was concerned. The overall number of carbon atoms in a straight chain appeared to be the main factor, as comparison of the CMC of branched tridecyl and n-dodecyl adducts (Schick, 1962), with the same number of ethylene oxide units, showed the latter to be approximately half that of the former. Experiments with synthesised (Corkill & others, 1961), and commercial compounds (Schick, 1962; Hsaio & others, 1956), have shown that for a given ethylene oxide chain the CMC decreased with increased length of the hydrophobic moiety. Schick (1962), however, found little difference in the CMC of fractionated octadecyl and dodecyl monoesters containing fourteen ethylene oxide units, and Lange (1960) found the generally accepted behaviour was invalid with polyoxyethylene ethers of paraffin chain alcohols greater than dodecyl.

Attempts at correlation between the values of CMC for different commercial alcohol adducts (Becher, 1959) showed the slopes of graphs of log CMC vs. ethylene oxide content decreased with increase of the number of carbon atoms in the straight chain of the hydrophobic group, and the series had a common intercept at a hypothetical zero ethylene oxide content. Unlike most published CMC results, concentrations in this work were based on % w/v; conversion of these results to the more common moles/litre designation of concentration have shown that the CMC for the lauryl and stearyl adducts decreased with ethylene oxide chain length, although the CMC for the (oxo-process) tridecyl alcohol adducts still increased. Despite this, for a given ethylene oxide chain, the CMC (moles/litre) decreased with lengthening of the aliphatic chain. Such results further stress the unsatisfactory nature of working with heterogeneous compounds.

The presence of a sharply defined CMC has been assumed in most of

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TABLE 1. CRITICAL MICELLE CONCENTRATIONS OF SYNTHETIC NON-IONIC DETERGENTS

Abbreviations: n-butyl = C<sub>4</sub>, n-octyl = C<sub>8</sub>, etc., branched chain hydrocarbon structures written in full; n<sub>6</sub> = -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>6</sub>OH, etc., \* is mean value of determinations by several methods.

Compound	CMC				Reference
	Moles/litre (upper line)		at °C (lower line)		
C <sub>4</sub> n <sub>6</sub>	0.80	0.76		0.71	Elworthy & Florence, 1964
Me <sub>2</sub> CH·CH <sub>2</sub> n <sub>6</sub>	20	30		40	<i>Ibid.</i>
	0.91	0.88		0.85	
C <sub>6</sub> n <sub>3</sub> (× 10 <sup>-3</sup> )	20	30		40	Corkill, Goodman & Harrold, 1964
	10.7	10.0		7.8	
C <sub>6</sub> n <sub>4</sub> (× 10 <sup>-3</sup> )	15	25		35	Donbrow & Jan, 1963
	9.0				
C <sub>6</sub> n <sub>5</sub> (× 10 <sup>-3</sup> )	20				<i>Ibid.</i>
C <sub>6</sub> n <sub>6</sub> (× 10 <sup>-3</sup> )	9.2				Elworthy & Florence, 1964
	20				
Et <sub>2</sub> CH·CH <sub>2</sub> n <sub>6</sub> (× 10 <sup>-3</sup> )	7.4	6.5		5.2	<i>Ibid.</i>
	20	30		40	
C <sub>8</sub> n <sub>3</sub> (× 10 <sup>-3</sup> )	10.0	9.3		8.7	Corkill, Goodman & Harrold, 1964
	20	30		40	
C <sub>8</sub> n <sub>4</sub> (× 10 <sup>-3</sup> )	9.3	7.5			<i>Ibid.</i>
	15	25			
C <sub>8</sub> n <sub>5</sub> (× 10 <sup>-3</sup> )	11.9	9.9	7.7	6.7	Corkill & others, 1961
	15	25	35	45	
(× 10 <sup>-3</sup> )	9.8				Balmбра & others, 1964
	25				
(× 10 <sup>-3</sup> )	11.3	8.9		7.2	Elworthy & Florence, 1964
	18	30		40	
Pr <sub>2</sub> CH·CH <sub>2</sub> n <sub>6</sub> (× 10 <sup>-3</sup> )	23	20			Corkill, Goodman & Harrold, 1964
	20	30			
C <sub>8</sub> n <sub>6</sub> (× 10 <sup>-3</sup> )	16	13		11	Corkill, Goodman & Harrold, 1964
	15	25		35	
C <sub>10</sub> n <sub>3</sub> (× 10 <sup>-4</sup> )	7.3	6.0		5.6	<i>Ibid.</i>
	15	25		35	
C <sub>10</sub> n <sub>4</sub> (× 10 <sup>-4</sup> )	14.5	11.2	9.8	9.0	Hudson & Pethica, 1964
	1	6.8	10	15	
(× 10 <sup>-4</sup> )	7.3	6.8			Carless, Challis & Mulley, 1964
	20	25			
(× 10 <sup>-4</sup> )	0.53*				Hudson & Pethica, 1964
	14.1	11.8	9.7	9.0	
C <sub>10</sub> n <sub>5</sub> (× 10 <sup>-4</sup> )	16	10	15	20	Donbrow & Jan, 1963
	5	7.6	7.2	6.8	
(× 10 <sup>-4</sup> )	8.1	30	35	40	Donbrow & Jan, 1963
	25				
(× 10 <sup>-4</sup> )	8.6*				Carless & others, 1964
	20				
(× 10 <sup>-4</sup> )	9.3*				Corkill, Goodman & Harrold, 1964
	20				
C <sub>10</sub> n <sub>6</sub> (× 10 <sup>-4</sup> )	11.4	9.0	6.6	6.4	Corkill, Goodman & Harrold, 1964
	15	25	35	45	
(× 10 <sup>-4</sup> )	9.0	6.6		4.3	Balmбра & others, 1964
	25	35		45	
(× 10 <sup>-5</sup> )	9.4*				Donbrow & Jan, 1963
	20				
Bu <sub>2</sub> CH·CH <sub>2</sub> n <sub>6</sub> (× 10 <sup>-5</sup> )	34	31		28	Elworthy & Florence, 1964
	15	20		25	
C <sub>10</sub> n <sub>6</sub> (× 10 <sup>-4</sup> )	21	17.2	14	11	Hudson & Pethica, 1964
	5	10	15	20	
C <sub>10</sub> n <sub>9</sub> (× 10 <sup>-4</sup> )	9	7.3			Corkill, Goodman & Harrold 1964
	25	35			
C <sub>10</sub> n <sub>9</sub> (× 10 <sup>-4</sup> )	14	13		11	Elworthy & Florence, 1964
	15	25		35	
Bu <sub>2</sub> CH·CH <sub>2</sub> n <sub>9</sub> (× 10 <sup>-4</sup> )	32	28		24	Donbrow & Jan, 1963
	20	30		40	
C <sub>12</sub> n <sub>3</sub> (× 10 <sup>-5</sup> )	4.2*				Lange, 1960
	20				
(× 10 <sup>-5</sup> )	5.7				Carless & others, 1964
	23				
(× 10 <sup>-5</sup> )	3.8*				Corkill & others, 1961
	20				
C <sub>12</sub> n <sub>6</sub> (× 10 <sup>-5</sup> )	10.8	8.7		7.2	Corkill, Goodman & Harrold, 1964
	15	25		35	
(× 10 <sup>-5</sup> )	8.7*				Donbrow & Jan, 1963
	20				
(× 10 <sup>-5</sup> )	7.9*				Carless & others, 1964
	20				

## PHYSICAL CHEMISTRY OF SOME NON-IONIC DETERGENTS

 TABLE 1—*continued*

Compound	CMC			Reference
	Moles/litre (upper line)	at ° C (lower line)		
C <sub>12</sub> N <sub>7</sub> (× 10 <sup>-5</sup> )	8.0			Lange, 1960
	23			
C <sub>12</sub> N <sub>9</sub> (× 10 <sup>-5</sup> )	10			<i>Ibid.</i>
	23			
C <sub>12</sub> N <sub>12</sub> (× 10 <sup>-5</sup> )	14			<i>Ibid.</i>
	23			
C <sub>13</sub> N <sub>8</sub> (× 10 <sup>-5</sup> )	11			Becher, 1964
	25			
C <sub>13</sub> N <sub>10</sub> × 10 <sup>-5</sup> )	12			<i>Ibid.</i>
	25			
C <sub>13</sub> N <sub>12</sub>	11			<i>Ibid.</i>
	25			
C <sub>14</sub> N <sub>6</sub> (× 10 <sup>-6</sup> )	10			Balmбра & others, 1964
	25			
C <sub>14</sub> N <sub>8</sub> (× 10 <sup>-6</sup> )	1			<i>Ibid.</i>
	35			
(× 10 <sup>-6</sup> )	1			Corkill & others, 1961
	25			
C <sub>16</sub> N <sub>8</sub> (× 10 <sup>-6</sup> )	1.7			Elworthy & Macfarlane, 1963
	25			
(× 10 <sup>-6</sup> )	97*			Carless & others, 1964
	27			
C <sub>16</sub> N <sub>7</sub> (× 10 <sup>-6</sup> )	1.7			Elworthy & Macfarlane, 1963b
	25			
C <sub>16</sub> N <sub>9</sub> (× 10 <sup>-6</sup> )	2.1			<i>Ibid.</i>
	25			
(× 10 <sup>-6</sup> )	38*			Donbrow & Jan, 1963
	20			
(× 10 <sup>-6</sup> )	36			Carless & others, 1964
	20			
C <sub>16</sub> N <sub>12</sub> (× 10 <sup>-6</sup> )	2.3			Elworthy & Macfarlane, 1962b
	25			
C <sub>16</sub> N <sub>15</sub> (× 10 <sup>-6</sup> )	3.1			<i>Ibid.</i>
	25			
C <sub>16</sub> N <sub>21</sub> × 10 <sup>-6</sup> )	3.9			<i>Ibid.</i>
	25			

the previously mentioned work on this subject, but Kushner & Hubbard (1954) claimed, from turbidimetric results on a sample of Triton X 100, that there was no well defined CMC but a gradual increase in the fraction of added detergent forming micelles up to a concentration of about 0.3 g/100 ml, where virtually all of each increment added to the solution became micellar. The authors suggested that this may have been caused by the effects of the chain length distribution; the shorter ethylene oxide adducts forming micelles at lower concentrations. Later work (Kushner, Hubbard & Doan, 1957) on molecularly distilled fractions still showed no sharp CMC. The concentration where the concentration/turbidity vs. concentration graph settled to a straight line was lower in the case of the fraction with the shorter mean ethylene oxide chain length. When considering these latter results it must be borne in mind that molecular distillation does not give a series of clear cut chemical entities, but at the best merely increases the incidence of molecules having an ethylene oxide content close to that of the mean. It has been suggested that this monomer saturation concentration is an artifact arising from non-equilibrated solutions (Becher & Clifton, 1959), but this time dependence of micellar breakdown has in turn been attributed to the presence of impurities (Corkill & others, 1961), and did not occur when chemically pure synthetic compounds were studied.

The determination of CMC of a series of homogeneous *n*-t-octylphenoxyethoxyethanols (containing from 1–10 ethylene oxide units) by Crook, Fordyce & Trebbi (1963), showed the general trend of increased CMC with polyoxyethylene chain lengthening.

Recent work on a synthetic dodecyl ether of hexaoxyethylene glycol (Balmbra, Clunie, Corkill & Goodman, 1962) gives another interesting aspect. Comparison of the CMC obtained from surface tension plots ( $c_0$ ) with that apparent from turbidity ( $c_1$ ) showed the latter to be much higher. The constant value for the surface tension observed at concentrations greater than  $c_0$  was taken to indicate that the activity of the monomers in equilibrium with the surface phase remained constant,  $c_1$  being caused by the micellar units between  $c_0$  and  $c_1$  having such low aggregation numbers that the solution turbidities are too small to be distinguished experimentally from the solvent turbidity, and only at concentrations greater than  $c_1$  does the micellar weight become appreciable and constant.

Furthermore, in a study of the light scattering of monohexadecyl- $n_6$  and monohexadecyl- $n_7$ , an association of small into large micelles has been detected (Elworthy & Macfarlane, 1962a); bearing out this idea of a second association concentration higher than the first CMC. The values of this second association concentration appear to decrease with increasing ethylene oxide chain length and may account for some of the apparently anomalous results obtained in studying these CMC values by different methods.

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