

ARTICLE

Effect of Short Chain Alcohols upon Viscosity of TTAB Solution

Yun-fei Yan, Hua-zhen Li, Hai-yang Yang*, Jia-sheng Qian, Ping-ping Zhu, Ping-sheng He

Department of Polymer Science & Engineering, University of Science & Technology of China, Hefei 230026, China

(Dated: Received on April 6, 2007; Accepted on May 29, 2007)

The effect of ethanol (C_2H_5OH), propanol (C_3H_7OH), and butanol (C_4H_9OH) upon the viscosity of tetradecyltrimethylammonium bromide (TTAB) solution in the presence or absence of KBr at 30 °C was investigated, where the surfactant concentration C_S is kept constant. In the absence of KBr, the relative viscosity η_r of TTAB solution increases linearly with the alcohol concentration C_A , indicating that the alcohols do not promote micelle formation of TTAB. In the presence of KBr, η_r linearly decreases with C_A for C_2H_5OH , but it exhibits a maximum with increasing C_A for C_3H_7OH or C_4H_9OH . The facts reveal that C_2H_5OH or C_4H_9OH promotes the micelle formation of TTAB. A possible explanation is that the hydrophobicity of the micellar interior is enhanced by KBr, so that C_2H_5OH or C_4H_9OH can dissolve in micelle and promotes micelle formation. In the presence of KCl, which is less efficient in promoting the micelle formation of cationic surfactant, both C_3H_7OH and C_4H_9OH have only a slight effect on the micelle formation. In contrast, due to the hydrophilicity, C_2H_5OH cannot dissolve in micelles in the presence of KBr or KCl.

Key words: Relative viscosity, Cationic surfactant, Organic additives, Hydrophobic interaction

I. INTRODUCTION

The effect of organic additives upon micellization of surfactants in solution has drawn considerable attention [1-32]. It is widely recognized that an organic additive with a long hydrocarbon chain can dissolve in micelle and promote micelle formation of surfactants either in the presence or absence of inorganic salts. On the other hand, the organic additive with a short hydrocarbon chain cannot dissolve in micelle because the hydrophobic interaction between the non-polar part of organic additive and the hydrophobic interior of micelle is not strong enough. In particular, the preferential solubilization of organic additives will decrease the surface energy of micelle. As a result, the micelles of surfactants break into small micelles in solution [30-31,33].

Kabir-ud-Din *et al* demonstrated that the effect of organic additives is enhanced by inorganic salts such as KCl [9-10,13,16-19]. Such an effect can be well characterized by viscosity measurement when the number of carbon atoms in the organic additives is greater than 4. On the other hand, the lower chain length additives (e.g. C_4OH , C_3OH , or C_4NH_2) show marginal effect on micelle formation even in the presence of KCl. This is in a good agreement with the results presented by Manabe *et al.* [34].

On the other hand, the hydrophobicity of micellar interior also has effect on the solubilization of the organic additives. Høiland *et al.* studied the distribution coefficients of hexanol and heptanol in sodium dodecyl sulfate (NaDDS) solutions in the presence of NaCl [27]. It was

suggested that the distribution coefficients were greatly associated with the hydrophobicity of the micellar interior which could be enhanced by addition of NaCl. It is well known that Br^- is more efficient in promoting micelle formation of cationic surfactants than Cl^- [35-37]. In the presence of KBr, the interaction of the non-polar part of organic additives with micellar hydrophobic interior should be stronger than that in the presence of KCl or NaCl. Accordingly, the additives even with short hydrocarbon chain (e.g., C_4OH , C_3OH) can dissolve in micelle and promote micelle formation in the presence of KBr. In this work, we investigated the effect of organic additives upon micellization of TTAB in the presence of KBr by viscometry.

II. EXPERIMENTS

A. Materials

The cationic surfactant tetradecyltrimethylammonium bromide (TTAB) was purchased from Alfa Aesar (purity of 99%). Ethanol, propanol, butanol, and potassium bromide were A.R. grade and used as received. Distilled water was used to prepare various solutions. Both the solvent and the solution were filtered with 0.45- μm filters prior to use.

B. Viscosity measurement

The viscosity measurements were carried out using a conventional Ubbelohde viscometer that was placed in a thermostatically controlled bath with a precision of 0.01 °C. Measurements were initiated after approximately 5-10 min equilibrium time. The flow time was determined from an average of several readings (more

* Author to whom correspondence should be addressed. E-mail: yhy@ustc.edu.cn, Tel: +86-551-3607549

than 5 readings). In this experiment, the surfactant concentration C_S is kept constant but the alcohol concentration C_A is progressively increased. The relative viscosity of micelle solution is calculated from the Eq.(1) [3,38,39].

$$\eta_r = \frac{t}{t_0} \quad (1)$$

where t and t_0 are the flow time of micelle solution and the distilled water respectively. Both t and t_0 are longer than 100 s so that the kinetic energy correction is neglected.

III. RESULTS AND DISCUSSION

A. Effects of alcohols on the viscosity of TTAB solution in the presence or absence of KBr

Figure 1(a) shows how the relative viscosity η_r of TTAB solution varies with C_2OH , C_3OH and C_4OH concentration C_A in the absence of KBr at 30 °C, where $C_S = 0.1$ mol/L. It can be seen that η_r increases linearly

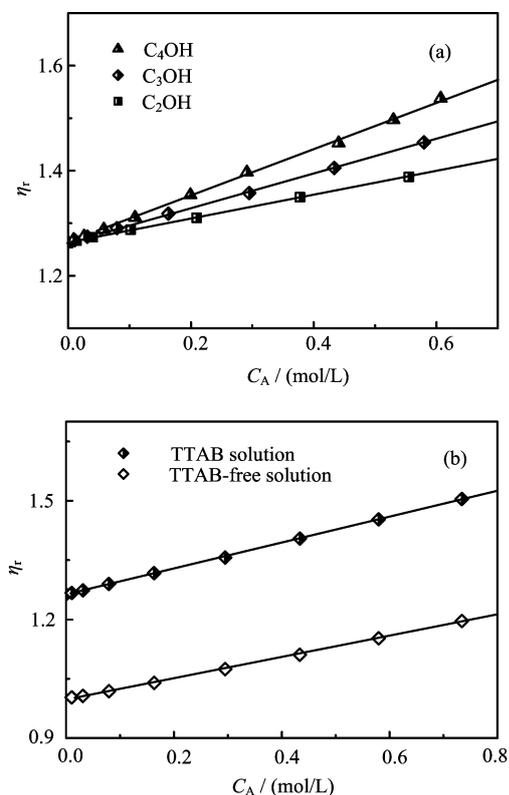


FIG. 1 (a). The relative viscosity η_r of TTAB solution varies with C_2OH , C_3OH and C_4OH concentration in the absence of KBr at 30 °C. (b) The relative viscosity η_r varies with C_3OH concentration in the presence and absence of TTAB at 30 °C. The concentration of TTAB is kept constant of 0.1 mol/L. η_r was determined by t/t_0 where t_0 is the flow time of the pure water.

with C_A in the whole range of concentration investigated. Note that such dependence does not imply that alcohols promote the growth of micelle size, because the solvent is distilled water instead of a mixture of distilled water and alcohol. Figure 1(b) shows that η_r increases linearly with C_A even in the absence of TTAB, suggesting that the dependence of η_r on C_A in Fig.1(a) should be due to the contribution of alcohols.

When a mixed solvent is used, we define the relative viscosity of TTAB solution as η_r' , where the contribution of alcohols to the relative viscosity of TTAB solution can be subtracted. Figure 2 shows that η_r' decreases perceptibly with C_A . It is well known that the preferential solubilization of alcohols in the surface of micelles decreases the surface energy. As a result, the aggregation number of TTAB in aqueous solution decreases [25-26,39]. This explains why η_r' decreases with increasing C_A as shown in Fig.2.

Figure 3 shows how the relative viscosity η_r of TTAB solution varies with KBr concentration at 30 °C, where $C_S = 0.1$ mol/L. We note that η_r sharply increases at the high KBr concentration, indicating TTAB micelles have changed from spherical micelles to rodlike micelles [11].

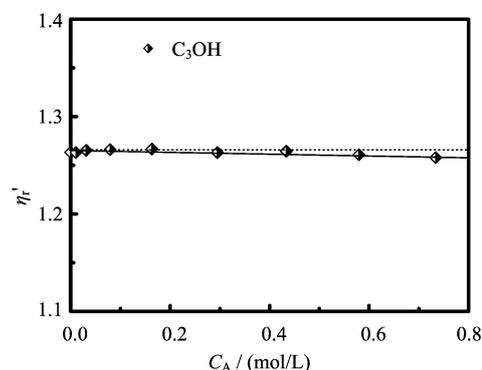


FIG. 2 The relative viscosity η_r' of TTAB solution varies with C_3OH concentration in the absence of KBr at 30 °C. η_r' is determined by t/t_0' where t_0' is the flow time of the mixed solvent of C_3OH and the distilled water.

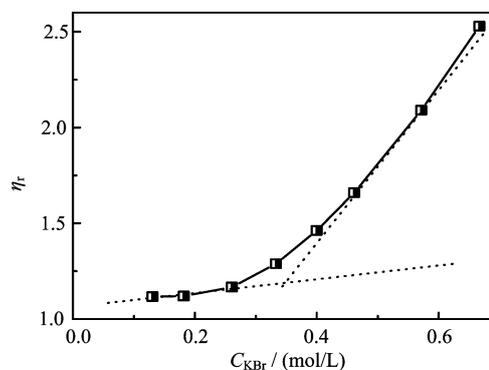


FIG. 3 The relative viscosity η_r of TTAB solution varies with KBr concentration at 30 °C.

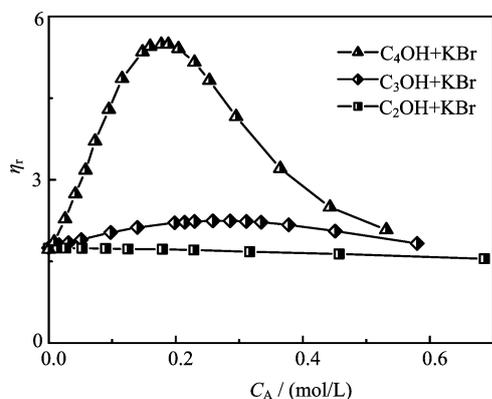


FIG. 4 The relative viscosity η_r of TTAB solution varies with $C_2\text{OH}$, $C_3\text{OH}$ and $C_4\text{OH}$ concentration in the presence of 0.5 mol/L KBr at 30 °C.

Figure 4 shows how the relative viscosity η_r of TTAB solution varies with alcohol concentration C_A in the presence of KBr at 30 °C. At $C_A=0$, $\eta_r \sim 1.7$ indicating TTAB micelles has changed from spherical micelles to rodlike micelles in the presence of KBr as indicated in Fig.3. Figure 4 also shows that η_r gradually decreases with the $C_2\text{OH}$ concentration, suggesting that the micelle size of TTAB decreases. This is quite different from the results shown in Fig.1(a), where the addition of $C_2\text{OH}$ increases the relative viscosity η_r . The dependence of η_r on C_A for $C_2\text{OH}$ in Fig.3 indicates that the contribution of the decrease in micelle size to η_r is greater than the contribution of $C_2\text{OH}$ to η_r . Note that the η_r with $C_2\text{OH}$, $C_3\text{OH}$, or $C_4\text{OH}$ exhibits different dependence. As the concentration of $C_3\text{OH}$ or $C_4\text{OH}$ increases, η_r exhibits a maximum. A possible explanation is that the hydrophobicity of the micellar interior increases due to the formation of TTAB rodlike micelles in solution. As a result, the hydrophobic interaction of alcohols with micelle increases accordingly. The alcohols with shorter chain (e.g., $C_4\text{OH}$, $C_3\text{OH}$), therefore, dissolve in micelle and promote micelle formation due to the hydrophobic interaction. This is why η_r initially increases with increasing C_A . However, the excessive alcohols would swell and even break the rodlike micelle into small micelles. As a result, η_r decreases with C_A when C_A is above a certain value. Since $C_4\text{OH}$ is a more hydrophobic molecule than $C_3\text{OH}$, the maximum of η_r for $C_4\text{OH}$ is greater than that for $C_3\text{OH}$. In contrast, $C_2\text{OH}$ is too hydrophilic to dissolve in micelle and promote micelle formation of TTAB even in the presence of KBr.

B. Effects of $C_3\text{OH}$ and $C_4\text{OH}$ on the viscosity of TTAB solution in the presence of KBr

Figure 5 shows how the relative viscosity η_r of TTAB solution varies with $C_3\text{OH}$ concentration in the presence of KBr at 30 °C. At $C_A=0$, η_r increases with increasing

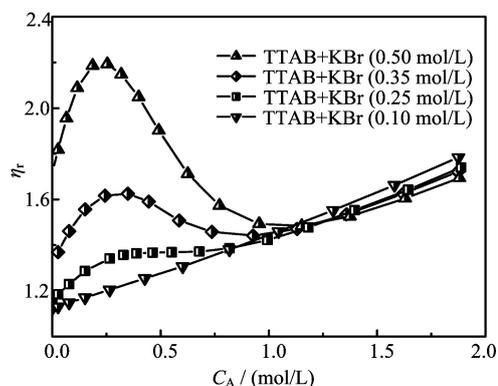


FIG. 5 The relative viscosity η_r of TTAB solution varies with $C_3\text{OH}$ concentration in the presence of KBr with various levels of concentration at 30 °C.

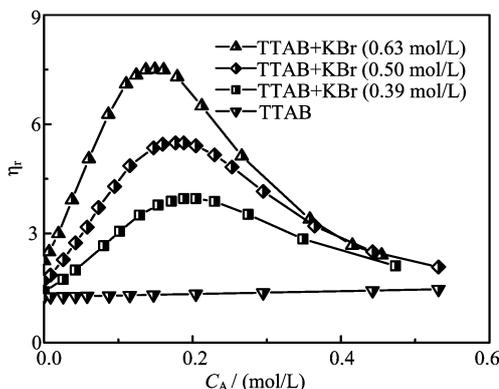


FIG. 6 The relative viscosity η_r of TTAB solution varies with $C_4\text{OH}$ concentration in the presence of KBr with various levels of concentration at 30 °C.

KBr concentration, indicating that the hydrophobicity of the micellar interior increases with KBr concentration. Namely, the hydrophobic interaction of alcohols with micelle increases with KBr concentration. Figure 5 also shows that η_r sharply increases and then decreases as C_A increases at high KBr concentration. When KBr concentration is 0.1 mol/L, η_r linearly increases with C_A , like the case in the absence of KBr (Fig.1). Note that the critical concentration of C_A or C_A^* , at which η_r exhibits the maximum, shifts to lower concentration as KBr concentration increases. Obviously, the hydrophobic interaction between alcohol molecules and the micelle becomes stronger at high KBr concentration. It is known that the distribution coefficient K (defined as $K=X_a^M/X_a^W$, where X_a^M and X_a^W are the mole fraction of alcohol in micelles and water phase, respectively [40]) is greatly associated with the hydrophobic interaction of alcohols with micelle. Thus, K for $C_3\text{OH}$ increases at high KBr concentration. This is why η_r exhibits the maximum at lower C_A in the presence of KBr.

Figure 6 shows how the relative viscosity η_r of TTAB solution varies with $C_4\text{OH}$ concentration for TTAB in the presence of KBr at 30 °C. By comparing Fig.6 with

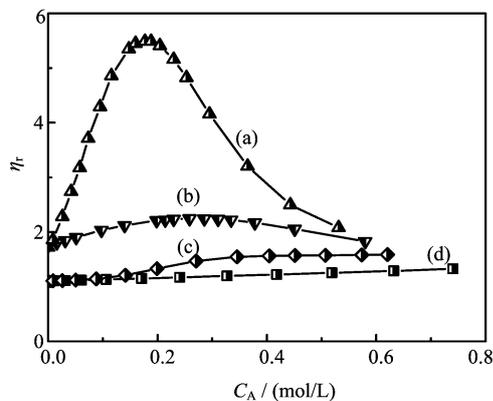


FIG. 7 The relative viscosity η_r of TTAB solution varies with $C_3\text{OH}$ and $C_4\text{OH}$ concentration in the presence of 0.5 mol/L KBr and 0.5 mol/L KCl at 30 °C. (a) TTAB+0.5 mol/L KBr+ $C_3\text{OH}$, (b) TTAB+0.5 mol/L KBr+ $C_4\text{OH}$, (c) TTAB+0.5 mol/L KCl+ $C_3\text{OH}$, (d) TTAB+0.5 mol/L KCl+ $C_4\text{OH}$.

Fig.5, we know that η_r also exhibits a maximum in the presence of $C_4\text{OH}$. Since $C_4\text{OH}$ is more hydrophobic than $C_3\text{OH}$, $C_4\text{OH}$ hydrophobically interacts with the micelles more strongly.

C. Effects of $C_3\text{OH}$ or $C_4\text{OH}$ on the viscosity of TTAB solution in the presence of KCl

As discussed above, as the hydrophobicity of the micellar interior increases, the short chain alcohol dissolves in micelle and promotes the micelle formation. KCl is less efficient than KBr in promoting micelle formation of cationic surfactants. Therefore, the dependence of η_r on C_A in the presence of KCl should be quite different from that in the presence of KBr. Figure 7 shows that $\eta_r \sim 1.1$ at $C_A = 0$ when KCl concentration is 0.5 mol/L, indicating KCl is indeed less efficient than KBr in promoting micelle formation of TTAB. In other words, the short alcohol ($C_3\text{H}_7\text{OH}$) is difficult to dissolve in the micelle. In contrast to $C_3\text{OH}$, $C_4\text{OH}$ is a more hydrophobic molecule. Figure 7 also shows $C_4\text{OH}$ has negligible effect upon the micellization of TTAB in the presence of KCl. Note that η_r in the presence of KCl is less than that of salt-free solution at $C_A = 0$. A possible explanation is that TTAB micelles associate together to some extent in a salt-free solution due to the mutual collision which makes different micelles sharing of the common part of the palisade layer belong to the different micelles. The addition of KCl screens the electric interaction and therefore breaks down the association of the micelles. The viscosity of micelle solution, therefore, decreases in the presence of KCl. Thus, the increase of η_r at high C_A in the presence of KCl indicates that the hydrophobic interaction between $C_4\text{OH}$ and the micellar interior is very weak.

IV. CONCLUSION

This report shows that the viscosity measurement can be used in studying the hydrophobic interaction between alcohols and TTAB micelle. Such a hydrophobic interaction depends on the hydrophobicity of both alcohol molecules and the micellar interior. In the absence of KBr, the hydrophobic interaction is not so strong that alcohol molecules cannot dissolve in micelles. In the presence of KBr, TTAB micelles change from spherical micelles into rodlike micelles, leading the hydrophobicity of the micellar interior to increase. As a result, even the less hydrophobic alcohols such as $C_3\text{OH}$ and $C_4\text{OH}$ can dissolve in micelle and promote micelle formation. In the presence of KCl, which is less efficient than KBr in promoting the micelle formation of cationic surfactant, either $C_3\text{OH}$ or $C_4\text{OH}$ shows little effect on the micelle formation of TTAB. $C_2\text{OH}$ is too hydrophilic to dissolve in micelles in the presence of KBr or KCl.

- [1] S. Kumar, Z. A. Khan, N. Parveen, and Kabir-ud-Din, *Colloid and Surfaces A Physicochem. Eng. Aspects* **268**, 45 (2005).
- [2] A. Desai, D. Varade, J. Mata, V. Aswal, and P. Bahadur, *Colloid and Surfaces A Physicochem. Eng. Aspects* **259**, 111 (2005).
- [3] H. Yang, S. Zhang, H. Liu, X. Xu, J. Zhang, and P. He, *J. Mater. Sci.* **40**, 4645 (2005).
- [4] G. S. Kalur, B. D. Frounfelker, B. H. Cipriano, A. I. Norman, and S. R. Raghavan, *Langmuir* **21**, 10998 (2005).
- [5] S. Kumar, D. Sharma, and Kabir-ud-Din, *J. Surfactants & Detergents* **7**, 271 (2004).
- [6] S. M. Zourab, R. F. El-Samak, and J. Dispersion, *Sci. Technol.* **25**, 41 (2004).
- [7] A. P. Romani, M. H. Gehlen, G. A. R. Lima, and F. H. Quina, *J. Colloid Interface Sci.* **240**, 335 (2004).
- [8] S. R. Raghavan and E. W. Kaler, *Langmuir* **17**, 300 (2001).
- [9] S. Kumar, A. Z. Naqvi, and Kabir-ud-Din, *Langmuir* **17**, 4787 (2001).
- [10] S. Kumar, A. Z. Naqvi, and Kabir-ud-Din, *Langmuir* **16**, 5252 (2000).
- [11] W. C. Zhang, G. Z. Li, Q. Shen, and J. H. Mu, *Colloids and Surfaces A Physicochem. Eng. Aspects* **170**, 59 (2000).
- [12] W. J. Kim and S. M. Yang, *Langmuir* **16**, 6084 (2000).
- [13] S. Kumar, D. Banasal, and Kabir-ud-Din, *Langmuir* **15**, 4960 (1999).
- [14] V. K. Aswal, P. S. Goyal, and P. Thiyagarajan, *J. Phys. Chem. B* **102**, 2469 (1998).
- [15] E. Caponetti, D. C. Martino, M. A. Floriano, and R. Triolo, *Langmuir* **13**, 3277 (1997).
- [16] Kabir-ud-Din, D. Banasal, S. Kumar, and D. Banasal, *Langmuir* **13**, 5071 (1997).
- [17] Kabir-ud-Din, S. Kumar, Kirtr, and P. S. Goyal, *Langmuir* **12**, 1490 (1996).

- [18] S. Kumar, Kirti, K. Kumari, and Kabir-ud-Din, *JAOCS* **72**, 817 (1995).
- [19] S. Kumar, Kirti and Kabir-ud-Din, *JAOCS* **71**, 763 (1994).
- [20] S. Kumar, V. K. Aswal, and H. N. Singh, P. S. Goyal, and Kabir-ud-Din, *Langmuir* **10**, 4069 (1994).
- [21] J. B. Hayter and J. Penfold, *J. Phys. Chem.* **96**, 1994 (1992).
- [22] G. M. Forland, J. Samseth, H. Hoiland, and K. Mortensen, *J. Colloid Interface Sci.* **164**, 163 (1994).
- [23] M. Paul, Lindemuth, L. Gary, and Bertrand, *J. Phys. Chem.* **97**, 7769 (1993).
- [24] A. M. Blokhus, H. Hoiland, E. Gilje, and S. Backlund, *J. Colloid Interface Sci.* **124**, 125 (1988).
- [25] I. Vikholm, G. Douheret, S. Backlund, and H. Hoiland, *J. Colloid Interface Sci.* **116**, 582 (1987).
- [26] P. Baglionit and L. Kevan, *J. Phys. Chem.* **91**, 2106 (1987).
- [27] H. Høiland, E. Ljosland, and S. Backlund, *J. Colloid Interface Sci.* **101**, 467 (1984).
- [28] M. Almgren and S. Swarup, *J. Colloid Interface Sci.* **91**, 256 (1983).
- [29] P. Stilbs, *J. Colloid Interface Sci.* **87**, 385 (1982).
- [30] P. Stilbs, *J. Colloid Interface Sci.* **89**, 547 (1982).
- [31] R. Zana, S. Yiv, C. Strazielle, and P. Lianos, *J. Colloid Interface Sci.* **80**, 208 (1981).
- [32] S. Yiv, R. Zana, W. Ulbricht, and H. Hoffmann, *J. Colloid Interface Sci.* **80**, 224 (1981).
- [33] R. Leung and D. O. Shah, *J. Colloid Interface Sci.* **113**, 484 (1986).
- [34] M. Manabe, K. Shirahama, and M. Koda, *Bull. Chem. Soc. Jpn.* **63**, 2904 (1967).
- [35] V. K. Aswal and P. S. Goyal, *Phys. Rev. E* **61**, 2947 (2000).
- [36] P. S. Goyal, S. V. G. Menon, B. A. Dasannacharya, and V. Rajagopalan, *Chem. Phys. Lett.* **211**, 559 (1993).
- [37] F. Quirion and L. J. Magid, *J. Phys. Chem.* **90**, 5435 (1986).
- [38] H. Yang, Y. Yan, P. Zhu, H. Li, Q. Zhu, and C. Fan, *Eur. Polym. J.* **41**, 329 (2005).
- [39] Y. Yun, H. Yang, W. Liu, P. Zhu, and P. He, *Chin. J. Polym. Sci.* **23**, 557 (2005).
- [40] S. Backlund, K. Bundt, K. S. Birdl, and S. Dalsager, *J. Colloid Interface Sci.* **79**, 578 (1981).