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ORIGINAL CONTRIBUTION

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Polymerisation of liquid crystalline phases in binary surfactant/water systems.

Part 4. Dodecyldimethylammoniumethylmethacrylate bromide

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Abstract The phase behaviour and polymerisation of a quaternary ammonium surfactant containing an ethylmethacrylate polymerisable moiety within the head group region has been investigated. The addition of this large flexible hydrophilic moiety alters significantly the inherent surface activity of the surfactant and the surfactant may be compared with the class of non-ionic polyethyleneoxide surfactants. Polymerisation of both self-assembled and non self-assembled states went to near completion with the resulting polymer being completely insoluble in water.

Key words Polymerisation – surfactant self-assembly – liquid crystals – dodecyldimethylammonium-ethylmethacrylate bromide

Introduction

In this the fourth paper in the series [1–3] on the polymerisation of liquid crystalline phases in binary surfactant/water systems an ethylmethacrylate polymerisable moiety has been incorporated into the head group of a C_{12} single-chain quaternary ammonium surfactant yielding dodecyldimethylammoniumethylmethacrylate bromide (DDAM, $CH_3-(CH_2)_{11}-N^+(CH_3)_2(CH_2-CH_2-O-CO-C(CH_3)=CH_2)Br^-$). The length of the polymerisable group is equivalent to that of a hydrocarbon chain containing six carbon atoms. The presence of two hydrocarbon chains affects the partitioning between the hydrophobic and hydrophilic regions of the surfactant and hence its self-assembling properties. The flexibility of the ethylmethacrylate group is extremely high, being comparable to that of an unbranched C_6 hydrocarbon chain and will therefore alter the inherent rigidity of the surfactant. By reason of this flexibility and the presence of a carbonyl group (containing oxygen, an electron donating atom), it has been proposed by Hamid and Sherrington [4] that the geometry shown in Fig. 1 is one of the possible configurations adopted by this surfactant. If this conformation is adopted the ethylmethacrylate is replacing a position traditionally included as part of the head group of a single-chain surfactant. Therefore the addition of the ethylmethacrylate group may increase considerably the number of degrees of freedom of the head group.

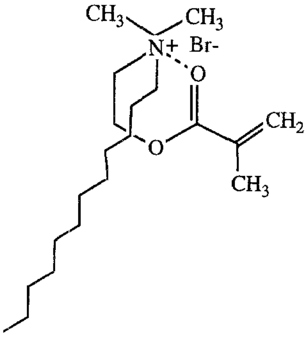

Fig. 1 One of the proposed [4] conformations adopted by the DDAM surfactant molecule in solution (note that the conformations adopted by DDAM are dependent upon the surfactant's environment and will, therefore, vary with both temperature and composition)

DDAM is very different from the surfactants discussed in the previous papers [1–3]. This difference may be categorised as follows. First, the increase in the number of configurations that the surfactant is capable of adopting in solution (i.e. the increased polydispersity in the surfactant packing parameters (e.g. head group area and volume)), affects directly the surfactant's self-assembling behaviour compared with those surfactants containing the allyl polymerisable moiety (where the flexibility of the head group is relatively reduced). Second, the ethylmethacrylate polymerisable group has an increased reactivity towards polymerisation over the allyl group. Due to the ability of this surfactant to polymerise to a high degree over a very short time scale it has been widely studied in the low concentration regime [4–10]. These two aspects of the surfactant were expected to influence the surfactants ability to retain its underlying geometry upon polymerisation and enable the surfactant to polymerise to a greater extent than has been found to occur in surfactants polymerised with the allyl moiety [1–3].

Experimental

Dodecyldimethylammoniumethylmethacrylate bromide (DDAM, $CH_3\text{–}(CH_2)_{11}\text{–}N^+(CH_3)_2(CH_2\text{–}CH_2\text{–}O\text{–}CO\text{–}C(CH_3){=}CH_2)Br^-$) was prepared at 20 °C as described previously [4, 5, 8, 9]. Elemental Analysis: Calculated for $C_{20}H_{40}O_2NBr$: C 59.10%; H 9.92%; N 3.45%. Found C 58.27%; H 10.05%; N 3.27%. m.p. 87–89 °C. NMR Analysis: Proton $C\underline{H}_3\text{–}(CH_2)_{11}$ 0.89 δ; $CH_3\text{–}(C\underline{H}_2)_8$ 1.23 δ; $CH_3\text{–}(CH_2)_8\text{–}C\underline{H}_2$ 1.32 δ; $CH_2\text{–}C\underline{H}_2\text{–}CH_2\text{–}N$ 1.75 δ; $C\underline{H}_3\text{–}C =$ 1.94 δ; $(C\underline{H}_3)_2\text{–}N$ 3.50 δ; $CH_2\text{–}CH_2\text{–}C\underline{H}_2\text{–}N$ 3.84 δ; $O\text{–}CH_2\text{–}C\underline{H}_2\text{–}N$ 4.16 δ; $C\underline{H}_2\text{–}O$ 4.85 δ; $\underline{H}\text{–}C{=}C(CH_3)$ 5.85 δ proton trans to methyl group, 6.13 δ proton cis to methyl group. Carbon 13 $\underline{C}H_2\text{–}CH_2$ 13.47 δ; $\underline{C}H_3\text{–}C =$ 17.66 δ; $CH_3\text{–}\underline{C}H_2$ 22.06 δ; $CH_2\text{–}\underline{C}H_2\text{–}CH_2\text{–}N$ 22.35 δ; $\underline{C}H_2\text{–}(CH_2)_2\text{–}N$ 25.65 δ; $CH_3\text{–}(CH_2)_2\text{–}\underline{C}H_2$ 28.68 δ; $CH_3\text{–}(CH_2)_3\text{–}(\underline{C}H_2)_5$ 28.98 δ; $CH_3\text{–}CH_2\text{–}\underline{C}H_2$ 31.26 δ; $(\underline{C}H_3)_2\text{–}N$ 51.24 δ; $N\text{–}\underline{C}H_2\text{–}CH_2\text{–}O$ 57.63 δ; $N\text{–}\underline{C}H_2\text{–}(CH_2)_{10}$ 61.57 δ; $\underline{C}H_2\text{–}O$ 64.83 δ; $=\underline{C}H_2$ 126.69 d; $\underline{C} =$ 134.55 δ; $\underline{C}{=}O$ 165.70 δ. FTIR Analysis: C=C stretch 1633.7 cm^{-1}; C=O stretch 1720.8 cm^{-1}; H–C= stretch 3019.3 cm^{-1}.

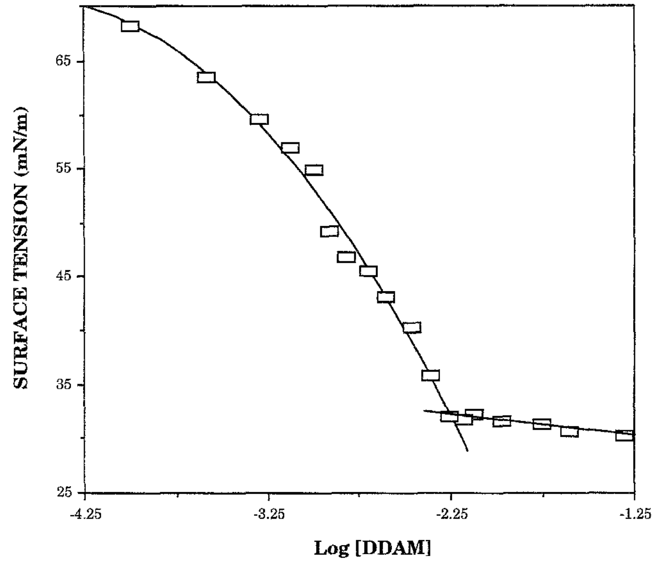

Fig. 2 Air/aqueous solution surface tension curve for DDAM measured at 25 °C. Errors are indicated by the size of the data points

Incorporation of the ethylmethacrylate functional group into the head group of the surfactant leads to DDAM polymerising readily, to the extent that the monomeric form of DDAM will polymerise on standing without any added initiators or any attempt to remove oxygen. Due to this rapid polymerisation care must be taken in storing the surfactant and it must be used within a week of preparation to ensure that contamination from polymeric DDAM is maintained to a minimum. The presence of any oligomer/polymer greatly affects the self-assembly, surface tension and conductivity of the surfactant, all of which may be used as indicators for the presence of polymeric DDAM.

All experimental techniques used were as described in the first paper of this series [1].

Results

Critical micelle concentration

Figure 2 shows the curve obtained from air/aqueous solution surface tension measurements by using the du Noüy ring method. Aggregation of the surfactant molecules manifests itself as a dramatic change in slope and subsequent plateau of the experimental curve. A polynomial of variable order can be used to fit a curve to the experimental data points obtained prior to the concentration at

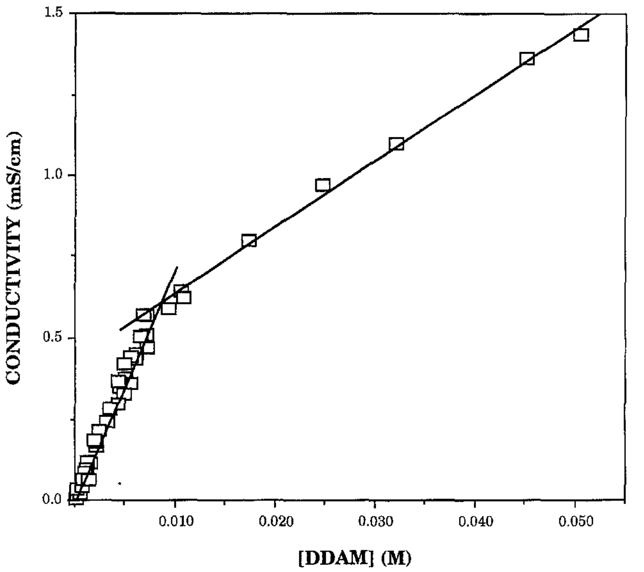

Fig. 3 Specific conductivity of DDAM in water measured at 25 °C. Errors are indicated by the size of the data points

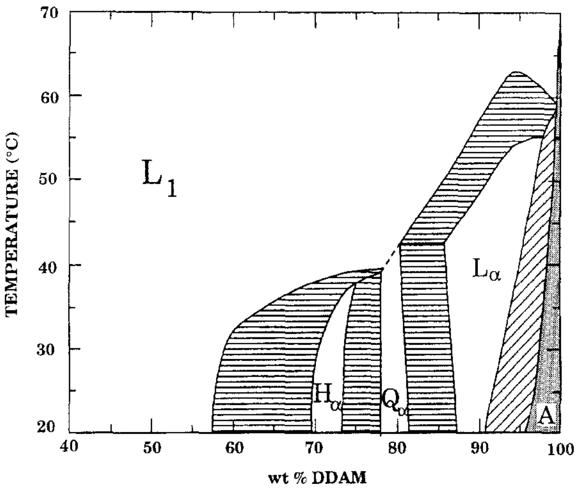

Fig. 4 Schematic diagram of the partial binary phase diagram determined for the DDAM/water system. L_1: micellar, H_α: normal hexagonal, Q_α: bicontinuous cubic (type Ia3d, Q^{230} or Gyroid IPMS), L_α: lamellar, and A: hydrated DDAM crystals. The horizontally shaded areas indicate regions where two phases coexist (i.e. these lines indicate the tie lines between the two phases). Diagonally shaded areas indicate regions where a liquid crystalline phase coexists with hydrated crystals of DDAM

which aggregation occurs [11]. For the DDAM/water system a polynomial of degree two gave an adequate fit to the data with a correlation coefficient equal to 0.990. By using this fit the critical micelle concentration (cmc) was determined to be 5.66×10^{-3} M. The surface excess concentration was calculated from the slope of the pre-micellisation curve close to the cmc and from this the area per polar head group at the interface. For the DDAM/water system the surface excess concentration of DDAM is $2.8 \pm 0.1 \times 10^{-3}$ mol·cm^{-2} and the area per polar head group is 58 ± 1 Å^2.

Some other experiments indicated that small amounts of polymeric DDAM may be detected by the presence of a minimum in the surface tension curve (not present in Fig. 2) and as the amount of polymer increases the solutions at higher concentrations become turbid.

The electrical conductivity curve for DDAM in water at 25 °C is shown in Fig. 3. The curve shows a distinct break at a concentration of 7.29×10^{-3} M DDAM corresponding to the initiation of surfactant aggregation. Evaluation of the percentage dissociation of the bromide counterion (β) was achieved by taking the ratio of the slopes of the two linear regions of the curve and by using this method β is 28.9%. A second method utilised the area per polar head group calculated from the surface tension measurements in conjunction with the monodisperse mass action model [12–15]. From this method the aggregation number is determined to be 51 and the percentage dissociation 29.4%.

The values determined for the cmc of DDAM by using specific conductivity and surface tension measurements compare favourably with those obtained by Nagai *et al.* [5] (cmc(DDAM) $\sim 6 \times 10^{-3}$ M using electrical conductivity and dye solubilisation measurements) but are considerably higher than the value obtained by Hamid and Sherrington [4] where the cmc was found to be in the range of 1.9 to 3.6×10^{-3} M depending upon the method used.

Monomeric self-assembly

The self-assembling behaviour of DDAM in water is shown in Fig. 4. DDAM forms three liquid crystalline phases at surfactant concentrations in excess of those where a micellar phase (L_1) is formed in the temperature range of 20° to 70 °C. At still higher concentrations hydrated DDAM crystals are also observed.

A normal hexagonal phase (H_α) forms at concentrations of DDAM between 69.6 and 73.8 wt%, this precedes a cubic phase (Q_α) between 78.1 and 81.7 wt%, prior to the formation of a lamellar liquid crystalline phase (L_α) between 87.3 and 91.0 wt%, at 20 °C. All phase transitions were observed to be first order. The Krafft discontinuity remains below 20 °C until concentrations exceeding 91.0 wt% are reached.

Thermotropic studies on the pure monomeric surfactant showed that on decreasing the temperature below the melting point of the surfactant (87–89 °C) the texture obtained is that shown in Fig. 5. This texture is first formed at

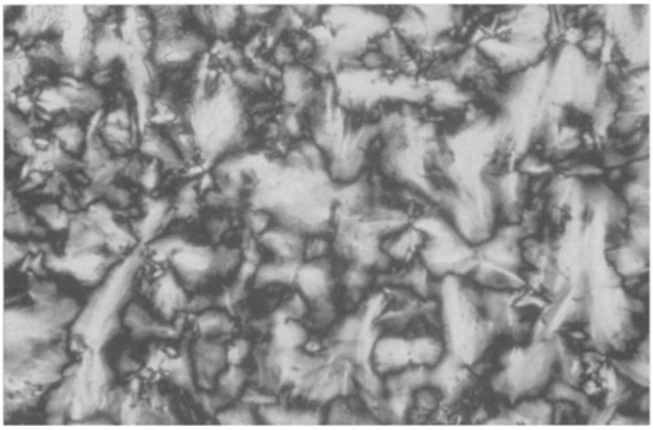

Fig. 5 Optical texture of pure monomeric DDAM at 75 °C observed under crossed polarising filters, magnification 480

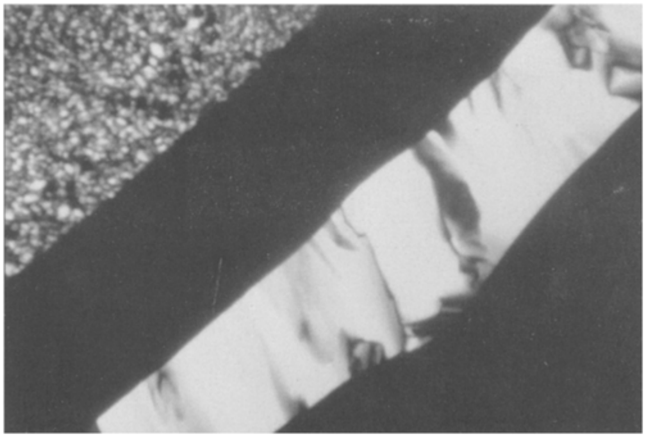

Fig. 6 Concentration gradient performed at 25 °C for the DDAM/water system (crossed polarising filters, magnification 240). From right to left micellar, hexagonal, cubic and lamellar phases are apparent

approximately 78 °C. If the temperature is subsequently increased again then the texture does not disappear at the melting point of the surfactant but is found to persist to varying temperatures. The reason for this persistence of the texture is due to the monomeric DDAM surfactant being thermally initiated at these moderate temperatures and the sample becoming contaminated by the presence of oligomer/polymer. It was also possible to determine the presence of the polymer and its continued formation at these temperatures due to the increased viscosity of the sample. If a sample of the monomeric surfactant is maintained at this temperature for a period of approximately 15 min then the sample is completely polymerised; forming a polymeric film which adheres to the surfaces of the slide and cover slip so that it is no longer possible to shear the sample (i.e. DDAM is able to thermally self-initiate in air).

The extent and rapidity of this polymerisation meant that all bulk DDAM/water samples were equilibrated at room temperature to reduce any polymer contamination.

Several attempts were made to determine DDAM's self-assembling behaviour by using added inhibitors (4-methoxyphenol, hydroquinone and methylhydroquinone) but these were found to be unsuitable due to a) the inhibitor reacting with the surfactant to produce deep red solutions exhibiting no liquid crystalline phase formation or b) the inhibitor altering the phase progression (in one case the hexagonal phase was no longer observed). Addition of inhibitor to the reaction mixture during the synthesis of the surfactant was also found to be unsuccessful. The phase diagram shown in Fig. 4 is that obtained by using no added polymerisation inhibitors and although considered to be accurate for the monomer, partial polymerisation cannot be totally ruled out. Equilibration at high concentrations was especially difficult to perform while avoiding formation of polymer.

Fig. 7 Optical texture for a bulk sample in the hexagonal region of the DDAM/water system (71.4 wt%, 30 °C, crossed polarising filters, magnification 240)

Concentration gradients performed at various temperatures revealed that no liquid crystalline phase formation occurred above 70 °C. Figure 6 shows a concentration gradient performed at 25 °C where the micellar, hexagonal, cubic and lamellar phases are formed.

A typical optical texture observed for a bulk sample within the hexagonal phase of the DDAM/water system under crossed polarising filters is shown in Fig. 7. The texture most closely resembles that described by Rogers and Winsor [16], comprised of striations. The "fan texture" is also observed to form during concentration gradients. From the textures displayed by the DDAM hexagonal phase it is evident that the length of the cylindrical aggregates is limited. The hexagonal phase is extremely unstable to changes of temperature and does not occur

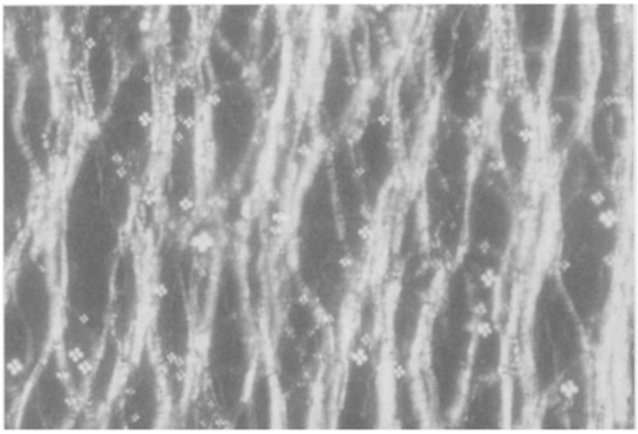

Fig. 8 "Oily streaks" texture observed for the bulk DDAM lamellar phase. The layers comprising the phase lie parallel to the glass slide, crossed polarising filters, 89.8 wt% sample at 25 °C, magnification 240

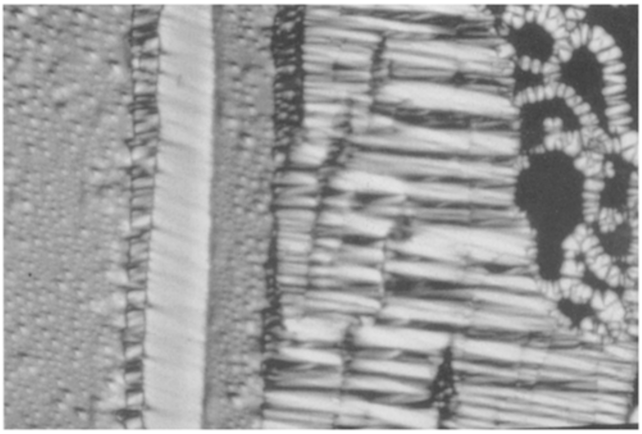

Fig. 9 Optical texture obtained during formation of the lamellar phase in the DDAM/water system from a 30 °C concentration gradient (crossed polarising filters, magnification 240)

above approximately 40 °C. The viscosity of this hexagonal phase, in comparison with hexagonal phases formed in many other surfactant/water systems, is also greatly reduced. Both the stability and viscosity may reflect the shortening of the cylindrical aggregates.

The cubic phase, which follows the hexagonal phase on increase in DDAM concentration, is also found to have a reduced viscosity and an instability to increases in temperature, melting at approximately 45 °C.

Figure 8 shows the optical texture observed for a bulk sample of the lamellar phase observed in the DDAM/water system under crossed polarising filters. The texture is typical for lyotropic lamellar liquid crystalline phases [17, 18] and is usually described as consisting of "oily streaks". The texture has been well studied in relation to the underlying geometry of the surfactant molecules and defects present (see references [19–21]). The oily streak texture, contrasts strikingly with the texture observed for the lamellar phase obtained during a concentration gradient, as shown in Fig. 9. This texture is not one classically ascribed to being formed by a lyotropic lamellar liquid crystalline phase and must, therefore, arise due to the presence of unusual orientational effects, anchoring and defects not normally found in lamellar liquid crystalline phases. Due to the instability of this surfactant towards polymerisation, further detailed investigation into the formation of this texture was not attempted.

Small-angle x-ray scattering (SAXS) was performed on the liquid crystalline phases observed by optical microscopy for the DDAM/water system. Several problems were encountered during these experiments. Due to the low flux of the x-rays generated by the SAXS equipment available in this laboratory, long exposure times were necessary (times from 12 to 60 h were often required to obtain a good diffraction pattern), but as stated previously samples allowed to stand are prone to polymerisation. When polymerisation did occur the diffraction pattern could not be indexed to one liquid crystalline phase only. If samples were run twice under identical conditions it was frequently found that the intensities of the observed Bragg peaks had altered (due to an increase in the amount of polymer present). On the occasions when a diffraction pattern from a pure monomeric liquid crystalline phase was obtained, only one Bragg peak was of reasonable intensity; where a second peak was observed the intensity was extremely low, making detection difficult (even when data collection was over a reasonable time period).

The results given in Table 1 are for those believed to be pure samples for each of the liquid crystalline phases observed in the DDAM/water system. Diffraction patterns were obtained for powdered samples and were comprised of Debye–Scherrer rings which were produced by all domains in the irradiated volume.

Samples within the DDAM micellar region produced one weak diffuse ring at small- and wide-angles ($Q = 2\pi/4.5 = 1.4\ \text{Å}^{-1}$), indicative of a random packing of surfactant aggregates [22, 23].

The hexagonal phase produced a small-angle diffraction pattern consisting of two rings with Q-values in the ratio of $1:\sqrt{3}$. The first ring was of medium intensity and the second was extremely weak. This pattern is suggestive of parallel cylinders packed in a two-dimensional hexagonal array (Table 1). The hydrocarbon chains were found to be in a liquid-like state producing one diffuse ring at wide-angles at $Q = 1.4\ \text{Å}^{-1}$ similar to the chains in the micellar, cubic and lamellar phases.

The DDAM cubic phase gave a diffraction pattern at small-angles comprised of two rings only, at best, often

Table 1 Structural parameters for DDAM/water mesophases at 27 °C

DDAM % (w/w)	Phase	Observed Q (Å^{-1})	Unit cell length (a) (Å)	Volume fraction Φ	Paraffin chain thickness (d_s) (Å)	Water and head group thickness (d_w) (Å)	Mean area per polar head (A) (Å^2)	hkl
41.0	L_1	0.175	–	0.20	–	–	–	–
70.4	H_α	0.179 0.310	40.4	0.34	24.8	15.7	56.7	$10\bar{1}0$ $11\bar{2}0$
73.0	H_α	0.281 0.314	40.0	0.35	24.9	15.1	56.3	$10\bar{1}0$ $11\bar{2}0$
80.7	Q_α (Ia3d)	0.184 0.212	83.6	0.39	–	–	–	211 220
89.7	L_α	0.193	32.6	0.43	13.9	18.7	50.5	001

only one weak ring was observed. Both rings were of low intensity, though the second was considerably less intense than the first. The rings were in a ratio of $\surd 6 : \surd 8$ which is attributable to one space group only, despite only two rings being observed, the Q^{230}(Ia3d). This cubic phase is assumed to be bicontinuous and of type I [24–28] and has been ascribed to the Gyroid infinite periodic minimal surface (IPMS) [29–34].

The lamellar liquid crystalline phase was observed to produce a diffraction pattern with only one ring at small-angles (this being the most difficult phase to equilibrate without any formation of polymer) and as such no conclusion as to the exact nature of the phase geometry can be drawn, but it is assumed to be comprised of parallel planer bilayers.

It was not possible to obtain a diffraction pattern for the thermotropic liquid crystalline phase formed by pure monomeric DDAM. All samples were found to contain polymer due to the temperatures at which the phase was formed.

Table 1 gives the structure parameters determined from the locations of the Bragg peaks for each of the liquid crystalline phases formed in the DDAM/water system. All equations were calculated at 27 °C by using the specific volume of the hydrocarbon chains and an assumed structure.

Polymeric DDAM

The monomeric form of DDAM was polymerised as an isotropic solution, in order to compare the self-assembling behaviour of the polymer with that of the monomeric surfactant and observe any differences between surfactant aggregation before and after polymerisation. The polymeric form of DDAM was prepared by thermal initiation via added α,α'-Azobis(isobutyronitrile) (AIBN, $(CH_3)_2C(CN)N{=}N(CN)C(CH_3)_2$, 5 mol% to surfactant) in a 0.25 M solution of the surfactant in chloroform, in which the surfactant was found to form an isotropic solution only (i.e. no aggregation of the surfactant molecules was observed when chloroform was used as the solvent). The sample was reacted at 60 °C for 1 day after which time polymerisation was essentially complete, with the polymer remaining soluble throughout the polymerisation. Direct initiation of the surfactant by using ultraviolet light also produced similar results.

NMR Analysis: Proton $C\underline{H}_3\text{–}(CH_2)_{11}$ 0.89 δ; $CH_3\text{–}(C\underline{H}_2)_8$ 1.24 δ; $OC\text{–}C(C\underline{H}_3)(C\underline{H}_2)$ shoulder to 1.24 peak; $CH_3\text{–}(CH_2)_8\text{–}C\underline{H}_2$ 1.54 δ; $CH_2\text{–}C\underline{H}_2\text{–}CH_2\text{–}N$ 1.75 δ; $O\text{–}C\underline{H}_2\text{–}CH_2\text{–}N$ 2.66 δ; $(C\underline{H}_3)_2\text{–}N$, $CH_2\text{–}CH_2\text{–}C\underline{H}_2\text{–}N$ and $O\text{–}CH_2\text{–}C\underline{H}_2\text{–}N$ broad peak centred at 3.41 δ. Carbon 13 $\underline{C}H_3\text{–}(CH_2)_{11}$ 13.71 δ; $\underline{C}H_3\text{–}C\text{–}$ 15.24 δ; $CH_3\text{–}\underline{C}H_2$ 21.90 δ; $CH_2\text{–}\underline{C}H_2\text{–}CH_2\text{–}N$ 24.76 δ; $\underline{C}H_2\text{–}CH_2\text{–}CH_2\text{–}N$ 25.14 δ; C 28.57 δ; $CH_3\text{–}(CH_2)_2\text{–}\underline{C}H_2$ 28.76 δ; $CH_3\text{–}(CH_2)_3\text{–}(\underline{C}H_2)_5$ 28.95 δ; $CH_3\text{–}CH_2\text{–}\underline{C}H_2$ 31.43 δ; $(\underline{C}H_2)_2\text{–}C\text{–}$ 31.62 δ; $(\underline{C}H_3)_2\text{–}N$ 50.29 δ; $N\text{–}\underline{C}H_2\text{–}CH_2\text{–}O$ 59.71 δ; $N\text{–}\underline{C}H_2\text{–}(CH_2)_{10}$ 62.48 δ; $\underline{C}H_2\text{–}O$ 62.86 δ; $\underline{C}{=}O$ 184.57 δ (compare with monomer).

Pure polymeric DDAM was found to be completely insoluble in water and no liquid crystalline phases were observed to form for all concentrations in the temperature range 20° to 100 °C. Hence the act of covalently bonding the surfactant molecules has either a) decreased the surfactant's solubility significantly, so that liquid crystalline phases may still form at very high temperatures or pressures or b) altered the surfactants amphiphilic nature to such a degree that the polymer can no longer be considered to have significant surfactant characteristics (i.e. the polymer does not behave as a polysoap).

If instead a mixture of both monomeric and polymeric forms of DDAM were combined in varying ratios a lamellar phase was observed to form having unusual elasticity properties which varied with the ratio of the two components (this however was extremely difficult to control due to the continued polymerisation of the monomeric surfactant). Hence although pure polymeric DDAM is insoluble in water its solubility is increased when combined with monomeric DDAM (the ratio of monomer to polymer for formation of the lamellar liquid crystalline phase was of the order of 90:10).

Polymerisation of liquid crystalline phases

Ampoules for polymerisation were prepared by the freeze–pump–thaw method. Polymerisation was, however, spontaneously initiated immediately following the removal of oxygen and equilibration of the concentrated liquid crystalline phases was not possible prior to commencement of polymerisation. Any attempt to form the micellar phase first and then remove water in order to induce equilibration of the more highly concentrated phases involved removal of water under vacuum which again induced polymerisation and could not be used as a method of preparation.

Due to the sensitivity of DDAM towards polymerisation it was not possible to conduct a reproducible study of the polymerisation of the liquid crystalline phases formed in the DDAM/water system and only polymerisation of the micellar solutions was quantitatively investigated.

Polymerisation in the micellar region was possible due to the ease of equilibration of these solutions. Controlled initiation had to be started immediately following sealing of the ampoule. Polymerisation was performed for both 5 and 40 wt% surfactant concentrations in the micellar region of the DDAM/water system, using both thermal and photochemical initiation. For all samples (i.e. all exposure times), polymer formation resulted in the precipitation of granular solid which remained dispersed at low conversion but settled out as the extent of polymerisation increased. Polymerisations were performed over the time scale of 15 min to 1 day.

Figure 10 shows the percentage conversions for 5 and 40 wt% DDAM micellar solutions initiated photochemically. Both concentrations show a trend of increasing polymerisation with time, with both being essentially 100% polymerised after approximately six hours.

Thermal initiation reached >95% conversion after the first 15 min for both the 5 and 40 wt% micellar solutions; indicating that the combination of an increase in temperature (which has been observed to initiate polymerisation of DDAM in air) and the presence of AIBN leads to a more efficient polymerisation.

The formation of a precipitate upon polymerisation of the micellar solutions indicates that intra-micellar polymerisation alone did not occur and hence a "polymerised micelle" was not obtained. The insolubility indicates that the molecular weight of the forming polymer chains is comparable to that of polymeric DDAM and, therefore, greater than the aggregation number of the micellar aggregates.

It was considered that due to the behaviour of both the pure polymeric DDAM and the observed consequences of polymerisation in the micellar solutions, that polymerisation in the higher liquid crystalline phases would have mirrored the results found in these two cases, i.e. formation of a completely insoluble polymer rendering retention of the liquid crystalline phases impossible. Qualitative visual observations also supported this proposition.

Discussion

The addition of the ethylmethacrylate polymerisable moiety has a marked effect on the observed aggregation of the surfactant molecules in comparison to dodecyltrimethylammonium bromide (DTAB, CH_3–$(CH_2)_{11}$–$N^+(CH_3)_3Br^-$ [35]), a non-polymerisable analogue, and allyldodecyldimethylammonium bromide (ADAB, CH_3–$(CH_2)_{11}$–N^+ $(CH_3)_3Br^-$, [1]), the allyl polymerisable moiety analogue. Changing the nature of the polymerisable functionality from a small slightly hydrophilic group, as is the case for the allyl polymerisable moiety to a large group with significantly increased hydrophilicity and flexibility has the direct consequence of reducing the concentration at which aggregation is initiated by approximately a factor of two. The extent of dissociation of the bromide counterion is, however, found to be similar for ADAB and DDAM. These results are mirrored when DDAM is compared with DTAB.

Both the area per polar head group and the surface excess concentration at the air/water interface are found to be similar for ADAB and DDAM. This supports the supposition that DDAM adopts the conformation shown in Fig. 1. It should, however, be noted that it cannot be inferred that this configuration is maintained upon aggregation (where the interface is now liquid/liquid).

The phase diagrams obtained for DDAM, DTAB [1, 35] and ADAB [1] indicate that the liquid crystalline phases formed in the DDAM/water system have a much lower stability towards changes in temperature. This lowering of the liquid crystalline phases stability must be a direct consequence of the presence of the ethylmethacrylate polymerisable moiety being neither a purely hydrophilic nor hydrophobic side group.

Although the phase progression for the three surfactants is the same, the surfactant volume in the DDAM case is larger than that for DTAB and ADAB and its head

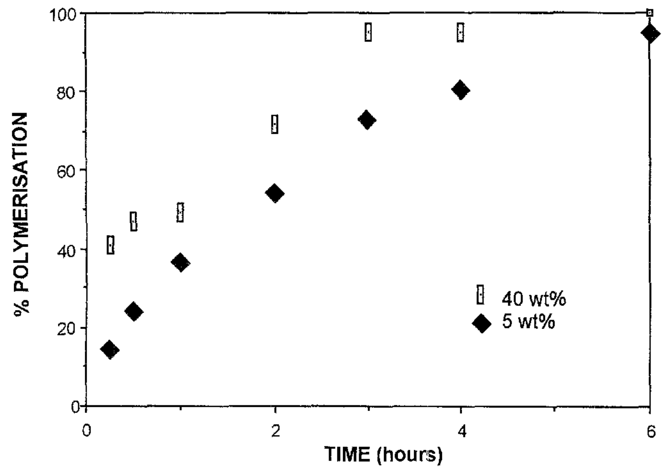

Fig. 10 Percentage conversion for 5 and 40 wt% DDAM micellar phases, initiated photochemically. Errors are indicated by the size of the data points

group has a greater degree of flexibility. The steric interaction between the surfactant molecules is also increased and the C_{12} hydrocarbon chain does not have the degree of orientational/translational freedom that is apparent in the other surfactants. The increased flexibility and the introduction of dual hydrophilic/hydrophobic characteristics into the head group region provides the possibility of a fluctuating polar/apolar interface. For a proportion of the surfactant molecules the hydrophilic/hydrophobic interface may be positioned further down the hydrocarbon chain with the interface fluctuating with time. In effect these surfactant molecules may no longer be considered as possessing a C_{12} paraffinic chain. This effective reduction in the length of the hydrocarbon chain and increase in the flexibility of the surfactant will increase the surfactant's solubility and reduce its ability to form stable liquid crystalline phases. The effect of reducing the length of the hydrocarbon chain is well known and in general self-assembly is not observed below a chain length of approximately eight. The effect of increasing the flexibility of the surfactant on self-assembly has been shown [36] in the case of non-ionic surfactants, where the head group contains large flexible ethylene oxide groups which like the ethylmethacrylate group have a dual hydrophilic/hydrophobic nature. Comparison of a series of C_{12} ethylene oxides [36] with sodium dodecyl sulfate (SDS, $CH_3\text{-}(CH_2)_{11}\text{-}SO_4\text{-}Na^+$) [37], for example shows that the solubility of this series of non-ionic surfactants is increased and the extent of surfactant self-assembly is reduced (in general, more phases are observed to form as the number of ethylene oxide groups increases). Where self-assembly does occur the stability of the liquid crystalline phases to increases in temperature is low. These results are, therefore, analogous to those found here for the self-assembly of DDAM compared with DTAB. This confirms the conclusion that the ethylmethacrylate introduces a large degree of freedom to the head group of the surfactant. The exact degree to which the ethylmethacrylate group influences the fluctuation of the position of the interface is impossible to determine experimentally and the position of the hydrophilic/hydrophobic interface is therefore unknown. It can, however, be assumed that a larger portion of the DDAM surfactant, in contrast to DTAB and ADAB, will reside in the water region of the liquid crystalline phases.

Polymerisation in the micellar region of the DDAM/water system has been previously performed at concentrations directly following aggregation using a variety of initiators (polymerisation has also been performed in benzene, in which the surfactant has been shown to form inverse micelles, and other non-aggregating solvents) by several groups [4–10]. Results have shown that in water, polymerisation occurs rapidly and to a high degree for all initiators used (including AIBN) and that molecular weight determinations gave the number of monomer units as greater than 20 000 (the experimental limit for the methods used) in some cases. Conversions and molecular weights were also found to be high in non-aggregating solvents (including chloroform).

These previous results for the dilute micellar region are analogous to those obtained during this study for relatively concentrated micellar regions and support the claim that polymerisation in the micellar region of the DDAM/water system does not produce a "polymerised micelle" formed by intra-micellar polymerisation.

Conclusions

The focus of this series of articles has been on elucidating the essential requirements for polymerisation of surfactant lyotropic liquid crystalline phases. To this effect five polymerisable surfactants were studied each differing in some critical aspect of the surfactant structure. The two polymerisable moieties investigated were the allyl group ($CH_2\text{-}CH=CH_2$) and the ethylmethacrylate group ($CH_2\text{-}CH_2\text{-}O\text{-}CO\text{-}CH(CH_3)=CH_2$). The ethylmethacrylate was found to be more readily polymerised and to produce polymers of higher molecular weight. The allyl polymerisable moiety (due to its relative smallness) introduces fewer disruptions into the surfactant's self-assembly than the much bulkier and more hydrophilic ethylmethacrylate group which tends to dominate the solution characteristics of the surfactant. In addition to altering the nature of the polymerisable moiety its position in the surfactant molecule also affects the surfactant's self-assembly and subsequent polymerisation.

Introduction of the allyl group into the head group changes both the hydrophilicity and rigidity of the head group. It also induces changes to the electrostatic interactions between the surfactant molecules and hence the solubility of the surfactant in water and the stability of the phases formed. Polymerisation of the allyl group in the head group of the surfactant limits the extent of conversion due to the large electrostatic interactions between the head groups of the surfactant monomers which acts to inhibit the reaction. The increased steric interactions due to the presence of the second paraffinic chain are such that in combination with the electrostatic interactions polymerisation is completely inhibited.

Placement of the allyl polymerisable group at the end of the hydrocarbon chain increases the rigidity of the paraffinic chains. Polymerisation in the non-self-assembled form is facilitated in this configuration due to isolation of the allyl group from the head group region. As the length of the hydrocarbon chain is decreased, the dominance of the polymerisable moiety over the surfactant self-assembly increases, with disruptions to the paraffinic chains being magnified resulting in a variation in the solution behaviour before and after polymerisation. Hence, there is a critical chain length below which the interactions between the surfactant paraffinic chains become increasingly important in determining the surfactant's behaviour in both the polymerised and non-polymerised forms.

The exact nature of the paraffinic chains (either molten, frozen or bound in a polymer chain) is critical in determining the self-assembly of both the monomeric and polymeric forms of a surfactant and also in the polymerisation of its lyotropic liquid crystalline phases. From these results it appears that retention of the underlying surfactant geometry during polymerisation requires the chains to be in a molten state (if polymerisation takes place within the tail of the paraffinic chain), such that the inherent rigidity of the chains is not the dominant influence in the self-assembly of the surfactant. Altering this dominance via polymerisation will induce a shift in the balance of interactions controlling surfactant self-assembly, inducing a phase transition.

The presence of the ethylmethacrylate group significantly alters the amphiphilic nature of the surfactant, and the interactions between the surfactant molecules, which reduces the stability of the liquid crystalline phases. Polymerisation in both isotropic solution and self-assembled forms was rapid and went to near-completion. The resultant polymer was completely insoluble in water. The molecular weight of the polymer chains was substantially increased as compared with those formed by the allyl polymerisable moiety. Therefore, not only is the nature of the polymerisable group and its position in the surfactant molecule important but also the length of the polymer chains which it forms.

Hence polymerisation of single-chained systems occurs more readily when the polymerisable moiety is placed at the end of the paraffinic chain, rather than in the head group of the surfactant, for isotropic polymerisations. This is due to reduced steric and electrostatic interactions. Once polymerisation occurs within the aggregated state of the surfactant though, the large mobility available to the tail (over the head group) and the cage-like effect of the surfactant aggregate decreases dramatically the extent to which polymerisation will occur. In contrast, the self-assembled form of the surfactant monomers had little or no effect on the extent or ease of polymerisation when the polymerisable group was contained within the head group of the surfactant. Leading to the conclusion that the best position for incorporation of a polymerisable group is neither at the end of the hydrocarbon chain nor within the head group but rather at a position where mobility is reduced (i.e. within the hydrocarbon chain situated close to the interface) but where head group interactions are no longer critical.

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