Review Article

Further aspects of the physical chemistry of some non-ionic detergents*

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SIZE, SHAPE AND HYDRATION OF MICELLES

The most interesting properties of detergents in solution are their surface and micellar behaviour and the factors affecting this. Aqueous solutions of non-ionic detergents are colloidal, thus the techniques applied in their study have been similar to those generally used in colloid science.

It has now been accepted that molecules of non-ionic detergents having a polyoxyethylene chain sufficiently large to produce water solubility of the hydrophobic moiety, orientate themselves in micelles with the hydrophobic moiety inside and the glycol chains outside. The glycol chain confers water solubility by trapping water molecules in some way (Goto, Sugano & Koizumi, 1954; Ferguson, 1955). The exact amount of water trapped and the means by which this is effected is conjectural as, until recently, no independent method of measuring the aqueous co-volume of the micelle had been reported. Hydroxonium ions, hydrogen bonding and various arrangements of the water molecules around the ether oxygens or within the glycol structure have been suggested (Chwala & Martin, 1937, 1947; Wurzchmitt, 1950; Trinchieri, 1952; Hsaio, Dunning & Lorenz, 1956; Kehren & Rosch, 1956; Rosch, 1956; Bailey & Callard, 1959; Schick, 1963b). From viscosity and micellar studies, Kushner & Hubbard (1954) estimated that there were 43 molecules of water per polyoxyethylene chain in a micelle of Triton X 100 (n_{10}). Of this number, they suggested 20 molecules were held by hydrogen bonding to the ether oxygens, the rest being physically trapped by the chain. Nakagawa & Inoue (1958) showed the number of hydrating water molecules per oxygen atom of the polyoxyethylene chain increased with chain length. Other workers (Karabinos, Hazdra & Ballun, 1955; Karabinos & Metziger, 1955; Kehren & Rosch, 1956; Reich, 1956; Rosch, 1956; Boehmke & Heusch, 1960), using data from viscosity, polarimetry, and heat of hydration, have given 1, 2, 3 or 4 water molecules per ether oxygen, depending on the chain length and the workers concerned.

We have recently described a method, based on vapour pressure measurements, of estimating the micellar hydration (Elworthy & Macfarlane, 1964). The vapour pressures over gels and concentrated solutions of detergents were measured as a function of detergent concentration and, by a suitable extrapolation procedure, the concentration determined at which the solution had (within experimental error), the same apparent

vapour pressure as water. The amount of water in this solution was taken as a measure of micellar hydration as it corresponds to the minimum amount necessary to cause separation of the micelles from one another. Although the method is empirical the values obtained for the hydration (w_1) agree well with those derived from the intrinsic viscosities of micelles which are spherical (Equation 2: Elworthy & Macfarlane, 1965).

As with much of the work on non-ionic detergents, most studies of micellar structure have been made with commercial detergents, and much of the conflicting data in the literature is due to the batch variation of only nominally similar compounds (Dunning, 1957; Dwiggens & Bolen, 1961; Dwiggens, Bolen & Dunning, 1960; Boon, Coles & Tait, 1961). As we have already discussed (Elworthy & Macfarlane, 1965), the polymerisation syntheses give rise to products having a range of ethylene oxide chain lengths; a range which varies depending on the experimental conditions. Although claims of "reproducible heterogeneity" have been made (Becher, 1961) these heterogeneous compounds are far from ideal for physico-chemical measurement.

The effect of fractionation of these materials on their physical properties has been studied and serves to further illustrate this point (Kushner, Hubbard & Doan, 1957; Stauff & Rasper, 1957). Molecular distillation of a sample of Triton X 100 gave two fractions, one giving a clear solution in water, the other being classed as "insoluble". Further redistillation of the two fractions gave one insoluble and one soluble subfraction from each. From light scattering studies of the two soluble subfractions, the micellar weights (M) obtained were:

	M	n	Aggregation number
Lower distilling fraction ..	208×10^3	8	373
Undistilled	90×10^3	10	139
Higher distilling fraction ..	53×10^3	12	73

(Where n is the mean number of ethylene oxide units per molecule.)

Recombination of the soluble and insoluble fractions gave a molecular weight the same as that of the undistilled compound.

The above values indicate a trend which is found with all surfactants of the polyoxyethylene type at a given temperature: this is that the micellar aggregation number for a given hydrophobic group decreases with increasing polyoxyethylene chain length (Kushner & others, 1957; Nakagawa & Kuriyama, 1957a; Stauff & Rasper, 1957; Nakagawa, Kuriyama & Inoue, 1960; Becher, 1961; Elworthy & Macfarlane, 1962a; 1963; Schick, Atlas & Eirich, 1962). Also, with standard polyoxyethylene chain length, the aggregation number increases with increasing length of the hydrophobic part of the molecule, i.e., by increasing the length of the paraffin chain (Corkill, Goodman & Ottewill, 1961; Kuriyama, 1962a; 1962b).

Several authors (Balmbra, Clunie, Corkill & Goodman, 1962, 1964; Elworthy & Macfarlane, 1963) have found that micellar weight, as determined from light scattering, appears to vary with solute concentration.

TABLE 1. MICELLAR WEIGHTS OF SYNTHETIC NON-IONIC DETERGENTS

Abbreviations C_{16} = n-hexadecyl, n_6 = six ethylene oxide units.

In each entry the micellar weight (M) is given on the upper line, the aggregation number (m) on the second, and the temperature (T) on the lower line. All micellar weights are $\times 10^5$.

Compound							Reference
C_8n_6 ..	M	0·12	0·16	0·20	0·33	0·82	Balmbra & others, 1964.
	m	30	41	51	82	210	Corkill & others, 1961
	T	18	30	40	50	60	
	M	0·125					
	m	32					
	T	25					
$C_{10}n_6$ ..	M	0·31	1·1	2·7	5·6		Balmbra & others, 1964
	m	73	260	640	1,330		
	T	25	35	45	50		
$C_{12}n_6$ ..	M	0·63	0·84	1·8	3·2		Balmbra & others, 1962
	m	140	186	400	710		
	T	15	18	25	30		
	M	6·3	10	18			
	m	1,400	2,220	4,000			
	T	35	42	45			
	M	0·78					Corkill & others, 1961
	m	173					
	T	25					
$C_{14}n_6$ ..	M	15	26	36	56		Balmbra & others, 1964
	m	3,100	5,400	7,500	11,700		
	T	25	30	35	40		
$C_{16}n_6$ ..	M	51	68	84			Ibid.
	m	10,500	13,300	16,600			
	T	28	32	34			
	M	12·3⎫					Elworthy & Macfarlane, 1963
	m	2,430 ⎬ Infinite dilution					
	T	25 ⎭					
	M	52⎫		63⎫			Ibid.
	m	10,300 ⎬ Zimm		12,500 ⎬ Dissymmetry			
	T	25 ⎭ plot		25 ⎭ method			
$C_{16}n_7$ ..	M	0·90	1·14	1·37	3·27		Elworthy & McDonald, 1964. Elworthy & Macfarlane, 1963
	m	162	207	250	590		
	T	15	17·5	20	25		
$C_{16}n_8$ ..	M	1·31	1·43	1·6	4·0		Elworthy & McDonald, 1964
	m	220	240	270	670		
	T	15	25	35	37·4		
	M	6·0	16·7				
	m	1,010	2,800				
	T	39·3	44·3				
$C_{16}n_9$ ..	M	1·4	1·8	3·5	6·4	8·8	Elworthy & McDonald, 1964. Elworthy & Macfarlane, 1962a
	m	220	240	550	1,000	1,380	
	T	25	45	50	53·5	57·5	
$C_{16}n_{12}$ ..	M	1·17					Elworthy & Macfarlane, 1962a
	m	150					
	T	25					
$C_{16}n_{21}$ ..	M	0·82					Elworthy & Macfarlane, 1963
	m	70					
	T	25					

Extrapolations of T–C plots (Elworthy & Macfarlane, 1965) do not pass through the CMC, but through a higher concentration C_L, which may be a second association limit. Thus plots of Hc/T against c curve upwards at low concentrations.

For the C_{16} n_6 and C_{16} n_7 detergents, Elworthy & Macfarlane (1963), found that, at 25°, the micellar weights at infinite dilutions were $1·2 \times 10^6$ and $0·33 \times 10^6$ respectively, while at higher concentrations, above C_L,

they were ca. 5×10^6 and 1×10^6 respectively. Balmbra & others (1962) report ca. $5 \cdot 1 \times 10^6$ for $C_{16}n_6$ at $28°$. Large dissymmetries develop at finite concentrations.

It is not yet clear if the small micelles first formed at the CMC grow steadily in size and reach a constant value at C_L, or whether the first formed micelles aggregate to form the larger ones.

It is undoubtedly time that a more precise experimental technique than light scattering was used in studying these systems.

Table 1 lists the micellar weights of synthetic non-ionic detergents.

Straight line relationships between the aggregation number and the reciprocal of the number of ethylene oxide units per molecule have been obtained for several detergent series, which would make it possible to predict an aggregation number for a given hydrophobe. Little work has been done on detergents containing ethylene oxide chain lengths such that monomers are formed at high concentrations, but it has been shown for some larger compounds (Schick & others, 1962) that, although there is a decreased aggregation number with increasing polyoxyethylene content, the actual micellar weights were greater than of those compounds with short polyoxyethylene chains. The rise in micellar weight together with a CMC lower than expected, has been attributed to a decrease in the solubility of the ethylene oxide moiety as its molecular weight increased. Unfortunately there is insufficient data to show whether a plot of aggregation numbers vs. ethylene oxide units per molecule passes through a minimum, or merely becomes asymptotic.

The shape of the micelle is a further factor to be determined. The three models most frequently used for micellar aggregates are spheres, discs or rods. It has been suggested that, in dilute solution, small micelles of ionic detergents with molecular weights of 10 to 50×10^3 (Debye & Anacker, 1951; Tartar, 1959) are spherical, whereas large micelles, with aggregate molecular weights of greater than 500×10^3, are rod shaped.

From intrinsic viscosity numbers, sedimentation constants, and light scattering dissymmetry ratios on a range of compounds, Schick & others (1962) claimed a similar pattern for non-ionic detergents, i.e., in the range $M = 45$ to 100×10^3, spheres appear the most probable shape, while for large micelles discs or rod-like shapes are likely. For Triton X 100 ($M = 90,000$), Kushner & Hubbard (1954), from light scattering and viscosity work, suggested a spherical micelle and Nakagawa & Inoue (1958) also suggested a spherical micelle for a series of compounds of micellar weight from 40 to 60×10^3 on the basis of constant effective specific volume. Becher (1961), on the other hand, pointed out that micelles of this size are so small that the light scattering dissymmetry values (Z_{45} close to unity) do not give much idea about the shape of the micelles. His calculations, based on surface area measurements and the hydrated volume of the micelle, suggested that, for micelles containing molecules with fairly long ethylene oxide chain lengths ($n_{15}-n_{30}$), the assumption of a rod-like micelle was to be favoured. However, Becher

made no allowance for the variation of hydration with polyoxyethylene chain length.

The use of viscosity in the determination of micellar shape is complicated by the presence of the co-volume of water in the micelle. Viscosity has therefore been used mainly in conjunction with other techniques. Raphael (1954) showed that the viscosity of a given molar concentration of an adduct decreased with decreasing ethylene oxide chain length, passed through a minimum, then rose again. This pattern of behaviour is perhaps illustrated more clearly by studies on a hexadecyl series of synthesised surfactants at 25° (Elworthy & Macfarlane, 1962, 1963; Elworthy & McDonald, 1964); hexadecyl-n_6 and hexadecyl-n_7 gave intrinsic viscosities of 22·7 and 9·7 respectively, and hexadecyl-n_8 gave the smallest value, 3·8, after which the values rose steadily; hexadecyl-n_9, 4·3; up to 6·8 c.c./g for hexadecyl-n_{21}, the largest compound studied.

In the first interpretation of these results, micellar shape factors for the lower members of the series were calculated by assuming maximum and minimum values for their hydration; the minimum level was set by assuming hexadecyl-n_6 to be unhydrated and hexadecyl-n_{21} hydrated and spherical, while the upper limit was obtained by letting hexadecyl-n_{15} and hexadecyl-n_{21} be spherical and hydrated and drawing an asymptote to a plot of g water/g detergent (calculated directly from the intrinsic viscosity) against the number of ethylene units in the detergents.

Correlation of these intrinsic viscosity results with the values obtained for micellar hydration by the vapour pressure method has, however, led to a re-appraisal of these shape factors (Elworthy & Macfarlane, 1964). The micelles formed by the first two members of the series, hexadecyl-n_6 and hexadecyl-n_7, were asymmetric and hydrated to the extent of 0·39 and 0·44 g water/g detergent respectively, but compounds containing more than eight ethylene oxide units per molecule formed spherical micelles, the increase in intrinsic viscosity with increasing chain length being accounted for by the increase in micellar hydration as the series was ascended.

CONFIGURATION OF THE ETHYLENE OXIDE CHAINS

Because of the lack of knowledge of micellar dimensions, much of the early speculation about the configuration of the oxyethylene chain in the micelle was based on viscosity and X-ray diffraction data of the glycols themselves. Lower molecular weight chains, i.e., with not more than ten ethylene oxide units, appeared to exist in the regular extended "zig-zag" or *trans* structure, whereas longer chains occurred as the more condensed "meander" or *gauche* form (Curme & Johnston, 1952). Coils, and "crumpled helical" and "highly convoluted" structures, particularly for very long chains, have also been suggested (Sauter, 1933; Hibbert & Lovell, 1940; Bailey & Callard, 1959).

Rosch (1957) has claimed that the "meander" form is the most likely in aqueous solution; a spiral chain being formed due to carbon-oxygen dipoles (forces which are said to be accentuated in water due to the presence of an onium structure) where each oxygen approached closely

and was attracted to a carbon atom separated from it by three other carbon atoms and one oxygen atom. Despite its being sterically possible, the "meander" form has been described as somewhat "crowded" (Becher, 1962) and may require stabilisation by a chain of hydrogen bond-linked water molecules between the adjacent chain oxygens. The polyoxyethylene chain might even be in a random mixture of both configurations, *trans* and *gauche*, as found in dioxane solution by dipole and infra-red measurements (Uchida, Kurita, Koizumi & Kubo, 1956; Kuroda & Kubo, 1957, 1959).

Although not strictly comparable with micellar structure, application of the Gibbs equation to surface tension data has shown the cross-sectional area of the polyoxyethylene chain in solution to be the controlling factor in the packing of the molecules in the interface (Hsaio & others, 1956; Schick, 1962; Elworthy & Macfarlane, 1962b), but the increment of area per ethylene oxide unit decreased as the number of ethylene oxide units per molecule increased. Coupled with a similar effect for surface potential measurements (Schick, 1963b), this has been interpreted as a coil formation of the polyoxyethylene chain in the aqueous phase, the size of the coils increasing as the chain lengthened without reaching complete randomness even with the longest chains studied by this technique (containing up to one hundred ethylene oxide units).

An expanding coil structure has also been described from measurements of micellar volume (Elworthy & Macfarlane, 1962a, 1964; Schick & others, 1962; Macfarlane, 1963). These measurements showed that, at 25°, the polyoxyethylene chains were contracted to well below their fully extended length but the dimensions calculated for these coils were dependent on the volume assigned to the hydrophobic core of the micelle, that of an oil droplet being considered the most probable.

EFFECTS OF TEMPERATURE

Solubility of detergent compounds, even in dilute solutions, is often limited to certain temperature ranges; only between a lower Kraft Point and an upper cloud point can a solution exist without phase separation. Thus, outside this temperature range, the detergent loses many of its most important properties. Little work appears to have been done on the Kraft Point as few of the non-ionic detergents exhibit this phenomenon, but the cloud point has been studied extensively.

As has been described, the micellar properties are influenced by the hydrophilic properties of the molecule, which, in turn, appear to be a function of the length of the polyoxyethylene chain and the amount of water "trapped". The cloud point has generally been assumed to be caused by a thermal dehydration of the micelle reaching a stage where the hydrophilic properties of the micelle were reduced to such a level that the detergent was thrown out of solution. Above the cloud point a phase rich in detergent separated out of solution (Maclay, 1956; Nakagawa & Tori, 1960), leaving a concentration of detergent in the co-existing aqueous phase which appeared to be dissolved as a monomer dispersion with virtually no micelles present.

Here, as with the other solution properties, altering the length of the polyoxyethylene chain for a given hydrophobe affected this behaviour; the cloud point rising on increasing the number of ethylene oxide units in the chain (Raphael, 1954; Elworthy & McDonald, 1964). For ether-linked adducts of constant glycol chain length, it fell with increasing size of the hydrophobic group in ascending a homologous series. Though cloud points are sometimes found to be constant over a fairly wide range of concentration (Maclay, 1956), some have been shown to vary with concentration (Balmbra & others, 1962), and certain discrepancies in the literature have been attributed to comparison at different concentrations.

Provided the compound is pure, the cloud point of polyoxyethylene ether adducts appears as a sharp change in turbidity, but as the hydrophilic chain is lengthened, the cloud point exceeds $100°$. To measure these high cloud points, pressure has been increased to obtain higher temperatures, or a substance which lowered the cloud point to a more easily measured temperature has been added. The values obtained are then extrapolated to zero additive concentration (Maclay, 1956).

For non-ionic detergents, clouding is a reversible procedure, the solution becoming clear again when the temperature drops below the critical point. Clouding is used to follow the polymerisation of ethylene oxide onto a hydrophobic group as the phenomenon can be adapted to give a quick idea of the progress of the reaction. Steele & Berger (1956) have characterised non-ionic detergents from plots of cloud points against apparent density. These plots showed that values for a particular type of detergent fell into a characteristic band which could be used as a method of identification.

In contrast to many ionic detergents (Kuriyama, 1962b, 1962c), the micellar weights of polyoxyethylene type non-ionic detergents increase with rising temperature (Dwiggens & Bolen, 1961; Balmbra & others, 1962), the rate of increase becoming greater as the cloud point is approached (Kuriyama, 1962a, 1962b). It is therefore necessary to consider the effects of temperature on micellar weight and structure.

Kuriyama (1962b) measured by light scattering the micellar weights and apparent second virial coefficients of a methoxydodecyl polyoxyethylene glycol over a range of temperatures up to the cloud point. He found the solute-solvent interaction decreased with increase in temperature, the rate of the interaction decreasing more rapidly as the cloud point was approached. He concluded that the phase separation occurred not because of a simple dehydration of micelles, but rather as a result of the decreased interaction between water and very large micelles.

Diffusion-viscosity experiments on a methoxypolyoxyethylene octanoate (Nakagawa, Inoue, Tori & Kuriyama, 1958) showed the increase in micellar weight with temperature was accompanied by an increase in hydration with the development of asymmetry near the cloud point.

The behaviour of micellar weight with temperature appears to depend on the balance of the hydrophobic and hydrophilic parts of the detergent molecules. Balmbra & others (1962, 1964) have reported an exponential rise of micellar weight with increasing temperature for $C_{10}n_6$, $C_{12}n_6$ and

$C_{16}n_6$. For C_8n_6 there was a more rapid increase at temperatures above 45° than below this temperature.

Elworthy & McDonald (1964) investigated the consequences of varying the hydrophilic part of the monomer on the temperature effects; they studied three synthesised detergents; hexadecyl-n_7, hexadecyl-n_8 and hexadecyl-n_9, by light scattering, viscosity, and vapour pressure techniques. Below temperatures of 22°, 33° and 45°, respectively, for these compounds, a slow increase in micellar weight with increasing temperature was found, but above these transition temperatures (designated T_h) there was an exponential rise in micellar weight which was accompanied by the development of much micellar asymmetry.

It can be envisaged that a compound containing a long polyoxyethylene chain would give a slow increase of micellar weight with temperature, while one containing a short chain would give the exponential increase only.

Below the transition temperature the micelles were reasonably spherical with the polyoxyethylene chains contracted to about 50% of their fully extended lengths but above T_h the micelles appeared to resemble prolate ellipsoids of revolution. The increasing micellar size was accompanied by an increase in micellar hydration, at least up to T_h. This finding, although somewhat surprising, fits in with the marked extension of the polyoxyethylene chains as more space is available for trapping water in the expanded micelles.

The use of commercially produced detergents in studies of the temperature variation of micellar weight obscures the sharpness of the transition at T_h, due presumably to the range of polyoxyethylene chain lengths present.

EFFECT OF ELECTROLYTES

One of the often quoted advantages for non-ionic detergents is their stability even in relatively high electrolyte concentration: this, however, does not mean that they are unaffected by the presence of electrolytes (Maclay, 1956; Bolle, 1960; Kuriyama, 1962b). Early work by Doscher, Myers & Atkins (1951) showed that sodium chloride strikingly raised the viscosity and turbidity of aqueous solutions of non-ionic detergents, whereas calcium chloride had a much smaller effect. The surface tension increased gradually with increase of the ratio of calcium chloride to detergent, whereas it decreased with sodium chloride. These effects were interpreted as sodium chloride "salting out" the non-ionic detergent whereas calcium salts "salted in" the hydrated calcium ions co-ordinating in some way with the ether oxygens. The isolation of a detergent-calcium chloride complex further substantiated this theory. Maclay (1956), and Bolle (1960), in an examination of the factors affecting solubility of non-ionic adducts, showed that, in dilute solution, the lowering of the cloud point by electrolytes was a linear function of the ionic strength, and the observed salting out effect for alkali metals and multivalent cations was roughly in the order of decreasing ion hydration. Kuriyama (1962b), however, pointed out that although calcium chloride exhibited a smaller effect on the cloud point when compared with sodium

chloride at the same ionic strength, if compared at the same molar strength it was equally effective. The effect of electrolytes on the cloud points is obviously integrated with the complex network affecting micellar structure, hydration, and aggregation number at different temperatures, but whether one can obtain an indication of the effects of electrolytes at lower temperatures from their effects on cloud points is doubtful, particularly in the light of studies on the effects of salts on micellar weights at different temperatures.

At 30°, the addition of sodium chloride to a methoxy polyoxyethylene dodecyl ether (n_{12}) gave a linear increase in micellar weight with increase of salt concentration whereas with calcium chloride, although the micellar weight increased initially, it was nearly constant over a range of 0·5–1·0M. At 50°, the effect of sodium chloride was greater than at the lower temperature, but at this higher temperature equimolar concentrations of calcium chloride were equal to or more potent than those of sodium chloride in their effect on micellar weight. To further complicate the issue, other workers have claimed that addition of electrolytes at a given temperature does not necessarily give an increase in micellar weight (Mankowich, 1955; Becher, 1962; Schick & others, 1962). Becher (1962), working on a series of commercial dodecyl ethers, showed that although a slight increase in micellar weight was found for the lower members of the series, the larger detergents showed, if anything, a slight decrease in micellar weight. Schick & others (1962), have shown similar effects with an octadecyl ether series but the decrease in micellar weight with added electrolytes did not appear until a much longer polyoxyethylene chain was present in the adduct (n_{100}). It has been suggested (Schick & others, 1962) that the increased length of the polyoxyethylene chain enhanced the adsorption of electrolyte to such an extent that it increased the overall solubility of the detergent, but it would appear that much depends on the particular series being studied.

In a further attempt to elucidate salting out mechanisms, the effect of added electrolyte on the CMC has been examined, and here the order of effectiveness in lowering the CMC followed a decrease in lyotropic number (Hsaio & others, 1956; Becher, 1962; Schick, 1962); the effect being more pronounced with the more hydrophilic longer oxyethylene chain compounds. A change in the lyotropic number of the anions had a larger effect in lowering the CMC than that of the cations. Surface moment and surface tension studies have suggested that the addition of sodium chloride produces a collapse of the ethylene oxide coil structure, in a manner similar to that observed for the glycols by Bailey & Callard (1959). Addition of a proton donor or acceptor also effects the CMC (Schick, 1963b), e.g., for a nonylphenyl adduct (n_{15}).

Solvent			CMC
0·86M HCl ..	..	..	150 μmol/litre
Water	..	..	110 μmol/litre
0·86M NaOH	..	..	80 μmol/litre

Hsaio & others (1956) have attributed this shift to oxonium ion formation in the polyoxyethylene chains; added protons increase the ionic character of the non-ionic detergents and consequently the CMC is increased, and vice versa. This has been taken by these authors to indicate that non-ionic detergents are weakly cationic in aqueous solution, and, by Becher (1962), to explain the electrolyte effects in the terms of a positive double layer in the outer layer of the micelle. Conductivity experiments made to clarify this last point (Becher, 1963) appear to be affected by the presence of polymerisation catalysts in the substance.

Mankowich (1955) has suggested that the lowering of the CMC in the presence of electrolyte does not occur because of any specific electrical property of the electrolyte but rather to its effect on the solvent. On the basis that sucrose would markedly lower the activity without affecting the electrical properties, the CMC has been measured in different concentrations of sucrose solutions (Becher, 1963). The values obtained showed little change, and together with the magnitude of the effects at given electrolyte concentrations, and the apparent specificity of the anions, they did not point to an effect on activity as a likely explanation.

Perhaps the most complete picture of electrolyte effects was that obtained from micellar and surface studies by Schick & others (1962) and Schick (1962; 1963b). On the basis of their results, these authors have postulated the following mechanism for "salting out" non-ionic detergents. The salting out of neutral molecules depends on the concentration and ionic radii of the electrolyte, and the dielectric constant of the non-electrolyte (Bailey & Callard, 1959). Small hydrated ions (low lyotropic number) are more effective in salting out than large hydrated ions (high lyotropic number). This was shown to follow with the non-ionic detergents studied; the salting out increased with increasing electrolyte concentration and with decreasing radii of hydrated ions. The hydration of the anions was more important than that of the cations. Thus, Schick & others claimed that there was first a removal of hydrogen bonded water molecules from the ether oxygens of the ethylene oxide chain by the increased electrolyte concentration, and second, that the extent of the dehydration of the ethylene oxide chain was determined by the closeness of approach of the cations to the ether oxygens, but this was partially counteracted by the tendency of the counter anions to be hydrated.

Undoubtedly, work with synthetic detergents is necessary for a better understanding of salt effects.

SOLUBILISATION

The ability of detergent solutions to dissolve organic compounds which are insoluble, or only slightly soluble in water, is one of their most striking properties. It is termed solubilisation. For ionic detergents, it is generally believed that with non-polar hydrocarbons uptake occurs into the interior of the micelle; for partially miscible polar compounds, such as octanol and phenols, there is adsorption on the micelle surface with the hydrocarbon inside and the polar group of the solubilisate in the aqueous phase. Water soluble polar substances, such as glycerol and

certain dyes, which are insoluble in hydrocarbons, are thought to be adsorbed on to the exterior of the micelles (Harkins, Mittelman & Corrin, 1949; Alexander & Johnson, 1950). With non-ionic detergents of the polyoxyethylene type there is another possible mode—that of incorporation into the polyoxyethylene chain part of the micellar structure.

In the study of solubilisation, as with electrolytes, much of the work and the conclusions from it have been based on the effects of solubilisates on cloud points (Weiden & Norton, 1953; Livingstone, 1954; Maclay, 1956; Bolle, 1960). The cloud point of Triton X 100 (Maclay, 1956) has been shown to be significantly raised by anionic detergents and aliphatic hydrocarbons, but, as the polarity of the solubilisate was increased by the introduction of double bonds or polar constituents, the effect on cloud points was much less marked. Aromatic and polar aliphatic additives caused the cloud points to be sharply decreased (Maclay, 1956).

The mode of incorporation may account for the difference in the effects of such compounds on cloud points. Dodecane is insoluble in a polyoxyethylene glycol and will be taken into the hydrophobic core of micelles; benzene, however, is miscible with the hydrophobic moiety, with polyoxyethylene glycols, and with concentrated aqueous solutions of the glycols, and may thus be partially present in the glycol structure, thereby decreasing the hydrophilic properties of the micelle.

Weiden & Norton (1953) attributed the lowering of the cloud point by benzene and phenol to a decrease of the hydrophilic properties of the micelles, but Livingstone (1954) suggested pH might also play an important part in the effect of phenols although this latter idea was refuted by Maclay (1956). Such effects have been used in attempts to develop methods of assay for non-ionic detergents in aqueous solution, either by ascertaining the length of the oxyethylene chain of the adduct or by gaining an idea of its properties in solution (Davis, Wattman & Speel, 1955; Karabinos, 1955).

The solubilisation of phenol and its analogues has also been said to occur by binding of the phenolic hydroxyl groups with the ether oxygens of the polyoxyethylene chains by hydrogen bonding (Mulley & Metcalf, 1956; Patel & Kostenbauder, 1958). Higuchi & Lack (1954), and Higuchi & Guttman (1956), have reported complex formation of phenolic substances with polyoxyethylene groups, and it has been observed that many phenolic substances were readily dissolved in concentrated solutions of polyoxyethylene glycols (Nakagawa, 1954; 1956).

The solubilisation of iodine (Osol & Pines, 1952; Allawala & Riegelman, 1953a; 1953b; Bartlett & Schmidt, 1957; Brost & Krupen, 1957; Hugo & Newton, 1963), and various dyes (Sheppard & Geddes, 1945; Rigg & Liu, 1953; Nakagawa, 1958; Riegelman, Allawala, Hrenoff & Strait, 1958), with their concomitant spectral changes, have similarly been the subject of varying opinion.

Examination of phase changes (Nakagawa & others, 1963) and construction of phase diagrams (McBain & Marsden, 1947; Winsor, 1960; Mulley, 1961; Balmbra & others, 1962; Mulley & Metcalf, 1962) in the presence of different solubilisates have also been made to try to obtain a

clearer insight to this problem. Solubilisation and some pharmaceutical aspects have been well reviewed by Mulley (1964).

Light scattering measurements have been made in a study of the effect of n-decane and n-decanol on the micellar weights of two methoxypoly-oxyethylene glycol monodecyl ethers by Nakagawa, Kuriyama & Inoue, 1960). These authors have shown that the micellar weights increased with the addition of solubilisates up to the saturation limit of the solubilisate, the increase originating not only from the simple incorporation of solubilisate molecules into the existing micelle, but also from the number of detergent molecules in the micelle increasing with added solubilisate. The solubilisation process was therefore accompanied by a reconstitution of the micelles in a manner analogous to that concluded from other techniques (Nakagawa & Inoue, 1957; Brady & Huff, 1958); the rate of increase in micellar weight being more rapid with shorter oxyethylene chain compounds.

The concept of "no solubilisation when there are no micelles" (though addition of a third component may lower the concentration at which micelles are formed), is also illustrated by this work. Peaks in the plots of R_{90} (Rayleigh's ratio) vs. concentration below the CMC for the pure compound, increased as the ratio of solubilisate to detergent was raised, and were interpreted as being caused by solubilisate or a solubilisate-surfactant complex, ejected into the aqueous phase by dilution below the CMC, forming small droplets which increased the amount of scattered light. The concentration at which this peak started to develop gradually decreased with the addition of solubilisate in a manner similar to that found for ionic detergents (Ralston & Eggenberger, 1948; Grieger, 1949).

Increasing the temperature of ternary systems, such as n-decane or n-decanol (Kuriyama, 1962a) in an aqueous non-ionic detergent solution, gave a rise in micellar weight, but the patterns of increase varied from each other, reflecting the different effects on the cloud point of the two compounds.

Addition of an anionic (Kuriyama, 1962c) to a non-ionic detergent gave a mixed micelle, the micellar weight showing virtually a straight line relationship between the micellar weights (at 30°) of the two pure compounds in aqueous solution, and increase of micellar weight of the non-ionic detergent with temperature elevation was progressively suppressed by increasing the amount of ionic detergent added, until a stage was reached when the micellar weight decreased on heating. Micellisation in mixed systems has been studied by Corkill & others (1961) and by Corkill, Goodman & Tate (1964).

SURFACE ACTIVITY

The adsorption of surface-active agents at an interface causes a reduction in the surface tension; the surface tension dropping rapidly with increasing concentration until a constant minimum value is reached at the CMC. The general theory of adsorption of surface-active compounds at the interfaces is that it is the result of the opposing tendencies of the hydrophobic and hydrophilic groups, the former tending to escape from

the surface of the water, provided the external phase is sufficiently sympathetic, the latter group tending to pull the molecule into solution.

With non-ionic detergents of the type under consideration it has been shown that for a given hydrophobic group, the surface tension at the air-water interface above the CMC increases with increasing glycol length, the actual value of the surface tension being a property of the hydrophobe in question (Fineman, Brown & Myers, 1952; Raphael, 1954; Schick, 1962), and the temperature; the surface tension decreasing with rise in temperature over moderate ranges (Corkill & others, 1961).

Measurement of the surface tension as a means of determining the CMC has the advantage that the solution may be examined without the addition of any extra component which may itself effect the value obtained. Application of the Gibbs Equation to measurements below the CMC allows the area per molecule at the interface to be calculated.

Surface ageing, though said to be absent with shorter compounds (Mulley & Metcalf, 1962) has been reported by Schick (1962; 1963b), Corkill & others (1961), and others, particularly as the concentration of the solution approached the CMC. Times allotted by different workers for the attainment of equilibrium vary widely and although a time of some 3 hr can be expected for a solution around 10^{-6} molar on the basis of time taken for diffusion of the molecules to the interface (Ward, 1949), times up to several days have been required for hexadecyl-n_6 at concentrations less than the CMC (Corkill & others, 1961; Elworthy & Macfarlane, 1962b). This, with other results, suggests that other factors are involved, e.g., orientation of the polyoxyethylene chains.

A further difficulty which arises in attempting to make measurements of surface activity at low concentrations (10^{-5}–10^{-6}) is that adsorption of detergents on to glass or other vessels may significantly affect the concentration. The equilibration of glassware and solutions by the method suggested by Pethica & Matijevic (1958) is therefore necessary.

Other methods of observing adsorption have been reported (Hsaio & Dunning, 1955; Kuno & Abe, 1961; 1962) but with much variation in the results, arising from the interfacial conditions and the mode of analysis; selective adsorption of shorter length ethylene oxide chain adducts often influencing the results to different extents.

Interfacial tensions between aqueous solutions of polyoxyethylene ether adducts and such substances as vegetable oils, benzene and toluene, gave minima with ethylene oxide contents of 14–20 units (Wrigley, Smith & Stirton, 1957; Raphael, 1954), and 7–12 units respectively (Cohen, 1951), while hexane followed a pattern similar to that existing at the air-water interface.

For single species p-t-octylphenoxyethoxyethanol, Crook, Fordyce & Trebbi (1963) have shown that there was a preferential adsorption of the shorter ethylene oxide chain length compounds at the air-water interface. At the iso-octane:water interface, the compounds with longer ethylene oxide chains were preferentially adsorbed.

Elworthy & Florence (1964) studied synthetic detergents with branched hydrocarbon chains at the air-water interface. An equation of the type

$(\pi - \pi_0)$ $(A - A_0)$ = constant fitted the results above π = 2 dynes/cm (π=surface pressure, A = area/molecule).

Lipophilic substances, such as carbon black, gave a Langmuir type adsorption for a range of nonyl-phenol adducts (Kuno & Abe, 1962), but with a hydrophilic powder, such as calcium carbonate, the type of adsorption depended on the compound examined and was very sensitive to change in chain length (Kuno & Abe, 1961). Compounds with less than four and more than nine ethylene oxide units per molecule showed no adsorption on to calcium carbonate, those with five and six gave Langmuir type, whereas seven and seven point five ethylene oxide units showed multilayer adsorption.

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