Study of the interaction between poly(N-ethyl-4-vinylpyridium bromide) and surfactants in aqueous solution

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Abstract

The interaction between cationic poly(N-ethyl-4-vinylpyridium bromide) (PEVPB) and SDS (sodium dodecyl sulfate) was investigated. It is proved that the polymer-bound micelles of SDS are formed below the CMC of SDS in pure water through fluorescence spectroscopy using pyrene as a probe. Also, it has been found that the PEVPB–SDS interaction depends on what type of confirmation of SDS is added into polymer solution: molecules or micelles. The two systems of PEVPB–SDS molecules and PEVPB–SDS micelles are studied by the measurements of reduced viscosity, fluorescence spectroscopy, conductivity and turbidity. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Studies of the interaction between polymer and dissolved surfactants or colloidal particles have their roots in biochemistry, for they originated from the study of protein–surfactant interaction. It was recognized that in the polymer–micelle complex, the properties both of the micelles and of the polymers are mutually modified. Polymer–micelle interaction plays an important role in the areas of polymer solubilization, [1, 2], conformational change in biopolymers [3, 4], mineral flotation and flocculation [5] and so on. At an early stage of the research in this field, many studies were concentrated on nonionic polymers such as PPO, PEO or PEG, ionic surfactants such as SDS or DTAB and so on [6–9]. Later, there was much discussion in the field of the interaction between polyelectrolytes and oppositely charged surfactants. Since the 1980 s, interaction between polymers (either nonionic or ionic) and cationic surfactants has been developed because of the commercial application of surfactant-selective electrodes [10, 11]. Dubin and co-workers published a system of poly(dimethyl-diallylammonium chloride)-SDS-(Triton X-100). One of the main conclusions was the formation of both intermolecular and intramolecular polymer–micelle complex when the concentration of surfactant was higher than the CMC, [12–14a].

However, little attention has been directed to the study of hydrophobicity changes of surfactants in the presence of polyelectrolytes in the literature. In this paper, hydrophobicity for the system of poly(N-ethyl-4-vinylpyridium bromide)-SDS was studied through several measurements such as reduced viscosity, conductivity, turbidimetry and fluorescence. It was found that the association of polyelectrolyte with SDS micelles can be formed although the SDS concentration was very low and a structure model was speculated. The hydrophobicity change of SDS in the presence of PEVPB was studied with fluorescence using pyrene as a probe.

2. Experiment

2.1. Materials

The preparation of the polyelectrolyte PEVPB is based on the literature [15]. The following scheme

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describes the structure of PEVPB. The degree of polymerization is 1375 by the viscosity measurement. Sodium dodecyl sulfate (SDS) and benzyl dimethyl dodecyl ammonium chloride (BDDAC) are analytically pure. Purified pyrene (Aldrich) was kindly received from the lab of the University of Groningen, the Netherlands (Scheme 1).

2.2. Methods

1. The measured solutions were made as follows: surfactant was added into PEVPB solution under agitation at 30°C. Two kinds of PEVPB–SDS solutions were prepared according to the concentrations of SDS used: system I uses 1.0×10^{-3} M SDS and system II uses 5.0×10^{-3} M SDS. The concentration of PEVPB (C_p) was 1 g/l except in the solutions for measuring reduced viscosity.
2. The viscosity measurements were carried out with Ubbelodhe viscometer in a water bath at 30°C.
3. Turbidimetry measurements were carried out with a spectrophotometer at a wavelength of 420 nm and an effective path length of 1.0 cm.
4. Conductivity was measured with a DDS-12A conductivity meter at 25°C.
5. Solutions for fluorescence measurement were made with the water saturated with pyrene (pyrene concentration is about 1.0×10^{-7} M). Fluorescence spectra were recorded with a RF-540 fluorophotometer at 25°C. The excitation wavelength was 335 nm and the emission spectra were recorded from 360 to 390 nm.

3. Results and discussion

3.1. The effects of charges of the head groups on interactions in the PEVPB–surfactant system

Because of the dissociation of PEVPB in aqueous solution, PEVPB chains with much more positive charges showed an extended conformation. It can be characterized through reduced viscosity. Similar to normal polyelectrolytes, η_{sp}/C_p of the PEVPB solution
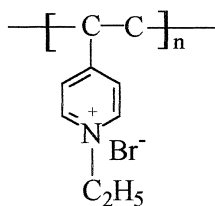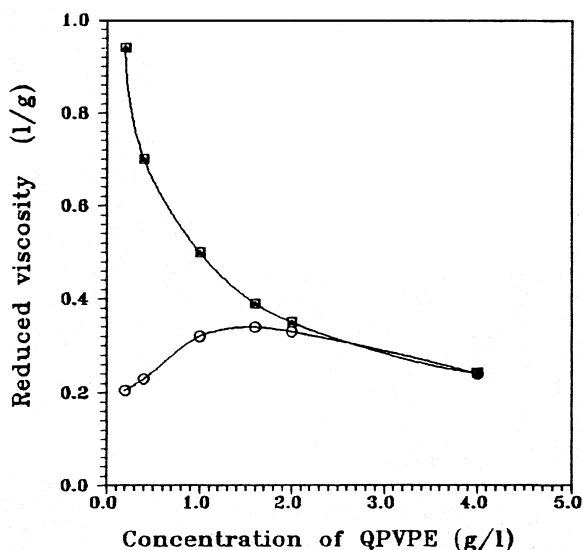

Scheme 1.

Fig. 1. Reduced viscosity (η_{sp}/C_p) of PEVPB in aqueous solutions in the absence and in the presence of low concentrations of surfactants at 30°C: $\square$ in pure water; $\blacktriangle$ in the presence of BDDAC (2.5×10^{-5} M); $\bigcirc$ in the presence of SDS (2.5×10^{-5} M).

increases with diluting solution. Fig. 1 shows that η_{sp}/C_p moderately decreases in the presence of anionic SDS (2.5×10^{-5} M). SDS seems to have no clear effect on η_{sp}/C_p when $C_p > 2.6$ g/l. However, the viscosity behavior in the presence of cationic BDDAC (2.5×10^{-5} M) is the same as the polymer solution without any surfactant. This illustrates that electrostatic action plays an important role in the interaction between polyelectrolytes and surfactants. The head groups with opposite charges (SDS) can interact with PEVPB chains and make their conformation change from extended to compact.

3.2. Study of interactions in the PEVPB–SDS system

Dubin reported that the precipitate was formed in a SDS-Triton X-100 mixed solution in the presence of poly(dimethyldiallylammonium chloride) and this precipitate, formed by a polymer–micelle complex, can not be dissolved again [14b]. Similar behavior was observed in this paper. The solution becomes turbid in an SDS solution in the presence of PEVPB, and a large amount of white fluccule precipitate was formed if the concentration of SDS was higher than the CMC. However, there is no precipitate if the SDS solution at low concentration (1.0×10^{-3} M) was slowly added into the PEVPB solution. It was found that the difference of turbidity is relative to the concentration of SDS used. Fig. 2 shows the difference in turbidity of Systems I and II. The solutions of system I were clear and stable, in contrast, all of the solutions of system II
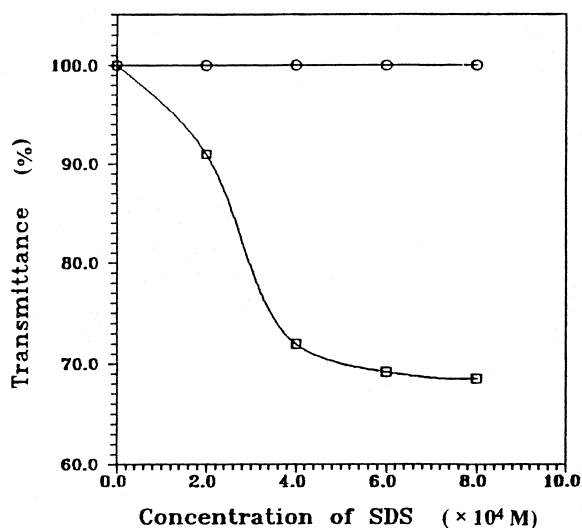
Fig. 2. Turbidity plotted as transmittance (%) vs SDS concentration for two PEVPB–SDS systems: ○ for system I; □ for system II.

Fig. 3. The comparison of conductivity of two PEVPB–SDS systems at 25°C: ○ for system I; □ for system II.

were turbid, although the concentration of SDS with diluted solutions in both systems was the same. The study of fluorescence spectra indicates that the concentration of the formation of SDS micelles in pure water is more than 3.0×10^{-3} M at 25°C (details about fluorescence spectra will be discussed later). Therefore, the formation of SDS micelles is impossible when the concentration is 1.0×10^{-3} M. Thus, the difference in both systems depends on what conformation of SDS is
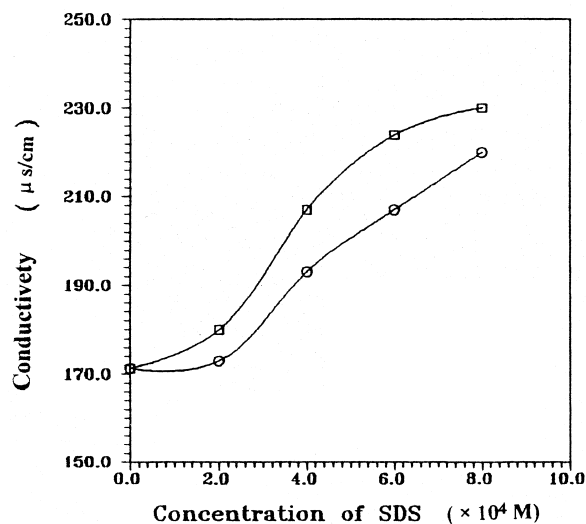
added to the PEVPB solution: micelles or molecules. Then, systems I and II represent two different interactions: PEVPB–SDS molecules and PEVPB–SDS micelles.

Fig. 3 shows the difference in conductivity of the two systems. Generally, the conductivity increases with the addition of electrolyte SDS. The conductivity of system I is slightly less than that of system II. As in the above discussion about the electrostatic action
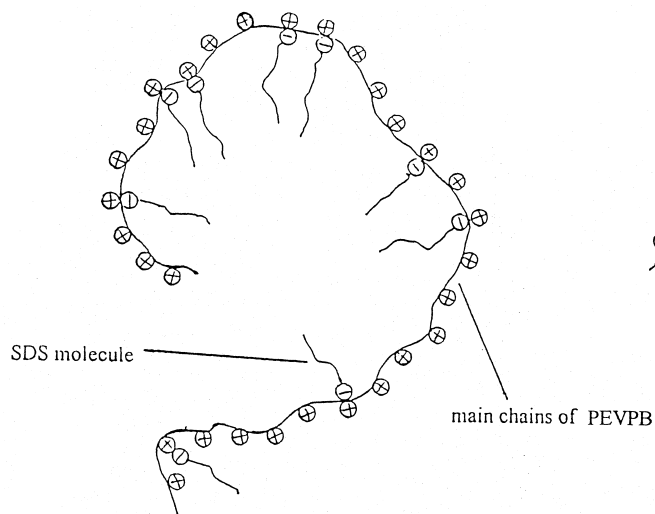
(1) Conformational model of the interaction between PEVPB and SDS molecules.
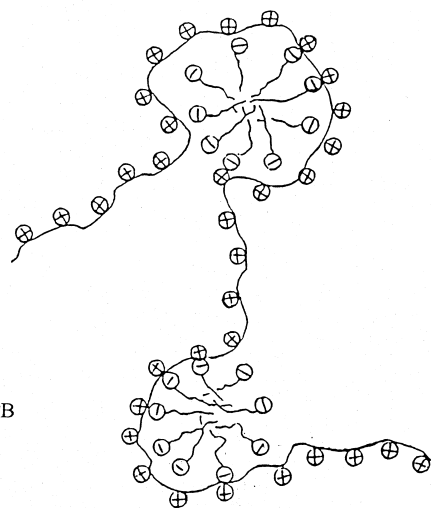
(2) Conformational model of the interaction between PEVPB and SDS micelles.

Scheme 2.

between main chains of PEVPB and head groups of SDS, the counteraction of electrostatic repulsion results in a reduction of conductivity in the system. In other words, PEVPB chains can bind with more SDS molecules. Because SDS micelles are spherical [16] and negative charge density is higher on micelles surfaces, electrostatic action exists between PEVPB and SDS micelles in system II. However, PEVPB chains may not touch and bind with enough SDS head groups because of the steric effect. This could be the reason for the difference of conductivity for the two systems. Scheme 2 describes the conformational models of the two systems when the SDS concentration is low.

3.3. The effect of PEVPB on the hydrophobicity of SDS

Pyrene is usually used as a fluorescence probe to study surfactant aggregation [17, 18] and the conformational state of polysoaps [19, 20]. Because pyrene is a very hydrophobic molecule, it can be very easily solubilized in hydrophobic microdomains (or micelles) for the characterization of hydrophobicity. Fig. 4 shows fluorescence spectra of pyrene in several aqueous solutions. The ratio of the first and third vibronic band (I_1/I_3) in the pyrene fluorescence spectrum is a sensitive indicator of the polarity of the pyrene microenvironment. Fig. 5 is a plot of I_1/I_3 vs concentration of SDS solution. It reveals that the concentration of the formation of SDS micelles is about 3×10^{-3} M at 25°C. Fig. 6 shows the hydrophobicity change of system I in the presence and absence of PEVPB (system II is impossible to measure because of its turbidity). It
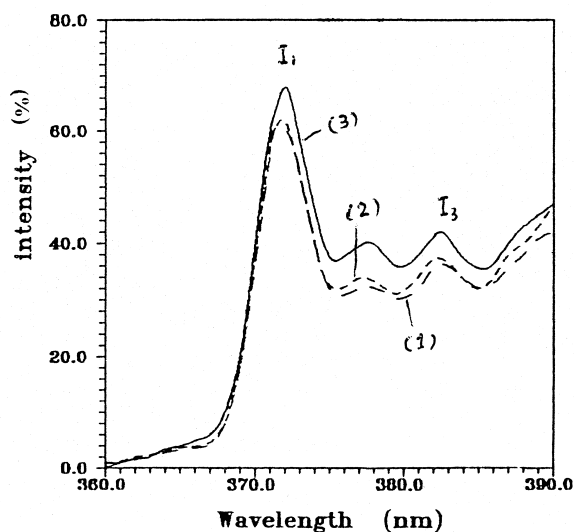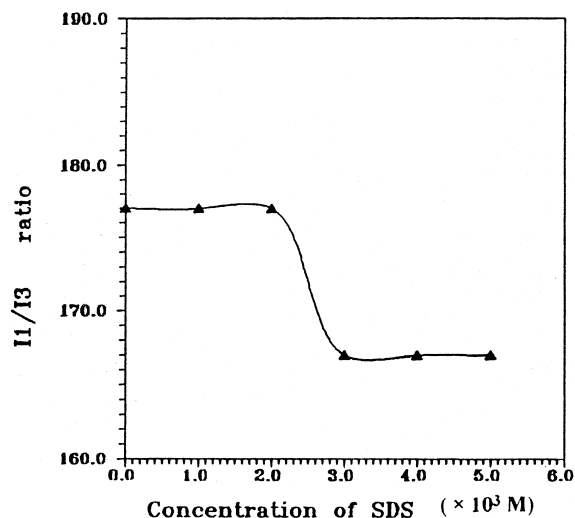

Fig. 5. The plot of I_1/I_3 of fluorescence spectra vs the concentration of SDS aqueous solution prepared by water saturated with pyrene.

clearly indicates that I_1/I_3 of the SDS solution in the absence of PEVPB is equal to that in pure water when the SDS concentration is in the studying range ($< 1 \times 10^{-3}$ M). But I_1/I_3 of system I decreases abruptly at 2×10^{-4} M after the addition of PEVPB (the concentration of PEVPB external solution was 1 g/l). Obviously, the driving force can be attributed to the hydrophobicity interaction in the solution. In the process of interaction between PEVPB and SDS, SDS molecules tend to bind to a site adjacent to other SDS molecules. In this case, the CMC of SDS may decrease (2×10^{-4} M) in the presence of PEVPB. The formation

Fig. 4. Pyrene fluorescence spectra in aqueous solutions at 25°C: (1) in pure water; (2) in the presence of PEVPB (1 g/l) and SDS (1×10^{-4} M); (3) in the presence of PEVPB (1 g/l) and SDS (2×10^{-4} M).
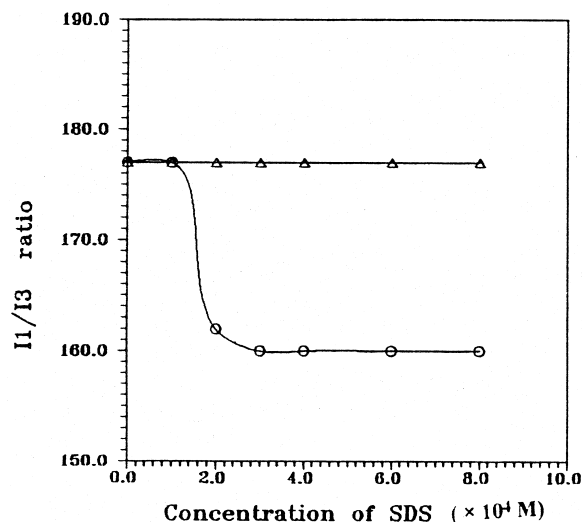

Fig. 6. Pyrene fluorescence in SDS solutions at 25°C: △ in the absence of PEVPB; ○ in the presence of PEVPB (1 g/l).

of so-called polymer-bound micelles is due to the contribution of the hydrophobic force.

4. Conclusion

The formation of polymer-bound micelles of SDS is possible below the CMC of SDS in pure water because of the electrostatic interaction between head groups of SDS and polyelectrolyte chains and the hydrophobic interaction among its alkyl groups. Two kinds of polyelectrolyte–surfactant interactions are dependent on what conformation of SDS is added into the polymer solution: molecules or micelles. Polyelectrolyte–surfactant micelle interaction may exist even though the surfactant concentration is lower than the CMC in pure water.

Acknowledgements

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