

INTERACTION OF POLY(SODIUM SULFODECYL METHACRYLATE) WITH CETYLTRIMETHYL AMMONIUM BROMIDE IN AQUEOUS SOLUTION*

Cong-hua Lu, Chuan-qiu Luo and Wei-xiao Cao**

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Abstract The interaction of poly(sodium sulfodecyl methacrylate) (PSSM) with cetyltrimethyl ammonium bromide (CTAB) was studied. It was found that the precipitate formed from PSSM and CTAB will be dissolved by excessive CTAB, resulting in the appearance of two maxima of the solution viscosity at the molar ratio (CTAB/ $-\text{SO}_3^-$) of ≈ 0.68 and ≈ 1.30 , respectively. The first one is related closely to the aggregation of polymer chains via CTAB molecules and the second one should be ascribed to the formation of the mixed micelles comprising surfactant and the polymer's hydrophobic chains. The effect of NaCl on the viscosity, the transmittance of the aqueous solution and the solubility of oil-soluble dye (dimethyl yellow) in the mixed system were also investigated.

Keywords Poly(sodium sulfodecyl methacrylate), Cetyltrimethyl ammonium bromide, Mixed micelle

INTRODUCTION

The interaction between surfactant and polyelectrolyte has received more and more attention in recent years due to both scientific and practical importance^[1–5]. The systems comprising surfactant and polyelectrolyte are related closely to many industrial fields, such as detergent, paint, food and pharmacy. Various techniques^[2, 3, 6–9] for characterizing these systems have been developed including surface tension, viscosity measurement, dye adsorption, surfactant ion-selective electrodes, nuclear magnetic resonance, neutron scattering, X-ray diffraction, cryo-transmittance electron microscopy (Cryo-TEM) *etc.*

It is well known that in dilute solution of such systems, the aggregation of surfactant on the side chains of polymer usually occurs and it is a cooperative process above the critical aggregation concentration (cac), which is far below the critical micelle concentration (cmc) of surfactant^[10]. But in concentrated solution, this phenomenon becomes rather complicated^[7].

The interaction of hydrophobically modified water-soluble polymers (HMWSP) with surfactants exhibits distinct characteristics especially in the rheological behavior. It is always encountered that with the addition of surfactant, the viscosity of HMWSP solution will reach a maximum, then drops rapidly^[11–14] and in certain cases, there exist two viscosity maxima^[15–19]. For example, Goddard *et al.*^[15] found that two viscosity maxima appear in the system consisting of sodium dodecyl sulfate (SDS) and hydrophobically modified cationic cellulose before and after phase separation, respectively. The first maximum was thought to be the result of interaction among a few surfactant molecules with polymer chains. The second maximum (even gelation) was ascribed to the intermolecular aggregation, or even cross-linking, via the mixed micelles from SDS and hydrophobic polymer chains. Furthermore, the rheological properties of the system are affected severely by concentration, the molar ratio of surfactant and polyelectrolyte, as well as the characteristics of the polymer such as hydrophobicity, charge density and its distribution and so on^[15, 17]. In the present article, a biocompatible and anticoagulant

* This work was supported by the National Natural Science Foundation of China (Contract No: 39870227 & 50173002).

** Corresponding author: Wei-xiao Cao (曹维孝), E-mail: wxcao@pku.edu.cn

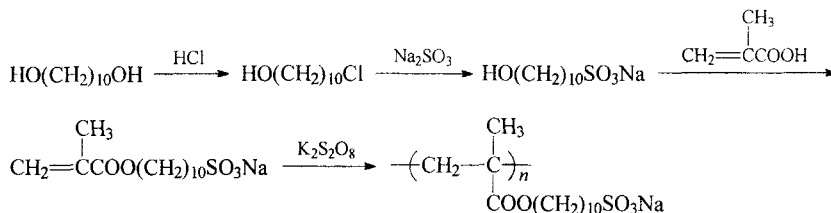
Received May 17, 2002; Revised June 27, 2002; Accepted July 9, 2002

poly(sodium sulfodecyl methacrylate) (PSSM) was selected as HMWSP, and the interaction with CTAB was studied. The results should be helpful in understanding the interaction between the biocompatible materials and organic tissues.

EXPERIMENT

Materials

Cetyltrimethyl ammonium bromide (CTAB) and myristyltrimethyl ammonium bromide (MTAB) were purchased from ACROS. Dimethyl yellow (DMY) was available from Beijing Chemical Reagents Corp. Poly(sodium sulfodecyl methacrylate) (PSSM) ($\eta_{sp}/c = 0.80 \text{ dL g}^{-1}$, determined in 0.5 mol/L NaCl solution) was synthesized according to Ref. [20], and the synthetic route is represented in Scheme 1. Other reagents used were analytically pure grade.



Scheme 1 The synthetic route of PSSM

Preparation of CTAB/PSSM and DMY Solutions

CTAB/PSSM solution was prepared by mixing aqueous stock solutions of PSSM (the concentration of SO_3^- is 0.05 mol/L) and CTAB (0.1 mol/L) in a given ratio of CTAB/ SO_3^- (R). The mixture was stirred thoroughly with a magnetic stirrer for 30 min at $\approx 30^\circ\text{C}$, and stood for 30 min before the measurements. If precipitation occurred, the mixture was filtered. DMY which was used as a spectrum probe for detection of the hydrophobic domain existing in CTAB/PSSM solution, is an oil-soluble dye and sparingly dissolves in water, so excessive DMY was added to CTAB/PSSM solution. After stirring for 12 h at room temperature, insoluble DMY was filtered out and the filtrate was diluted with a mixed solvents composed of ethanol and water ($V/V = 1/1$) to 100 times.

Measurements

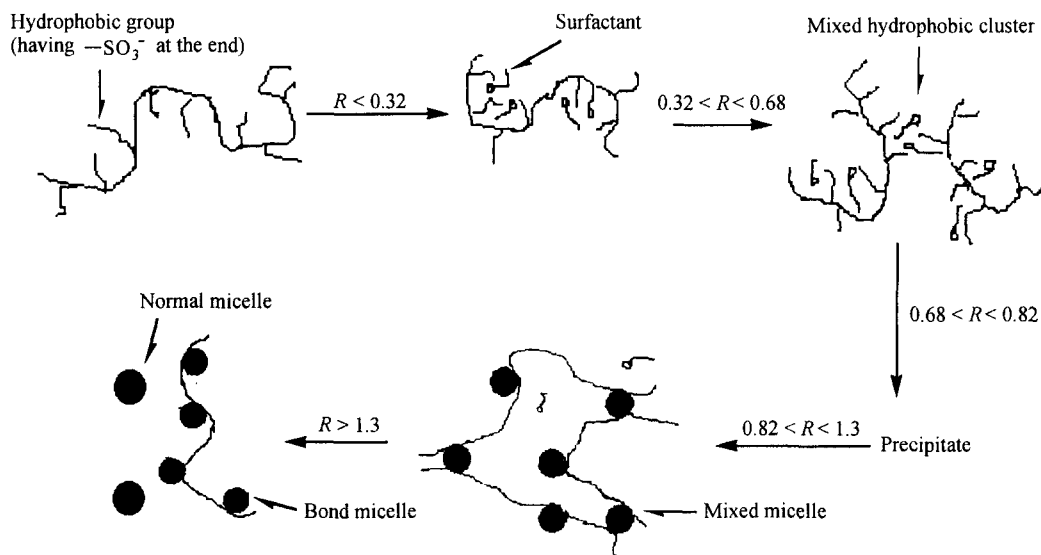
The viscosity of the aqueous solution was measured at $30 \pm 0.1^\circ\text{C}$ using a capillary viscometer equipped with a glass jacket for circling water from a thermostat^[18, 19]. The relative viscosity was obtained as $\eta = t/t_0$, where t and t_0 are the flow time of the solution and the solvent (water) respectively. The light transmittance of CTAB/PSSM aqueous solution (at 700 nm wavelength) and the light absorbance of DMY at 420 nm were determined on a Shimadzu UV-2100 spectrophotometer at room temperature.

RESULTS AND DISCUSSION

Effect of Molar Ratio of CTAB/ SO_3^- (R) on the Viscosity

Figure 1 shows the variation of viscosity with the molar ratio of CTAB/ SO_3^- in CTAB/PSSM aqueous solution. It was found that there exist two viscosity maxima appearing at $R \approx 0.68$ and ≈ 1.3 respectively. The decrease of viscosity in the $0 < R < 0.32$ region is considered to arise from the negative charges (SO_3^-) of PSSM being neutralized partly by CTAB, resulting in the conformational change of PSSM chain from extending rod to coil. In the $0.32 < R < 0.68$ region, the solution viscosity increasing with addition of CTAB is attributed to the aggregation of polymer chains via CTAB molecules^[11, 16]. With further addition of CTAB, precipitate was formed at $0.68 < R < 0.82$ due to the neutralization of the negative charge of PSSM molecules by CTAB. Following the addition of more CTAB, the precipitate was then dissolved, resulting in the appearance of second viscosity maximum at $R \approx 1.3$. It is reasonable to consider that excessive CTAB causes the formation of mixed micelles with hydrophobic chains of PSSM; when all of the PSSM chains take part in forming the mixed

micelles, the solution viscosity reaches its maximum^[11–19]. It is very interesting that the solution viscosity in the $0.82 < R < 1.3$ region is quite susceptible to the time. For instance, the viscosity is lower when it was determined immediately than after waiting for 30 min. This phenomenon means that there exists an equilibrium process for destroying and rebuilding the aggregation. Referring to the model described by Mogny *et al.*^[11], the interaction process between CTAB and PSSM can be illustrated schematically as follows:



Scheme 2 Schematic representation of the interaction existing in the solution of CTAB/PSSM

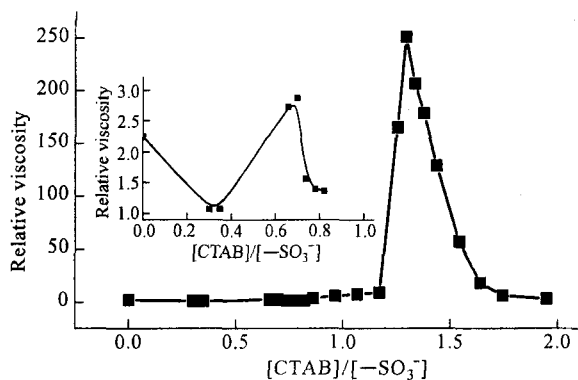


Fig. 1 Relative viscosity of CTAB/ PSSM aqueous solution changes with the molar ratio of CTAB/ $-\text{SO}_3^-$

Effect of NaCl on the Viscosity

Figure 2 shows the effect of NaCl on the viscosity of CTAB/ PSSM aqueous solution. The results show that the maximum value of the viscosity increases markedly especially for the second maximum, as compared with that in the absence of salt (see Fig. 1). This effect should be attributed to the screening effect of NaCl on the charge of PSSM and the decrease of cmc of the surfactant in salt solution^[21]. Therefore, the presence of NaCl is favorable to the hydrophobic interaction between CTAB and PSSM, and thus enhances the solution viscosity.

Light Transmittance of CTAB/PSSM Aqueous Solution

Figure 3 shows the relationship between the light transmittance of CTAB/PSSM solution and the molar ratio of CTAB/ $-\text{SO}_3^-$ at room temperature. We can see that in the region of $0.32 < R < 0.68$, the transmittance decreases (the turbidity increases) rapidly until the appearance of precipitate (phase separation), upon which ($R \approx 0.65$)

the transmittance reaches a minimum. The solution becomes turbid due to aggregation of polymer chains with the surfactant molecules^[22]. In the region of $R > 0.68$, the transmittance increases until all of the precipitate is dissolved.

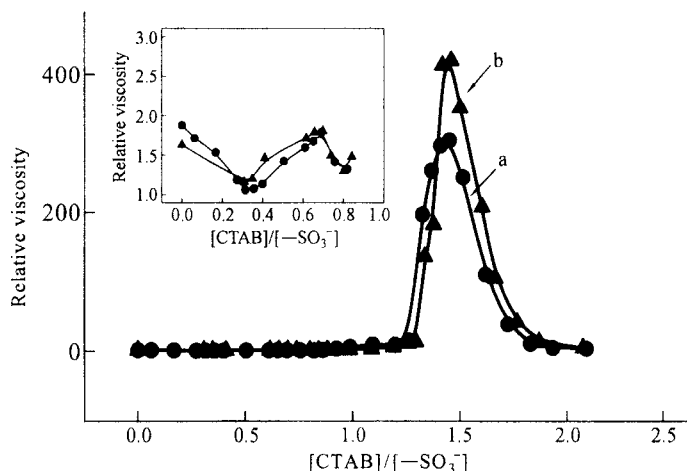


Fig. 2 The effect of NaCl on the relative viscosity of CTAB/PSSM aqueous solution [NaCl]: a) 0.025 mol/L; b) 0.05 mol/L

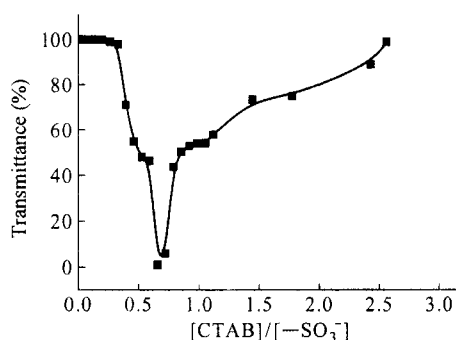


Fig. 3 The transmittance at 700 nm changes with the molar ratio of CTAB/ $-\text{SO}_3^-$ in CTAB/PSSM aqueous solution

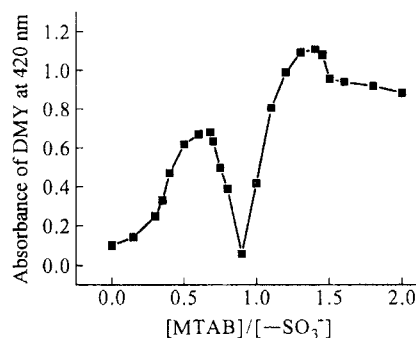


Fig. 4 The absorbance of DMY at 420 nm changes with the molar ratio of MTAB/ $-\text{SO}_3^-$ in MTAB/PSSM aqueous solution

Detection of the Hydrophobic Domains by DMY

Using myristyltrimethyl ammonium bromide (MTAB) instead of CTAB, the changes of the viscosity of the MTAB/PSSM solution are very similar to those of the CTAB/PSSM system. The first and second maxima of viscosity appear at R (MTAB/ $-\text{SO}_3^-$) ≈ 0.68 and ≈ 1.4 respectively. It is known that oil-soluble dye such as dimethyl yellow (DMY) can be used as a spectrum probe to detect the hydrophobic domain in aqueous solution^[18]. Figure 4 shows the absorbance of DMY changes with the molar ratio of MTAB/ SO_3^- in the MTAB/PSSM system. We can see that two maximum absorbance peaks appear at $R \approx 0.68$ and ≈ 1.4 respectively. It is in accord well with the viscosity results determined and shows that the hydrophobic domains, where DMY molecules enter easily, exist at $R \approx 0.68$ and ≈ 1.4 in MTAB/PSSM solution. At $R > 1.4$, the decrease of the absorbance of DMY with further addition of MTAB indicates that the intermolecular aggregation of PSSM is destroyed by excessive MTAB. It is reasonable that similar changes of hydrophobic domains with different R in CTAB/PSSM solution occur.

REFERENCES

- 1 Jönsson, B., Lindman, B., Holmberg, K. and Kronberg, B., "Surfactants and Polymers in Aqueous Solution", John Wiley & Sons Ltd, England, 1998, Chapter 11
- 2 Leung, P.S. and Goddard, E.D., *Colloids Surfaces*, 1985, 13: 47
- 3 Goddard, E.D., *Colloids Surfaces*, 1986, 19: 301
- 4 Liu, J., Nakama, M., Takisawa, N. and Shirahama, K., *Colloids Surfaces, A*, 1999, 150: 275
- 5 Kim, B.S., Ishizawa, M., Gong, J.P. and Osada, Y., *J. Polym.Sci, A-1*, 1999, 37: 635
- 6 Winnik, F.M. and Regismond, S.T.A., *Colloids Surfaces, A*, 1996, 118: 1
- 7 Thalberg, K. and Lindman, B., *Langmuir*, 1991, 7: 277
- 8 Kamenka, N., Kaplun, A., Talmon, Y. and Zana, R., *Langmuir*, 1994, 10: 2960
- 9 Goldraich, M., Schwartz, J.R., Burns, J.L. and Talmon, Y., *Colloids Surfaces, A*, 1997, 125: 231
- 10 Cabane, B. and Duplessix, R., *J. Phys. (Paris)*, 1982, 43: 1529
- 11 Magny, B., Iliopoulos, I., Zana, R. and Audebert, R., *Langmuir*, 1994, 10: 3180
- 12 Tanaka, R., Meadow, J., Williams, P.A. and Phillips, G.O., *Macromolecules*, 1992, 90: 304
- 13 Persson, K., Wang, G. and Olofsson, G., *J. Chem. Soc. Faraday Trans.*, 1994, 90: 3555
- 14 Thuresson, K., Lindman, B. and Nyström, B., *J. Phys.Chem., B*, 1997, 101: 6450
- 15 Goddard, E.D. and Leung, P.S., *Colloids Surfaces*, 1992, 65: 211
- 16 Guillemet, F. and Piculell, L., *J. Phys. Chem.*, 1995, 99: 9201
- 17 Kästner, U., Hoffmann, H., Dönges, R. and Ehrler, R., *Colloids Surfaces, A*, 1996, 112: 209
- 18 Meng, Z.Y., Lu, Y.X. and Cao, W.X., *J. Macromol. Sci. Pure*, 2001, 38: 233
- 19 Zheng, X.L., Meng, Z.Y. and Cao, W.X., *Acta Polymerica Sinica*, 2000, 3: 386
- 20 Chen, W.Y., Xu, B.Z. and Feng, X.D., *J. Polym. Sci, Polym. Chem. Ed.*, 1982, 20: 547
- 21 Clint, J.H., "Surfactant Aggregation", Blackie & Son Ltd., New York, 1992, p.108
- 22 Kästner, U., Hoffmann, H., Dönges, R. and Ehrler, R., *Colloids Surfaces, A*, 1994, 110: 279