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A cationic surfactant is bound to poly(vinylpyrrolidone) in high pH media

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Abstract: Interaction of tetradecylpyridinium bromide with poly(vinylpyrrolidone) was studied by use of an electrode sensitive to the cationic surfactant. In a neutral medium, there was no sign of interaction: potentiometric titration response was in agreement with Nernst equation irrespective of absence and presence of the polymer. But in a medium with pH 11.3, deviation from Nernst response appeared in a PVP solution showing binding of the cationic surfactant onto the polymer which had been thought indifferent to cationic surfactants in spite of strong affinity to anionic surfactants. The result is interpreted in terms of deprotonation from PVP at higher pH media.

Key words: Tetradecylpyridinium bromide – poly(vinylpyrrolidone) – surfactant selective electrode – pH dependence/binding isotherm

Introduction

Among a variety of intriguing phenomena which surfactants show, interaction with polymers is interesting and important from the view points of academic research as well as of applications. Actually, a lot of knowledge has been accumulated and documented in review articles [1–3], but still leaving some to be studied. One such leftover is why cationic surfactants are less affinitive toward neutral water-soluble polymers such as poly(vinylpyrrolidon)[PVP], poly(vinylalcohol) [PVA], poly(ethylene oxide) [PEO], and methylcellulose [MC], while anionic surfactants are very strongly bound to these polymers [2]. The dissymmetry with respect to electric charge is, however, not observed in polyelectrolyte systems [1–3]: cationic surfactants are equally strongly bound to anionic polyelectrolytes as anionic surfactants are bound to cationic polyelectrolytes. Ruckenstein and Hoffmann ascribed the difference to the bulkiness of cationic head group [4], but could not explain another important feature: the order of interaction strength. For anionic surfactants (say, alkyl sulfates), the interaction becomes stronger in the order of PVP > PEO > PVA. But for cationic surfactants, Saito reported a quite reversed order: PVP scarcely bind the cationic surfactants in spite of its strongest hydrophobicity [5, 6]. The same tendency was confirmed on binding isotherms [7].

This dissymmetry with respect to electric charge is not limited to surfactants. Scholtan reported that alkyl sulfonate dyes are strongly bound by PVP, but corresponding cationic dyes are not [8, 9]. So this problem should have wider significance beyond surfactant chemistry.

This reversal of interaction order may be explained by assuming a very minute amount of protonation to these "neutral" polymers with a probable order of "basicity" of the polymers. Even a small amount of charge may be effective for binding anionic surfactant, but reject cationic surfactant. Molyneux also made a similar assumption to explain the binding of phenols to PVP [10, 11]; a slightly positively charged PVP has affinity to slightly negatively charged phenols in combination with other mechanisms such as hydrogen bonding and van der Waals interaction.

In the present study, we carried out some experiments to see how the pH of media affects interaction between PVP and tetradecylpyridinium bromide (TDPBr), a typical cationic surfactant, by means of an electrode selective to the surface-active cation. The experimental result will be interpreted in terms of a possible protonation to PVP.

Experimental

Materials

The *N*-tetradecylpyridinium bromide was synthesized by treating 1-bromotetradecane with dry pyridine and purified by recrystallization from acetone three times after decoloration by active charcoal from methanol solution. Poly(vinylpyrrolidone) (PVP, K-30) is commercially available and purified by dialysis against doubly distilled water for 3 days.

Surfactant-selective electrode: The electrode is based on a concentration cell as follows [12, 13]:

Ag/AgCl/1 M KCl Agar bridge/standard solution ||M|| sample solution /1 M KCl agar bridge/AgCl/Ag ,

where M is the surfactant-selective membrane which is a jelly mixture of 20% poly(vinylchloride) and 80% dioctylphthalate cast from a tetrahydrofuran solution. The electromotive force of the cell was measured with a digital multimeter (Advantest TR6845) with a very high input resistance (> 1000 Mohm). All measurements were carried out in 5 mM NaBr solution at 25 °C.

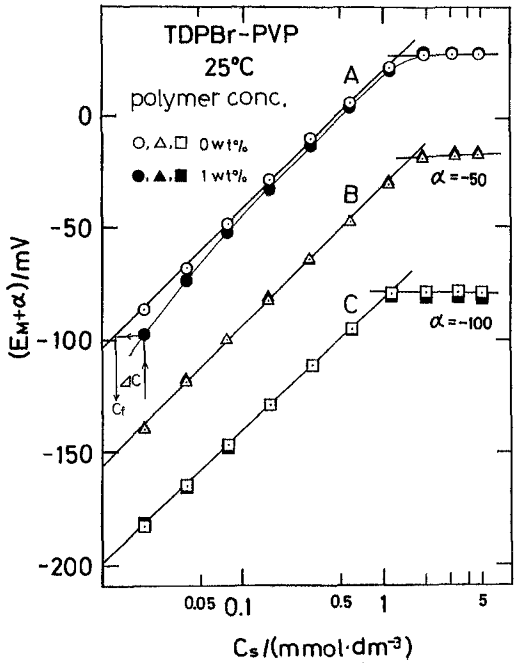

Fig. 1. Potentiograms. Open marks refer to the systems without PVP and filled marks to those with PVP. Medium: A: 2.5 mM Na_2CO_3 (pH = 11.3); B: 2.5 mM Na_2CO_3, pH adjusted to 7 by adding HCl; and C: pH = 6–7 not adjusted (medium is distilled water)

Results and discussion

Figure 1 shows that the electrode is functioning excellently and showing the Nernstian response, i.e., the slopes are nearly 59 mV/dec, and the asymmetric potentials are usually within a few mV (open marks: without PVP). The breaks found around 1 mM TDPBr also confirm the sensitivity of the electrode to TDP cation, since the CMC of the surfactant in the medium lies there. The three pairs of potentiograms (Fig. 1A–C) have displaced each other by 50 mV for clarity. Figure 1C displays experimental results performed without adjusting pH (about 6–7) in the absence and presence of 1% PVP. There is no difference between the two titration curves (open and filled squares), meaning that PVP does not bind the surfactant in the neutral medium in accordance with our previous result [7]. However, in a medium containing 2.5 mM Na_2CO_3 (pH = 11.3), a deviation from the Nernstian response is evident which is a sign of binding TDPBr to PVP. The same experiments were repeated in a medium where the pH was adjusted to 7 by adding a small amount of concentrated HCl to the 2.5 mM sodium bicarbonate solution, and the results are shown in Fig. 1B. Again, the two potentiograms coincide with each other irrespective of the presence of PVP. A preliminary experiment at pH 11 by adding NaOH also resulted in a deviation seen in Fig. 1A. So, it is not carbonate ions that caused the binding of TDPBr, but a high pH is thought to induce the binding. Change in ionic strength will also alter binding affinity, as reported before [14]. However, a slight change in ionic strength, as in the present work, would not introduce an appreciable difference. From the deviation a binding isotherm is constructed by plotting $X = \Delta C/C_p$ vs. $\log(C_f)$, where $\Delta C = C_s - C_f$ is a difference between the total (C_s) and equilibrium

(C_f) concentrations with C_p being the polymer concentration, and the logarithmic plot may facilitate presentation at low surfactant concentration region. It is seen in Fig. 2 that the binding increases with the equilibrium surfactant concentration towards the CMC. This tendency is the same as observed with partially acetylated PVA that is rather affinitive to cationic surfactants among the neutral polymers [7, 15], and it may be understood that protons which have coordinated, even if minutely, to PVP and thus caused repulsive force against cationic surfactants are now removed in an alkaline medium from the polymer which becomes neutral and thus behaves as "normally" as partially acetylated PVA. It might be too difficult to measure the basicity of pyrrolidone ring. The basicity is inferred to be very weak because of the effect of carbonyl group adjacent to nitrogen atom, but it should still be basic. Binding occurs independently (Langmuir type) at a lower concentration region followed by low cooperative binding which emerges by ordinary micelle formation [14]. This binding scheme is a little different from systems involving anionic surfactants which show a sudden binding at somewhere below half the CMC; the binding is saturated just before the ordinary micelle formation starts, and further addition of surfactant only increases the number of micelles. The alkaline medium condition alone does not impose on PVP a very strong affinity to cationic surfactants, while PVP is affinitive to anionic surfactants. The problem is whether or not the cooperative binding begins far below the CMC. Once the cooperative binding starts, polymer molecules will be promptly saturated with bound surfactant molecules before ordinary micellization sets out. The question is why cationic surfactant would not start cooperative binding far below the CMC. One factor may be the bulkiness of the head groups of cationic surfactants as suggested by Ruckenstein et al. [4]. Another factor should be a weaker interaction of PVP with cationic surfactants than with anionic ones. It is speculated that there is also a difference in hydrophobic hydration around methylene groups adjacent to the charged head group. The hydrophobic hydration of that part might be weakened somehow in cationic surfactants, while it might be relatively intact in anionic surfactants, just as was suggested by Robb [16]. Actually, ^{13}C-NMR [17] suggested that polymer chains are lying along the water-hydrocarbon interface of surfactant aggregates, in agreement with thermodynamic consideration [18, 19]. So it is advocated to examine the difference in the hydration around 2–3 methylene groups adjacent to the charged head groups of cationic and anionic surfactants in connection with neutral polymer-surfactant interaction.

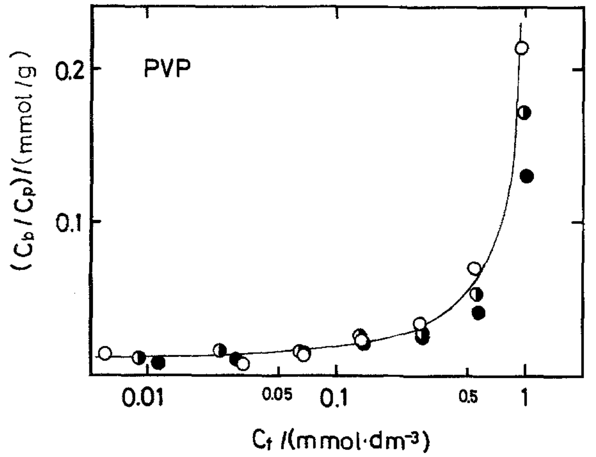

Fig. 2. Binding isotherms of tetradecylpyridinium bromide to PVP in alkaline media. Open and half-filled circles: 2.5 mM Na_2CO_3 (pH = 11.3); filled circles: pH adjusted to about 11 by adding NaOH

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