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Phase Studies of a Mixed Trimethyltetradecylammonium Bromide–Hexadecyltrimethylammonium Bromide System

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A phase studies was carried out on the phase equilibria in the three component systems of single and binary mixture (1 : 1) of trimethyltetradecylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (HTAB) with water and 1-hexanol at 30 °C. The phases were separated by repeated centrifugation. The birefringence was observed under cross polarizers and their consistency, texture and optical pattern were examined under the polarizing microscope. On the basis of the results obtained, a phase diagram was drawn that consists of two phases of isotropic solution and two mesophases. Results also showed a larger region for the lamellar liquid crystalline in the mixed system. The critical micelle concentration for the micellar region of the mixture was found at 0.0014 mol dm^{-3}.

Mixtures of surfactants are not only exhibiting superior properties as compared to only singular surfactant but also can be produced at a relatively lower cost. The superiority in performance for mixture of similar or dissimilar surfactant is largely attributed to the synergistic interaction amongst the mixture molecules.[1] The formation of aggregated structure i.e. mixed micelles at a critical concentration, cmc can be totally different in solutions containing only single surfactant. Antagonistic interactions, however, do occur in some mixtures resulting in higher cmc value than those of single component.[2,3] It is therefore imperative to study the phase equilibria of this mixtures as it forms the basis for the different behaviour or interactions encountered by them.

Phase equilibria, systems of water/surfactant/co-surfactant, are by now well known and a great number of articles[4] are available. Nevertheless, it is however important to note that such studies involved mainly single component of surfactant. With the much interest in mixed surfactants of late,[5—8] it is thought that such studies in binary mixture of surfactants might be intriguing and of some importance. The surfactants used i.e. TTAB and CTAB have been studied quite extensively by several workers as a single component system.[9—11] Data on their mixtures is however still lacking.

The results of these studies are illustrated by means of triangle diagram of the usual type. The final phase diagram takes into account of all the results and the location of the various phases. The optical pattern of the lamellar liquid crystalline phase and the formation of mixed micelle will also be presented.

Experimental

Materials. The TTAB, HTAB, and 1-hexanol were obtained from Sigma, Merck, and Fluka, respectively, and were used without further purification. The high purity of surfactants was confirmed by the absence of any detectable minimum in the measured surface tension, γ versus surfactant concentration curves of the aqueous solutions of each surfactant. Doubly distilled water was used.

Determination of Phase Equilibria. The phase equilibria were determined by titration to turbidity for the solution part of the system. The samples were then vortexed for mixing purposes. The samples were allowed to equilibrate in a water bath kept at 30 °C. The phases were separated by means of centrifugation at high speed.

Surface Tension Measurement. A Fisher (model 215) surface tension analyzer was used for measuring the interfacial tension. The samples of 50 ml with various concentration of surfactants were prepared and ran at a speed range of 0.1 in min^{-1}. The temperature was controlled at 30±0.01°C.

Photomicroscopy. A Will (model V 365) polarizing microscope, attached to an Olympus camera (model OM-2) was used for photomicroscopy. Precleaned microscope slides and covers were selected, and then buffed with lint-free tissue immediately before use. A small sample was transferred from the sample tube onto the glass slide and sheared between the cover and was left for a few minutes for equilibration. The appearance of the sample was then observed

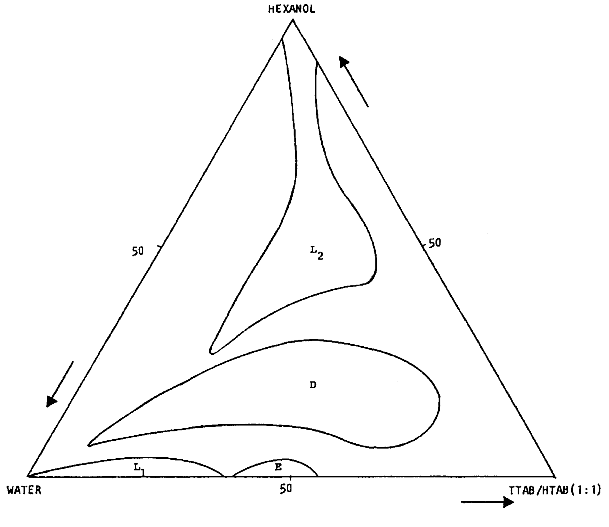

Fig. 1. Phase equilibria at 30 °C of mixture of TTAB and HTAB (1 : 1)/water/1-hexanol.

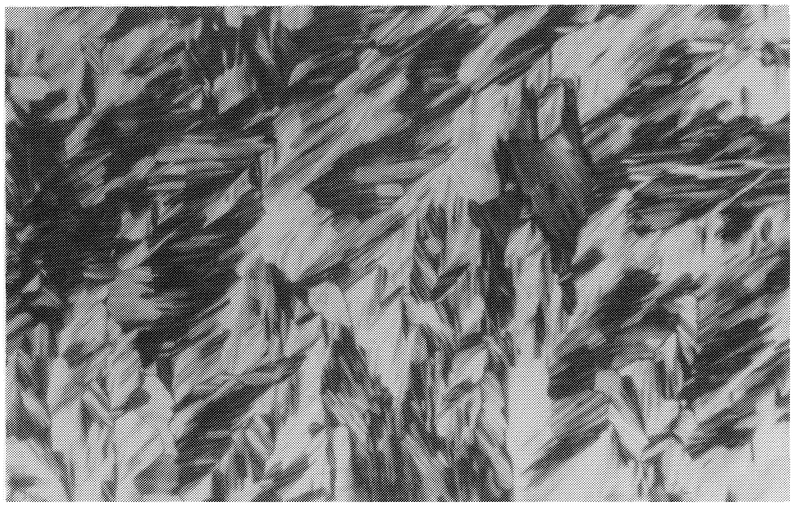

Fig. 2. Optical pattern of typical hexagonal liquid crystalline structure at 50% by weight of both water and mixed surfactant.

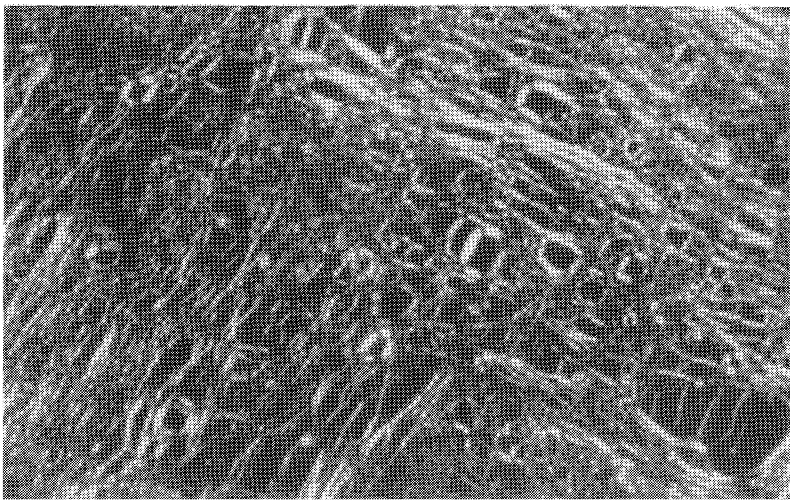

Fig. 3. Optical pattern of typical lamellar liquid crystalline structure at a representative region of phase D.

between cross polarizers. A representative region was then selected and photographed at a magnification of 100.

Results and Discussion

Result showed the existence of two region of homogeneous isotropic solution as in Fig. 1. One in the part with high aqueous content and the other with high alcohol content. These regions are designated as L_1 and L_2 respectively.[4)] The limits of these areas were determined by titrating to turbidity with a smallest amount of one component to the homogeneous solution.

In the part of the system with a higher content of TTAB and HTAB, liquid crystalline phases occurred. In the alcohol-free state, the mixed surfactant formed hexagonal liquid crystalline, E with water content ranging from 45 to 60 percent. The phase was identified by the rodlike projection pattern when observed under the polarizing microscope as in Fig. 2. This phase maintains its structure up to about 5 weight percent of hexanol.

In the central part of the system another phase was observed and when looked under the polarizing microscope exhibited a typical lamellar liquid crystalline, D pattern as in Fig. 3. This region has a minimum water content of 13 percent and a maximum of 85 percent. When the results of these observation were entered in the phase diagram, Fig. 1 was obtained. The results is a typical three component system employing water/surfactant/co-surfactant components. It is however interesting when comparison are made with their pure components system as in Fig. 4. The results obtained for the single surfactant system is consistent with work done by Ekwall.[4)] From the phase equilibria (Fig. 4), it is obvious there exist some differences, even though not to a large extent, in the respectives region especially the boundaries of each region.

Graph of weight fraction of water versus weight fraction of surfactant is plotted to facilitate comparison between the two systems. Figure 5 shows the region for the micellar solution, L_1 of the system. The region between 0.65 to 1.0 surfactant fraction is shifted upward about 0.5 weight fraction of water for the mixed surfactant indicating a lower amount of 1-hexanol is solubilized in the micellar region. The critical micelle concentration, cmc of the mixed surfactants of 0.0014

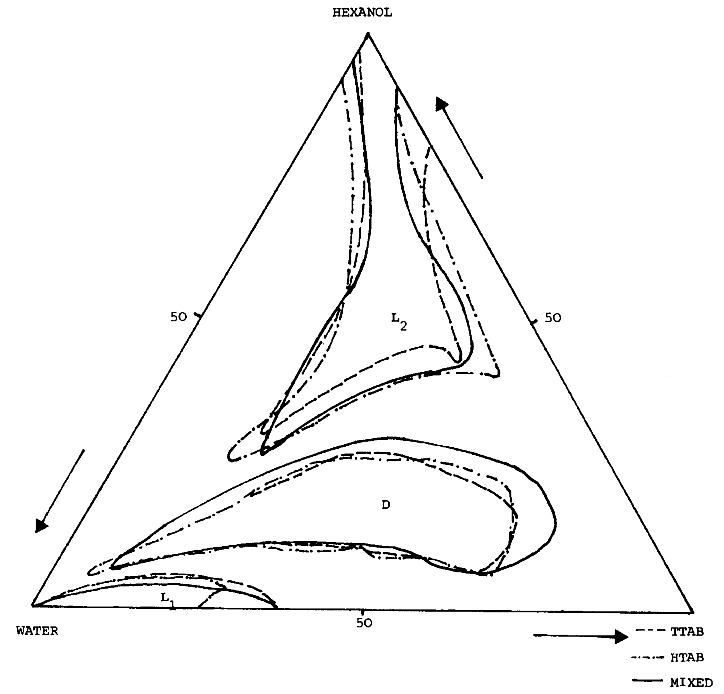

Fig. 4. Phase equilibria at 30 °C of: — water/TTAB-HTAB (1 : 1)/1-hexanol, --- water/TTAB/1-hexanol, –•– water/HTAB/1-hexanol.

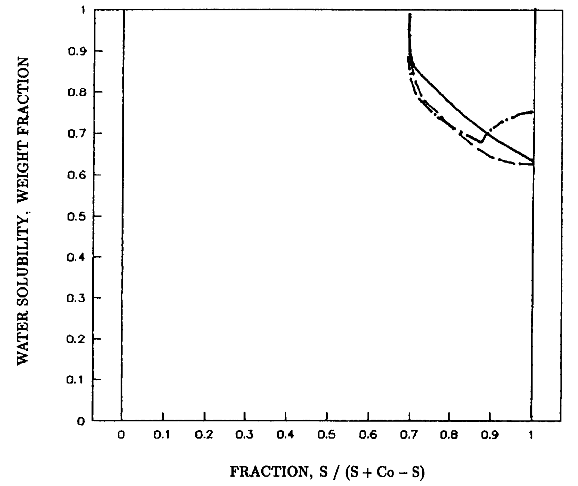

Fig. 5. The solubility of water (weight fraction) in TTAB : HTAB(S)/1-hexanol(Co–S) (—), TTAB-(S)/1-hexanol(Co–S) (---), and HTAB(S)/1-hexanol-(Co–S) (–•–) mixture (weight fraction) for the micellar, L₁ phase.

mol dm^{-3} is found to be intermediate of that of the cmc of the single component (Fig. 6). This is attributed to the formation of mixed micelle by the TTAB and HTAB molecules thus altering the property of the singular component and changes the cmc value. A formal calculation, adopting the mixed micelle theory,[6] for the theoretical value based on equation

$$\frac{1}{\mathrm{CMC}} = \frac{\alpha}{\mathrm{CMC}_1} + \frac{(1-\alpha)}{\mathrm{CMC}_2} \tag{1}$$

where α is the mole fraction of surfactant 1, gives a value

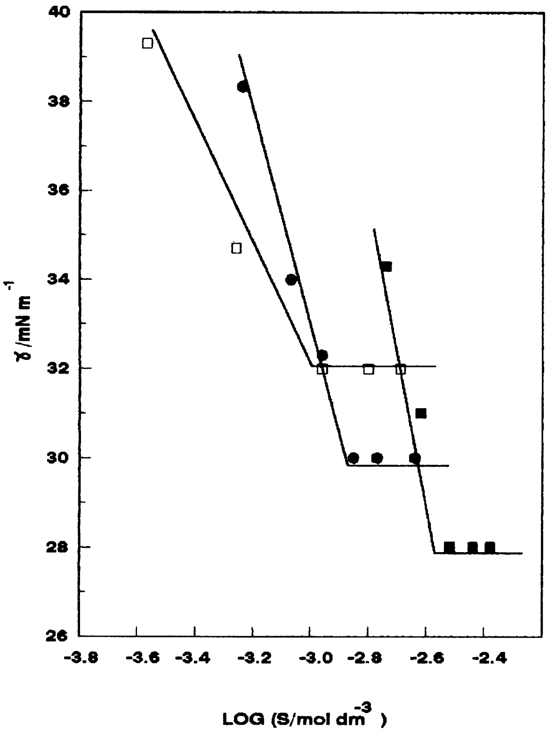

Fig. 6. The surface tension versus logarithm of concentration; □ HTAB, ■ TTAB, and ● TTAB : HTAB (1 : 1) systems.

of 0.0015 mol dm^{-3} which indicates a possible ideal behavior for this mixture.

For the inverse micellar phase, L_2 (Fig. 7), studies show that the existence of a maximum and minimum

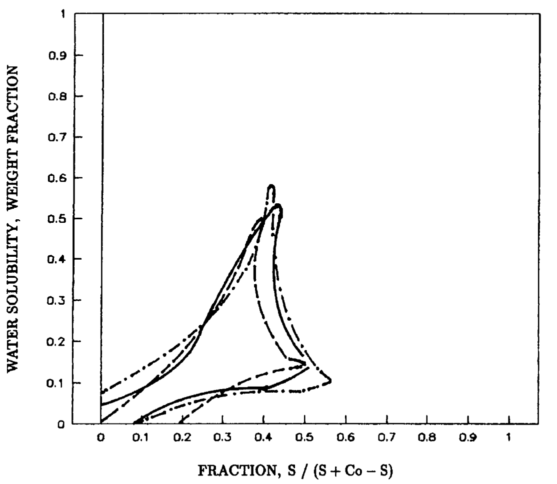

Fig. 7. The solubility of water (weight fraction) in TTAB : HTAB(S)/1-hexanol(Co–S) (—), TTAB-(S)/1-hexanol(Co–S) (- - -), and HTAB(S)/1-hexanol-(Co–S) (– • –) mixture (weight fraction) for the inverse micellar, L_2 phase.

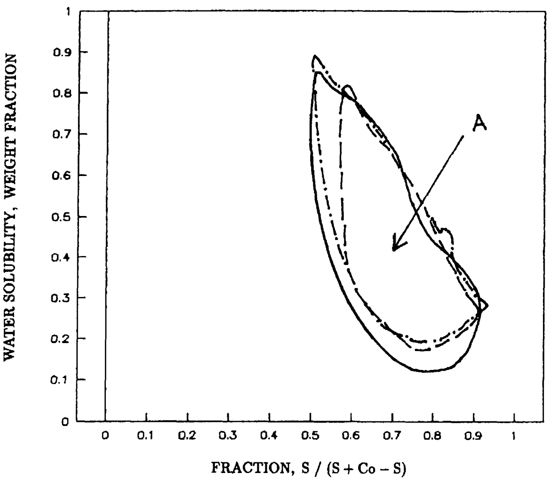

Fig. 8. The solubility of water (weight fraction) in TTAB : HTAB(S)/1-hexanol(Co–S) (—), TTAB-(S)/1-hexanol(Co–S) (- - -), and HTAB(S)/1-hexanol-(Co–S) (– • –) mixture (weight fraction) for the lamellar liquid crystalline, D mesophase.

water solubility region at about 0.4 and 0.5 surfactant fraction respectively. The maximum water for the mixture is found at 52 percent, intermediate of its constituent component, but a slight shift to the right side. The minimum water is however the same with TTAB that is 15 percent water, an increase of 5 percent if compared to HTAB. The region also exhibits a higher solubility of water between 0.25 to 0.35 surfactant fraction for the mixture.

Figure 8 shows a typical lamellar liquid crystalline, D located in the middle part of the diagram. The figure shows an extended region for the mixed surfactant at the lower part of the water solubility region between 45 to 90 percent surfactant fraction. The maximum water is again intermediate of its constituent single component, but a reduction of about 10 weight percent of surfactant if compared to TTAB. The minimum water intake is found at 13 percent whereas 17 and 18 percent for the single component. The extended region for the whole phase shows a good indication of a better stability for the mixed system.

In order to illustrate the arrangement of the surfactant molecules in these system and the presence of lamellar liquid crystal, a representative region A, (Fig. 8) consisting of 40, 70, and 30 percent water, surfactant and cosurfactant respectively is selected and observed the dislocation of the optical pattern under the polarizing microscope.[12] The TTAB and HTAB at this composition shows an optical pattern typical of a lamellar liquid crystal structure with maltese crosses interchelating with oily streaks and oily streaks respectively as in Fig. 9. While the mixture containing the mixed surfactant exhibits another typical lamellar liquid crystal with striated pattern (Fig. 9). The results gave evidence of the possible molecular arrangement of the surfactant molecules in the lamellar liquid crystal. The presence of TTAB and HTAB molecules obviously created a temporary disorder in the molecular arrangement and changes the optical pattern of the whole organization, but still maintaining the overall lamellar liquid crystalline structure. It is important to note here that this is purely a speculation as this method is not precise in making such conclusion.

Comparison for the hexagonal liquid crystalline region is however omitted as we are mainly interested in the lamellar state. Therefore such an investigation and comparison would have insignificant relevance for further examination and is considered unwarranted.

The above results demonstrate that there are indeed differences in a mixed surfactant system. This is largely due to the formation of a mixed micelle containing amphiphilic molecules of different hydrocarbon chain length which in this case C-14 and C-16, an increase of about 0.504 nm in length. The stability of the system is also increased as shown by the increase of the lamellar liquid crystalline region. Further investigation will be reported on the stability of this system by use of light scattering and low-angle X-ray diffraction and will be published elsewhere. Nevertheless, it is however important to realize that the phase equilibria studies presented gives a quantitative distinction between single and mixed surfactant systems.

Summary

The studies disclose indeed there exist differences in mixed surfactant against their consituent single component. These changes are largely attributed to the formation of mixed micelle which exhibit synergistic interaction among the mixed molecules, resulting in higher stability of the system.

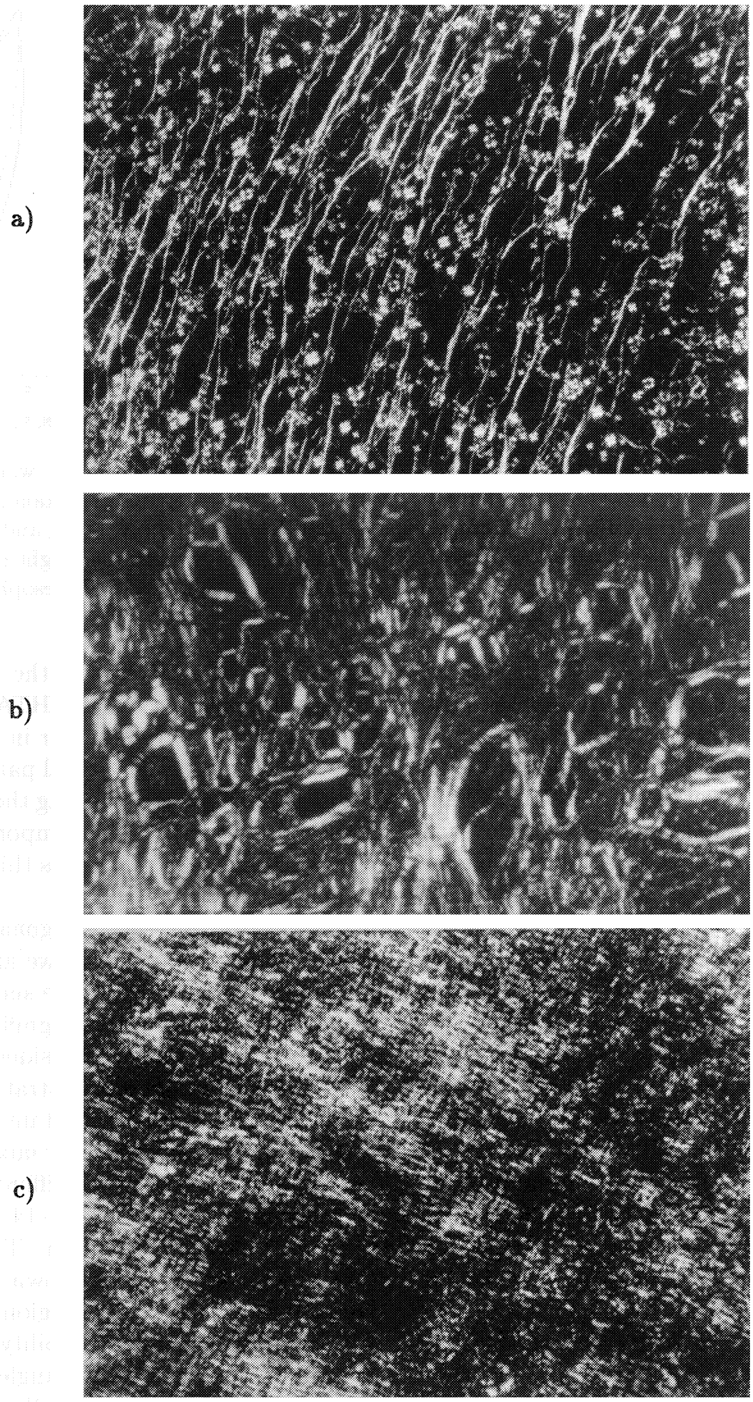

Fig. 9. Optical pattern of 40, 70, and 30 percent water, surfactant and cosurfactant shows: a) maltese crosses in oily streaks for TTAB, b) oily streaks for HTAB, c) striated pattern for TTAB : HTAB mixture.

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