Studies on the micellization and intermicellar interaction of CTAB in dilute solution

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Association of amphiphilic surfactants forms various microstructures such as spherical micelle, wormlike micelle, vesicle, hexagonal liquid crystal and lamellar liquid crystal [1]. Among this associate colloidal structure, viscoelastic wormlike micelles have attracted much interest in recent years [2–10]. The entangled wormlike micelles increase the viscosity of the fluids like polymer. Under shear, these wormlike micelles can break and re-form. Hence, it was sometime called 'living polymer'. Applications of wormlike micelles have been found in different areas from oil fields, drag reducing agents in district heating systems, home and personal care products to templates for asymmetric and aligned nanostructures [11–15].

Among cationic, zwitterionic and anionic type surfactants, the cationic surfactant is most widely studied [2]. The cationic surfactant, Cetyltrimethylammonium bromide (CTAB), is an amphiphile used very commonly. The basics of its micellization and related behaviors have been essentially studied [6,8–10,16– 18]. However, there are a limited number of studies dedicate to investigating the viscosity of CTAB solutions in terms of micellar structure and intermicellar interaction [8,18]. It is well known that organic counterions such as sodium salicylate (NaSal) are more efficient in promoting wormlike micelle formation than weakly binding inorganic salt. Salicylate ions not only adsorb on a Stern layer of micelle surface but also penetrate into micelles, which is of different from simple inorganic salts such as KBr [19]. The excess adsorption and penetration of salicylate ions, however, induce negative net charge of micelles. Simultaneously micelle size decreases to small micelles because of electrostatic repulsion in "anionic" micelles. This suggests that the micellar structure and intermicellar interaction of CTAB is greatly dependent on the ratio of CTAB/NaSal in dilute solution. Ubbelohde viscometer is efficient in determine the viscosity of dilute solution. Different from the flow time measurement carried out by Ostwald viscometer, the flow time of the liquid carried out by Ubbelohde viscometer is independent of the volume of the liquid in viscometer. As a result, the flow time and thus the viscosity of solutions with a series of concentrations can be achieved by adding the solvent into the viscometer successively. Based on this characteristic of the Ubbelohde viscometer, we present here a general procedure for investigating the influence of CTAB/NaSal ratios upon micellization and intermicellar interaction of CTAB in dilute Solution. In our approach, the aqueous NaSal solution, instead of the distilled water, is selected as the solvent, similar to the technique developed to study polymer-polymer interactions in ternary solutions [20, 21]. The relative viscosity of CTAB with a series of concentrations in aqueous NaSal solution, therefore, can be achieved by adding NaSal solution into the viscometer successively. Obviously the ratios of CTAB/NaSal in solution will also change successively with dilution. This suggests that the process of dilution is essentially the process by which the influence of CTAB/NaSal ratios upon the viscosity of CTAB

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solutions can be 'scanned' and investigated. Application of this approach results in a better understanding of micellization and intermicellar interaction of CTAB in dilute solutions. For comparison, the viscosity of CTAB in aqueous KBr solutions is also measured.

The surfactant CTAB was purchased from Sigma Co. and was used as received. The salt NaSal and KBr are A.R. grade products of Shanghai reagent Co., China. The relative viscosity of CTAB in either NaSal solution or KBr solution at 30 °C were carried out by Ubbelohde viscometer with the capillary diameter of 0.55 mm that was placed in a thermostatically controlled bath with a precision of ±0.02 °C. The flow time of either NaSal solution or KBr solution, namely t_0, was measured using a thoroughly cleaned viscometer at first. After drying the viscometer, the flow time of CTAB with a series of concentrations in either NaSal solution or KBr solution, namely t, was achieved by adding the either NaSal solution or KBr solution into the viscometer successively. The relative viscosity was calculated from the equation

$$\eta_r = \frac{t}{t_0} \tag{1}$$

It should be noted that application of Equation 1 was practical in case that the measuring conditions corresponding to either t or t_0 would be just the same [22].

The relative viscosity of CTAB in NaSal solution 30 °C is shown in Fig. 1. The initial concentration of CTAB is 100 mM. It can be seen that the relative viscosity of CTAB exhibits the double-peak behavior in the presence of NaSal solution with the concentration of either 5.0 mM or 3.4 mM for NaSal, but disappearsin 10 mM NaSal solution. To make the discussion easier to be understood, the viscosity behavior of CTAB in 10 mM NaSal solution is studied at first. From Fig. 1 it can be seen that the relative viscosity of CTAB decreases slightly with the successive adding of NaSal solution into the viscometer, reaches minimum when the concentration of CTAB is approximately 40 mM. With

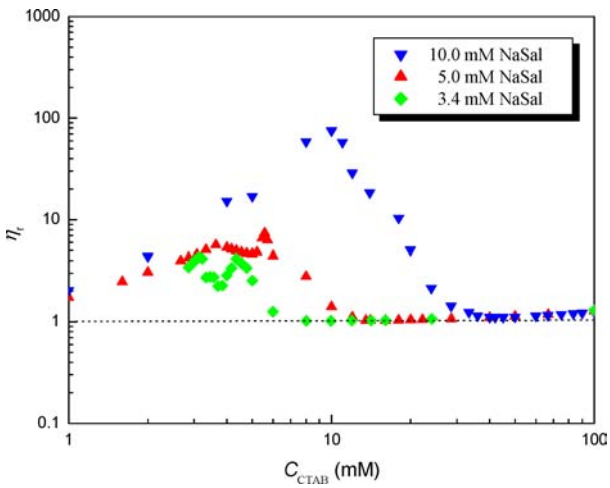

Figure 1 The relative viscosity versus concentration for CTAB in aqueous NaSal solution with the different concentration for NaSal at 30 °C.

the further adding of NaSal solution into the viscometer, the relative viscosity of CTAB increases rapidly, reaches maximum when the concentration of CTAB is approximately 10 mM. Excessive adding of NaSal solution results in the rapid decrease of the relative viscosity of CTAB as shown in Fig. 1. The relative viscosity of CTAB decreasing to minimum with dilution can be interpreted in terms of the decrease of the volume ration of micelles in solution. When the concentration of CTAB is greater than 40 mM, the ratio of NaSal/CTAB is sufficiently less and the electrostatic repulsion between the head groups of CTAB cannot be compensated efficiently by counterions. As a result, the increase of the relative viscosity of CTAB induced from the contribution of the growth of micelles in solution is negligible. On the other hand, the volume ratio of micelles decreases with dilution. However, when the concentration of CTAB is less than 40 mM, the influence of NaSal/CTAB ratio upon the growth of micelles in solution is notable. Therefore, the volume ratio of micelles and thus, the intermicellar interaction in solution increase considerably and the relative viscosity of CTAB increases to maximum with dilution as shown in Fig. 1. It has been pointed out that the excess adsorption and penetration of Salicylate ions decreases micelles to small size because of electrostatic repulsion in "anionic" micelles [19]. From Fig. 1 it can be seen that when the concentration of CTAB is less than 10 mM, or the ratio of NaSal/CTAB is greater than one, the relative viscosity of CTAB decreases rapidly, suggesting that micelle size should have decreased to small micelles because of electrostatic repulsion in "anionic" micelles in such a case.

Of peculiar interest is that the relative viscosity of CTAB exhibits the double-peak behavior in the presence of NaSal solution with the concentration of either 5.0 mM or 3.4 mM for NaSal. From the above discussion it can be seen that CTAB micelles grows to maximum at a certain ratio of NaSal/CTAB. The intermicellar interaction and thus, the relative viscosity of CTAB, however, depend not only on the length of micelles but also on the volume of micelles in solution. The length of wormlike micelles in solution is chiefly dependent on the ratio of NaSal/CTAB. On the other hand, the volume ratio of wormlike micelles in solution depends not only on the ratio of NaSal/CTAB but also on the concentration of CTAB in solution. In case that the concentration of NaSal is fixed as presented in this study, both the maximum length of micelles and the maximum volume of micelles in solution is greatly associated with the concentration of CTAB. However, the critical concentration of CTAB corresponding to either the maximum length of micelles or the maximum volume of micelles in solution is not the same. This explains why the relative viscosity of CTAB exhibits the double-peak behavior in the presence of NaSal solution with the concentration of either 5.0 mM or 3.4 mM for NaSal. The left peak in Fig. 1 indicates that micelles of CTAB have grown to the maximum length, whereas the right peak indicates the volume of micelles becomes the maximum in solution. It can also be seen from Fig. 1 that the double-peak shifts to the higher concentra-

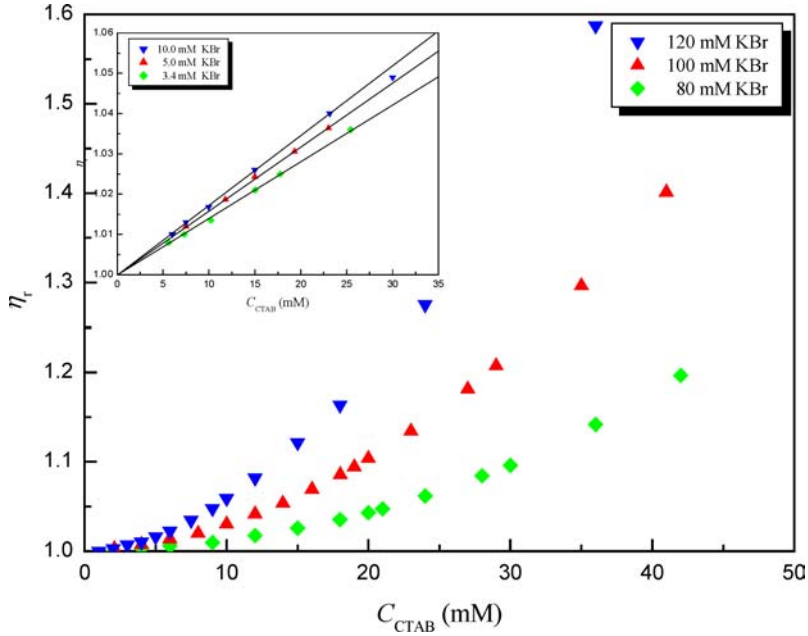

Figure 2 The relative viscosity versus concentration for CTAB in aqueous KBr solution with the different concentration for KBr at 30 °C.

tion of CTAB in solution with the higher concentration of NaSal. In case that NaSal in solution is fixed to be 10 mM, the length of wormlike micelles of CTAB grows rapidly at high concentrations of CTAB. On such an occasion, micelles have interpenetrated each other and the slight decrease of micellar length due to the improper ratio of NaSal/CTAB makes little contribution to the relative viscosity of CTAB solution. As a result, the relative viscosity reaches maximum on condition that the volume of micelles becomes maximum in solution. It is the reason why the double-peak behavior disappears in the presence of NaSal solution with the concentration of 10 mM for NaSal.

Fig. 2 shows the relative viscosity of CTAB in aqueous KBr solution at 30 °C. It can be seen that the relative viscosity of CTAB in the presence of KBr solution with the concentration of 3.4, 5.0 and 10.0 mM for KBr increases linearly with concentration of CTAB, critically different from the viscosity behavior of CTAB in the presence of NaSal as shown in Fig. 1. In particular, the relative viscosity of CTAB in the presence of KBr is much less than the relative viscosity of CTAB in the presence of NaSal, indicating NaSal is more efficient in promoting micelle formation than KBr. It has been reported that the transition of CTAB from monomer to spherical micelle in water is 0.8 mM [19]. In our experiment, the concentration of CTAB in the presence of KBr solution with the concentration of 3.4, 5.0 and 10.0 mM for KBr is greater than 0.8 mM, suggesting that the spherical micelle has formed in solution. Considering that the relative viscosity of CTAB increases linearly with concentration, we believe that CTAB keeps the spherical micelle in the concentration investigated. In case that the concentration of KBr is greater than 80 mM, the relative viscosity of CTAB increases rapidly with concentration of CTAB as shown in Fig. 2. This suggests the formation of wormlike micelle in solution. Compared with the relative viscosity of CTAB solution in the presence of NaSal, the relative viscosity of CTAB solution in the presence of KBr is much less, indicating that the length of wormlike micelle of CTAB in aqueous KBr solution is much less that in aqueous NaSal solution.

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