Negative Thixotropy in the Aqueous Mixtures of Cationic-anionic Surfactants

Zhao Guoxi Xiao Jinxin

(Department of Chemistry, Peking University, Beijing 100871)

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Negative thixotropy is a rheological phenomenon defined as a reversible increase in viscosity with time when a liquid flows at constant shear rate. This phenomenon was found only in some polymers^[1] and very few dispersing systems^[2] in the past. In the present paper, we report the negative thixotropy found in some aqueous mixtures of cationic-anionic surfactants. Fig.1 shows the region in which the aqueous mixtures of dodecyltriethylammonium bromide ($C_{12}NE$) and sodium dodecylsulfate ($C_{12}S$) display negative thixotropy.

1 Features of Negative Thixotropy Solutions

(1) For the mixtures of $C_{12}NE$ and $C_{12}S$, negative thixotropy was observed only in the nonequimolar mixtures with $C_{12}S$ in excess.

(2) The systems displaying negative thixotropy were in the region between the mediate and high concentrations (It has been shown that^[3] the mixtures form transparent homogeneous solutions at very dilute and high concentrations, and heterogeneous solutions at mediate concentrations).

(3) Some negative thixotropy solutions were transparent and homogeneous, such as the mixed solution of $C_{12}NE$ and $C_{12}S$ with the total concentration of $0.01\text{mol}\cdot\text{dm}^{-3}$ and molar ratio of 1:2, some were opalescent or turbid, such as the mixed solution of $C_{12}NE$ and $C_{12}S$ with the total concentration of $0.05\text{mol}\cdot\text{dm}^{-3}$ and the molar ratio of 1:1.5. These opalescent or turbid solutions were usually quite stable, no obvious change of their appearances could be observed on standing for a long time.

(4) The solutions displaying negative thixotropy were usually viscoelastic.

Fig.1 The region of negative thixotropy solutions of $C_{12}NE$ - $C_{12}S$ (25 °C)

2 Possible Mechanism of Negative Thixotropy

Up to now, there has been no theory of general agreement to explain the negative thixotropy of different systems. For the aqueous mixtures of cationic-anionic surfactants, we thought that the negative thixotropy might be due to the existence of lamellar micelles with certain sizes.

When the solution flows, it is the sliding of bilayers in lamellar micelles with each other that leads to low viscosity of the solution. With the increase of shearing time, the parallel arrangement of bilayers would be gradually destroyed and become disordered, and consequently, the viscosity increases with time. When the flow stops, the bilayers would return to the parallel arrangement gradually, which leads to the decrease of viscosity with time.

In lamellar micelles, most of the surfactant molecules assume parallel arrangement form. In order to form lamellar micelles, it should satisfy two conditions: the proper charge density on the micellar surface and the small polar groups of surfactants, especially the former one. Too low a charge density induces precipitation or turbidity because of the coacervation or flocculation between micelles. Too high a charge density induces the formation of rodlike or spheric micelles. The charge density on the micellar surface is decided mainly by surfactant concentration and the molar ratio of two kinds of surfactants, it increases with the increase of surfactant concentration and the amount of excess of component. On this ground, we might demonstrated the fact that negative thixotropy was observed only on the boundary between the mediate concentration region in which precipitation or turbidity occurs and the high concentration region in which the mixtures form transparent homogeneous solutions^[3], and the total concentration forming lamellar micelles decreases with the increase of the amount of $C_{12}S$.

Since the polar group of $C_{12}NE$ is larger than that of $C_{12}S$, the increase of the amount of $C_{12}NE$ is analogous to that of the average size of polar groups, so it is not easy to form lamellar micelles when $C_{12}NE$ is in excess. Conversely, with $C_{12}S$ in excess, the mixtures form lamellar micelles more easily. This might be the reason that negative thixotropy was observed only in the mixtures with $C_{12}S$ in excess.

This mechanism of negative thixotropy could be proved by the fact that the lamellar liquid crystal could be observed by polarizing microscope in some negative thixotropy solutions which were on standing for a long time, such as the mixture of $C_{12}NE$ and $C_{12}S$

with the total concentration of $0.04\text{mol}\cdot\text{dm}^{-3}$ and the molar ratio of 1:1.5. The lamellar liquid crystal could be regard as the result of growth of lamellar micelles.

Reference

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正、负离子表面活性剂混合体系的负触变性

赵国玺 肖进新

(北京大学化学系, 北京 100871)

摘要 报导正、负离子表面活性剂混合体系的负触变性(负触变性通常只存在于某些高分子溶液及极少数粗分散体系中). 总结出负触变性的形成规律, 提出了负触变性的形成机理, 认为负触变性的产生是由于溶液中存在具有一定大小的层状胶团, 当溶液流动时, 层状胶团双层之间的平行排列方式被打乱, 导致溶液粘度随时间而增加.

关键词: 正、负离子表面活性剂, 负触变性