Model of Rod-to-sphere Transition of the Mixed Micelles of Cationic-Anionic Surfactants

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It has been known that[1][2], with the increase of surfactant concentration, the micelles of mixed cationic-anionic surfactants undergo a transition from sphere to rod at dilute concentrations. The sphere-to-rod transition of micelles and the coacervation or flocculation of long rodlike micelles have been used successfully to explain the occurrence of precipitation or turbidity of the aqueous mixtures of cationic-anionic surfactants at dilute concentrations (usually slightly above CMC)[1,2]. It has been found that with the continuing increase of surfactant concentration, the aqueous mixtures of cationic-anionic surfactants with precipitate or turbidity turn into homogeneous transparent solutions at high concentrations [2,3,4]. This unusual phenomenon can't be explained by the model of sphere-to-rod transition of mixed micelles. In the present paper, we propose the model of rod-to-sphere transition of micelles. In this model, it is thought that, at relative high concentration, with the continuing increase of surfactant concentration, the micelles of mixed cationic-anionic surfactants undergo a transition from long to short rod, and then to spherical shape.

1　Mechanism of Rod-to-sphere Transition of Micelles

In this paper, we use a simplified model to interpret the process of rod-to-sphere transition.

At first, we discuss the nonequimolar mixed systems of cationic-anionic surfactants. For such systems, at low concentrations, micelles are nearly uncharged (the molar ratio of two surfactants in micelle is nearly 1:1). With the increase of concentration, the molar ratio of the two surfactants in the micelle will deviate from 1:1 and approach that in the solution gradually. As a result, the micelles will become charged. Because of the electrostatic repulsion between the polar groups of like electric charge, it is more stable for the surfactant molecules which are in excess in a micelle to adopt radiation-like arrangement than parallel arrangement in micelles, which induces a long rodlike micelle to split into several short

rodlike micelles. In this way, more surfactant molecules which are in excess in a micelle will be in the semi-ball position of a rodlike micelle and adopt radiation-like arrangement. With the further increase of concentration, the short rodlike micelles will be not stable as well, and will split into shorter rod. We can imagine that the last result of rodlike micelle splitting would be the spheric micelle. It is only in the spheric micelle that the distance between the polar groups of like electric charge is the largest, and the energy of the micelle is the lowest.

As can be seen, the rod-to-sphere transition of a micelle at high concentration and the sphere-to-rod transition of a micelle at low concentration are two opposing processes, but their essences are identical, both are energy-advantageous. The driving force of sphere-to-rod transition is the electrostatic attraction between unlike electric charge of the polar groups in a equimolar mixed micelle. The driving force of rod-to-sphere transition is the electrostatic repulsion between the polar groups of like electric charge in a nonequimolar mixed micelle.

For equimolar mixed systems, the surfactant molecules in unit volume of a micelle increase with increasing surfactant concentration. Therefore, at high concentration, surfactant molecules will take stagger arrangement (two kinds of polar groups are in different planes respectively). Such arrangement is not energy-advantageous: (1) the surface of a micelle seems to be covered by the polar groups of like charge which is analogous to micellar surface charged; (2) the polar groups of like charge being in the same plane get relatively close to each other, so there will be certain electrostatic repulsion between them, and there is the tendency that the polar groups of like charge are away from each other as far as possible. Therefore, such equimolar mixing micelles, like nonequimolar mixing micelles above-mentioned, will also undergo a transition from long to short rod, and then to spherical shape at high surfactant concentrations.

2 Experiment Evidences of Rod-to-sphere Transition of Micelles

It is a very strongly evidence for the rod-to-sphere transition of micelles that the cationic-anionic surfactant mixtures with precipitate or turbidity turn into homogeneous transparent solutions with increasing surfactant concentration. Besides, we performed light-scattering and rheological property measurements of such mixtures to illustrate the rod-to-sphere transition of micelles.

2.1 Dynamic Light-Scattering Measurement

Table 1 shows the micellar sizes of the mixtures of dodecyltriethylammonium bromide ($C_{12}NE$) and sodium dodecylsulfate ($C_{12}S$) determined by dynamic light-scattering. As can be seen, the micellar size decreases with increasing surfactant concentration at higher concentration region. It should be pointed out that, since the micelles in this system are charged highly, the strong interaction between charged micelles makes the formula by which the micelles size calculated [1,2] not to fit this system quite well, the values in table 1 should be regarded as the "apparent" micelle sizes. At any rate, the data in Table 1

do clearly show the relative size change during the rod(or lamella)-to-sphere transition of micelles.

2.2 Rheological Property Measurement

Table 2 shows the rheological properties of the aqueous mixtures of $C_{12}NE$ and $C_{12}S$. Our studies have shown that[3,6], at the boundary of the mediate concentration region where mixtures form heterogeneous solutions and the high concentration region where mixtures form homogeneous transparent solutions, some solutions exhibit viscoelasticity and negative thixotropy; with the increase of concentration, viscoelasticity and negative thixotropy vanish gradually and the solutions become clear like water. We have shown that[3,6] viscoelasticity and negative thixotropy are deduced by "giant micelles", such as very long rodlike and large lamellar micelles. So we can deduce qualitatively that the micelles are very large at the above-mentioned boundary, and become small with the increase of concentration.

We can see that the dependence of the apparent viscosity upon the surfactant concentration at high concentration region is very peculiar: the viscosity initially decreases with increasing concentration, passes through a minimum, and then increases again. That viscosity decreases with increasing concentration can be considered as a result of the decrease of micellar size with the increase of surfactant concentration. The increasing of viscosity with concentration above 0.01 mol·dm^{-3} can be considered as a result of micellar concentration fluctuation because the increasing extent of viscosity is small, which may be demonstrated by the Einstein viscosity equation with the correction for solvation effect[5]

$$\eta = \eta_0[1 + 2.5(1 + 3\Delta R/R)\phi] \tag{1}$$

Table 1 The micellar sizes of mixed $C_{12}NE$-$C_{12}S$ solutions (molar ratio: $[C_{12}NE]/[C_{12}S]$=1:5, 25 ℃)

c_{Tot}/mol·dm^{-3}	d/ Å
3.5×10^{-3}	1263.4
4.0×10^{-3}	186.8
5.0×10^{-3}	113.7
6.0×10^{-3}	70.9
8.0×10^{-3}	65.4
1.0×10^{-2}	49.0
5.0×10^{-2}	21.0
1.0×10^{-1}	20.0

Table 2 The rheological properties of mixed $C_{12}NE$-$C_{12}S$ solutions[a] (molar ratio: $[C_{12}NE]/[C_{12}S]$=1: 5,25 ℃)

c_{Tot}/mol·L^{-1}	$10^3\eta$/Pa·s	viscoelasticity	Negative thixotropy
0.10	1.07	no	no
0.05	0.98	no	no
0.01	0.90	no	no
8.0×10^{-3}	0.88	no	no
6.0×10^{-3}	0.96	yes	yes
5.0×10^{-3}	1.03	yes	yes
4.0×10^{-3}	1.06	yes	yes
3.0×10^{-3} [b]	--	--	--

[a] For the negative thixotropy system, the viscosity is that at a time $t=0$ (minimum viscosity)
[b] Precipitation or turbidity occurs below 3.0×10^{-3}mol·dm^{-3}

Where η and η_0 are the viscosity of solution and solvent respectively, ϕ is the volume

fraction of micelles, and ΔR is the increment of the micellar radius (R) due to solvation. Here we regarded the micelles as spheres when the total concentration of surfactants is above 0.01mol·dm^{-3}, which can be seen from table 1. The ionic micelles are highly solvated and then the $\Delta R/R$ value would be appreciably large. Given $\Delta R/R=1$, equation (1) becomes

$$\eta = \eta_0(1 + 10\phi) \tag{2}$$

When the total concentration of surfactants goes up from 0.05mol·dm^{-3} to 0.1mol·dm^{-3}, the viscosity calculated by equation (2) increases from 0.983×10^{-3} to 1.037×10^{-3} Pa·s at 25 ℃, if the volume fractions are 0.01 and 0.02 for 0.05 and 0.1mol·dm^{-3} solutions, respectively. These values are consistent quite well with that in Table 2.

To sum up, it can be concluded that, at high concentration, micellar size decrease with increasing surfactant concentration.

It should be point out that, before the rod-sphere transition there is usually a transition from lamellar to rodlike micelles with the increase of concentration in some micellar solutions, such as the mixtures shown in table 1-2. Around 4.0×10^{-3} mol·dm^{-3}, they are lamellar micellar solutions, which might be proved by their negative thixotropy[5]. With the continuous increase of surfactant concentration from 3.5×10^{-3} to 1.0×10^{-1} mol·dm^{-3}, the micelles undergo a transition from lamellar to rod, and then to spherical shape.

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正、负离子表面活性剂混合胶团棒 - 球转变模型

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摘要 提出正、负离子表面活性剂混合胶团的棒-球转变模型. 认为在溶液浓度较高时, 随浓度进一步增大, 正、负离子表面活性剂混合胶团经历了一个长棒变短、短棒变为球状的转变过程. 并通过混合胶团溶液的相行为、光散射及流变性质测定等加以证实.

关键词: 正负离子表面活性剂,   胶团,   棒 - 球转变