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THE EFFECT OF BENZYL ALCOHOL ON THE MICELLAR PROPERTIES OF CTAB IN KBr SOLUTION

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ABSTRACT

The effect of benzyl alcohol on the micellar size and shape of CTAB in KBr solution has been investigated by means of viscosity, LLS (laser light scattering), and NMR measurements. The surfactant CTAB (cetyltrimethylammonium bromide) and KBr content are kept constant at 0.01 mol.L^{-1} and 0.1mol.L^{-1}. The data from the various techniques are quantitatively in agreement. The viscosity of 0.01mol.L^{-1} CTAB/ 0.01mol.L^{-1} KBr micellar system has a marked maximum at benzyl alcohol content 0.6% (v/v), where the size of rod micelles are largest. The results from ^{1}H-NMR spectra of CTAB molecules show that before the maximum viscosity, benzyl alcohol is located in the interfacial region of CTAB micelles in the presence of KBr salt. If more benzyl alcohol is added, it starts solubilizing in the palisades of the micelles.

INTRODUCTION

Recently, the size and structure of ionic micelles in the presence of additives has been extensively studied. For most aqueous ionic surfactant solutions above best close to the critical micelle concentration (cmc), the micelles are regarded as spherical in

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shape.[1] Several authors have shown that short and medium chain length alcohol may lead to a decrease in the micellar size.[2-5] On the other hand, addition of medium to long chain alcohol increases the aggregation number producing larger alcohol-surfactant mixed micelles.[2,6] These changes in micellar size are often explained in terms of differences in the solubilization mechanism of the alcohol. The principal location of alcohol molecules in aqueous micellar solution depends on the alcohol structure. As a contrast to the behavior of long chain alcohol, short chain alcohols mainly affect the micelles through their effect on the solvent.[7]

Addition of neutral salt decreases the electrostatic interaction between monomers in the micelle and may cause structural changes. These depend on the type of surfactants, their concentration and the salt content. There is now very strong evidence for an entangled micellar phase in several aqueous cationic detergent systems in the presence of added salt, such as cetyltrimethylammonium bromide or chloride (CTAB or CTAC) with added KBr or sodium salicylate (NaSal); cetylpridinium bromide(CPyBr)+KBr; cetylpridinium salicylate(CPySal)+NaSal etc. The last years have seen a growing interest in structure and size of them and the number of conferences dealing with them has considerably increased.[8-13] However, there has been relatively few contributions on the effect of the additives on the micellar properties of these systems.

In this article we will show the influence of benzyl alcohol on the shape and size of micelles in the CTAB dilute solution with the addition of KBr salt. These results, obtained from viscosity measurement, LLS and ^{1}H-NMR spectra of CTAB molecules in micelles with solubilized benzyl alcohol are quantitatively consistent.

EXPERIMENTAL

The CTAB was obtained by recrystallization from solution of analysis grade CTAB. All of reagents in this study are of the analysis grade purchased from Shanghai Chemical Reagent Co..

The measurements of viscosity were performed on Ubbelohde Viscometer.

A commercial laser light scattering equipment (ALV/SP-150) equipped with a solid-state laser (ADLAS DPY425 II, output power≈400mW at λ =532nm) as the light source and an ALV-5000 multi- τ digital correlator was used. The samples were filtered through a 0.5um Millipore filter into the cylindrical light scattering cell. In static light scattering, the angular dependence of the time-averaged scattered light intensity was measured, which led to the weight-averaged molar mass M_w and the *z*-average square-root-mean radius of gyration $\langle R_g^2\rangle_z^{1/2}$ (or written as $\langle R_g\rangle$).

In dynamic LLS, the intensity-time correlation function $G^{(2)}(\tau, \theta)$ in the self-beating mode was measured, where τ is the delay time and θ the scattering angular. $G^{(2)}(\tau, \theta)$ can be related to the normalized first-order electric field time correlation function $|g^{(1)}(\tau,\theta)|$ as

$$G^{(2)}(\tau,\theta)=\langle I(0,\theta)I(\tau,\theta)\rangle=A[1+\beta\ |g^{(1)}(\tau,\theta)|^2] \qquad \text{<1>}$$

where A is the measured baseline; β, a parameter depending on the coherence of the detection; and τ, the delay time. For a polydisperse sample, $|g^{(1)}(\tau,\theta)|$ is related to the line-width distribution $G(\Gamma)$ as

$$|g^{(1)}(\tau,\theta)|=\langle E(0,\theta)E^*(\tau,\theta)\rangle=\int_0^\infty \Gamma G(\Gamma)e^{-\Gamma\tau}d\Gamma \qquad \text{<2>}$$

$G(\Gamma)$ can be calculated from the Laplace inversion of the measured $G^{(2)}(\tau,\theta)$ on the basis of eqs 1 and 2. The CONTIN program developed by Provencher[14] was used. For a diffusive relaxation, at infinite dilution and $\theta\to 0$, $(\Gamma/q^2)\to D$, where q is the scattering vector and D is translation diffusion coefficient. D can be converted to the hydrodynamic radius (R_h) by using the Stokes-Einstein equation:

$$R_h=\kappa_B T/6\pi\eta D \qquad \text{<3>}$$

Where η, κ_B and T are the solvent viscosity, the Boltzmann constant, and the absolute temperature.

The specific refractive index increment (dn/dc) used in static light scattering was determined by a novel and precise differential refractometer.[15] For CTAB in 0.1mol.L^{-1} KBr solution, the value of dn/dc is 0.155mL/g. In this study, the dn/dc for the mixed CTAB and benzyl alcohol micelle adopted the same value in 0.1mol.L^{-1}KBr solution.

^{1}H-NMR spectra were recorded using a Varian Unity Inova-300 instrument. The ^{1}H chemical shifts are reported in δ units (ppm) relative to TMS (tetramethylsilane) as external standard (δ =0.00 ppm).

All measurements were conducted at temperature of 30±0.5°C.

RESULTS AND DISCUSSION

Effect of Benzyl Alcohol Concentration on the Viscosity of CTAB/KBr Micellar Solution.

Figure 1 shows the viscosity change of CTAB micellar system when benzyl alcohol is added to this solution. In the presence of 0.1mol.L^{-1} KBr salt, the relative viscosity of 0.01mol.L^{-1}CTAB systems increases with increasing amount of benzyl alcohol to a value of approximate 1.9 for a benzyl alcohol content of 0.6% (v/v). If more benzyl alcohol is added, the viscosity is decreased. In the absence of KBr salt, the viscosity of 0.01mol.L^{-1}CTAB solution increases slightly with addition of alcohol due to the increase of volume fraction of mixed micelles.

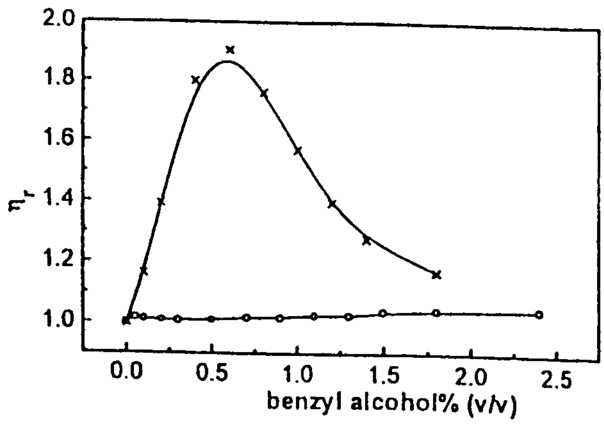

Figure 1 The effect of benzyl alcohol concentration on the relative viscosity of 0.01 mol.L^{-1} CTAB/KBr micelle system. (O):0 mol.L^{-1}KBr; (X):0.1mol.L^{-1}KBr

Effect of Benzyl Alcohol Concentration on R_g and R_h of Mixed Benzyl Alcohol and CTAB Micelles in the Presence of KBr Salt.

The light scattering data are given in table 1. In order to compare conveniently the data of LLS with the data of relative viscosity, We list also the latter in Table 1. The R_g and R_h of micelles go through a marked maximum upon additions of benzyl alcohol in CTAB/KBr system and the largest size of micelles corresponds to the highest viscosity in the micellar system.

Imae[9] has shown that CTAB rod-like micelles are formed in aqueous solution having NaBr concentration higher than 0.06mol.l^{-1}. In our 0.01mol.L^{-1} CTAB/0.1mol.L^{-1} KBr micellar system, the exact values of the $<R_g>$ and M_w can not be obtained due to the electrostatic interaction between the micelles, but the results of LLS show that M_w of CTAB micelle is order of 10^5 and the R_h is 7.8nm. This suggests that the micelle is a rod.

The rate of R_g/R_h is 0.775 for spheres and 2 for rigid rods according to theoretical prediction[8]. From the table 1, before benzyl alcohol concentration 0.6 % (*i.e.* the highest viscosity), the rate of R_g/R_h increases up to 4 and M_w up to 4.52×10^6 with increasing benzyl alcohol content. If more benzyl alcohol is added, the rate of R_g/R_h is reduced to 1.5 and M_w to 1.15×10^6 at which benzyl alcohol content is 1.8%. The above data suggests that at low concentration alcohol, the rod micelles grow larger and longer with an increasing amount of alcohol. After the highest viscosity, the size of micelle decreases and the rod micelles[9] change to an oblate ellipsoid. Obviously, the change of shape of the micelles causes the reduction of viscosity.

In order to elucidate the mechanism of effect of benzyl alcohol on the size and shape of CTAB micelles, we measured the position of benzyl alcohol in CTAB/KBr micellar system.

Table1 The variance of $\langle R_g \rangle$, R_h, M_w and $\langle R_g \rangle / R_h$ of micelles with benzyl alcohol concentration in 0.01mol.L^{-1}CTAB/0.1mol.L^{-1}KBr micellar system

Benzyl alcohol%(V/V)	$\langle R_g \rangle$/nm	Rh/nm	$\langle R_g \rangle$/Rh	Mw	η_r
0		7.8			1
0.1	49.76	19.34	2.57	7.31E+05	1.162
0.2	65.72	24.59	2.67	1.22E+06	1.392
0.4	82.28	30.07	2.73	1.55E+06	1.792
0.6	134.4	33.43	4.02	4.52E+06	1.903
0.8	57.76	31.87	1.81	1.56E+06	1.761
1.2	45.22	28.77	1.57	1.56E+06	1.397
1.8	30.88	20.15	1.53	1.15E+06	1.17

The Variations of Solubilization Position of Benzyl Alcohol with Benzyl Alcohol Concentration in CTAB/KBr Micellar System.

Surfactant micelles can be pictured as having a highly non-polar interior and a relatively polar interfacial region. Between them is a palisade layer. Solubilized molecules with relatively high polarity such as alcohol are generally considered to be located primarily in the palisades of micelles, they are oriented in such a manner that the polar functional groups are absorbed closely to the micellar surface and the hydropholic ones are directed towards the micellar interior.[16] Generally, intercalation of aromatic group between head-groups or the long chain methylenes of surfactant in micelles results in an upfield shifts of some of protons of surfactant monomers in the aggregates as a result of a ring current-induced shift.[17]

In the presence of 0.1mol.L^{-1} KBr salt, the dependence of chemical shifts of $-CH_3$, $-(CH_2)_{13}$ and $N-(CH_3)_3$ on benzyl alcohol concentration are showed in figure 2. Figure 2 shows the peak of the long chain methylenes of CTAB molecules in mixed benzyl alcohol and 0.01mol.L^{-1} CTAB/ 0.1mol.L^{-1} KBr micellar system to have a marked line broadening as to a new signal when benzyl alcohol concentration is in excess of 0.6% where the viscosity of mixed benzyl alcohol and CTAB/KBr micellar system is highest and the size of micelle is biggest.

The variations of ^1H chemical shift ($\Delta\delta = \delta_0 - \delta$. Where δ_0 is ^1H chemical shift of CTAB molecules in 0.01mol.L^{-1}CTAB/0.1mol.L^{-1}KBr system without benzyl alcohol and δ is ^1H chemical shifts of the same system with benzyl alcohol.) directly indicate the effect of benzyl alcohol concentration on ^1H chemical shift of CTAB molecules. In the presence of 0.1mol.L^{-1} KBr salt, The variations of ^1H chemical shift of resolved signals of CTAB molecule on benzyl alcohol concentration are showed in figure 3. $\Delta\delta > 0$ means upfield shift of ^1H chemical shift.

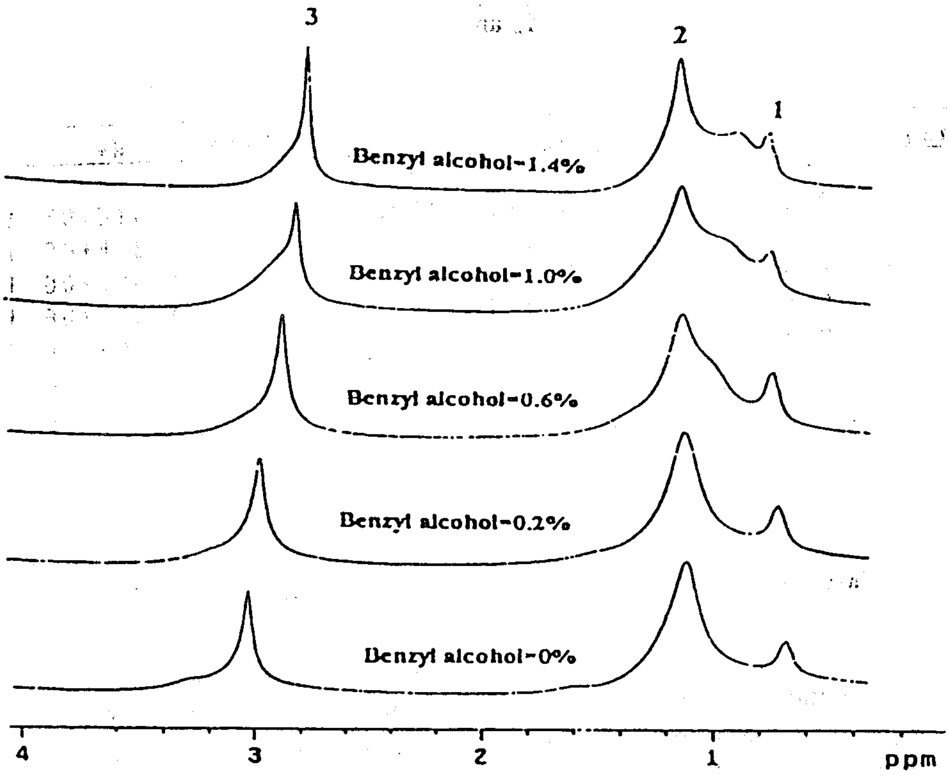

Figure 2 The effect of benzyl alcohol concentration on ^{1}H-NMR spectra of CTAB molecule in 0.1mol.L^{-1} KBr solution. 1: $-CH_3$; 2: $-(CH_2)_{13}$; 3: $N-(CH_3)_3$

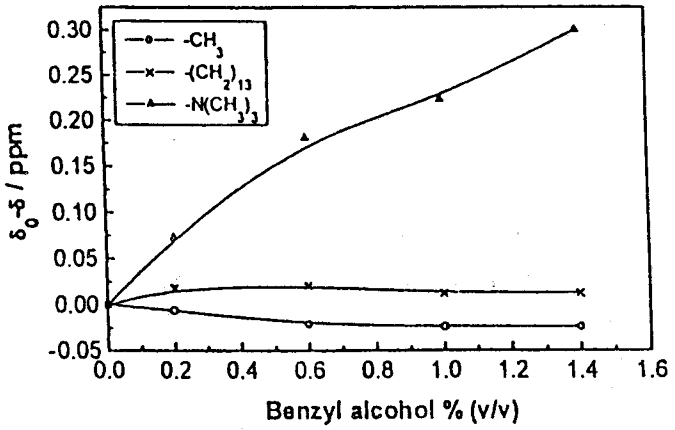

Figure 3 The variations of chemical shifts of protons of CTAB molecules in micelles with benzyl alcohol concentration in 0.1mol.L^{-1}KBr solution

The results of figure 3 show that the addition of benzyl alcohol results in an rapidly upfield shift of protons of $N\text{-}(CH_3)_3$, whereas the variance of $\Delta\ \delta$ of $-(CH_2)_{13}$ and $-CH_3$ is insignificant.

The above results suggest that the aromatic ring of benzyl alcohol molecules locates among $N\text{-}(CH_3)_3$ groups and that the –OH groups are directed towards the bulk solution till benzyl alcohol content reaches 0.6%. In lower concentration than this value the electric field of ring current of benzyl alcohol induces the upfield change of the ^1H chemical shift of $N\text{-}(CH_3)_3$ and does not have apparent influence on the long chain methylenes of CTAB molecules. If more benzyl alcohol is added, it is solubilized in the palisades and the aromatic ring of benzyl alcohol locates among the part of the long chain methylenes which is near the polar group of CTAB molecule. Due to the effect of ring current of benzyl alcohol, there is an upfield shift for the signals of protons of long chain methylenes near the aromatic ring and the ^1H-NMR band of the long chain methylenes starts to broaden and split. At that concentration, the rod micelles change to oblate. The polar interfacial region solubilizes more alcohol molecules. In this case, ^1H chemical shifts of $N\text{-}(CH_3)_3$ tend still to upfield.

Israelachvili et al.[18] have considered the geometric limitations which place restriction on allowed shapes of micelles. They gave a critical condition for the structure of micelles:

Rod micelles: $V/a_0 l_c = 1/2 \sim 1$ <4>

Oblate spheroid micelles: $V/a_0 l_c = 1/3 \sim 1/2$ <5>

Sphere micelles: $V/a_0 l_c = 0 \sim 1/3$ <6>

Where l_c is roughly equal to but less than the fully extended length of the [illegible] referred to as the optimal surface area per factant molecule, being that area at which the free energy per surfactant molecule a micelle is a minimum. V dominates hydrocarbon core volume per surfactant lecule in micelle.

At the same time they believed that the oblate spheroid micelles formed by ionic d zwitterionic amphiphiles are unacceptable. Because the peripheral regions of em have too great a curvature while the central regions are too thick, the oblate heroid micelle is energetically unfavorable due to electrostatic repulsion from the lar groups of surfactants. In CTAB/KBr micellar system, the addition of neutral salt creases the electrostatic interaction between monomers in micelle and can bring out the possibility of existence of oblate spheroid micelles.

In the absence of salt, alcohol is solublized in the palisades of micelles and bring out the decreasing size of micelles.[3] In contrast with the case, benzyl alcohol is solubilized in the interfacial region of CTAB rod micelles in KBr solution, consequentially, micelles will become larger and longer due to the structure being hardly disturbed by alcohol. When alcohol is solubilized in the palisades, it is like a wedge among surfactant in micelle. In this case, a_0 will increase fast. In this process, v and l_c are almost constant. Once $v/a_0l_c<1/2$, the rod micelles will undergo a transition to oblate spheroid. At that stage, the size of mixed alcohol and surfactant micelles decreases. As a result of these transitions, the viscosity of this system decreases.

CONCLUSION

The results obtained in this study clearly show the complexity for the viscosity, size and shape of CTAB micelles in the KBr solution with the addition of benzyl alcohol. A little amount of alcohol solubilized in the interfacial region of aggregates promotes rod micelles to be larger and longer. As a result of the process, the viscosity of the systems will rise. At that stage, the variance of a_0 is insignificant. When the alcohol content is higher, it will be solubilized in the palisades of micelles and a_0 will increase fast, as a result of this process, the rod micelles transfer gradually into oblate spheroid ones. Consequentially, the viscosity of micellar system decreases.

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