



Interactions Between Poly(N-vinyl pyrrolidone) and Sodium Dodecyl Benzene Sulfonate in Aqueous Solution

XIAOMING CHEN^{1,2,*}

¹Department of Polymer Materials and Engineering, Anhui Jianzhu University, Hefei 230601, P.R. China

²School of Chemistry and Chemical Engineering and Anhui Province Key Laboratory of Environment-Friendly Polymer Materials, Anhui University, Hefei 230039, P.R. China

*Corresponding author: E-mail: chenxmyn@hotmail.com

Received: 18 February 2014;

Accepted: 5 May 2014;

Published online: 6 November 2014;

AJC-16199

Poly(N-vinyl pyrrolidone) is a nonionic water-soluble amphiphilic polymer. The nitrogen atom of side group in poly(N-vinyl pyrrolidone) macromolecular chain possesses a partial positive charge. Therefore, electrostatic interactions between the nitrogen atom in poly(N-vinyl pyrrolidone) and the anionic surfactant headgroup of sodium dodecyl benzene sulfonate should be taken into account in PVP-SDBS system. As a result the viscosity, conductivity and surface tension measurements show that the interaction between poly(N-vinyl pyrrolidone) and sodium dodecyl benzene sulfonate can be explained by the two-stages interaction model which originally is suggested for polyelectrolyte-surfactant systems. In the first stage the anionic headgroups of sodium dodecyl benzene sulfonate individually bind to the "cationic" side groups of poly(N-vinyl pyrrolidone) chain due to electrostatic attraction. When the surfactant concentration increases, the second stage of the micellization of polymer-bound surfactant occurs.

Keywords: Poly(N-vinyl pyrrolidone), Sodium dodecyl benzene sulfonate, Interaction.

INTRODUCTION

The polymer-surfactant systems have been found many applications in industry¹⁻⁶ and are closely related with life science. One of the key problems in polymer-surfactant system is the interactions between macromolecules and surfactant molecules and the resulting micellization of polymer-bound surfactant⁷.

For polyelectrolyte-surfactant systems, both theory and experiments indicated^{7,8} that the interactions between polyelectrolyte and surfactant molecules with oppositely charge could be separated into two processes. Firstly, the surfactant molecule will associate with ionic group in macromolecular chain by the electrostatic interaction of oppositely charged ions in surfactant and polyelectrolyte and form electrostatic salt (initiation process) and secondly the surfactant bounded with macromolecule form micelle-like aggregates by the hydrophobic interaction between adjacently hydrophobic chain, which stabilizes the micelle-like aggregation (cooperative process). This is sometimes called two-stage interaction model^{7,8}.

For nonionic water-soluble amphiphilic polymer-surfactant systems^{9,10}, it has been well recognized that the interactions between macromolecules and surfactant molecules could be taken place when the surfactant concentration is well above

so called the critical aggregation concentration (CAC). If the surfactant concentration reached critical aggregation concentration the surfactants bind onto the polymers in the form of micelle-like aggregates and cause a chain expansion due to electrostatic repulsions between bound micelles. At the critical concentration named polymer saturation point (PSP), the polymer-bound micelles become saturated. The excess addition of surfactants will induce the formation of free micelles in solution. The dimension of polymer chain reaches maximum at the saturation of binding and then decrease due to the screening of electrostatic repulsions by excess ions.

Cabane¹⁰ proposed that micelle-like aggregates combined by surfactant with macromolecular chain will exist and distribute along the extending chain in the way of a coil conformation. The small fraction of segments on the chain will have interaction directly with polar end groups and hydrated methylene groups located on the micelle-water surface in order to reduce the surface free energy, but the main part segments on the chain will stay in the water as the coil-form. The electrostatic interaction and the hydrophobic interaction are the main driving forces in the nonionic water-soluble amphiphilic polymer-surfactant systems.

Poly(N-vinyl pyrrolidone) (PVP) is a nonionic water-soluble amphiphilic polymer, the interaction between PVP and

surfactant seems to obey the Cabane's model, *i.e.* the formation of micelle-like aggregates will take place when the surfactant concentration is beyond the critical aggregation concentration. However the situation is more complicated for the PVP-surfactant system. In the presentation we studied interaction of poly(N-vinyl pyrrolidone)-sodium dodecyl benzene sulfonate system (PVP-SDBS) by means of viscosity, conductivity and surface tension in detail and found that the behaviour of PVP-SDBS system had some similarity with the polyelectrolyte-surfactant systems and could even be explained by the two-stage interaction model.

EXPERIMENTAL

Poly(N-vinyl pyrrolidone) (PVP) with MW = 360000 Da was purchased from Sigma Chemical Company. Sodium dodecyl benzene sulfonate (SDBS purity > 99 %) was obtained from China Xuzhou Second Chemical Company and used without further purification. Two stock solutions were prepared, both containing the desired concentrations of PVP. A high concentration of surfactant was also included in one of the solutions. Known quantities of the stock solutions were mixed to give any desired concentration of surfactant. This procedure was used for all experiments here in which it was desired to vary the surfactant concentration systematically. All water used was distilled and deionized.

All viscosity measurements were carried out using a conventional Ubbelohde capillary viscometer (inner diameter $\phi = 0.55$ mm) at 30 ± 0.1 °C maintained with a thermostatic water bath. Measurements were initiated after approximately 5-10 min equilibrium time. Each flow time was determined by repeating at least five time measurements and kept long to neglect the kinetic corrections to the observed data. The precision of the measurements was ± 0.01 s and the reproducibility was ± 0.1 s. The viscometer was thoroughly cleaned with concentrated chromic acid and deionized distilled water after each experiment.

The conductivity measurements were carried out with a digital conductometer (Peiying Chemical Engineering Technology Co., Ltd., Shanghai, China, model DDY-3C). A conductivity cell with a double-walled jacket to circulate the thermostated water at 30 ± 0.1 °C was used for all measurements.

Surface tension measurements were carried out at 30 ± 0.1 °C with DP-AW surface tension experimental equipment (Sangli Electrical Equipment Co. Ltd., Nanjing, China) using maximum bubble pressure method.

RESULTS AND DISCUSSION

The electrostatic repulsion between polymer-bound surfactant will bring on the extension of macromolecular chain, thus the solution viscosity will increase very much. Therefore the viscosity should be a simple and affective mesure to indicate the interaction between polymer and surfactant. Fig. 1 shows the relative viscosity (η_r) of PVP-SDBS aqueous solutions at fixed PVP concentration as a function of the concentration of SDBS at 30 °C. The most salient feature in Fig. 1 is the sharp increase of the viscosity when $C_{\text{SDBS}} \geq 0.3$ mmol/L. Then, when $C_{\text{SDBS}} \geq 1.7$ mmol/L the viscosity increased more slowly as

can be seen in the difference of the slope of the viscosity curves. However when $C_{\text{SDBS}} \geq 3.2$ mmol/L, $C_{\text{SDBS}} \geq 4$ mmol/L and $C_{\text{SDBS}} \geq 4.3$ mmol/L in the case of $C_{\text{PVP}} = 0.0005$ g/mL, $C_{\text{PVP}} = 0.001$ g/mL and $C_{\text{PVP}} = 0.0015$ g/mL, respectively the viscosity decreased at polymer saturation point (PSP).

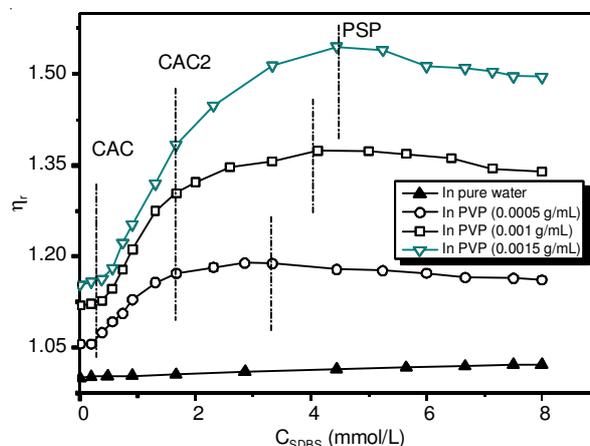


Fig. 1. Relative viscosity (η_r) of SDBS aqueous solutions at fixed poly(N-vinyl pyrrolidone) (PVP) concentration as a function of the concentration of SDBS at 30 °C

Poly(N-vinyl pyrrolidone) is a nonionic water-soluble amphiphilic polymer instead of polyelectrolyte, but it has a side-group of pyrrolidone ring in the chain. As Takagishi and Kuroki¹¹ suggested that the nitrogen located in the side group of PVP chain in water possesses a partial positive charge because the unpaired electron will join together into a conjugate system with pyrrolidone ring, which results in the electron cloud moving to oxygen atom. As a result the nitrogen atom with part positive charge and oxygen atom with part negative charge will be formed (Fig. 2). After oxygen atom protonated by water the PVP will possess positive charge more or less. Therefore the electrostatic interactions between the nitrogen atom in PVP and anionic surfactant headgroup should be taken into account in PVP-SDBS system. The viscosity behaviour of PVP-SDBS system may be explained by the two-stage interaction model of the polyelectrolyte-surfactant systems.

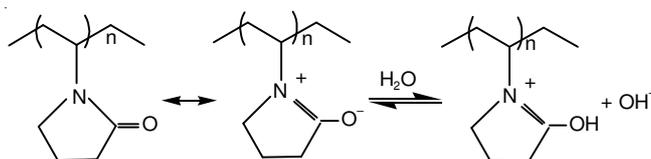


Fig. 2. Schematic illustration of partial positive charge on poly(N-vinyl pyrrolidone) (PVP) side group

Obviously the first turning point in η_r - C_{SDBS} curve corresponds to the initiation of the PVP-SDBS interaction, *e.g.* the critical aggregation concentration (CAC). And it is 0.3 mmol/L. The SDBS molecules bind onto the macromolecules and cause a chain expansion due to electrostatic repulsions between bound SDBS ions.

It is noticed that there are another turning point before the polymer saturation point (PSP) in η_r - C_{SDBS} curve for PVP-SDBS system. We call SDBS concentration corresponding to the second turning point as the second critical aggregation

concentration (CAC2). It is not difficult to understand the critical aggregation concentration² if we follow the two-stage interaction model of the polyelectrolyte-surfactant systems. According to the model critical aggregation concentration² is the concentration beyond which the micellization of polymer-bound surfactant will take part in. In PVP-SDBS system when $0.3 \text{ mmol/L} \leq C_{\text{SDBS}} \leq 1.7 \text{ mmol/L}$ the anionic headgroups of SDBS individually bind to the cationic side groups of PVP chain due to electrostatic attraction. When $C_{\text{SDBS}} \leq 1.7 \text{ mmol/L}$ the micellization of polymer-bound surfactant occurs.

At last the polymer saturation point (PSP) will be reached. They are 3.2, 4 and 4.3 mmol/L for the PVP-SDBS systems with $C_{\text{PVP}} \leq 0.0005$, $C_{\text{PVP}} \leq 0.001$ and $C_{\text{PVP}} \leq 0.0015 \text{ g/mL}$, respectively. The screening of electrostatic repulsions by excess SDBS ions and counterions results in the decrease of solution viscosity.

The formation of larger surfactant micelles or polymer-surfactant complex makes that the mobility of SDBS ions decreases, much like sphere to rod transition of micelles¹². As a result the conductivity increases more slowly with the surfactant concentration. Fig. 3 shows the conductivity of SDBS aqueous solutions at fixed PVP concentration as a function of the concentration of SDBS at 30 °C. Three turning point with different slope can be seen distinctly in κ - c curves corresponding to critical aggregation concentration, critical aggregation concentration² and PSP respectively. It can be also seen in Fig. 4 which shows the surface tension of SDBS aqueous solutions at fixed PVP concentration as a function of the concentration of SDBS at 30 °C. The addition of PVP significantly lowers the surface tension of the surfactant solution. This so-called synergistic effect is well documented in the literature¹³. The surface tension curves of PVP/SDBS systems also display three distinct characteristic concentrations where the surface tension changes quite sharply, corresponding to critical aggregation concentration, critical aggregation concentration² and PSP respectively.

Conclusion

In this paper we studied interaction of poly(N-vinyl pyrrolidone)-sodium dodecyl benzene sulfonate system (PVP-SDBS

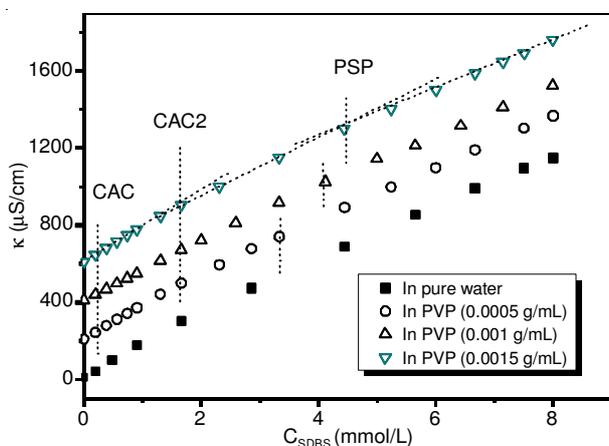


Fig. 3. Conductivity of sodium dodecyl benzene sulfonate (SDBS) aqueous solutions at fixed poly(N-vinyl pyrrolidone) (PVP) concentration as a function of the concentration of SDBS at 30 °C. (○, shifted by +200 μS/cm; Δ, shifted by +400 μS/cm; ▽, shifted by +600 μS/cm)

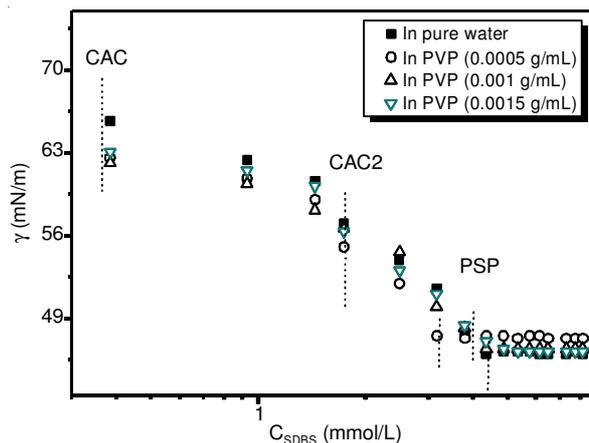


Fig. 4. Surface tension of sodium dodecyl benzene sulfonate (SDBS) aqueous solutions at fixed poly(N-vinyl pyrrolidone) (PVP) concentration as a function of the concentration of SDBS at 30 °C

system) by means of viscosity, conductivity, surface tension and steady-state fluorescence and found that the behaviour of PVP-SDBS system had some similarity with the polyelectrolyte-surfactant systems and could even be explained by the two-stage interaction model which originally is suggested for polyelectrolyte-surfactant systems. The interaction takes place when the surfactant concentration is higher than the critical aggregation concentration (CAC). At polymer saturation point (PSP), the polymer-bound micelles become saturated. The excess addition of surfactants induce the formation of free micelles in solution. The dimension of polymer chain reaches maximum at the saturation of binding and then decrease due to the screening of electrostatic repulsions by excess ions.

ACKNOWLEDGEMENTS

This work was supported by Key Project of Anhui Provincial College Natural Science Foundation (KJ2013A065, KJ2012A052), Anhui Province Key Laboratory of Environment-friendly Polymer Materials Research Fund (KF2012003) and Anhui Provincial Natural Science Foundation (1308085QE88, 1208085ME82).

REFERENCES

1. E. Hoff, B. Nyström and B. Lindman, *Langmuir*, **17**, 28 (2001).
2. D. Dhara and D.O. Shah, *Langmuir*, **17**, 7233 (2001).
3. S. Dai and K.C. Tam, *J. Phys. Chem. B*, **105**, 10759 (2001).
4. E. Feitosa, W. Brown, K. Wang and P.C.A. Barreleiro, *Macromolecules*, **35**, 201 (2002).
5. L. Bernazzani, S. Borsacchi, D. Catalano, P. Gianni, V. Mollica, M. Vitelli, F. Asaro and L. Feruglio, *J. Phys. Chem. B*, **108**, 8960 (2004).
6. A.P. Romani, M.H. Gehlen and R. Itri, *Langmuir*, **21**, 127 (2005).
7. E.D. Goddard, *Colloids Surf.*, **19**, 255 (1986).
8. C. Wang and K.C. Tam, *Langmuir*, **18**, 6484 (2002).
9. A.D. Bó, B. Schweitzer, A.C. Felipe, D. Zanette and B. Lindman, *Colloids Surf. A*, **256**, 171 (2005).
10. B. Cabane, *J. Phys. Chem.*, **81**, 1639 (1977).
11. T. Takagishi and N. Kuroki, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 1889 (1973).
12. A. Desai, D. Varade, J. Mata, V. Aswal and P. Bahadur, *Colloids Surf. A Physicochem. Eng. Asp.*, **259**, 111 (2005).
13. E.D. Goddard, *J. Colloid Interf. Sci.*, **256**, 228 (2002).