

PHASE DIAGRAMS OF A NONIONIC SURFACTANT/ OCTAN-1-OL/WATER IN THE PRESENCE OF ANIONIC AND CATIONIC SURFACTANTS

**Hamdan Suhaimi*, Lim Wen Huei, Zaizi Desa, Anuar Kassim,
Dzulkefly Kuang and Faujan B.H. Ahmad**

Surfactant Research Group
Chemistry Department
Faculty of Science and Environmental Studies
Universiti Pertanian Malaysia, 43400 Serdang,
Selangor Darul Ehsan, Malaysia

RINGKASAN: *Gambarajah fasa dengan komponen ketiga yang mengandungi polioksietilina 10 lauril eter ($C_{12}E_{10}$) bercampur dengan tetradeciltrimetilammonium bromida (TTAB) dan dengan natrium dodesil sulfat (SDS) telah disediakan pada 30°C. Keputusan menunjukkan kehadiran dua fasa larutan isotropik dan dua mesofasa. Keputusan juga menunjukkan kawasan hablur cecair lamela yang lebih besar dalam kedua-dua sistem campuran berbanding dengan sistem $C_{12}E_{10}$ tulen. Kelarutan air pada kepekatan oktan-1-ol yang tinggi adalah lebih banyak dalam SDS iaitu surfaktan yang bercas negatif daripada surfaktan bercas positif yang mengandungi atom nitrogen TTAB.*

ABSTRACT: Phase diagrams with a third component consisting of polyoxyethylene 10 lauryl ether ($C_{12}E_{10}$) mixed with tetradecyltrimethylammonium bromide (TTAB) and with sodium dodecyl sulphate (SDS) were prepared at 30°C. Results showed the presence of two phases of isotropic solution and two mesophases. The results also showed a larger region for the lamellar liquid crystalline in both of the mixed system when compared to the pure $C_{12}E_{10}$ system. The solubilization of water at higher concentration of octan-1-ol was greater in SDS, i.e., the negatively charged surfactant, than the positively charged surfactant containing a nitrogen atom TTAB.

KEYWORDS: Mixed surfactant, detergents, liquid crystal, phase diagrams.

* To whom all correspondence should be addressed.

INTRODUCTION

Mixtures of nonionic and anionic surfactants are an important aspect in the formulation of many detergents. Recently, Friberg and Chiu (1992) have reported the phase diagrams of water and anionic surfactant combined with nonionic surfactant. Information on the phase behaviour of water and cationic surfactant combined with nonionic surfactant is, however, not tractable from the above results; an obvious impediment to the progress in the field and especially in toiletries. Furthermore, it has been pointed out that positively charged or nitrogen-containing surfactants give a high solubilization of water at higher cosurfactant content (Venable and Viox, 1984).

In our previous study (Hamdan and Lim, 1994), we have found that mixed surfactant systems, which contain both nonionic and ionic surfactants, possess many interesting properties which are quite different from those of systems where only nonionic or the ionic surfactant is present. The experimental results showed that at 30°C, the systems of a mixed nonionic-ionic surfactant and water deviated from ideality with a nonideal parameter of -7.0. This merits further investigation of all the phase regions in systems consisting of mixed nonionic-ionic surfactant/cosurfactant/water in order to better understand their behaviour.

With that, we present the phase diagrams of a nonionic surfactant polyoxyethylene 10 lauryl ether, C₁₂E₁₀ mixed with a cationic surfactant, tetradecyltrimethylammonium bromide, TTAB and with an anionic surfactant, sodium dodecyl sulphate, SDS, each at equal molar ratio. Similar method from a previous contribution (Sagitani and Friberg, 1980; 1983) is adopted in this study.

MATERIALS AND METHODS

Materials

The tetradecyltrimethylammonium bromide >99% (Sigma), sodium dodecyl sulphate >99.5% (Mallinckrodt), polyoxyethylene 10 lauryl ether >97% (Sigma) and octan-1-ol 99% (Merck) were used without further purification. Doubly distilled and deionized water was used.

Determination of Phase Diagram

The phase diagrams 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 5000 rpm. The boundaries between the turbid to clear transitions were visually estimated. The presence of liquid crystalline mesophase in the sample was

detected with crossed polarizers and identified under a microscope with a polarized light by comparing the textures with those of photomicrographs in the literature (Rosevear, 1954). A Will (model V 365) polarizing microscope, attached to an Olympus camera (model OM-2) was used for photomicroscopy.

RESULTS AND DISCUSSION

$C_{12}E_{10}$ /Octan-1-ol/Water

Figure 1 shows the solubility region for the ternary system of $C_{12}E_{10}$ /octan-1-ol/water. Two regions of homogenous isotropic solutions were observed, one emanating from the part with high aqueous content and the other, extending from the water free axis. These regions are designated, following Ekwall's (1975) nomenclature, as L_1 and L_2 , respectively. The aqueous micellar region, L_1 , was able to solubilize up to about 5 percent weight of octan-1-ol. On the other hand, L_2 showed a complete solubilization of the nonionic surfactant in octan-1-ol. The resulting alcoholic solution was able to solubilize about 35 percent of water at a weight ratio of octan-1-ol and $C_{12}E_{10}$ of almost unity. The solubility area was found to be narrower at higher octan-1-ol content.

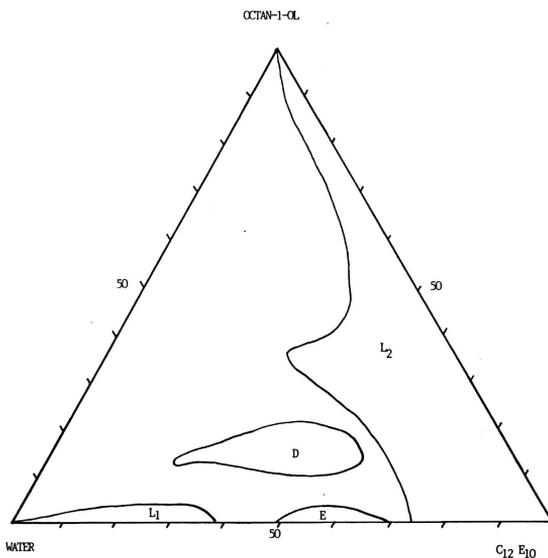


Figure 1. Ternary phase diagram of polyoxyethylene 10 lauryl ether ($C_{12}E_{10}$)/octan-1-ol/water at 30°C.

In the area of the system with a higher content of $C_{12}E_{10}$, liquid crystalline mesophases were observed. In the octan-1-ol-free axis and low content of octan-1-ol, the surfactant

formed a hexagonal liquid crystalline, E. Observation under polarized light confirmed the structure of E by exhibiting a “fan-like texture” (Rosevear, 1954). At the central part of the system, another mesophase was detected and when observed under the polarized light microscope exhibited “mosaic textures” of typical lamellar liquid crystalline, D. The results obtained are consistent with previous workers (Mitchell *et al.*, 1983).

(C₁₂E₁₀ + TTAB)/Octan-1-ol/Water

Figure 2 shows an equivalent data but for system with mixed C₁₂E₁₀ and TTAB at equal molar ratio. The phase diagram again shows the existence of two regions of homogenous isotropic solutions and two mesophases. L₁, emanating from the water apex in the same fashion as in the pure C₁₂E₁₀ system. On the contrary, L₂ shows a noticeable transition by requiring a minimum amount of water for it to form. This region extends towards the octan-1-ol free axis to about 24 percent of octan-1-ol. Octan-1-ol was not significantly soluble in water. By combining with approximately equal weight of the mixed C₁₂E₁₀-TTAB its solubility in water is increased to 27 percent by weight (Figure 2). The water solubility in the mixed system was, however, lower than in the corresponding C₁₂E₁₀ system.

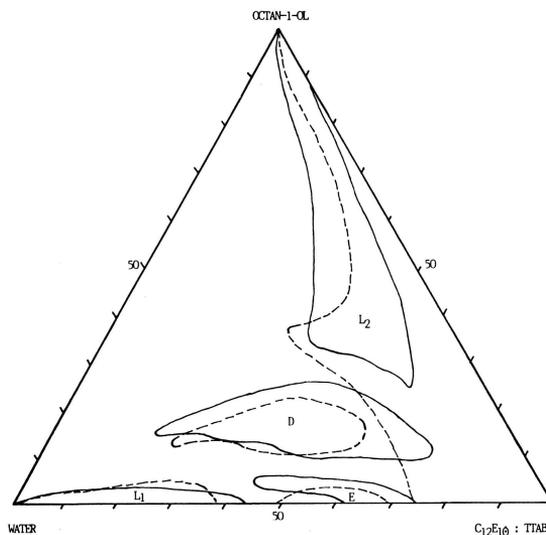


Figure 2. System of Figure 1 (broken lines) but with a third component consisting of an equimolar ratio of C₁₂E₁₀ and tetradecyltrimethylammonium bromide (TTAB).

At mixed surfactant concentrations in excess of those in the aqueous micellar solution, L₁, a liquid crystalline mesophase, E, was observed with a structure of hexagonally arranged

cylinders. This mesophase maintained its structure up to about 5 weight percent of octan-1-ol and projected towards the water apex to about 54 percent of water. Another liquid crystal region was observed at the intermediate part of the system and exhibited textures under polarized light, typical of a lamellar liquid crystalline, D. This region has a minimum water content of 17 percent and a maximum of 66 percent. The content of octan-1-ol ranged from 9 to 24 weight percent.

$(C_{12}E_{10} + SDS)/\text{Octan-1-ol/Water}$

Figure 3 shows the equivalent phase diagram upon replacing some of the $C_{12}E_{10}$ with SDS at equimolar amount. Once again, the phase diagram was characteristic of such systems with an aqueous micellar solution, L_1 , a liquid crystal array of cylinders, E, a lamellar liquid crystal, D and a octan-1-ol solution with inverse micelle, L_2 . The continuous octan-1-ol solution, L_2 region required a minimum amount of water ranging from 2 to 10 percent water.

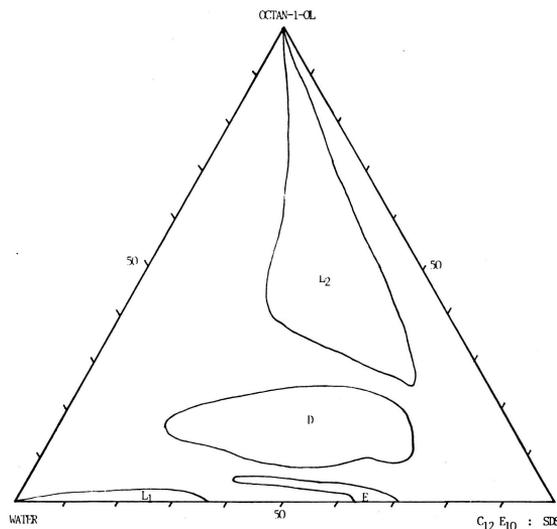


Figure 3. Ternary phase diagram of octan-1-ol, water and a third component consisting of an equimolar ratio of $C_{12}E_{10}$ and sodium dodecyl sulphate (SDS).

The hexagonal liquid crystal exhibited the same trend by requiring a minimum amount of octan-1-ol for its formation between 40 and 60 water content at the alcohol free axis. The amount of octan-1-ol solubilized was increased to 10 percent. The lamellar liquid crystalline, D region for the $C_{12}E_{10}$ -SDS was significantly increased compared to those of $C_{12}E_{10}$ system. This region has a lower minimum water content of 20 percent and a maximum of 64 percent. The alcohol contents range from 7 to 25 weight percent.

Comparison between the Phase Diagrams of Cationic and Anionic Surfactants

As mentioned earlier, it has been suggested that a combination of an alcohol with a nitrogen-containing (cationic) surfactant may be highly desirable to achieve a high solubilization of water at high alcohol content (Venable & Viox, 1984). In order to see whether there is a distinction of the aforementioned phenomenon between cationic and anionic surfactants, the L_2 region of the above phase diagrams are superimposed as shown in Figure 4. The L_2 region where the cationic surfactant (TTAB) is solubilized, was found to require a lesser amount of water than the anionic counterpart. However, the overall solubility region, and especially at higher content of octan-1-ol, is smaller than the corresponding anionic surfactant (SDS).

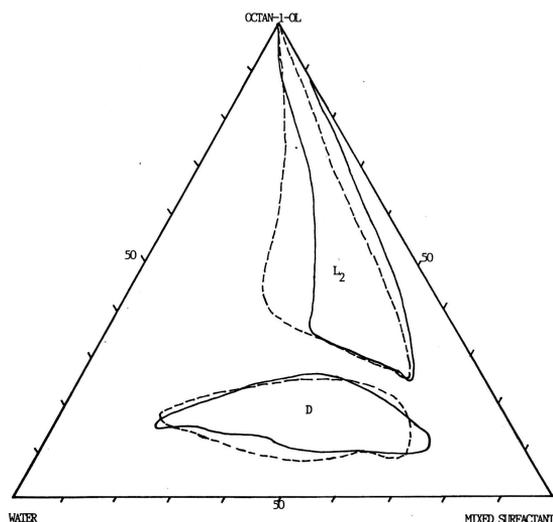


Figure 4. The solubility area in systems of water, octan-1-ol and a third component consisting of: (—), $C_{12}E_{10}$ -TTAB; (----), $C_{12}E_{10}$ -SDS for the L_2 and the lamellar liquid crystalline, D region.

The difference in the influence of the cationic and anionic surfactants on the stability of the systems (Friberg *et al.*, 1969) can be obtained from the comparison of the lamellar region for the $C_{12}E_{10}$ -TTAB and $C_{12}E_{10}$ -SDS systems (Figure 4). It is observed that the differences are modest which implied an almost equal stability for both of the mixed systems or a slightly higher stability for the SDS counterpart. Another important observation from this comparison is the shift in the surfactant ratio to achieve the maximum water solubility. It was observed that the surfactant fraction is lower for the mixed $C_{12}E_{10}$ -SDS

system. Obviously, fewer SDS molecules are needed to orient themselves in a lamellar structure with the C₁₂E₁₀ and octan-1-ol molecules. This resulting stable structure is sufficient to anchor the water molecules in its polar region.

CONCLUSION

The phase diagrams provided insight pertaining to the association phenomenon of the mixed molecules which is largely attributed to the formation of a mixed micelle containing amphiphilic molecules of different charges. In addition, the stability of the mixed surfactant systems is increased as illustrated by the extension in the solubility area of the lamellar liquid crystalline region. However, the positively charged surfactant failed to show its superior solubilization characteristics at higher alcohol content. Therefore, a specific combination of certain types of surfactant cannot be treated individually but rather should be considered in terms of the systems behaviour.

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