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ORIGINAL CONTRIBUTION

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The catanionic system dodecyltrimethylammonium hydroxide–*n*-dodecanephosphonic acid–water. Triangular phase diagram

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Abstract The triangular phase diagram of the system dodecyltrimethylammonium hydroxide (DTAOH)–dodecanephosphonic acid (H_2DP)–water was studied by several techniques. The DTAOH-rich zone could not be studied because DTAOH decomposed when it was dried. Pure H_2DP only forms lamellar mesophases with water. The inclusion of DTAOH in the system produces the appearance of cubic and hexagonal mesophases. The gradual increase in DTAOH proportion lead to the gradual reduction in the existence of the lamellar mesophase domain, and increase of the hexagonal liquid crystal domain. At high DTAOH content, the lamellar mesophase disappeared. This behavior was explained by the gradual destruction of the hydrogen-bonded structure in the polar headgroup layer of liquid crystal aggregates. H_2DP-rich anhydrous crystals were triclinic.

Key words Catanionic surfactants – mesophases – triangular phase diagram – dodecyltrimethylammonium hydroxide–*n*-dodecanephosphonic acid – liquid crystals

Introduction

Considerable work has been done on aqueous mixtures of catanionic (cationic–anionic) surfactants [1–5]. This kind of surfactants are of interest in pharmacy [6], analytical chemistry [6–9], wastewater treatments [10], chemical kinetics [11], textile wetting and detergency [12]. The phase behavior of catanionic mixtures has been studied extensively in recent years. General observations include precipitation in equimolecular mixtures and the formation of mixed micelles in an excess of one of the components [13–20].

The behavior of the bicomponent systems *n*-dodecanephosphonic acid (H_2DP)–water and dodecyltrimethylammonium hydroxide (DTAOH)–water was reported elsewhere [21–23]. The critical micelle concentration of the tricomponent system DTAOH–H_2DP–water was studied as a function of the H_2DP:DTAOH ratio in another paper [24]. The triangular phase diagram reported in this work not only resumes the information given in the preceding papers, but gives much new information and evidences some interesting aspects of the tricomponent system behavior.

Experimental

The preparation of H_2DP and DTAOH has been reported elsewhere [25, 26]. The samples with different H_2DP:DTAOH ratios were prepared by weighing solid H_2DP and then adding the appropriate volume of DTAOH solution of known concentration. Double-distilled, CO_2-free water was employed. Samples with solid or solid-like residues were centrifuged to separate the residue and the supernatant. Both parts were analyzed to establish their proportion and composition. Water content was determined by difference of weight of samples before and after evaporation under vacuum at low temperature. The DTAOH content was determined by adding a known amount of HCl solution to a weighed sample and then titrating the remaining HCl with NaOH. The H_2DP content was determined by adding a known amount of NaOH solution to a weighed sample and then titrating the remaining NaOH with HCl conductimetrically. All concentrations are w/w.

The samples were studied in the microscope using polarized and non-polarized light. Liquid samples were studied by slow peripheral evaporation, and the samples were left between slides to form crystals. The angles between edges, extinction angles and the homogenity of the crystals were determined. The crystals were also studied by peripheral dilution with double-distilled water. The residues were also studied by microscopy.

The crystals of the proportion 1:0.5 were studied by X-ray diffraction. The diffractogram was analyzed by the method of Vand [27, 28]. The diffractogram was determined in a Rigaku computerized X-ray diffractometer Geiger Flex D-max 3C, with Cu anode, Ni filter, 35 kV, 15 mA, $K_{\alpha 1}\lambda = 0.15404$ nm.

Results and discussion

The triangular phase diagram is shown in Figs. 1–3 at different scales.

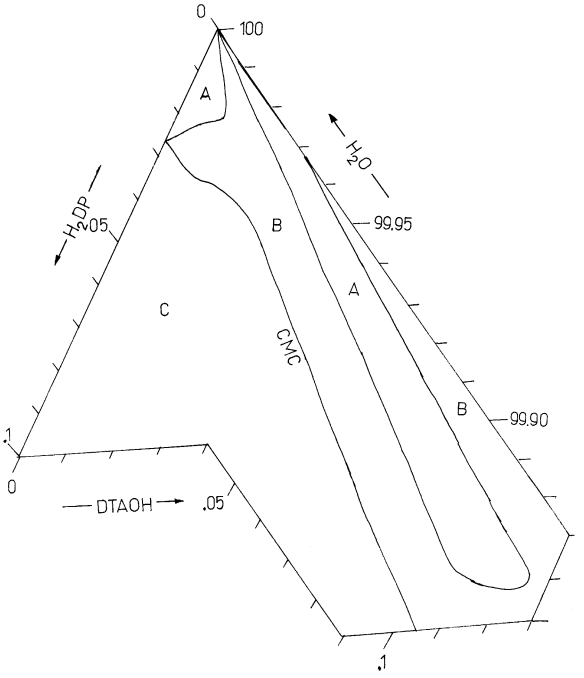

Fig. 1 Very low concentration zone of the tricomponent system phase diagram. A: molecular-dissolved surfactant solution, B: fully ionized small aggregates, C: micellar solution

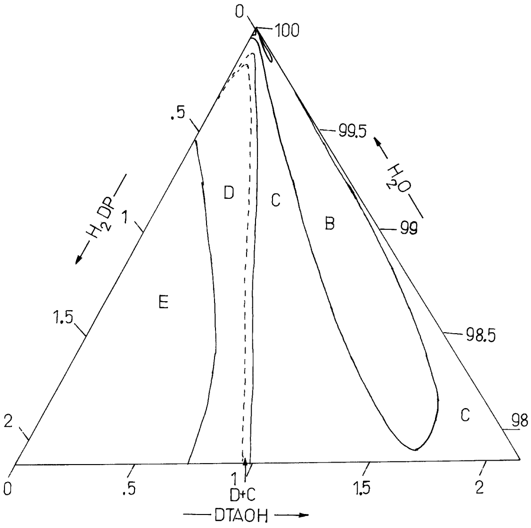

Fig. 2 Low concentration zone of the tricomponent system phase diagram, showing the domains of B: fully ionized small aggregates, C: micellar solution, D: liquid crystals, E: hydrated crystals

The binary system H_2DP–water

This side of the triangular phase diagram was performed on the basis of literature data [21]. H_2DP is a weak acid with $pK_1 = 4.03$ and $pK_2 = 8.42$ [26]. The critical micelle concentration (cmc) is 0.00104 mol dm^{-3} [22, 29, 30], which corresponds to 0.026 wt%. At 0.5 wt% H_2DP, a solid with waxy texture appears. By FTIR analysis it was found that the structure of this solid is similar to that of the anhydrous crystal, whose polar network is bound by hydrogen bonds. These hydrogen bonds are weaker than those in anhydrous crystals, because of the interaction with water. The hydrocarbon network was partially melted at 28 °C [21]. At H_2DP contents above 91 wt%, fully solid crystals appeared with some water. The DSC analysis of the interaction between water and surfactant showed that it is very weak, and it may not be considered as hydration, but occluded [31]. At 30 °C, the acid solubility is enough to produce lamellar liquid crystals in equilibrium with micellar solution. Typical mielyn figures may be seen peripheral dilution. There is a different lamellar mesophase at temperatures above 50 °C, and H_2DP does not form hexagonal nor cubic mesophases [21].

The anhydrous crystals are triclinic, with the following crystallographic characteristics [32]: number of molecules

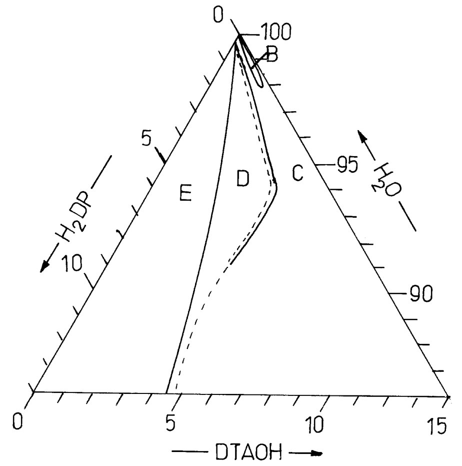

Fig. 3 The partial tricomponent system phase diagram, showing the different domains: B: fully ionized small aggregates, C: micellar solution, D: liquid crystals, E: hydrated crystals

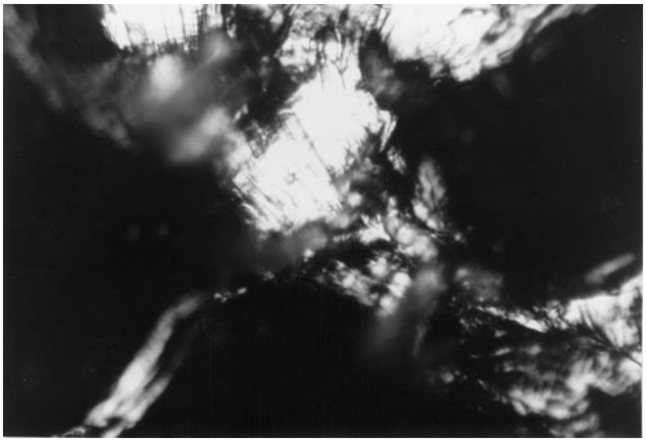

Fig. 4 Concentrated DTAOH–water system obtained by fast peripheral desiccation of dilute solution. Non-geometrical striated texture. Crossed polaroids X 150

in the unit cell (Z) = 4, $a = 0.940 \pm 0.002$ nm, $b = 0.5964 \pm 0.0007$ nm, $c = 3.088 \pm 0.005$ nm, $\alpha = 93.89 \pm 0.02^\circ$, $\beta = 81.38 \pm 0.02^\circ$, $\gamma = 79.78 \pm 0.023^\circ$, cross section of a molecule: $ab \sin \beta/2 = 0.2771 \pm 0.0009$ nm^2, narrow to wide thickness of the chain ratio, $\varepsilon = 0.642 \pm 0.002$, angle of tilt of the chain with respect to the $\{0\,0\,1\}$ plane $\tau = 54.4 \pm 6.3^\circ$, angle of tilt of the chain zig–zag with respect to the $\{0\,0\,1\}$ plane $\sigma = 73.77 \pm 0.28^\circ$.

The binary system DTAOH–water

DTAOH is a relatively strong base, with $pK_b = 2.8901 \pm 0.0003$ [25]. The phase diagram side of this system is incomplete because DTAOH dehydration was followed by the decomposition of the surfactant. Many different techniques were intended, but all of them failed in obtaining stable anhydrous DTAOH. In the desiccation procedures no solid formation was seen. The anhydrous system was a waxy-like semisolid, having DTAOH and products of decomposition. This decomposition was verified by dissolving the residue in double-distilled, CO_2-free water and conductimetrically titrating with HCl. Clearly, part of the residue did not redissolve and remained as a fine emulsion. The base content was lower than that in the original DTAOH solution, and became lower and lower as the time between desiccation and redissolution increased.

By fast desiccation of a small sample on a slide, we observed striated non-geometrical textures which are typical of hexagonal mesophases (Fig. 4). By peripheral dilution with double-distilled, CO_2-free water, immediately after desiccation, the sequence hexagonal mesophase–cubic mesophase–isotropic solution was seen. The cubic mesophase was not visible between crossed polaroids, but it was clearly visible as a granulated zone by intercalation of a selenite retardation plate. This zone showed high viscosity when the slides were pressed.

A slow desiccation between slides gave small birefringent crystals of unknown characteristics, but because of the very scarce amount of them and the decomposition verified in macroscopic samples, they were not studied by X-ray diffraction.

In the binary system DTAOH–water the aggregation follows a step mechanism [23]: at concentration $(1.300 \pm 0.041) \times 10^{-3}$ mol dm^{-3} (3.14×10^{-4}% w/w) monomers joined to form full-ionized submicellar aggregates, which captured counterions to form true micelles at $(1.108 \pm 0.010) \times 10^{-2}$ mol dm^{-3} (2.71×10^{-3}%). At $(3.02 \pm 0.28) \times 10^{-2}$ mol dm^{-3} (7.36×10^{-3}%) the micelles changed their structure, increasing their solubilization power [33]. The present study showed that at higher concentration a viscoisotropic (cubic) mesophase appeared, which in turn gave an hexagonal mesophase at much higher concentrations. Because of the DTAOH decomposition we could not determine the concentration at which the transitions isotropic (micellar) solution ↔ cubic mesophase ↔ hexagonal mesophase occur.

The binary system DTAOH–H_2DP

This side of the phase diagram could only be determined partially because samples with H_2DP : DTAOH proportions equal or larger than 1 : 2 decomposed when they were desiccated. We determined the crystalline structure of the

1:0.5 sample, which produced tabular crystals by peripheral evaporation between slides (Fig. 5). The angles between edges were 66.9 ± 2.9°, 114.0 ± 2.8°, 80.4 ± 4.8°, and 99.7 ± 2.4°. Figure 6 shows the powder X-ray diffractogram. The elementary cell was triclinic with the following crystallographic parameters: $a = 1.27$ nm, $b = 2.02$ nm, $c = 2.22$ nm, $\alpha = 120.44 \pm 0.73°$, $\beta = 101.9 \pm 1.3°$, $\gamma = 68.2 \pm 6.2°$, $\sigma = 41.8°$, $\tau = 35.3°$. The elementary cell had 18 molecules. Each half cell had three DTAOH and six H_2DP molecules. Even though the cell increased to maintain the repetitivity of the structure through the entire crystal, the triclinic form was retained.

Samples with different H_2DP:DTAOH proportions also gave tabular crystals when they were evaporated between slides. At proportions above 1:0.5, the crystals showed extinction patches (Fig. 7). This optical inhomogeneity indicates an inhomogeneous composition of the crystals. The angles between edges were 117.3 ± 2.5°, 63.9 ± 3.1° and 32.3° in samples whose proportion was 1:1, and 96.4 ± 3.2° and 112.2 ± 5.9°, and in some cases 80.99 ± 0.56°, and 99.7° in samples with a proportion of 1:1.5. Fast desiccation of samples with proportions above 1:2 did not give crystals but a semisolid gel. Slow desiccation gave crystals similar to that of the other samples. All crystals showed oblique extinction.

The constancy in habit of crystals when the H_2DP:DTAOH ratio changed (including angles between edges and the kind of extinction) suggested that in general, their structure was similar, i.e., they were triclinic. We did not study the crystals with H_2DP:DTAOH > 1:0.5 because of their inhomogeneity and the DTAOH decomposition, since the results might be strongly dependent on the zone of the crystals in which the sample was extracted, and on the age of crystals.

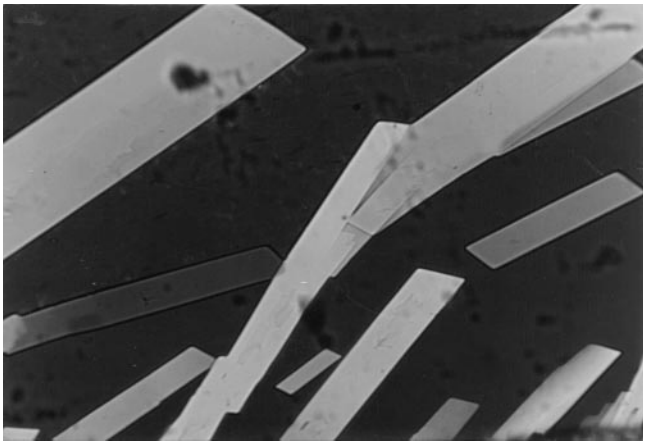

Fig. 5 Crystals obtained by slow peripheral evaporation between slides, 1:0.5 H_2DP:DTAOH sample, crossed polaroids and selenite retardation plate intercalated

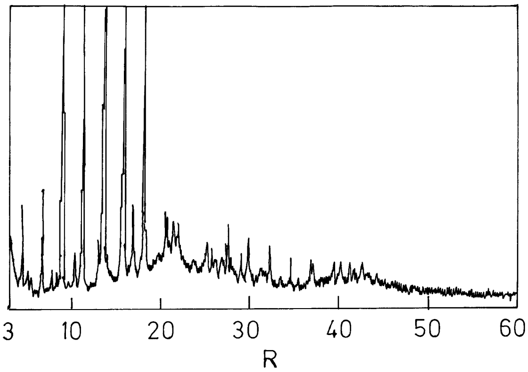

Fig. 6 Powder X-ray diffractogram, 1:0.5 H_2DP:DTAOH sample anhydrous crystals

Pseudotricomponent system

In mixtures of cationic and anionic surfactants in water, the cationic salts (DTA.HDP and DTA_2DP) may be viewed as phase compounds that exist in the ternary system, but alternatively may be viewed as a separate component [34]. We took the former point of view, because the system was closed and all catanionic salts were formed by the reaction of the added acid and base.

The best studied zone of the tricomponent system was that of low concentrations, in which several domains were determined. Figures 1 and 2 showed this zone, mainly (but not fully) extracted from previous papers [22, 23, 35]. At very low concentrations (Fig. 1) there were two zones of molecular solutions, one DTAOH-rich solution and another H_2DP-rich. Among these zones and that of the micellar solution there was a region in which

Fig. 7 1:0.5 H_2DP:DTAOH crystals showing extinction patches. Crossed polaroids X 200

small aggregates were fully ionized (no counterions were attached to the aggregates). This last region extended to fairly high concentrations in the DTAOH-rich region of the diagram.

In Figs. 2 and 3 the partially delimited zones of existence of solid and liquid crystals may be seen. These phases were situated in the H_2DP-rich side of the triangle. In H_2O-rich systems, the residue was composed of a gel-like mixture of waxy solid and liquid crystal. When solid and liquid phases coexisted in equilibrium, the composition of these phases was different. As an example, the sample with $H_2DP:DTAOH$ 1:1.5 had a supernatant with the ratio 1:1.16 and a residue (a gel-like mixture of waxy crystals and lamellar mesophase) with total proportion 1:0.61. This may be the cause of inhomogeneities in the crystals formed by evaporation: first, H_2DP-rich crystals precipitated, and then, they acted as crystallization nuclei for the remaining liquid, which became more and more rich in DTAOH. The final compositions were too rich in DTAOH, and became unstable to desiccation, giving rise to the decomposition of the base. This explains why we were unable to obtain crystals with $H_2DP:DTAOH >$ 1:0.5 without partial decomposition of the DTAOH in the sample.

The question arose if dilute solutions of DTAOH decompose with time. We titrated samples of the same DTAOH solution at different times along two weeks without significant differences in the results.

H_2DP only gives lamellar mesophases with water [21], but the inclusion of DTAOH gradually leads the system to the formation of other kinds of mesophases. As an example, peripheral evaporation between slides of a sample with $H_2DP:DTAOH = 1:0.5$ gave a sequence (from dilute to concentrate regions) micellar solution – hexagonal mesophase with coarse mosaic texture – cubic mesophase – lamellar mesophase with fine mosaic texture and some positive units. The 1:1 sample showed only hexagonal mesophase textures by fast desiccation, but peripheral dilution of the same (fastly) dried sample with water showed mielyn figures, which are typical of lamellar mesophase. When the total sequence of quasi-equilibrium was established, the lamellar domain was relatively narrow, and it was followed by a cubic and then an hexagonal mesophase, and then an isotropic micellar solution. The 1:1.5 and 1:2 samples showed the sequence of crystals – cubic – hexagonal – isotropic solution by peripheral dilution. No lamellar mesophase could be detected. The sample with $H_2DP:DTAOH \geq 1:2.5$ only showed hexagonal and isotropic (cubic and micellar) phases.

Summarizing the effect of the changes in the composition of the mesophases which appeared in the catanionic system, it may be said that the inclusion of DTAOH first allowed the formation of lamellar mesophase below 30° (pure H_2DP with water only forms this phase above 30 °C). When increasing the proportion of DTAOH, new cubic and hexagonal mesophases appeared. The increase of DTAOH proportion gradually increased the domain of existence of the hexagonal mesophase, whereas that of lamellar mesophase was gradually reduced and disappeared at $H_2DP:DTAOH \geq 1:1.5$. Lamellar mesophases in H_2DP–water systems have their polar interfaces strongly structured by hydrogen bonds between $-PO_3H_2$ groups [21]. The neutralization of these groups by the $-N(CH_3)_3^+$ polar heads, giving $-PO_3H^-$ and $-PO_3^=$ groups, and the separation between these by the intercalation of trimethylammonium groups caused the gradual reduction in hydrogen bonds between phosphonate groups. Both phosphonate and trimethylammonium groups have approximately the same volume, and if they are not hydrogen-bonded, the convex curvature of the interphase is favoured to form cubic and hexagonal mesophases, similar to the behavior of alkyltrimethylammonium halides.

As was already pointed out, fast desiccation of a small sample of DTAOH solution showed cubic and hexagonal textures. Since this surfactant decomposes when dehydrated, it may not be sure that the observed textures corresponded to pure DTAOH. However, the contamination with decomposition products might not be very high in the first minutes after desiccation, and the sequence hexagonal – cubic – micellar solution which was seen by peripheral dilution is probably that of the pure DTAOH–water system.

We could not determine the limits of existence of the various mesophases in the system because of the above difficulties. Therefore, in Figs. 2 and 3 the limits of the biphase regions were suggested with dashed lines, and the zone of existence of liquid crystals was drawn without any indication of the kind of mesophase.

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