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Technical

Phase Behavior of Polymeric Surfactants Containing Polyethyleneoxide with n-Decane

M.S. ASTON, C.J. BOWDEN, T.M. HERRINGTON* and **S.S. SAHI**, Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, England

ABSTRACT

The phrase behavior of six amphiphilic copolymers with n-decane is reported, and three phase diagrams are discussed in detail. The copolymers are representative of three different types of intramolecular ordering. The phase diagrams show that the extent of anisotropic gel phase formation and liquid crystalline behavior depends on the length of the hydrophilic chain in the copolymer and not the percentage amount of hydrophile.

INTRODUCTION

Many solid organic compounds, on being added to a suitable solvent, do not form an isotropic solution but instead form a viscous anisotropic liquid or semi-solid. These states of matter represent ordering intermediate between that of a liquid and a truly crystalline state and are known as liquid crystals or anisotropic gels. A liquid crystal is formed when the forces within a crystal are reduced so that some mobility of the molecules can occur but not enough to form a liquid. The resulting liquid crystal still has one or two degrees of order. Surfactants are the most common type of molecule to adopt a lyotropic liquid crystalline phase, as their structure encourages the formation of domains of solvent molecules (1). The most extensive series of nonionic surfactants so far studied are the n-alkylpolyethylene oxides, which form a series of lyotropic liquid crystalline phases with water (2). In the pure state these surfactants are not liquid crystalline, i.e., they are not thermotropic liquid crystals. In the present work the lyotropic behavior of a series of nonionic copolymers was studied. These copolymers are amphiphilic and their structures are tailor-made for use as oil-in-water or water-in-oil emulsifiers. Of the six copolymers investigated, five were found to show both thermotropic and lyotropic mesomorphic behavior.

EXPERIMENTAL

Materials

Six polymeric polyesters were studied: they were designated B1, B2, B3, A1, A2 and A3. They were prepared from commercial grade raw materials by standard condensation polymerization techniques at temperatures between 200 and 250 C, using xylene as an entraining solvent (3). The samples studied contained less than 1% of xylene which could not be removed by vacuum evaporation. Reagent grade n-decane was used.

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*To whom correspondence should be addressed.

B1, B2 and B3 are XYX block copolymers formed from poly(12-hydroxystearic acid), containing an average of five to six monomer units, and polyethylene glycol. B1 ($M_n \cong 3500$ g mol^{-1}) is made from PEG 1500. B2 is made from PEG 4000 and has a much higher molar mass ($M_n \cong 7000$ g mol^{-1}). B3 has a varied polyoxyethylene chain length, as it is made from a mixture of PEG 1500 and PEG 4000 and has a molar mass intermediate between B1 and B2. All three are waxy solids at 20 C, soluble in aliphatic hydrocarbons; B1 is a wide spectrum water-in-oil emulsifier. (B1 has a calculated HLB ~ 6.)

A1 and A2 are nonionic amphiphilic polymers prepared from predominantly C18 monocarboxylic acids, trimellitic anhydride, glycerol, pentaerythritol and polyethylene glycol. The major difference between A1 and A2 is that A1 contains 30% of PEG 1500 by weight, and A2 has 40% of PEG 600. Both have high molar masses and are polydisperse ($M_\omega : M_n \cong 20{:}1$). They have a branched complex structure but can be regarded as consisting of a number of loops and chains of the hydrophilic polyoxyethylene moieties linked through a relatively polar ester 'block' to the oleophilic chains. They are pale yellow, sticky solids; A1 (HLB ≅ 6) and A2 (HLB ≅ 8) are used as emulsifiers.

A3 is a random-structured ester containing 30% by weight of PEG 600. It is made by reacting polyisobutenylsuccinic anhydride ($M_n \cong 1000$) with polyethylene glycol in the presence of small amounts of glycerol, neopentyl alcohol and monocarboxylic fatty acids. Thus, large portions of the molecule are PIBSA-PEG-PIBSA chains. It is soluble in paraffinic media and is used as a water-in-oil emulsifier (HLB ≅ 6).

Techniques

Optical microscopy was used to identify phase structures. Phases were examined and photographs taken using a Leitz polarizing microscope fitted with a hot-stage. Lamellar and hexagonal phases were identified by comparison of their textures with literature photomicrographs (4) and by their characteristic conoscopic figures. Cubic phases and micellar solutions are optically isotropic but may be distinguished by large differences in viscosity and refractive index. Electron microscopy and low angle X-ray diffraction-confirmed phase structures and phase transitions were verified by Differential Scanning Calorimetry (DSC).

The phase diagram of each polymer with n-decane was determined by measurements on 15-30 binary mixtures. On the phase diagrams, all compositions are expressed in weight per cent. Homogeneity of mixing was attained using a vibromixer. Stirred and sealed samples were heated and cooled in a water bath between crossed polars. Care was taken to ensure that equilibrium was reached at each temperature. The phase sequence observed as a function of concentration and temperature was checked using the microscope penetration technique on the hot stage; clear adhesive film was used to minimize evaporation at the higher temperatures. The concentration gradient at the polymer/n-decane boundary allows the phases to develop as distinct bands, so their sequence can be monitored as a function of temperature; it must be borne in mind, however, that the true phase equilibrium is not reached under these conditions.

RESULTS

B1 + n-Decane

Pure B1 is anisotropic, transmitting light when contained between crossed polars. Under the polarizing microscope it shows large areas of uniform color with virtually no textures. The conoscopic figure is positive, typical of a lamellar phase. Electron microscopy of a freeze-fractured preshadowed platinum-carbon replica clearly shows a stratified morphology of repeat unit ~ 17 nm; this is shown in Figure 1. Low angle X-ray diffraction results are consistent with a lamellar phase of interplanar spacing 17.3 nm (5); this is equivalent to two moieties of poly(12-hydroxystearic acid) each containing five 12-hydroxystearic acid monomer units placed end to end. This anisotropic phase has been assigned as a gel phase because of its high viscosity and absence of the characteristic mosaic texture of the lamellar phase. The enthalpy of transition of pure B1 at 33.2 C is 147 kJ mol^{-1}, confirming a gel to isotropic liquid phase change. The proton Nuclear Magnetic Resonance (NMR) line width is broader than would be expected for a lamellar liquid crystal consistent with a lack of mobility of the hydrocarbon chains. The anisotropic phase will be designated Gel (L_β^1). It is thought to be very similar to the lamellar phase but with the localized liquid crystalline order which produces the typical mosaic (small domain) texture now extending over many more molecules to produce a juxtaposition of macroscopic-scale domains.

The phase diagram of B1 with n-decane is shown in Figure 2. The gel ($L_{\alpha\beta}^1$) phase extends toward the n-decane axis; the uniform areas encountered in the textural studies of this phase show that the B1 molecules readily incorporate n-decane between the layers, forming large aligned lamellar domains. DSC scans confirmed the inner boundary delineating the liquid crystal region. Pure B1 changes from an isotropic, yellow, waxy solid to a straw-colored isotropic liquid at 33.2 C. The stability of the two component gel phase is decreased by an increase in temperature, the temperature stability decreasing as more n-decane is incorporated into the structure. The gel phase behaves as an anisotropic liquid at compositions from 9 to 19%; at compositions up to 31% similar behavior is shown for some 3 to 5 C below the two-phase region. Marked birefringence in the two-phase region, on streaming between crossed polars, is shown by compositions of 14-50% at temperatures above 26 C. Streaming birefringence is shown to a lesser extent over the whole

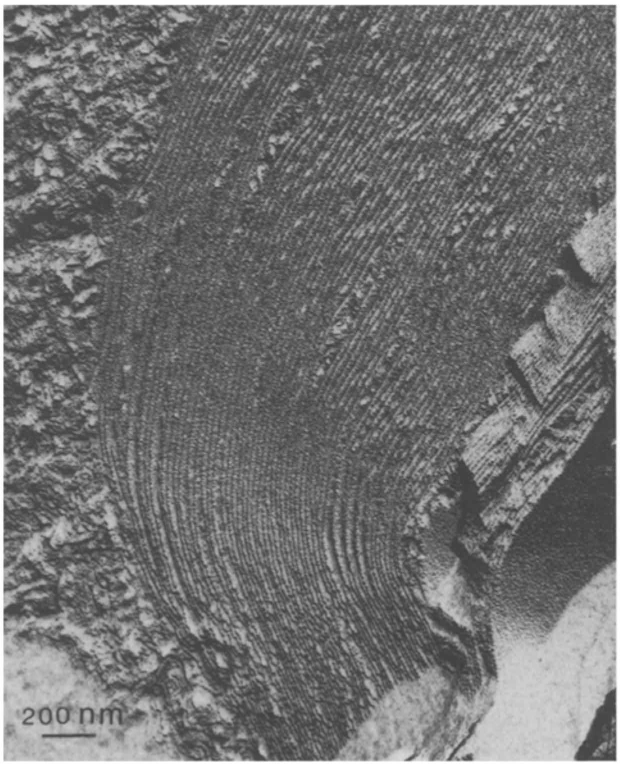

FIG. 1. Electron micrograph of pure B1; 1 cm ≡ 200 nm.

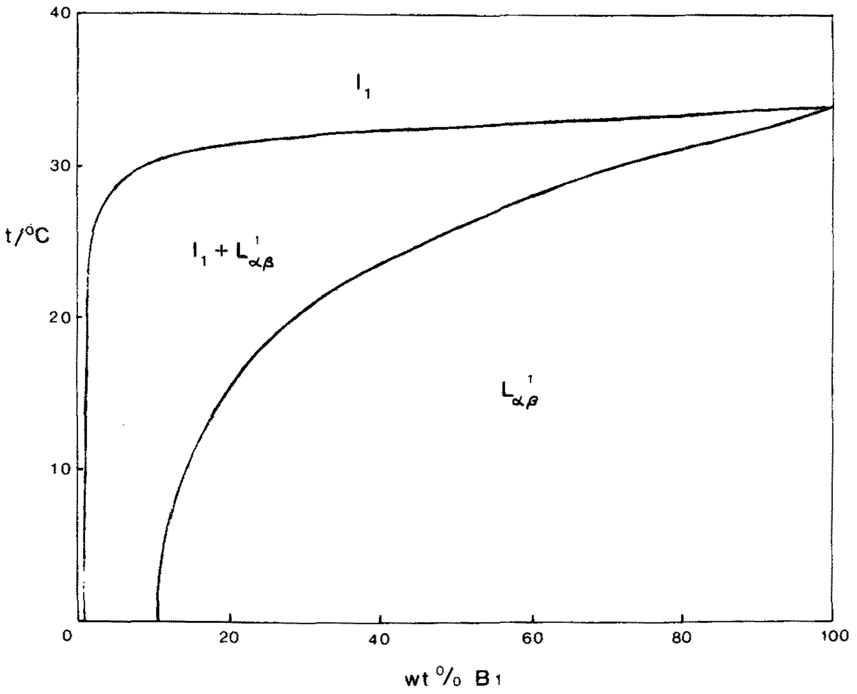

FIG. 2. Phase diagram of B1 + n-decane. I_1, isotropic liquid phase: $L^1_{\alpha\beta}$, anisotropic gel or liquid crystalline phase.

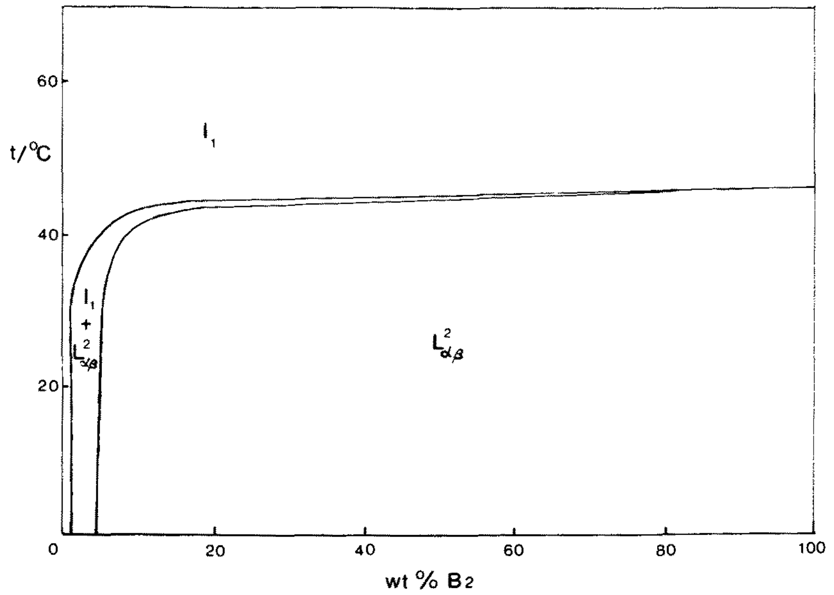

FIG. 3. Phase diagram of B2 + n-decane. I_1, I_2 and I_3 are isotropic liquid phases: $L^2_{\alpha\beta}$ and $L^{22}_{\alpha\beta}$ are anisotropic gel or liquid crystalline phases.

two-phase region at compositions greater than 14%. Low angle X-ray diffraction shows that the repeat spacing increases on adding n-decane; at 60% B1 the periodicity has increased by 10%.

B2 + n-Decane

B2 is a pale yellow, anisotropic waxy solid. Under the polarizing microscope it has a spherulitic texture and positive uniaxial conoscopic figures. After heating and cooling, large areas with a mosaic texture are displayed. The smooth-textured domain areas are smaller in extent than in B1. Low angle X-ray diffraction gives a repeat unit of 6.4 nm, suggesting that the poly(12-hydroxystearic acid) residues are randomly inclined in the layers. This anisotropic phase appears to be of a similar type to that exhibited by B1 but with less ordering present; it is designated Gel (L^2_{β}).

The most striking feature of the phase diagram of B2 with n-decane, shown in Figure 3, is the very extensive region of anisotropic gel $L^2_{\alpha\beta}$ phase, covering a much greater extent of T-composition space than that of B1 + n-decane. The extent of the mosaic texture exhibited by this phase increases with increasing n-decane content. The low angle X-ray repeat spacing increases on adding n-decane to 6.8 nm at 60% B2, but then decreases to 6.0 nm at 50% B2.

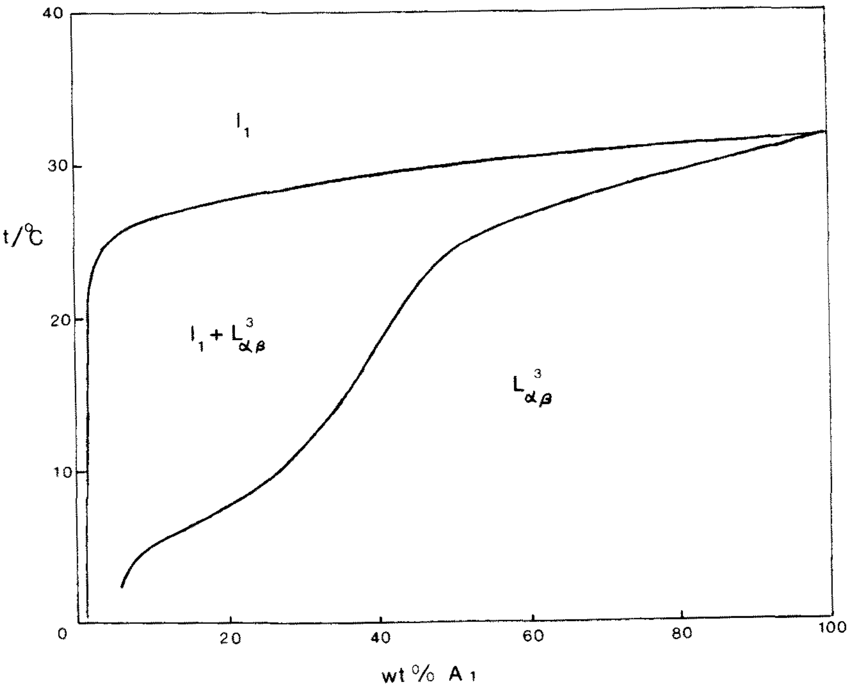

FIG. 4. Phase diagram of A1 + n-decane. I_1, isotropic liquid phase: $L^3_{\alpha\beta}$, anisotropic gel or liquid crystalline phase.

B3 + n-Decane

B3 is a yellow, anisotropic, waxy solid. Under crossed polars a coarse-grained mosaic texture is observed together with large smooth-textured areas, and a positive uniaxial interference figure characteristic of the lamellar phase is shown. The large smooth-textured domains are not as extensive as in B1. Anisotropic gel phases are formed with n-decane of an extent intermediate between B1 and B2.

A1 + n-Decane

A1, a yellow waxy solid, shows a large scale mosaic texture, with a few small non-textured areas, under the polarizing microscope, and a positive uniaxial conoscopic figure. This is indicative of a gel phase with small-scale lamellar-type domains, with considerably less ordering than in B1, B2 and B3, and is designated Gel (L^3_β).

In the phase diagram with n-decane (Fig. 4), quite extensive anisotropic behavior is shown especially at high A1 compositions. This phase shows the very fine-grained mosaic texture typical of a lamellar liquid crystal; at compositions below 51% it is, in fact, a pale yellow viscous anisotropic liquid even at 5 C. In the two-phase region the upper liquid phase shows pronounced streaming birefringence at compositions greater than 21% and between the temperatures 23 to 29 C.

A2 + n-Decane

A2 is a yellow sticky solid and isotropic. It is soluble in n-decane up to 50% (by wt) and at temperatures up to 50 C. At higher proportions of n-decane two liquid phases are formed which readily form a stable emulsion at lower temperatures. The phase diagram with n-decane shows no anisotropic regions in the temperature range 0 to 50 C.

A3 + n-Decane

In the pure form and under crossed polars, A3 shows large smooth-textured areas intermingled with a broken mosaic texture; it also shows a positive uniaxial interference figure characteristic of the lamellar phase. The phase diagram with n-decane shows an extensive anisotropic region and is similar to that of B1 and A1.

DISCUSSION

The five copolymers B1, B2, B3, A1 and A3 show both lyotropic liquid crystalline behavior in solution in n-decane and also thermotropic liquid crystalline behavior. The viscosity of the liquid crystalline phase increases with the copolymer content, and gels are formed.

The extent of the anisotropic region shown by mixtures of B2 and n-decane is greater than that of B1. This is to be expected, as B2 has a much longer polyoxyethylene chain than B1. Interestingly, although both polymers alone in the gel phase have a lamellar structure, because B2 is a much longer molecule than B1 it must to some extent bend back on itself so that a more random structure is obtained; thus there is a reduction in alignment of B2 relative to B1 so that B2 does not have such extensive planar domain areas in its textures. B3, with varied polyoxyethylene chain length, shows properties intermediate between those of B1 and B2.

The A1 + n-decane system shows quite extensive anisotropic behavior especially for A1 rich samples. In comparison with A2 the difference is quite startling. A2 is completely isotropic both on its own and with n-decane. This is thought to be due to the doubling in length of the polyoxyethylene chains of the A1 copolymer over A2. It suggests that the length of the polyoxyethylene chain has a very important effect on the physical properties of the surfactant. The very fine mosaic textures displayed by the liquid crystals formed by A1 is to be expected when one considers the random nature of the surfactant, i.e., if the surfactant itself has a random structure than it is not surprising that the liquid crystals it forms will reflect this and so will exist only in small units. It is surprising that, despite the randomness of the structure of A1, which includes unsaturated fatty acids not crystalline at ambient temperatures, the behavior is dominated by the tendency of the PEG 1500 to form its own phase. Both B1 and A1 are made from PEG 1500; in

A1 the fatty acids are in a more random arrangement than in B1, a block copolymer containing poly(12-hydroxystearic acid) crystalline at ambient temperatures. A2 has little tendency to order compared with A1, whereas B1 is more ordered.

On the intramolecular scale A3 is more ordered than A1 but less so than B1. Like A2 it contains PEG 600 but the hydrophobe is polyisobutenylsuccinic anhydride, a viscous liquid very different from the poly(12-hydroxystearic acid) of B1, showing no tendency to crystallize, even at temperatures as low as -40 C, whereas the latter crystallizes near 40 C. Polyisobutylene itself forms a coiled chain with the methyl groups staggered around a central axis; it is suggested that it is this effect that gives the polyisobutenyl groupings in A3 the tendency to form a separate phase, but no giant domains are observed, as the total structure is random.

For the degrees of order necessary for liquid crystal formation to occur, alignment of the surfactant molecules is required. Because polyoxyethylene chains interact favorably with each other, they produce the alignment necessary for the formation of a liquid crystal. This alignment is encouraged by the surfactant molecules having a regular structure. B1, an XYX block copolymer, exemplifies the molecular arrangement for this regular repeatable structure to occur, whereas with A2 the lack of regular molecular structure combined with shortness of the polyoxyethylene chains means there are insufficient interactions to produce the alignment necessary for the formation of liquid crystals.

This work was part of a project to determine the efficacy of these compounds as emulsifiers. B1 is an excellent oil+water+electrolyte emulsifier, and the low angle X-ray spacing found is in agreement with the thickness of its bilayer lipid film (6). However, better emulsifiers for the same system do not show liquid crystalline behavior in the same temperature range.

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Surface Properties in Binary Mixtures of Aerosol OT and Nonionic Surfactants

JUNG-HUNG CHANG, YASUSHI MUTO, KUNIO ESUMI* and KENJIRO MEGURO, Department of Applied Chemistry and Institute of Colloid and Interface Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162, Japan

ABSTRACT

The surface tensions of the mixed systems consisting of sodium di-2-ethylhexyl sulfosuccinate (Aerosol OT) and homogeneous polyoxyethylene glycol-n-dodecyl ether (nED; n=5 to 8) were measured in the absence and presence of sodium chloride (NaCl) by a modified Wilhelmy plate method.

In the case of the system containing nED and Aerosol OT, the nED concentrations were fixed at various amounts, and all the surface tension curves approached 32 or 33 mN/m as the concentration of Aerosol OT approached 1×10^{-3} mol/l. On the other hand, when the Aerosol OT concentration was fixed at 1×10^{-3} mol/l, the surface tension curves for the mixed system showed a flat portion in the range where mixed micelle in the solution and the two dimensional ones on the water surface were formed. Further, molecular interaction parameter B was calculated by the Rosen extension of the regular solution treatment of Rubingh. The average values of B in the nED-AOT systems increased as the value of n increased. The values of B increased with increasing activity of AOT.

In the case of the system containing 6ED, AOT and NaCl, the surface tension curves showed inflection points shifted to higher concentrations of AOT as the concentration of nED increased.

INTRODUCTION

There have been many studies on the interactions of nonionic and anionic surfactants in aqueous solution (1-11), in which the mixed micelle formation of mixtures has been studied by measuring the surface tension and by solubilization methods (1-11).

Recently, Meguro et al. (7,12) reported the properties of mixed micelles among sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS) and a series of homogeneous polyoxyethylene glycol-n-dodecyl ether (nED), and they have confirmed that the surface tension curves of nonionic surfactants have a flat portion in combination with SDS or STS. Further, they have interpreted the flat portion as the mixed micelles region.

On the other hand, sodium di-2-ethylhexyl sulfosuccinate (AOT) is an important practical anionic surfactant widely used in nonaqueous as well as in aqueous solutions. Although the micelle formation and solution behavior of AOT in water have been studied by several workers (13-16), there are a few reports about the interactions of AOT with other surfactants.

In this work, the surface properties of mixtures of nonionic surfactants and AOT were investigated by measuring their surface tensions and by calculating the interactions by measuring their surface tensions and by calculating the interaction parameter between them. The effect of salt on the mixtures containing nonionic and AOT surfactants also was examined.

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*To whom correspondence should be addressed.