Aggregation and Surface Properties of Synthetic Double-chain Non-ionic Surfactants in Aqueous Solution

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Abstract

Double-chain non-ionic surfactants have been synthesized with the general formula $2C_nMPEG_{750}$, where n is the number of carbons in the alkyl chains and 750 is the molecular weight of the monomethoxypolyoxyethylene (MPEG) head group. The aggregation and surface properties in dilute aqueous solution (< 1·0% w/w) of surfactants with n = 8, 10 and 12 have been determined.

Each of the surfactants formed clear, foaming, non-birefringent solutions. Total-intensity light scattering indicated the presence of micelles with aggregation numbers of 36, 68 and 74 for the $2C_8$, $2C_{10}$ and $2C_{12}$ surfactants, respectively, whereas photon-correlation studies yielded radii, assuming spherical aggregates, of 59–103 Å. Surface-tension measurements gave critical micelle concentrations for the surfactants in the range $1·15–7·24 \times 10^{-6}$ M; these, as expected, decreased when the number of carbon atoms in the alkyl chains was increased.

Such studies are important in the design of new surfactants as vehicles for drug delivery because it is imperative to be able to predict the type of aggregate formed by a surfactant.

It is well established that the molecular geometry of a surfactant influences the nature of the aggregate it forms when dispersed in aqueous solution at low concentrations (Israelachvili et al 1976). For example, double-chain surfactants with long hydrophobic chains, such as the naturally occurring phosphatidylcholines (lecithins) tend to form lamellar phases, whereas their single-chain equivalents of similar hydrophobic chain-length, namely the lysolecithins, form micellar aggregates (Arvidson et al 1985). However, with a few notable exceptions such as the lecithins and lysolecithins (Tausk & Overbeck 1976; Bain & Roberts 1992) and to a lesser extent the gangliosides (Corti et al 1991), very little work has examined, in detail, the relationship between the length and number of the hydrophobic and hydrophilic chains in a surfactant and the nature of the aggregate it forms. Yet an understanding of this relationship is of paramount importance in the design of new surfactants to provide vehicles for drug delivery, because it is imperative to be able to predict which type of aggregate a surfactant will form before synthesis. If this is not known with reasonable certainty, considerable time might be wasted synthesizing surfactants with inappropriate aggregation behaviour for their intended purpose.

As part of our study investigating the relationship between surfactant molecular structure and aggregation behaviour we have synthesized a large number of non-ionic surfactants with the general structure shown in Fig. 1 (Lawrence et al 1996a). In this text the structure of the surfactants is expressed by the general formula $2C_nMPEG_{750}$, where n is the number of carbons in the alkyl chains and 750 is the average molecular weight of the polydisperse monomethylpolyoxyethylene glycol (MPEG) head group. Surfactant molecules with hydrocarbon chain-lengths of fourteen or greater carbons and hydrophilic head groups of chain lengths between 12–16 ethylene oxide

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units form vesicles, whereas those with similar head groups but shorter hydrophobic chains form micelles (Lawrence et al 1996a). The physicochemical properties of the vesicles formed by surfactants from this series with alkyl chain lengths greater than 14 carbons have previously been reported (Lawrence et al 1996b). The current paper reports the aggregation and surface properties in dilute aqueous solution of three of the short double-chain surfactants from the same series, namely $2C_8MPEG_{750}$, $2C_{10}MPEG_{750}$ and $2C_{12}MPEG_{750}$.

Materials and Methods

Synthetic surfactants
The novel surfactants examined in this study were synthesized as described by Lawrence et al (1996a) and stored in-vacuo over calcium chloride at 277K until required. Elemental analysis, IR and NMR spectra for all the surfactants were consistent with the expected structures. Immediately before use the non-ionic surfactants were tested for purity by IR to ensure the absence of any carbonyl impurities. Once dispersed in triple-distilled water all preparations were stored at 277K in glass vials until used.

Methods
Cloud point determinations. The cloud point (or lower consulate temperature) was determined by heating the solutions at
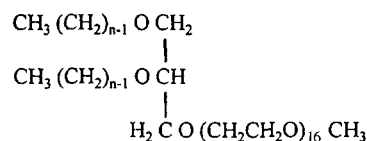
$$CH_3 (CH_2)_{n-1} \, O \, CH_2$$
$$|$$
$$CH_3 (CH_2)_{n-1} \, O \, CH$$
$$|$$
$$H_2 \, C \, O \, (CH_2CH_2O)_{16} \, CH_3$$

FIG. 1. The molecular structure of the novel non-ionic surfactants.

1 K min^{-1} and observing visually for the onset of turbidity and then cooling the solutions at a rate of 0·5 K min^{-1} until they cleared. Clouding and clearing temperatures determined in this way were not usually coincident, with the clouding temperature being 1–2 K higher than the clearing temperature. The values recorded are the means of four separate determinations.

Surface-tension measurements. Surface tensions (γ) of the aqueous surfactant solutions at 298 ± 0·1 K were measured by the detachment of a platinum ring suspended from a microforce balance (Cl Electronics, UK) attached to an intelligent digital multimeter (Thurly 1905a; Radio Spares, UK). The required range of concentrations was prepared by repeated dilution of the non-ionic surfactant solutions with triple-distilled water. All solutions were initially prepared using triple-distilled water. Before any measurements the microforce balance was calibrated with a series of known weights. Throughout surface tension determination the surface tension of pure water was frequently checked. The usual precautions were taken to ensure clean glassware and to prevent the adsorption of surfactant by the glassware.

Total-intensity light scattering and photon-correlation spectroscopy studies. Light-scattering measurements were performed at 298 ± 0·1 K using a Malvern 4700c digital auto-correlator equipped with a 75-mW argon-ion laser operating at 488 nm. All surfactant solutions for total-intensity light scattering (TILS) and photon-correlation spectroscopy (PCS) studies were clarified by ultrafiltration through a 0·1-μm cellulose acetate filter (Millipore, UK). Both TILS and PCS measurements were routinely performed at 45°, 90° and 135° to the incident beam. In all the surfactant samples tested the ratio of scattering intensities (for TILS) and of diffusion coefficients (for PCS) at angles of 45° and 130° were always in the range 1·0 ± 0·05, and so no further measurements were performed at other angles. For photon-correlation measurements, data were analysed using the cumulants assay of Koppel (1972). For TILS measurements the instrument was calibrated with a dust-free sample of benzene (AnalaR, BDH Chemicals, UK) using an R$_{90}$ for benzene at 488 nm and 298 K of 32·00 × 10^{-6} cm^{-1} from the data of Gulari et al (1979) and a refractive index for benzene at 488 nm and 298 K of 1·50993. Specific refractive-index measurements (dn/dc) required for analysis of the total-intensity light scattering data were determined using an Abbe 60 ED precision refractometer (Bellingham and Stanley, UK).

Results

Cloud-point determination

Cloud points, or lower consulate temperatures, were determined for the novel surfactants over the same concentration range as used for the light-scattering studies, 2·50–10·00 g L^{-1} (Table 1). Unfortunately, because of the limited number of compositions tested, it was not possible to establish the absolute minimum in the cloud-point curve and the concentration at which it occurred. It is this temperature that is generally quoted as 'the cloud point' for a particular surfactant (Rupert 1992). The primary purpose of our measurements was to confirm that the conditions of concentration and temperature used in this investigation for the various physicochemical determinations were far removed, that is at least 30° below, the surfactant-clouding temperature, thereby ensuring the absence of any perturbations in the system arising as a result of critical phenomena (Corti et al 1984).

To the best of the authors' knowledge this is the first time a cloud point has been reported for a double-hydrophobic-chain surfactant. By way of comparison an upper consulate temperature has been reported for micelle-forming short-chain lecithins (Tausk & Overbeek 1976). Although the observed trend was as expected, in that the cloud point decreased as alkyl chain length increased, it is of note that the influence of each additional CH$_2$ is not as great in these double-chain surfactants as might be expected from a comparison with single-chain polyoxyethylene ether surfactants. Thus in the current study an increase of four CH$_2$ units reduced the cloud point by only ~5°, whereas for a single-chain surfactant a similar increase in the length of the hydrophobic chain causes a reduction which is generally of the order of 22° (Gu & Sjoblom 1992). Furthermore, it is worth noting that the cloud points for the double-chain surfactants are higher than for the single-chain surfactant of the same carbon length. That these double-chain surfactants did not reduce the cloud point to the same extent as single-chain surfactants was perhaps not surprising, as almost certainly the two hydrophobic chains of the surfactant monomer associate closely, thereby reducing the effective area of the hydrophobic chain compared with that of the surfactant with a single hydrophobe of the same carbon number.

Surface-tension measurements

Surface tension (γ) was measured at 298 K for the three surfactants at several concentrations within a range of two decades about their critical micelle concentrations (CMC) (Fig. 2). Plots of γ against log$_{10}$C, where C is the bulk concentration,

Table 1. Cloud points of aqueous solutions of 2C$_8$MPEG$_{750}$, 2C$_{10}$MPEG$_{750}$ and 2C$_{12}$MPEG$_{750}$.

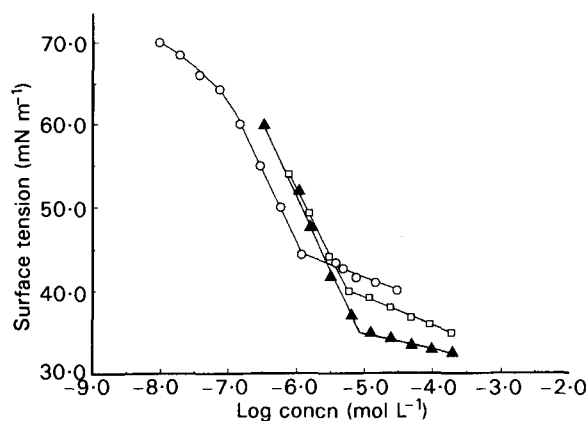| Non-ionic surfactant	Concentration of surfactant (g L^{-1})				
	2·50	5·00	6·50	7·50	10·00
2C$_8$MPEG$_{750}$	84 ± 1·1	80 ● 0·8	80 ± 0·9	80 ± 0·9	83 ● 0·8
2C$_{10}$MPEG$_{750}$	80 ± 0·9	74 ± 1·0	ND*	74 ± 0·6	74 ± 0·7
2C$_{12}$MPEG$_{750}$	70 ± 0·8	69·5 ± 0·9	70·5 ± 0·7	ND	ND

*Not determined.

FIG. 2. Surface tension, γ, as a function of log concentration for the surfactants $2C_8MPEG_{750}$ (▲), $2C_{10}MPEG_{750}$ (□) and $2C_{12}MPEG_{750}$(○) in water at 298 K.

enabled clear definition of the CMC as the intersection of two straight lines fitted to the experimental points. Values of CMC and the corresponding values of γ are listed in Table 2. Interestingly, the value of γ at the CMC is highest for the longest-chain surfactant, i.e. $2C_{12}MPEG_{750}$ and lowest for the shortest-chain surfactant, $2C_8MPEG_{750}$. This trend is opposite to that for single-chain polyoxyethylene ether surfactants (Attwood & Florence 1983) short-chain lecithins (Bain & Roberts 1992) and diacyl phosphatidic acids (Garigapati et al 1995); for these compounds increasing the length of the hydrophobic chain(s) of the surfactant generally leads to a greater reduction in surface tension. Furthermore, although no minima in γ were observed at the CMC for any of the surfactants, indicating the absence of significant amounts of surface-active impurities, γ surprisingly continued to decrease in a regular manner above the CMC.

From the slope of the plot of γ against logC just below the CMC, an excess surface concentration (F) was calculated by means of the Gibbs equation $F = -(1/RT)(d\gamma/dlogC)$. Because the CMC is low, the surface-excess concentration can be equated with the surface concentration and the area per molecule at the surface, A_{obs}, can be calculated from $A_{obs} = 1/(N_A\gamma)$, where N_A is Avogadro's constant. Values of A_{obs} for the surfactants under study are listed in Table 2. Clearly, because the surface areas of the three surfactants are similar and the cross-sectional area of a single hydrocarbon chain is approximately 21 $Å^2$, it seems that the head group is controlling this parameter and that the alkyl chains stand at the interface in a nearly vertical orientation. However, for each surfactant the area per molecule obtained at the air–water interface was surprisingly low, far lower than would be

expected for a micelle-forming surfactant with such a large head-group. By comparison, for example, the single-chain non-ionic surfactant $C_{12}E_{10}$ has an area per molecule of approximately 67 $Å^2$ (Warisnoichareon 1996 unpublished); the slightly longer head group of about 16 oxyethylene units present in the surfactants under study would be expected to increase this area significantly. The values obtained for the area per molecule in the current study were, however, of a similar order to that found for dioctanoylphosphatidylcholine, i.e. 51·4 $Å^2$ (Bain & Roberts 1992).

Although the value obtained for the CMC of the novel $2C_{10}MPEG_{750}$ surfactant was similar to that reported for didecylphosphatidylcholine, 5×10^{-6} M (log $-5·30$), the CMC observed for $2C_8MPEG_{750}$ was lower than that recorded for dioctanoylphosphatidylcholine (i.e. $2·7 \times 10^{-4}$ M (log $-3·57$); Marsh 1990). The CMC of the novel surfactants are, however, of a very similar order to those quoted for the structurally related 1,3-dialkyl polyoxyethylene glycerol ethers (Ohakata et al 1981).

From the value for the CMC and assuming a sufficiently large extent of association, it is possible to calculate the standard free energy of micellization of a non-ionic species, ΔG_m, from the approximation $\Delta G_m = RTln(CMC)$. With the CMC in M, ΔG_m refers to the free energy change associated with the transfer of 1 mol of chains from their ideally dilute solution-standard state in water (ideally dilute c = 1 M) to a hypothetical micellar standard state. Values of ΔG_m calculated from this equation are given in Table 2. As the decrease in log(CMC) (and ΔG_m) with alkyl chain length is not linear, there is no constant contribution per methylene group to the free energy of micellization of these surfactants. Using the data of Barry & El Eini (1976) for $C_{16}E_{17}$, for which they determined the free-energy change associated with the transfer of an oxyethylene group into the micelle as $+0·63$ kJ mol^{-1}, it is possible to calculate the approximate changes in ΔG_m arising from the transfer of an average methylene group into the micelle. From this approximation values of $-2·5$, $-2·0$ and $-1·8$ kJ mol^{-1} were obtained for $2C_8MPEG_{750}$, $2C_{10}MPEG_{750}$ and $2C_{12}MPEG_{750}$, respectively. These values are all smaller than the $-2·7$ kJ mol^{-1} per methylene unit which is the accepted value per methylene group for the micellization of single-chain polyoxyethylene alkyl ether surfactants. It was not unexpected that the value per methylene group was lower for these double-chain surfactants. A similar reduction in ΔG_m has previously been observed for lecithins when compared with lysolecithins; here ΔG_m was reduced by approximately 25% in the double-chain series, and this was considered to correspond to the fraction of the surface area of the two chains that were in mutual contact (Marsh & King 1986).

Table 2. Surface properties and thermodynamic parameters for micellization of $2C_8MPEG_{750}$, $2C_{10}MPEG_{750}$ and $2C_{12}MPEG_{750}$ in water at 298 K.

Non-ionic surfactant	Surface tension at CMC (mN m^{-1})	Log CMC (M)	Area per molecule ($Å^2$)	ΔG_m† (kJ mol^{-1})
$2C_8MPEG_{750}$	35·50	$-5·14$	52·6	29·3
$2C_{10}MPEG_{750}$	40·00	$-5·24$	61·3	29·9
$2C_{12}MPEG_{750}$	44·25	$-5·94$	56·8	33·9

† For solution standard state of 1 M; for a standard state of unit mole fraction add 4·0RT to ΔG_m.

Total-intensity light-scattering results

The total-intensity light-scattering results are presented (Fig. 3) as plots of S_{90} as a function of concentration (C) where S_{90} is the scattered light intensity at 90° arising from the surfactant solution expressed relative to that from a calibrated standard. Because the lowest concentration used in this study exceeded the CMC by several orders of magnitude, no corrections were made, apart from the normal subtraction of solvent scattering from solution scattering. It is apparent that the plots of S_{90} against C were linear for each of the surfactants. Similarly, plots of C/S_{90} were linear, with a slope insignificantly different from zero for all the systems (data not shown). These observations imply that the state of aggregation is not changing over the range of concentrations studied. It is of interest to note that the aggregates formed by short-chain (diheptanoyl and dioctanoyl) lecithins are known to grow with increasing surfactant concentration over the same concentration range as that examined in this study (Tausk & Overbeek 1976). Furthermore, other workers (Denkinger et al 1990) have observed time-dependent aggregation behaviour in micelles formed from non-ionic short-chain disaccharide surfactants in that, whereas small spherical micelles were immediately formed upon dispersing the surfactant in water, these aggregates grew considerably in size over several days. No such time-dependent effects on aggregation behaviour were seen for any of the surfactants in the current study when examined over a period of three days after preparation. The weight-average micellar weight, M, and the aggregation number, N, as calculated from the Debye equation are given in Table 3. Also given in Table 3 are the molecular weights of the surfactants, and their refractive index increments.

From a knowledge of the micelle aggregation number and the density of the hydrophobes calculated assuming they behave as liquids in the micellar core, it is possible to obtain an estimate of the radius of the hydrophobic core of the micelle and the average area per molecule of the surfactant at the core-mantle interface. As a consequence of the hydrocarbon chains in the core of the micelle being considered to be liquid-like, the length of the hydrophobic chain used in these calculations was
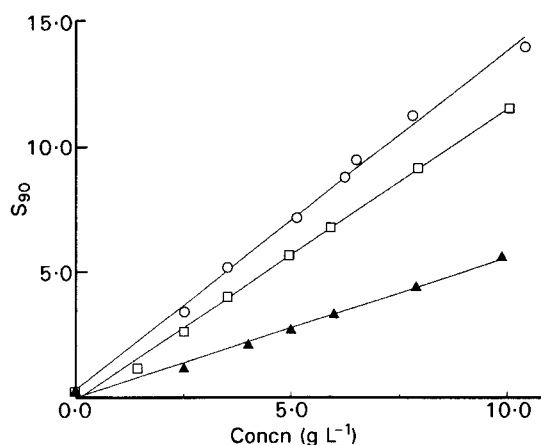

FIG. 3. Variation of the scattering ratio, S_{90}, with concentration for the surfactants $2C_8MPEG_{750}$ (▲), $2C_{10}MPEG_{750}$ (□) and $2C_{12}MPEG_{750}$ (○) at 298 K.

taken to be 80% of its extended chain length, obtained using the formula proposed by Tanford (1980). Furthermore, in these calculations, in line with other workers (e.g. Tanford 1980) the first methylene of the hydrophobic chain is considered as part of the head group.

Assuming that the polyoxyethylene chains of the surfactants adopt a random coil conformation in the aggregate, the radius of the whole micelle can also be estimated. Note that because of the uncertainty in estimating the length of the glyceryl group, this region has not been accounted for in the estimated micelle size; however this omission is thought only to result in underestimation of the radius by a maximum of 3·5 Å and will not alter the following discussion. The values obtained from these analyses are shown in Table 4. In each case, as the core radii are significantly greater than even the fully extended hydrophobic chain lengths (l_{ext}) of the corresponding surfactant, the aggregates can not be considered to be spherical, but must instead be ellipsoidal, because it is impossible for there to be a hole in the centre of the hydrocarbon core of the aggregate! In fact, the maximum allowable aggregation number

Table 3. Total-intensity light-scattering results for $2C_8MPEG_{750}$, $2C_{10}MPEG_{750}$ and $2C_{12}MPEG_{750}$ in water at 298 K.

Non-ionic surfactant	Molecular weight	dn/dc $(cm^3\,g^{-1})$	S_{90}/c $(L\,g^{-1})$	Aggregate weight	Aggregation number
$2C_8MPEG_{750}$	1008	0.141	0.602	36 500	36
$2C_{10}MPEG_{750}$	1064	0.142	1.209	72 500	68
$2C_{12}MPEG_{750}$	1120	0.142	1.477	82 500	74

Table 4. Dimensions of micelle of $2C_8MPEG_{750}$, $2C_{10}MPEG_{750}$ and $2C_{12}MPEG_{750}$, calculated assuming spherical aggregates.

Non-ionic surfactant	Fully extended chain length of hydrophobe (Å)	Volume of hydrophobic region per surfactant (Å)	Volume of hydrophobic core (Å³)	Radius of equivalent sphere (Å)	Surface area per molecule at core/mantle interface (Å²)	Radius of micelle (Å)†
$2C_8MPEG_{750}$	10·4	434	15 624	15·5	83·0	36·3
$2C_{10}MPEG_{750}$	12·9	542	36 856	20·6	78·9	41·4
$2C_{12}MPEG_{750}$	15·4	650	48 100	22.6	86·7	43·4

† Calculated assuming random coil length of 1.3 Å per ethylene oxide unit.

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for formation of spherical micelles of each of the surfactants was calculated to be 5·5, 8·5 and 12 for 2C$_8$MPEG$_{750}$, 2C$_{10}$MPEG$_{750}$ and 2C$_{12}$MPEG$_{750}$, respectively.

Unfortunately, because the sizes of these surfactant aggregates are too small for any asymmetry to be detected by light-scattering techniques, it is not possible to determine unambiguously the precise form of the ellipsoid or its axial ratios. Ideally some other complementary technique, such as viscosity measurement, is required whereby a reasonable estimate of the shape of the ellipsoid can be made by assuming a level of solvation of the aggregate. The use of a combination of analytical techniques to determine aggregate shape has been used successfully by a number of workers (see, for example, Tanford et al 1977; Evans et al 1990). Because of lack of material, it was not possible to perform viscometric measurements on the surfactant solutions. However, for purposes of illustration, from a knowledge of the extended alkyl chain length for each of the surfactants it is possible to calculate the dimensions of an oblate (disc-like) and prolate (rugby-ball-shaped) ellipsoid having an equivalent hydrophobic volume (Table 5). For illustration purposes only ellipsoids with a minor axis corresponding to 80% of the extended chain length (l_{ext}) of the hydrophobe are reported. From Table 5, it is clear that, whatever the nature of the aggregates formed by these surfactants, they are likely to have pronounced asymmetry and if the ellipsoid minor axis is set at < 0·8 l_{ext} the calculated asymmetry is increased even further. It should be noted, however, that the asymmetry is not as great when the dimensions of the whole aggregate are taken into account. Furthermore, despite the likely asymmetry of the micelles, the maximum dimension of the aggregate is most likely to be less that 1/20th of the wavelength of the incident light (here 244 Å), as aggregates would have to be very asymmetric before any dissymmetry would be seen using light scattering. Using the above example for 2C$_{10}$MPEG$_{750}$, an axial ratio of almost 10:1 is required for a prolate ellipsoid before any asymmetry is likely to be seen. Consequently, the lack of any significant dissymmetry observed from the light-scattering experiments is not unexpected.

It is worth commenting here, however, that Robson & Dennis (1977) have proposed that whereas polyoxyethylene surfactants forming aggregates with high aggregation numbers cannot be spherical on simple geometric grounds, they might still be able to assume spherical form by enabling mixing of the hydrophilic ethylene oxide chains with the hydrocarbon chains constituting the micellar core. Although this hypothesis is still controversial, there is mounting evidence in its favour. For example, Elworthy and coworkers (Arnason & Elworthy
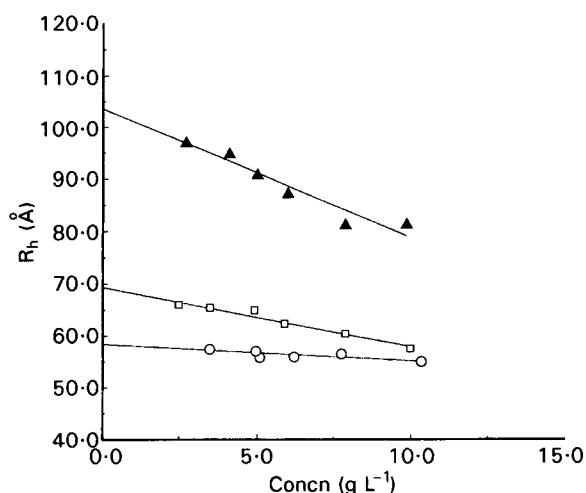

FIG. 4. Variation in apparent hydrodynamic radius (R$_h$) with concentration for the surfactants 2C$_8$MPEG$_{750}$ (▲), 2C$_{10}$MPEG$_{750}$ (□) and 2C$_{12}$MPEG$_{750}$ (○) at 298 K.

1980, 1981; Elworthy & Patel 1984a, b) have used a range of physicochemical techniques to postulate that such mixing occurs in polyoxyethylene n-alkyl ether surfactants with long hydrocarbon chains. Furthermore, Barlow and coworkers (see, for example, Ma et al 1994; Barlow et al 1995) have also observed mixing of the hydrocarbon chains and polyoxyethylene head groups in mono-layers formed from 2C$_{18}$MPEG$_{550}$. It might therefore be that the aggregates are rather more spherical than the above calculations suggest.

Results from photon-correlation spectroscopy

To ensure the absence of any inter-particulate effects, it is important to measure the effective diffusion coefficient over a range of concentrations and extrapolate to infinite dilution to obtain the true diffusion coefficient. The diffusion coefficients obtained in this manner, together with the hydrodynamic radii of micelles calculated assuming spherical aggregates, are shown in Table 6. It should be noted that although the ratios of the diffusion measurements at the angles of 45° and 135° for all surfactants were in the range 1 ± 0·05, micelle sphericity cannot be assumed from analysis of the total-intensity light-scattering data. The coefficient of polydispersity from the cumulants analysis obtained for the 2C$_8$MPEG$_{750}$ were very high (of the order of 0·3–0·35) suggesting a very disperse population of particles. In contrast, the values recorded for 2C$_{10}$MPEG$_{750}$ and 2C$_{12}$MPEG$_{750}$ were consistently less than

Table 5. Dimensions of micelle of 2C$_8$MPEG$_{750}$, 2C$_{10}$MPEG$_{750}$ and 2C$_{12}$MPEG$_{750}$, calculated assuming ellipsoidal aggregates.

Non-ionic surfactant	Effective length of hydrophobe. minor axis (b) of core (Å)	Prolate ellipsoid major axis (a) core (Å)	Axial ratio of core (ρ)† assuming prolate ellipsoid (Å)	Oblate ellipsoid major axis (a) core (Å)	Axial ratio of core (ρ) assuming oblate ellipsoid (Å)
2C$_8$MPEG$_{750}$	8·3 (29·1)‡	54·1 (74·9)‡	0·15	21·2 (42·0)‡	0·39
2C$_{10}$MPEG$_{750}$	10·3 (31·1)	82·9 (103·7)	0·12	29·2 (50·0)	0·35
2C$_{12}$MPEG$_{750k}$	12·3 (33·1)	75·9 (96·7)	0·16	30·6 (51·4)	0·40

† Axial ratio, $\rho = b/a$, minor axis/major axis. ‡Values in brackets are the dimensions (Å) of the whole micelle, calculated assuming random coil conformation of the polyoxyethylene chains.

Table 6. Diffusion coefficients and hydrodynamic radii of the micelles obtained by photon-correlation spectroscopy and calculated assuming spherical aggregates.

Non-ionic surfactant	Diffusion coefficient $(m^2 s^{-1})$	Hydrodynamic radius of equivalent sphere (Å)
$2C_8MPEG_{750}$	2·38 e-11	103·0
$2C_{10}MPEG_{750}$	3·53 e-11	69·5
$2C_{12}MPEG_{750}$	4·15 e-11	59·0

0·1, implying the presence of a monodisperse population of particles. However, for each of the surfactants a negative slope to the graph of the hydrodynamic radius (R_h) of the micelles, calculated assuming spherical aggregates, against concentration suggests the existence of repulsive inter-particulate interactions over the range of concentrations studied (Fig. 4).

It can be seen from Table 6 that, surprisingly, the diffusion coefficient decreases for the aggregates formed by the longer-alkyl-chain surfactants, yet from total-intensity light-scattering experiments the aggregation number is increased upon lengthening the hydrophobic chain of the surfactant. A possible explanation of this unexpected effect might be that some of the polyoxyethylene chains penetrate into the hydrophobic core of the micelle, thereby reducing the number of ethylene oxide units available for hydration and, as a consequence, reducing the effective hydrodynamic size of the aggregate. Because this penetration would be expected to be greatest in surfactants with the longest hydrophobic chains, it might explain the apparent discrepancy between the TILS and PCS results, which suggest that although $2C_8MPEG_{750}$ forms aggregates with the lowest aggregation number, the effective size of the micelles as determined by PCS is greatest for this surfactant.

Alternatively, changes in the shape of the aggregates formed by the various surfactants might be the reason for the observed trend in diffusion coefficients. For example, Evans et al (1990) have reported diffusion coefficients that initially increased then decreased upon increasing the molar ratio of water to lecithin when dispersed in trichlorotrifluoroethane and that this corresponded to a change in shape from oblate ellipsoid through spherical to prolate ellipsoid. However, in the absence of any complementary physicochemical data it is not possible to determine whether shape-changes are the cause in this instance.

Discussion

Surface tension and light-scattering data have been reported for a novel series of 1,2-dialkyl polyoxyethylene glycerol ether surfactants. The surfactants $2C_8MPEG_{750}$, $2C_{10}MPEG_{750}$ and $2C_{12}MPEG_{750}$ have all been shown to form micelles, with relatively low aggregation numbers in the range 36–74. On the basis of TILS measurements and simple packing arguments the conclusion is reached that these micelles are most probably asymmetric, and by analogy with the short-chain lecithins (Lin et al 1990) possibly prolate ellipsoidal structures. The asymmetry of the micelles is attributed to the bulk of the surfactants' hydrophobes, which are too large (in relation to the $MPEG_{750}$ head group) to be accommodated within a spherical micelle, and yet too small to form lamellar structures. It should

be noted, however, that if the polyoxethylene chains in the longer alkyl-chain surfactants do intrude into the hydrophobic core of the aggregate it is possible that the micelles might be less asymmetric than predicted from geometric constraints. To determine aggregate shape other techniques such as neutron scattering need to be applied.

In previous work we have shown that other surfactants in this series, containing either an MPEG head group of either 750 or 550 molecular weight, but with alkyl chains greater than or equal to C_{14}, can form stable vesicles in aqueous media (Lawrence et al 1996a). A similar variation in aggregate form as a function of surfactant alkyl chain length has also been noted for the related 1,3-dialkyl polyoxyethylene glycerol ethers (Ohakata et al 1981) which formed micelles or vesicular structures, respectively, when alkyl chains were eight or twelve carbon atoms long. For the phosphatidylcholines (PC) the micelle-forming lipids are those with alkyl chains less than or equal to C_8, although long rod-like micelles are formed by the diheptanoyl and dioctanoyl PC. For the 1,2-dialkyl non-ionic surfactants examined here the cut-off for micelle formation is a carbon number of 12, with the head group involving either 12 or 16 oxyethylene units (Lawrence et al 1996a). From the surface-tension data obtained for the 1,2-dialkyl polyoxyethylene glycerol ethers, the interfacial areas occupied by the surfactant molecules are calculated as 52·6–61·3 $Å^2$. These area estimates are anomalously low, being little more than the sum of the cross-sectional areas of the two surfactant alkyl chains, and comparable, in fact, with the areas determined for monoalkyl polyoxyethylene surfactants of similar head-group length (Attwood et al 1990; Warisnoichareon 1996, personal communication). We note, however, that a similar interfacial area was calculated on the basis of Langmuir trough data for the vesicle-forming surfactant $2C_{18}MPEG_{750}$, and that this anomaly was explained (on the basis of neutron-reflectance measurements) by the formation of multi-layers at the air-water interface (Ma et al 1994).

Similar multi-layer formation might be the reason for the small areas per molecule seen at the CMC for the surfactants in this study. The existence of such multi-layers might also account for the odd trend in surface tension at the CMC and the continued reduction in the surface tension observed above the CMC. Although it is generally assumed that micellar surfactants form only mono-layers at the air–water interface, there are a few reports in the literature in which researchers have proposed the presence of such surfactant multi-layers below the CMC. For example, Imae et al (1986) have suggested that dimethyloleylamine oxide forms a layer at least four molecules thick at the air–water interface. Currently we are using the technique of neutron reflectance to understand the nature of the behaviour of this class of non-ionic surfactant at the air–water interface.

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