An Unusual Variation of Surface Tension with Concentration of Mixed Cationic-anionic Surfactants

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There are two platforms in the surface tension vs. concentration curve (γ-lg$C$ curve) of cationic-anionic surfactant mixtures. The first platform is the same as that of common surfactant solution, and the cross point is the CMC. After the CMC, the mixtures form precipitate. At higher concentration, the mixtures form homogeneous solution again. When the mixtures form homogeneous solution at high concentration, surface tension increases with concentration, then becomes constant. So the γ-lg$C$ curve exhibits the second platform. The surface tension at the second platform increases by increasing molar ratio of two surfactants and polar group size of surfactants, and decreases with adding inorganic salts.

Keywords   Surfactants, cationic-anionic surfactants, catanionic surfactants, surface tension

Introduction

It is a common understanding that surface tension of surfactant aqueous solution almost maintains constant after surfactant concentration reaches CMC (critical micelle concentration).[1] However, for the aqueous mixtures of cationic-anionic surfactants, the situation is quite different. In a previous paper,[2] we reported that there are three concentration regions for mixed cationic-anionic surfactants, that is, the mixtures form homogeneous solutions at very low concentration. Above the CMC, the mixtures usually form precipitate or become turbid.[3] With the further increase of concentration, at relatively high concentration (much higher than CMC, but still rather dilute), the mixtures form homogeneous solutions again. In this paper, the surface tension of aqueous mixtures at the three concentration regions was measured. An unusual variation of surface tension with concentration was observed.

Experimental

$C_{12}H_{25}N(CH_3)_3Br$ ($C_{12}NM$), $C_{12}H_{25}N(C_2H_5)_3Br$ ($C_{12}NE$), $C_{12}H_{25}N(C_3H_7)_3Br$ ($C_{12}NP$), $C_{12}H_{25}N(C_4H_9)_3Br$ ($C_{12}NB$), and $C_{12}H_{25}SO_4Na$ (SDS) were prepared and purified in the same way as that in Ref. 4.

No surface tension minima were found for surfactants, which implies that no surface active impurities exist in them.[1]

Surface tension was measured by drop volume method.[1]

Results and discussion

Fig. 1 shows variation of surface tension with concentration. It is shown that there are two platforms in the surface tension vs. concentration curve (γ-lg$C$ curve). The first platform is the same as that of common surfactant solution and the turning point is the CMC. After the CMC, cationic-anionic surfactant mixtures usually form precipitate or become turbid, which was shown in dotted line in γ-lg$C$ curve. With the further increase of concentration, mixtures form homogeneous solution again (in this paper, we called this homogeneous solution as hyper-homogeneous solution). When the mixtures form hyper-homogeneous solution, surface tension increases with concentration, then becomes constant. So the γ-lg$C$ curve exhibits the second platform.
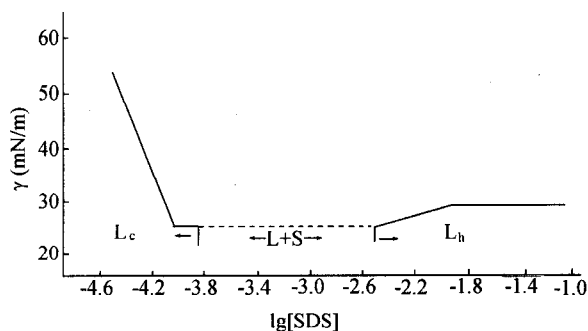
Fig. 1   Surface tension of C_{12}NE-SDS (molar ratio: 1 : 5) (25 ℃) (L_c: dilute homogeneous solution, L_h: hyper-homogeneous solution, L + S: Liquid + solid).

The surface tension in the second platform may be expressed as γ_{csc}. We investigated the effects of molar ratio of two surfactants, polar group size of cationic surfactants and inorganic salts on γ_{csc}.

Table 1 shows the effect of molar ratio of cationic surfactant to anionic surfactant in bulk solution on γ_{csc}.

Table 1   Effect of molar ratio of C_{12}NE to SDS in bulk solution on γ_{csc} (20 ℃)

Molar ratio	CMC (mol/L)	γ_{CMC} (mN/m)	γ_{csc} (mN/m)
1:0	4.2×10^{3}	39.2	
1:2	1.3×10^{4}	24.5	27.0
1:5	1.5×10^{4}	24.8	28.2
2:1	1.4×10^{4}	24.8	28.1
5:1	1.5×10^{4}	25.1	29.1
0:1	2.4×10^{3}	35.0	

Note: CMC is expressed in total concentration of cationic-anionic surfactants.

It can be seen from Table 1 that CMC and γ_{CMC} of mixed cationic-anionic surfactants almost keep constant, but γ_{csc} increases with increasing excess components.

It can also be seen that when C_{12}NE is in excess, the γ_{csc} values are higher than the γ_{csc} value when SDS is in excess.

Table 2 shows the effect of inorganic salts on γ_{csc}.

It can be seen that, when adding inorganic salts, CMC and γ_{CMC} do not change, but γ_{csc} decreases with increasing concentration of inorganic salts.

Table 3 shows the effect of sizes of ionic head groups of cationic surfactant on γ_{csc}.

It can be seen that, from C_{12}NM-SDS to C_{12}NB-SDS, γ_{CMC} and γ_{csc} increase.

Table 2   Effect of NaBr in bulk solution on γ_{csc} of C_{12}NE-SDS (20 ℃)

C_{NaBr} (mol/L)	CMC (mol/L)	γ_{CMC} (mN/m)	γ_{csc} (mN/m)
0	1.5×10^{4}	25.1	29.1
0.01	1.5×10^{4}	25.1	28.5
0.03	1.5×10^{4}	25.0	27.8
0.05	1.5×10^{4}	25.2	27.2

Note: molar ratio of C_{12}NE to SDS in bulk solution is 5:1.

Table 3   Effect of sizes of ionic head groups of cationic surfactant on γ_{csc} (20 ℃)[a]

Mixed surfactant	CMC (mol/L)	γ_{CMC} (mN/m)	γ_{csc} (mN/m)
C_{12}NM-SDS	1.9×10^{4} [b]	23.4[b]	26.0
C_{12}NE-SDS	1.5×10^{4}	25.0	29.1
C_{12}NP-SDS	1.3×10^{4}	25.5	30.5
C_{12}NB-SDS	1.5×10^{4}	26.3	31.3

[a] molar ratio of cationic surfactants to anionic surfactants in bulk solution is 5:1. [b] measured at (60 ℃).

It has been known that surface tension is decided by the composition of surface adsorbed layer.[1-4] The closer the arrangement of surfactant molecules at the surface, the lower the surface tension. There is strong electrostatic interaction between opposite charged ionic head groups for cationic-anionic surfactant mixtures, which makes surfactant molecules arrange more closely at the surface. As a result, the aqueous mixtures of cationic-anionic surfactants have lower surface tension than that of single cationic or anionic surfactants (as shown in Table 1).

Because of the strong electrostatic interaction between opposite charged ionic head groups, at low concentration, both the surface layer and micelles of cationic-anionic surfactant mixtures are close to equimolar although the bulk solution is nonequimolar (at relatively large molar ratio range).[3-5] This can be demonstrated by the fact that CMC and γ_{CMC} (surface tension at CMC) does not change when adding inorganic salts,[3-5] which is shown in Table 2.

The equimolar mixed micelles are uncharged, they grow to large size and precipitate out. With increase of total concentration of mixed surfactants, the monomer concentration of excess surfactants increases. It was shown that, when the monomer concentration of excess surfactants reaches it's CMC, precipitate of cationic-anionic surfactants can be solubilized,[7] which induces formation of the hyper-homogeneous solution.

We have showed that, at high concentration, the

composition of micelles would gradually be close to that of bulk solution with increasing concentration.[6] So for hyper-homogeneous solution, the micelles and surface layer would be charged if the bulk solution is nonequimolarly mixed. Because of the electrostatic repulsion between the same charged ionic head groups of the excess component, the surface tension will increase. When the composition of surface layer is the same as that of bulk solution, the surface tension will not change with concentration. So the second platform appears.

As mentioned above, at low concentration, both the surface layer and micelles of cationic-anionic surfactant mixtures are close to equimolar although the bulk solution is nonequimolar (at relatively large molar ratio range), so CMC and γ_{CMC} almost keep constant at relatively large molar ratio range. However, for hyper-homogeneous solution, the surface layer is charged, and the charge of surface layer is related to the amount of excess components. γ_{csc} is effected by the charge of surface layer. The more the charge of surface layer, the higher the γ_{csc}. On the basis of this, we can explain the fact that γ_{csc} increases with increasing excess components (Table 1).

It is well known that γ_{CMC} of single ionic surfactants decreases when inorganic salts are added because the dielectric layer of charged surface is depressed.[1] Since the surface layer of hyper-homogeneous solution is charged, the dielectric layer of charged surface can also be depressed by inorganic salts. So γ_{csc} decreases with increasing concentration of inorganic salts, as shown in Table 2. It is understandable that CMC and γ_{CMC} of

mixed cationic-anionic surfactants would not change when adding inorganic salts because micelles and surface layer are uncharged at low concentration.

In the previous paper,[4] we discussed the effect of sizes of ionic head groups of cationic surfactant on γ_{CMC} of cationic-anionic surfactants. It was shown that, with increase of ionic head group size (from C_{12}NM-SDS to C_{12}NB-SDS), electrostatic interaction between oppositely charged ionic head groups was reduced, so γ_{CMC} increased. In the same way, we can explain why γ_{csc} increases with increase of the ionic head group size (Table 3). We can also explain the fact that when C_{12}NE is in excess, the γ_{csc} values are higher than the γ_{csc} value when SDS is in excess because the ionic head group of C_{12}NE is larger than that of SDS (Table 1).

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