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Phase Diagram of the Binary System Water-(Dodecyldimethylammonio)propanesulfonate

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The phase diagram and some physicochemical properties of the binary system water-(dodecyldimethylammonio)propanesulfonate have been studied. Most of the experimental observations were focused on determining the role played by water on the stability of the observed phases. Results from deuterium quadrupole splittings of D_2O have been rationalized on thermodynamic grounds by introducing a binding equilibrium constant for water at interfaces.

Introduction

Betaine-like surfactants are long-chain zwitterionic compounds bearing in the same molecule a quaternary ammonium and an anionic group. Depending on the nature of the ammonium group and on the location of the hydrocarbon chains with respect to it, these betaine-like surfactants can be divided into different subclasses.¹ Among them, sulfobetaines, or more correctly, ammonioalkanesulfonates, are of interest because the combined effect of acid and basic groups² makes their solution properties independent of pH and ionic strength. The above features make them compatible with either cationic and anionic surface-active agents.

Apart from intrinsic interest in their solution properties, ammonioalkanesulfonates have peculiarities which make them suitable in the formulation of pastes, shampoos, and fine detergents,³ as softeners in laundry products,⁴ as antistatic products in photographic emulsions,⁵ in mild antibacterial media,⁶ and in the recovery of biologically active membrane proteins.⁷ The latter property is probably related with the properties of the ionic groups.

Physicochemical investigations on these compounds have been performed in the past^{1,8,9} and have received renewed

interest in recent years.¹⁰⁻¹⁵ However, with the partial exception of Nilsson et al.¹¹ no information has been reported on the lyotropic phases that ammonioalkanesulfonates can form with water.

In this paper, we report studies on the phase diagram of the system formed by water and (dodecyldimethylammonio)propanesulfonate (DDAPS), by combining observations obtained from optical polarizing microscopy, NMR experiments, and other ancillary techniques.

Experimental Section

Materials. DDAPS was a Sigma high-purity product. Its purity has been checked from the melting point, T_f , and from surface tension. No minima in the plot of surface tension versus log molality have been observed.

The samples for the melting point determination were dehydrated by dissolution in hot ethyl alcohol, filtered, and vacuum-dried. In this way, a comparison with available literature data³ and with T_f values from the purveyor is possible. The accuracy on the fusion temperature is to within 1.5 °C.

Water, twice distilled, deionized, and degassed, has conductance close to $1 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ at 25 °C.

Deuterium oxide, 99.7% isotopic enrichment, was from Merck.

The samples were prepared by weighing the components in glass tubes which were sealed off, heated at 90-100 °C for 1 day, and centrifuged back and forth several times soon after heating. In this way, problems arising from the trapping of solution, or middle phase, in a viscous isotropic matrix are overcome. The whole procedure was repeated until no changes could be detected through crossed Polaroids.

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(1) Tori, K.; Nakagawa, T. *Kolloid Z. Z.-Polym.* **1963**, *187*, 14; **1963**, *188*, 47-50; **1963**, *191*, 42-48.

(2) Gonenne, A.; Ernst, R. *Anal. Biochem.* **1978**, *87*, 28.

(3) Ernst, R.; Miller, E. J., Jr. In *Amphoteric Surfactants*; Bluestein, B. K., Hilton, C. R., Eds.; Marcel Dekker: New York, 1982; Vol. 12, Chapter 2.

(4) Lehman, H. D. German Patent 2,207,251, to Unilever, N.V., 1972.

(5) Wild, W.; Stemming, B.; Neumann, A.; Seibt, H.; Ruche, J.; Ball-schuh, D. German Patent (East) DD 152,867, 1981.

(6) Distler, H.; Widder, R. *Tenside* **1969**, *6*, 241.

(7) Beckett, A. M.; Woodward, R. J. *J. Pharm. Pharmacol.* **1963**, *19*, 422.

(8) Herrmann, K. W. *J. Colloid Interface Sci.* **1966**, *22*, 352.

(9) Swarbrick, J.; Daruwala, J. *J. Phys. Chem.* **1970**, *74*, 1293.

(10) Lianos, P.; Zana, R. *J. Colloid Interface Sci.* **1981**, *84*, 100.

(11) Nilsson, P. G.; Lindman, B.; Laughlin, R. G. *J. Phys. Chem.* **1984**, *88*, 6357.

(12) Mallaris, A.; Le Moigne, J.; Sturm, J.; Zana R. *J. Phys. Chem.* **1985**, *89*, 2709.

(13) Kamenka, N.; Haouche, G.; Facompré, B.; Brun, B.; Lindman, B. *J. Colloid Interface Sci.* **1985**, *108*, 451.

(14) Zana, R.; MacKay, R. A. *Langmuir* **1986**, *2*, 109.

(15) Faucompré, B.; Lindman, B. *J. Phys. Chem.* **1987**, *91*, 383.

The samples were stored at 20 °C at least 1 week before each set of measurements.

Methods. NMR experiments were performed by a Varian XL-300, working in an FT mode on proton and deuterium nuclei. Experimental conditions were as follows: acquisition time, 50 ms; number of transients, 2000; number of pulses, 400. For proton NMR, the number of transients was 1500, and other parameters were as before. Experiments were run from -10 to 100 °C; the temperature was constant within 0.2 °C.

Optical polarizing microscopy studies were performed by a Leitz Laborlux 12 microscope provided with a Linkam 600 thermoregulable cell. The assignment of textures was confirmed by experiments with λ - γ quarter-wave red compensators and consequent conoscopic investigation.¹⁶

Samples were prepared for optical microscopy in three different ways. A drop of concentrated micellar solution was put between glass slides, and the phase sequence was inferred from peripheral evaporation at the required temperature. The above procedure allows us to make conoscopic investigations on large anisotropic optical domains.

Alternatively, small amounts of water-DDAPS mixtures were pressed between glass slides. These were sealed off by a heat-resistant epoxy resin to avoid solvent losses. In some other cases, the samples were sealed in glass capillaries, heated at about 90–100 °C, and stored at the selected temperature for some hours.

The microscopic investigations were performed by scanning the temperature 2 or more times. The thermal transitions were also confirmed by macroscopic observations of samples heated in a glycerol bath.

The accuracy on the phase boundaries, detected by microscopy and optical methods, is within ± 2 °C.

Experiments by differential thermal analysis, DTA, were performed on anhydrous and/or air-equilibrated samples by a Mettler TG50 thermobalance, coupled with a Mettler TC10-TA processor system and a print swiss matrix. The heating rate used was 10 °C min⁻¹, and the atmosphere was an air stream at flow rate of 100 mL min⁻¹. The heating rate has no influence on the transition temperatures of both anhydrous and air-equilibrated solid samples, as confirmed by DSC experiments.¹⁷

Results and Discussion

Phase Diagram. The phase diagram of the system water-DDAPS, reported in Figure 1, was constructed by combining visual observations with those from optical polarizing microscopy, NMR, and DTA.

a. Solution Phase. A solution region, L_1 , extends from 0 to 48.5 DDAPS wt %, at 20 °C. In this domain, a molecularly dispersed subregion occurs up to 0.1 wt % of surfactant. Micelles begin to form above 3.6×10^{-3} M.¹⁷ From the fluidity of the samples, it can be argued that nearly spherical micelles are present in the whole solution region. This hypothesis is supported by fluorescence decay data.^{12,18}

Up to about 40 DDAPS wt %, proton NMR spectra for dodecylsulfobetaine aqueous solutions do not show signal broadening, thus excluding the onset of anisometric micellar aggregates.¹⁹

The fluidity of betaine solutions and the features from ¹H NMR spectra suggest that weak repulsive intermicellar interactions do occur, in spite of the absence of neat charges on the micellar surface. According to Evans and Ninham,²⁰ this behavior indicates the occurrence of nearly globular micelles up to the phase separation limit.

Optical studies performed at temperatures close to 0

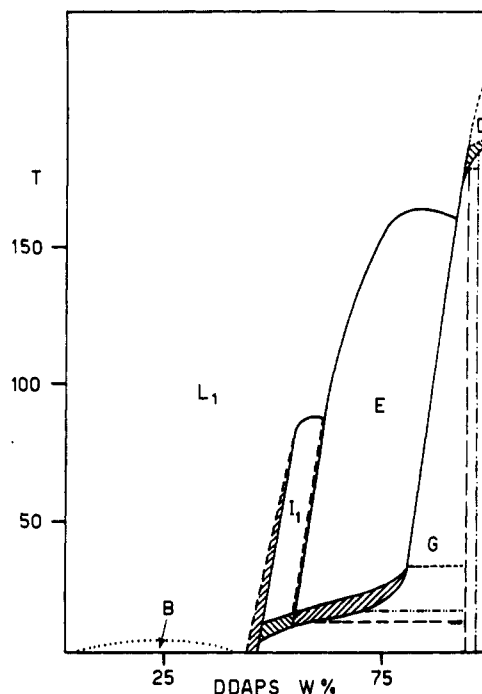


Figure 1. Phase diagram of the system water-DDAPS. L_1 is the solution region, I_1 a viscous isotropic mesophase, E the hexagonal mesophase (middle phase), and D a lyotropic phase with presumed lamellar structure. The gel phase is indicated G. The dotted area below the solution region marked B indicates upper consolute boundaries.

Table I. Chemical Shifts of Main Peaks in ¹H NMR Spectra of DDAPS-D₂O Mixtures*

micellar phase, ^b ppm	viscous phase, ^c ppm	assignment
4.709	4.752	terminal methyl
5.159	5.141	chain methylenes
5.589	5.641	N methyl groups
5.787	5.798	α methylenes

* Taken relative to the inner reference signal. ^b 43.5 DDAPS wt %. ^c 54.2 DDAPS wt %.

°C indicated the occurrence of consolute phenomena, close to the Krafft point. The kinetics of phase separation, the clouding processes, and the stability of the two phases have been discussed in detail by Nilsson et al.¹¹ and shall not be discussed here.

b. Viscous Isotropic Mesophase. A viscous isotropic mesophase, I_1 , extends from 49.5 to 63 DDAPS wt %. The lower limit of the phase was inferred by the absence of optical discontinuities in the refracting index. The thermal transitions L_1 - I_1 were inferred from microscopy in drying experiments. The transition temperatures are within ± 2 °C.

In some cases, a Pasteur pipet was introduced in the solution at the required temperature to determine the onset of the cubic phase. Further evidence came from the analysis of the samples discussed in the Experimental Section.

Proton and deuterium NMR spectra, as well as the optical properties of the above phase, strictly resemble those of the L_1 phase. The main proton NMR signals for two selected samples in micellar and viscous phases are reported in Table I. They indicate that the molecular environments sensed by DDAPS in the two phases are quite similar and suggest that, even if the fluidity of the two phases is extremely different (more than 4 orders of magnitude), the aggregates in micellar and I_1 phases should be similar in shape.

(16) (a) Cockx, G. C.; Jelley, E. E. In *Physical Methods of Chemistry*; Weissberger, A., Rossiter, B. W., Eds.; Wiley: New York, 1972; Vol. IIIA, Chapter III, p 119. (b) Hertel, G.; Hoffmann, H. *Prog. Colloid Polym. Sci.* 1988, 76, 123.

(17) Sesta, B.; La Mesa, C.; in preparation.

(18) Mallaris, A.; Lang, J.; Zana, R. *J. Colloid Interface Sci.* 1986, 110, 237.

(19) Ulmuis, J.; Wennerstrom, H. *J. Magn. Reson.* 1977, 28, 309.

(20) Evans, D. F.; Ninham, B. W. *J. Phys. Chem.* 1986, 90, 226.

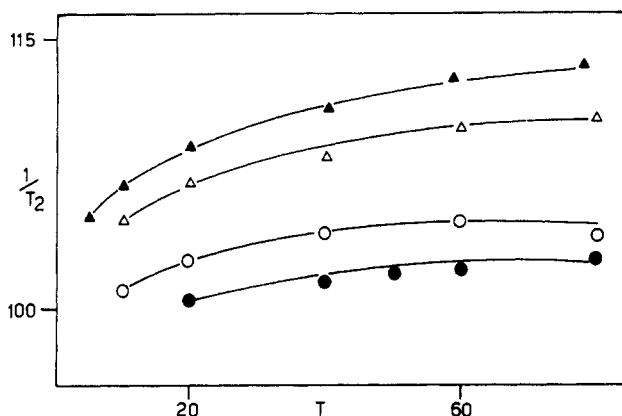


Figure 2. Transverse relaxation rates of D_2O , in s^{-1} , as a function of temperature for micellar solutions, \bullet , and viscous isotropic phases, \blacktriangle . Composition is 42.8 (\bullet), 46.3 (\circ), 52.8 (\triangle), and 57.1 (\blacktriangle), DDAPS wt %, respectively.

The I_1 phase could be formed by short rods arranged in a cubic array, (axial ratios in the range 1–2.5), because a three-dimensional structure of interconnected spherical micelles is not consistent with the surfactant volume fraction.

The transverse relaxation rates of D_2O , obtained by the deuterium signal amplitude at half-height, are nearly the same as bulk deuterium oxide and slightly affected by temperature changes, as indicated in Figure 2. In addition, the stiffness of the viscous phase implies that the displacement of the aggregates each apart from the other is difficult to realize. Systems showing similar peculiarities were described by Fontell.²¹

The region of existence of the I_1 phase and its location in the phase diagram suggest significant similarities with the location of the I_1 phase in the binary system dodecyltrimethylammonium chloride–water.²²

If we compare the structural moieties of the quaternary ammonium group of DDAPS with that of the alkyltrimethylammonium halide, we can reasonably ascribe the observed similarity to functional groups and sterical arrangements of their bulky head groups.

c. Middle Phase. A lyotropic mesophase with hexagonal symmetry, E, extends from about 65 to 87 DDAPS wt %, at room temperature. In polarized light, the samples show strongly birefringent fanlike and/or curdy textures, depending on composition. Samples obtained by peripheral evaporation or by penetration techniques show well-developed fanlike textures; when observed by conoscopy, these samples show negative birefringence and uniaxial character, in agreement with statements of Winsor.^{23a,b} A detailed description of optical axial character in lyotropics and their links with NMR has been recently reported by Hoffmann et al.¹⁶

The spectra show a splitting in I peaks, where I is the spin quantum number of deuterium, Figure 3, depending on the nonisotropic molecular environment sensed by D_2O molecules.

Information on the curvature of the polar interfaces can be obtained from the spectral profiles.²⁴ The com-

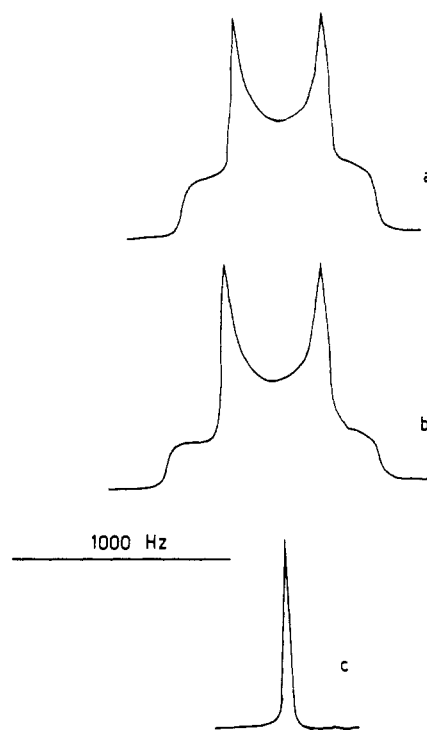


Figure 3. NMR spectral profiles for D_2O in cubic phase, c, and in hexagonal mesophase, a and b.

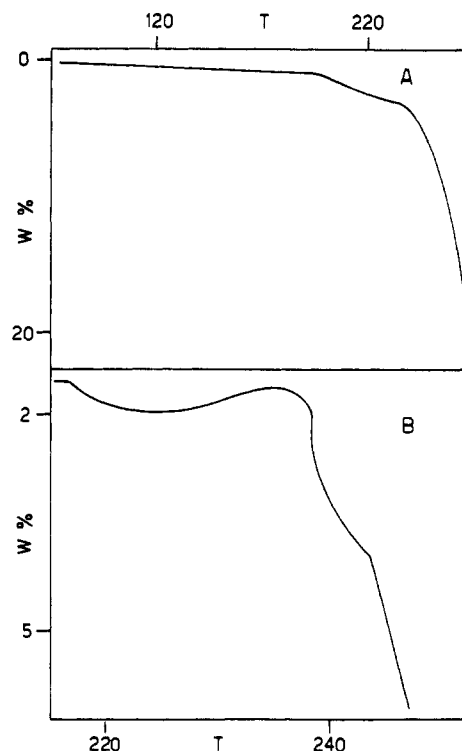


Figure 4. DTA analysis for crystalline, hydrated, dodecylammoniopropanesulfonate.

bined evidence from optical microscopy and from 2H quadrupole splittings indicates that the phase is hexagonal.

d. Solid Phase. A solid (hydrated) surfactant phase extends from 90 DDAPS wt % upward. Its appearance in polarizing microscopy is as in gels.²⁵ The DTA analysis of the solid hydrated surfactant, Figure 4, indicates that, close to 200 °C, the ammoniopropanesulfonate group releases part of its hydration water. According to the

(21) Fontell, K.; Fox, K. V.; Hansson, E. *Mol. Cryst. Liq. Cryst.* **1985**, *1*, 9.

(22) Balmbra, R. R.; Clunie, J. S.; Goodman, J. F. *Nature* **1969**, *222*, 1159.

(23) (a) Winsor, P. A. *Chem. Rev.* **1968**, *68*, 1. (b) Gilchirst, G. A.; Rogers, J.; Steel, G.; Vaal, E. G.; Winsor, P. A. *J. Colloid Interface Sci.* **1967**, *25*, 409.

(24) Chidichimo, G.; Vaz, N. A. P.; Yaniv, Z.; Doane, J. W. *Phys. Rev. Lett.* **1982**, *49*, 1950.

(25) Rosevear, F. B. *J. Am. Oil Chem. Soc.* **1954**, *31*, 628.

weight loss of the samples during the transition, the following equilibrium can be supposed:



Mixtures containing more than 90 wt % of surfactant undergo a thermal transition close to 200 °C. Optical microscopy revealed the existence of an anisotropic phase with lamellar textures and an oily streak appearance. The phase border is close to the decomposition temperature, and no efforts have been made to define in detail the region of existence of this phase.

Hydration Features of Mesophases. Average hydration numbers per amphiphilic molecule, N , can be obtained by deuterium NMR. In fact, nuclei with spin quantum numbers $S > 1/2$ located in anisotropic environment split their signal in two I peaks. The difference among the two resonances signals, Δ , contains information on the solvent interactions with interfaces.

Since Δ is a time-average value of contributions due to different binding sites,²⁶ the observed splittings can be assumed to be due to water in free and bound states. Accordingly

$$\Delta = IP_f D_f + P_b D_b I \quad (2)$$

where P_b and P_f are the relative contributions of water in bound and free states and D_b and D_f are the splittings of bound and free water, respectively. In mole fraction units

$$\Delta = ID_f + (nX_a/1 - X_a)(D_b - D_f)I \quad (3)$$

where X_a is the surfactant mole fraction.

Lindman and co-workers²⁷ modified eq 3 by assuming that bound water molecules are those located within a certain distance, d , from the polar interface. However, our data, analyzed by eq 3 and according to ref. 27, do not give significant differences in hydration numbers, which range from 6 to 7.

The loss of rotational degrees of freedom for water molecules due to binding is well accounted for in micellar solutions²⁸ and lyotropic mesophases.²⁹ We can account

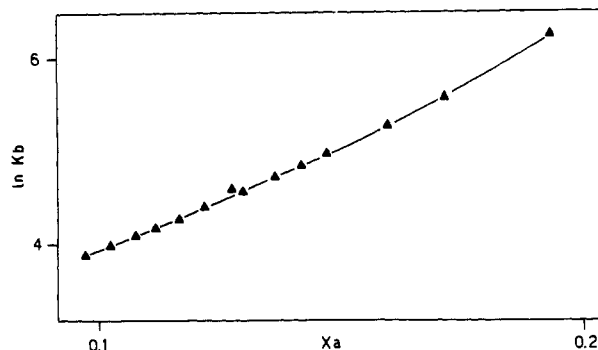


Figure 5. Binding constant, K_{bind} , for water at interfaces as a function of surfactant mole fraction, at 25 °C.

for binding according to

$$A + nW \rightleftharpoons A(nW) \quad (4)$$

$$K_{\text{bind}} = A(nW)/[(X_a - A)(1 - nA)^n] \quad (5)$$

where A is the amount of surfactant molecules taking place in hydration.

The free energy of binding

$$\Delta G_{\text{bind}}^\circ = -RT \ln K_{\text{bind}} \quad (5')$$

where K_{bind} (as in eq 5) ranges from 7.5 to 10.5 kcal mol⁻¹, increasing as T is raised. The trend of the equilibrium constant as a function of composition is reported in Figure 5.

Unexpectedly, such values increase slightly from 20 to 80 °C. The variation is just higher than the experimental error, but it is systematic throughout the whole phase region.

According to data calculated by eq 5 and 5', an increase in temperature is concomitant with an increase in the area per polar head group, thus supporting the hypothesis of increasing interactions with the solvent at high temperatures.

The hydration numbers of micellar DDAPS are about 2 times higher than values for the E phase.¹⁷ Accordingly, the thermal transitions from E to L_1 phases should be sensitive to variations in average hydration numbers. Work is in progress in this direction.

Registry No. H₂O, 7732-18-5; betaine surfactant, 14933-08-5.

(26) Lindblom, G.; Wennerstrom, H.; Lindman, B. *Chem. Scr.* 1974, 6, 81.

(27) Sward, M.; Schurtenberger, P.; Fontell, K.; Jonsson, B.; Lindman, B. *J. Phys. Chem.* 1988, 92, 2261.

(28) Sesta, B.; La Mesa, C.; Bonincontro, A.; Cametti, C.; Di Biasio, A. *Ber. Bunsen-Ges. Phys. Chem.* 1981, 85, 798.

(29) Rendall, A.; Tiddy, G. J. T. *J. Chem. Soc., Faraday Trans. 2* 1983, 79, 48.