Study on aqueous two-phase systems of the mixture SDS/CTAB surfactants

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Abstract: The phenomenon of two dilute aqueous phases composed of sodium dodecylsulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) was investigated under various conditions such as concentrations and molar ratios of the two surfactants, the addition of sodium chloride and temperature. Vesicles formation was found in the both phases by TEM image.

Keywords: aqueous surfactant two-phase (ASTP); cationic-anionic surfactants; vesicles

Introduction

Aqueous two-phase systems were introduced as a separation method for biomolecules in 1950's (Albertsson, 1956; 1958), and the studies about this were reported in recent years (Wormuth, 1991; Yin, 2002; Miao, 2002). In general, the two-phase system can be formed by combing two "incompatible" polymer in water. Above a certain critical concentration, the system separates into two water-rich phases (near 95%, w/w). The phase behavior of aqueous two-phase system consisting of polymer and non-ionic surfactant has been examined (Zhao, 1998; Piculell, 1992; Clegg, 1994). A very similar, an aqueous surfactant-two phase (ASTP), was also observed with the aqueous mixture of cation/anionic surfactant, where the solution demix into two macroscopic phases. One of phase is enriched in the anionic surfactant and the other is depleted (Xiao, 2001; Zhao, 1996; Zhu, 1999). Two kinds of different ASTP systems formed when cationic and anionic surfactants are in excess, respectively called ASTP-C, and ASTP-A, rather dilute surfactant aqueous solutions. The coexistence of two phases contains large amount of water, more than 95% both in general. When the cationic or anionic surfactant is excessive in a mixture of two different surfactants, the phase system is named "cationic aqueous two phase (ASTP-C)" or "anionic aqueous two phase (ASTP-A)" (Zhao, 1998). If there are vesicles in both phases, the system is named "vesicle two phase" (Piculell, 1992).

The exploitation of two-phase systems for separation, purification and concentration of biomolecules is gaining important in biotechnology. Aqueous polymer two-phase (APPT) systems have been applied in analysis and separation of chemical and biochemical materials. In this paper, the formation and some properties of ASTP with the mixture surfactants of SDS/CTAB are reported.

1 Experimental

Chemicals: CTAB (A. R.) is obtained from Shanghai Yuanji Limited Company; SDS (A. R.) was the product of Chinese Zhengya Chemical Plant of Suzhou. Sodium chloride (A. R.) was purchased from the Chemical Reagent Factory of Guangzhou. And water used was twice distilled.

Preparation of the system: The sample solutions are of various total surfactants concentrations and molar ratios. After surfactants mixed, proper amount of water was added in a stopper burette, then shook the burette, and kept them under a constant temperature.

Image observation: TEM image observations were carried out of above system by Hitachih-300 Electron Microscopy and Olympus Nicol Prism Microscopy, and the density were measured by pycnometer.

2 Results and discussion

2.1 Formation of ASTP systems

Almost all the mixed cationic-anionic surfactant solutions which were studied in our laboratory could form ASTP, it might be a common feature for such mixture systems. In our experiment, it has been shown that at equimolar of anionic/cationic surfactants, the aqueous solution of mixtures surfactant forms precipitate and with the increase of one composition content, the aqueous becomes clear. It was reported that the ASTP systems were formed at a narrow molar ratio region around the equimolar (Albertsson, 1958). In this work, ASTP was observed in the two molar ratio regions at SDS/CTAB from 6:1 to 2:1 and from 1:2 to 1:6 in the SDS/CTAB system. Figs. 1-3 show the variation of the total concentration against the molar ratio of SDS/CTAB in the region between 6:1 to 2:1 and 1:2 to 1:6 at various temperatures: 30°C, 40°C, 50°C. Fig. 1a and 1b illustrate that the total surfactant concentration increases abruptly and reaches a maximum at 1:3 and 4:1 of molar ratio of SDS/CTAB respectively. No ASTP occurs when temperature reach 40°C and 50°C under the molar ratio of SDS/CTAB from 1:2 to 1:6.

It is a common understanding that the aqueous mixtures of cationic/anionic bring out a precipitate above the CMC (Albertsson, 1956). ASTP-A and ASTP-C systems turn to milky homogeneous solutions at lower concentrations. But with the increase of concentration, ASTP-A would become clear, on the other hand, the multiphase separation appears in the aqueous mixture systems with excessive cationic surfactant. In this paper, we just discuss the systems of two phases.

2.2 Appearance and structure of ASTP systems

In the ASTP-C systems, the upper phases are clear and transparent, and the lower phases are opalescent solutions. There is an interesting phenomenon: firstly, the upper phases are milky, the lower phases are clear and transparent; however, after several days, the appearances of the upper phase and the lower phase alternate. At last, all the ASTP-C systems would disappear in about one week, the clear and transparent homogeneous solution come into being.

On the contrary, in ASTP-A systems, the lower phases are clear and transparent. But the appearances of upper phase vary with concentration and temperature. For example, most of upper phases are milky, but the upper phase of SDS/CTAB system with total surfactant concentration 0.1 mol/L is like oil at 40°C.

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The structure of two phases was measured by the Nicol Prism Microscope. All the two phases of ASTP systems can refract light. It implies that there exist orderly aggregates which have unsymmetrical structure in the system. The image is shown in Fig. 4.

Vesicle formation was also observed in both phases, the typical TEM images by using the negative-staining method are shown in Fig. 5 and Fig. 6. Drops of the sample solution were applied to carbon-coated Cu grids and dried, then, a drop of the agent was added as the staining agent. Extra droplet was instantly removed by using a filter paper.

2.3 The stability of ASTP systems

In our experiment, it was also shown that the separation time of two liquid phases for ASTP-A systems was much shorter than that for ASTP-C systems. The former, the separation time was from about 3 min to 2 h, and the latter, it lasted several hours, even tens hours. It could be noted that the rate of phase separation increased with increasing concentration.

The two phases of an ASTP system are completely immiscible, just like an oil-water system. When the two phases were shook up, the system turned turbid firstly, and then hold for a while, they would separate into two phases again, and the volume ratio of the ASTP newly formed was the same as the former.

At the respective temperature, the ASTP-A systems are very stable, no obvious change of their appearances could be observed even though standing for a month. While the ASTP-C systems would turn into a clear and transparent homogeneous from two-phase system after about one week.

The temperature affects the formation of ASTP systems
deeply. All ASTP systems turned turbid when the temperature decreased. While the temperature increased, the ASTP-C systems and the ASTP-A systems at low concentration became clear and transparent, but the ASTP-A systems at high concentration came into multiphase. When NaCl with 0.01 mol/L was added in the ASTP system, the ASTP-C system disappeared faster than without NaCl. In the ASTP-A system, the volume of upper phase reduced, the volume of lower phase increased.

2.4 Densities of ASTP Systems

Obviously the density of lower phase is much heavier than that of upper phase. Fig. 8 shows the densities of lower phases of SDS/CTAB at 30°C as a function of the total concentration for molar ratio 5:1 and 6:1 respectively. Fig. 7 shows that the density increases with the increasing NaCl concentration.

![Graph showing density as a function of total surfactant concentration.](image)

Due to the upper phases of ASTP-A systems very sticky, viscosity measurements could not be in progress exactly and perfectly by pycnometer.

It was reported that the ASTP systems are formed at the concentrations much higher than the CMC (Piculell, 1992). But in the range of ASTP-C systems formed here, the concentration of anionic surfactants would be lower than CMC. Table 1 shows the water content at different temperatures and molar ratio when the two dilute aqueous phases formed and disappeared. It is also known that the water content of ASTP is more than 95% (Zhu, 1999), but our results shown in Table 1 displayed the situation in ASTP systems. The water content are different at the mechanism of vesicle formation and characteristic phase behaviors for these systems can be discussed simply as follows: The equimolar mixed cationic and anionic surfactants formed precipitate will solubilize with surfactant in excess respectively. When cationic or anionic surfactant with a high amount of molar ratio, vesicle aggregations incorporated and partition, which results in two-phase forming.

3 Conclusions

The aqueous mixtures of SDS/CTAB surfactants form ASTP systems. When cationic or anionic surfactants are in excess, two kinds of ASTP systems (ASTP-C and ASTP-A) are formed. ASTP systems region varied with total surfactant concentration, molar ratio of anionic/cationic surfactant and temperature.

In appearance, the upper phases of ASTP-C systems are water-like phase, and the lower phase is milky. In ASTP-A system, the lower phases are clear and transparent and the upper phases are opaque, and very sticky. The two phases are completely immiscible, and they both contained vesicles.

### Table 1. The water content of ASTP-A

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>Water content</th>
<th>2:01 (SDS/CTAB)</th>
<th>3:01 (SDS/CTAB)</th>
<th>4:01 (SDS/CTAB)</th>
<th>5:01 (SDS/CTAB)</th>
<th>6:01 (SDS/CTAB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>F.D.</td>
<td>F.D.</td>
<td>F.D.</td>
<td>F.D.</td>
<td>F.D.</td>
<td>F.D.</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td>0.9908</td>
<td>0.8223</td>
<td>0.9939</td>
<td>0.8039</td>
</tr>
<tr>
<td>40</td>
<td>0.9814</td>
<td>0.8405</td>
<td>0.9878</td>
<td>0.8432</td>
<td>0.9879</td>
<td>0.8910</td>
</tr>
<tr>
<td>50</td>
<td>0.9813</td>
<td>0.8400</td>
<td>0.9877</td>
<td>0.8212</td>
<td>0.9879</td>
<td>0.8027</td>
</tr>
</tbody>
</table>

Notes: - means no ASTP system formed; F.D.: forming or disappearing of "F" (forming), "D"(disappearing)

ASTP systems may be taken for a new partition system to be used in the partitioning and analysis of biomaterials.

The conclusions above maybe give us some hints that finer conditions for other uses, such as environmental analysis, are that concentration of surfactants forming aqueous two-phase systems below 30°C is more clear, and more anion surfactants ratio is favorable for forming aqueous two-phase.

### References


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