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ORIGINAL CONTRIBUTION

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Binding of a surfactant counterion to low-charge-density poly(acrylic acid) and poly(methacrylic acid)

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Abstract The binding of a cationic surfactant, dodecylpyridinium (C12Py) chloride, with a low-charge-density poly (methacrylic acid) (PMA) was investigated in buffer solutions under the condition of constant pH. The binding isotherms with PMA consisted of two and three steps at a pH lower and higher than 3.2, respectively. Bindings in the first step were independent of pH and this step was considered to correspond to the solubilization of the hydrocarbon chains of C12Py into the nonpolar region of the compact form of PMA. This is the indication of the compact form from the binding isotherm. At pH higher than 3.2, the second step was discriminated and it depended on the pH. In the third step, a sharp rise in the degree of binding (β) was observed accompanying the solubilization of the precipitates of the PMA–C12Py complex. The binding with poly(acrylic acid) (PAA) and PMA in conventional unbuffered NaCl solutions was also examined and the pH profile of the solution during the binding process was determined. In the case of unbuffered NaCl solutions, the binding with PAA took place cooperatively at the critical association concentration (cac). The binding isotherm consisted of two steps and the pH decreased with the increase in β. The binding isotherm of PMA, on the other hand, consisted of three steps: the pH decreased slightly in the first step and considerably in the second step with the increase in β but it increased with β in the third step, exhibiting a pH minimum around 3.2. The binding in the first step coincided with that obtained in the buffered solutions. Linear relationships between β and the pH were found for both polymers. In the case of PMA, no cac was observed in both buffered and unbuffered NaCl solutions.

Keywords Surfactant ion binding · Poly(acrylic acid) · Poly(methacrylic acid) · Compact form

Introduction

The interaction between strong polyelectrolytes and oppositely charged surfactant counterions has been extensively investigated mainly in terms of binding isotherms [1–5]. The binding isotherms obtained have been analyzed after the treatment by Satake and Yang that is based on the Zimm–Bragg theory for the helix–coil transition of polypeptide [6, 7]. On the other hand, the interaction between weak polyelectrolytes and surfactant counterions has been examined less extensively [8–12]. In the case of weak polyelectrolytes, the proton dissociation equilibrium couples with the counterion binding. It has been reported that pH values of solutions change with the counterion binding [9, 10, 13]. Accordingly, the total number of binding sites and the pH of the solution become functions of the degree of counterion binding (β). This situation has caused

complications that prevent us from a quantitative analysis of the binding isotherms obtained. In order to circumvent the difficulty, a binding isotherm should be measured under the condition of constant pH using a buffer solution. We have investigated the binding of dodecylpyridinium counterion ($C12Py^+$) with low-charge-density poly(acrylic acid) (PAA) at constant pH in buffer solutions [13]. The critical association concentration (cac) decreased with the increase in the charge density of PAA and the binding isotherms obtained at different pH consisted of two steps: the first, the cooperative binding step and, the second, the gradual binding step. We determined binding parameters in the cooperative binding step by taking into consideration the protonation equilibrium and obtained a relatively large cooperativity parameter (u).

It has been pointed out that poly(methacrylic acid) (PMA), a popular weak polyelectrolyte, adopts a compact form at low charge densities [14–19]. It is interesting, therefore, to examine the binding of a surfactant counterion with low-charge-density PMA and to compare the result with that of PAA. The binding of tetradecyltrimethylammonium bromide (TTAB) with PMA was investigated by Kiefer et al. [10] in the presence of unbuffered 0.01 M NaBr. They found significantly low cooperative binding to low-charge-density PMA (the degree of ionization, $i = 0.25$) compared to high-charge-density PMA ($i = 1.0$).

In the present work, we study the binding of C12Py with low-charge-density PMA at constant pH in buffer solutions. In addition, we also investigate the binding behavior of C12Py with PAA and PMA in conventional unbuffered NaCl solutions with due to attention to the pH changes accompanying the counterion binding.

Experimental

PAA was purchased from Aldrich Chemical Co. (molecular weight about 450,000). PMA was purchased from Polysciences (molecular weight about 100,000). The polymer was purified by dialyzing it against pure water and was freeze-dried. C12PyCl was purchased from Tokyo Kasei Kogyo Co. and was purified by recrystallization four times from acetone.

We employed a 0.05 $molkg^{-1}$ glycine/HCl and 0.05 $molkg^{-1}$ NaCl solution (pH 2.8, 3.0, 3.3, 3.5, and 3.8). We also employed 0.1 $molkg^{-1}$ and 0.01 $molkg^{-1}$ NaCl solution as unbuffered NaCl solutions. Polymer stock solutions were prepared by dissolving NaCl solution and the polymer concentrations were determined by potentiometric titration with NaOH in the presence of 1 $molkg^{-1}$ NaCl. Surfactant stock solutions were prepared by dissolving C12PyCl in buffer solution or unbuffered NaCl solution. All sample solutions were prepared by mixing them with polymer stock solution, buffer solution or unbuffered NaCl solution, and surfactant stock solution in this sequence. The polymer concentration ($c_p = 9.0 \times 10^{-3}$ and 1.0×10^{-3} $molkg^{-1}$) referred to residue. Deionized and distilled water was used in all the experiments.

The free $C12Py^+$ ion concentration (c_f) was determined potentiometrically using a cationic surfactant-selective electrode. The surfactant-selective solid membrane was prepared according to the method of Takisawa et al. [20]. In the case of the measurements in an unbuffered NaCl solution, the following cell was used for the binding measurements,

$$\begin{aligned}&\text{Ag/AgCl} \mid \text{KCl (3.3 M) salt bridge} \mid \text{sample solution} \parallel \\ &\text{internal solution } (c_f \approx 1 \times 10^{-3}\ molkg^{-1} \text{ in unbuffered} \\ &\text{NaCl solution}) \mid \text{KCl (3.3 M) salt bridge} \mid \text{Ag/AgCl},\end{aligned} \quad (1)$$

where $\parallel$ denotes the cationic surfactant-selective solid membrane. In the case of a buffer solution, the following cell was used for the binding measurements,

$$\begin{aligned}&\text{Ag/AgCl} \mid \text{sample solution} \mid \text{internal solution} \\ &(c_f \approx 1 \times 10^{-3} molkg^{-1} \text{ in buffer solution same as sample solution}) \mid \\ &\text{Ag/AgCl}.\end{aligned} \quad (2)$$

The electromotive force (emf) of the cell was measured with an Advantest TR8652 or an R8240 digital electrometer with a stability of $\pm$ 0.05 mV. Calibration curves, relationships between the emf and log c_f in polymer-free solution showed very good linearity and the slopes were within 56.0 and 58.0 mV/decade.

The values of pH of the solutions were measured with an Horiba 6028-10T multiple-electrode and an Orion Research EA920ion analyzer. The accuracy of the measurement was ± 0.02. The sensitivity of the instrument was 0.001 pH units in an unbuffered NaCl solution and 0.01 pH units in a buffer solution. A series of sample solutions of nearly identical polymer concentrations and different C12Py concentrations were prepared for the measurements. All measurements were performed at 25 $\pm$ 1 °C.

Results

Binding of C12Py with PAA in unbuffered NaCl solution

The binding isotherms of $C12Py^+$ with PAA and the pH changes of the solutions in the course of the surfactant binding in unbuffered 0.1 and 0.01 $molkg^{-1}$ NaCl solution at 25 °C are shown in Fig. 1. The binding isotherm is the relationship between the degree of binding (β) and the logarithm of the free surfactant ion concentration ($\log c_f$), and β is defined in the present study as follows,

$$\beta = (c_0 - c_f)/c_p \ , \quad (3)$$

where c_0 denotes the total surfactant concentration. Bindings take place in a highly cooperative manner at well-defined concentrations and these concentrations refer to as the critical association concentration (cac). The values of the cac ($\pm 0.2 \times 10^{-4}$ mo kg^{-1}) were 2.3×10^{-4} and 1.3×10^{-4} $molkg^{-1}$ for 0.1 and 0.01 $molkg^{-1}$ unbuffered NaCl solution, respectively. The increase in the cac with the ionic strength is generally expected owing to the decrease in the electrostatic interaction [1]. The shape of the binding isotherms shown in Fig. 1 is scarcely affected by the ionic strength and consists of two steps: the initial cooperative binding step and the following gradual binding step. This shape is similar to that observed in buffered solutions [13]. The comparison of the binding isotherms reveals that the

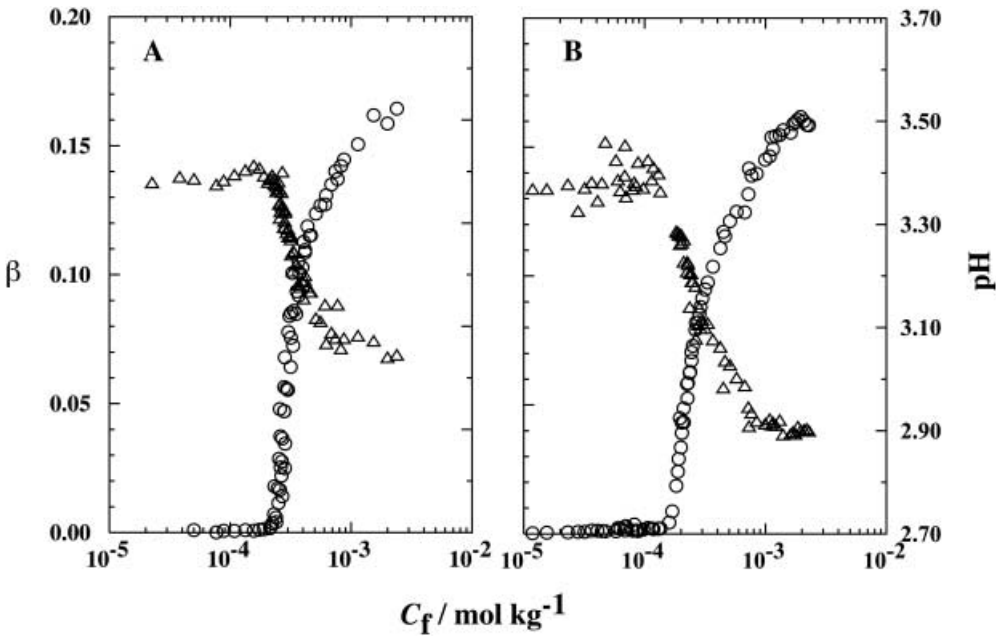

Fig. 1A, B Binding isotherms of dodecylpyridinium ion ($C12Py^+$) with poly(acrylic acid) (*PAA*) in unbuffered NaCl solutions and the relationship of pH values versus $\log c_f$ at $c_p = 9 \times 10^{-3}$ molkg^{-1} and 25 °C. c_{NaCl}: **A** 0.1, **B** 0.01 molkg^{-1}. β (○) and pH (△)

difference is observed in the first step but they coincide with each other in the second step. This fact suggests that the electrostatic interaction mainly dominates the binding behavior in the first step and the contribution of the hydrophobic interaction becomes more important in the second step.

The values of the pH of the solutions practically remained constant when c_f was lower than the cac, decreased steeply in the first step, and much less in the second step. The solutions became turbid when c_f exceeded the cac and then white, sticky precipitates were formed. Dissolution of the precipitates was not observed within the c_f range measured. Kiefer et al. [10] also described the decrease in pH during the addition of TTAB to PAA with a degree of ionization of 0.10. On the other hand, Shimizu [9] reported different results for binding of C12Py with alternating copolymer of maleic acid with ethylene (MAE) and styrene (MASt) at high charge densities. He pointed out that the pH values increased in the sharp rise step of the binding isotherms and then decreased in the leveling-off phase of the binding process in the case of MAE ($i = 0.2$, 0.3, 0.5, 0.6, and 1.0) and MASt ($i = 0.1$, 0.15, 0.2, 0.25, and 0.3). He also described that the relationship of the pH versus $\log c_f$ exhibited a characteristic double-peaked curve corresponding to the two-step binding isotherms in the case of MASt ($i = 0.5$, 0.75, and 1.0).

Binding of C12Py with PMA in unbuffered NaCl solution

The binding isotherm of $C12Py^+$ with PMA and the concomitant pH changes in unbuffered 0.1 molkg^{-1} NaCl solution at 25 °C are shown in Fig. 2. Figure 2 clearly indicates that the binding behavior of C12Py with PMA is different from that with PAA. In the first place, no definite cac was discriminated in the binding isotherm of PMA. The onset concentration of binding was significantly lower than the cac of PAA. Kiefer et al. [10] also found that the binding isotherm of TTAB with PMA ($i = 0.25$) did not show a definite cac. In addition, Fig. 2 indicates that the cooperativity of binding of

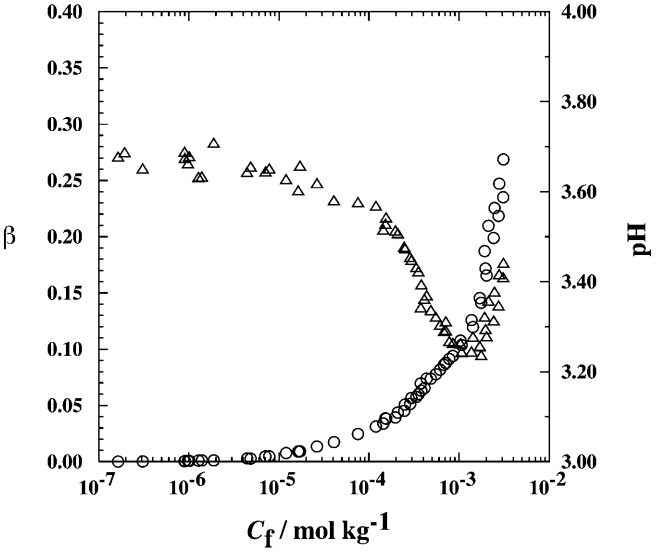

Fig. 2 The binding isotherm of $C12Py^+$ with poly(methacrylic acid) (*PMA*) in unbuffered 0.1 molkg^{-1} NaCl solution and the relationship of pH values versus $\log c_f$ at $c_p = 9 \times 10^{-3}$ molkg^{-1} and 25 °C. β (○) and pH (△)

C12Py with PMA is significantly lower than that of PAA.

In the second place, it should be pointed out that the binding isotherm consists of three steps: the induction step ($10^{-5} < c_f/\text{molkg}^{-1} < 10^{-4}$), the second step ($10^{-4} < c_f/\text{molkg}^{-1} < 10^{-3}$), and the steeply increasing step ($10^{-3} < c_f/\text{molkg}^{-1}$). The pH of the solutions decreased gradually to about 3.55 in the first step and then decreased steeply to about 3.25 in the second step. The solution became turbid and white precipitates were formed in the second step. In the third step, to our surprise, the pH increased and solubilization of the precipitates took place. In this way, the pH passed through the minimum value around 3.25.

Relationships between β and pH

The relationships between β and pH in the first step in the case of PAA and in the second step in the case of PMA are shown in Fig. 3. Figure 3 indicates clearly that the pH values of the solutions decrease linearly with β as follows,

$$\text{pH}(\beta) = \text{pH}(\beta = 0) - A\beta \ . \quad (4)$$

The values of A for PAA are 2.1 and 3.2 in 0.1 and 0.01 molkg^{-1} NaCl solution, respectively and 4.1 for PMA in 0.1 molkg^{-1} NaCl solution. The linearity will be discussed later in detail.

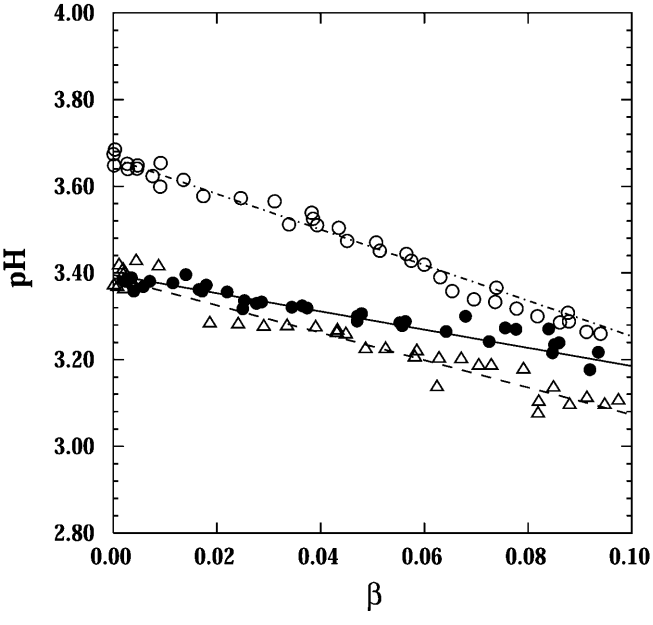

Fig. 3 Relationships of pH values versus β in unbuffered NaCl solution at 25 °C. PAA $c_{NaCl} = 0.1$ molkg^{-1} (●), PAA$c_{NaCl} = 0.01$ molkg^{-1} (△), and PMA $c_{NaCl} = 0.1$ molkg^{-1} (○)

The binding model of C12Py with low-charge-density PMA

A schematic binding model of C12Py with low-charge-density PMA is shown in Fig. 4. In the absence of surfactant ion, it is known that PMA adopts a compact conformation at a pH lower than 5 [14–19].

1. In the first step, surfactant counterions can dissolve in compact regions of PMA by hydrophobic interaction until the maximum solubilization. No cac will be observed because of the relatively low cooperativity of this process.
2. In the second step, surfactant counterions bind with ionized binding sites of PMA by electrostatic interaction. So, a fraction of unionized carboxyl groups dissociate because of the shift of the protonation equilibrium. Binding sites will be formed and the pH of the solution will decrease. In addition, the aggregation of PMA–C12Py complexes may take place by the extra hydrophobicity introduced by the hydrocarbon tails of bound surfactant counterions.
3. In the third step, the binding of surfactant counterions proceeds further and the solubilization of aggregates of PMA–C12Py complexes occurs. The solubilization mechanism is considered to be as follows. Surfactant counterion bind with PMA–C12Py complexes with the hydrocarbon chain facing toward the inside of the complex and charged head group toward the solution. As a result, the surface of the PMA–C12Py complex will become more hydrophilic and the dissolution of aggregates will take place. On the other hand, the degree of ionization after binding (α) of PMA will increase in order to counteract positive charges introduced by bound surfactant head groups. Here, α is defined as the molar ratio of COO^- groups to the sum (COO^- + COOH). Therefore, the pH values of the solutions will increase. The hydrophobicity of PMA–C12Py with $\beta = 0.1$ may be sufficient to form the second layer of bound surfactant.

Binding of C12Py with PMA at constant pH in buffer solution

Recently, we studied the binding behavior of C12Py counterion with PAA at low but constant pH values in buffer solutions [13]. We have applied this approach to PMA in the present study. An example of the binding isotherm and the pH value of solution is shown in Fig. 5. The constancy of the pH was better at a low c_p (Fig. 5b) than at a high c_p (Fig. 5a). Figure 5 also indicates that the binding isotherm does depend on the PMA concentration c_p.

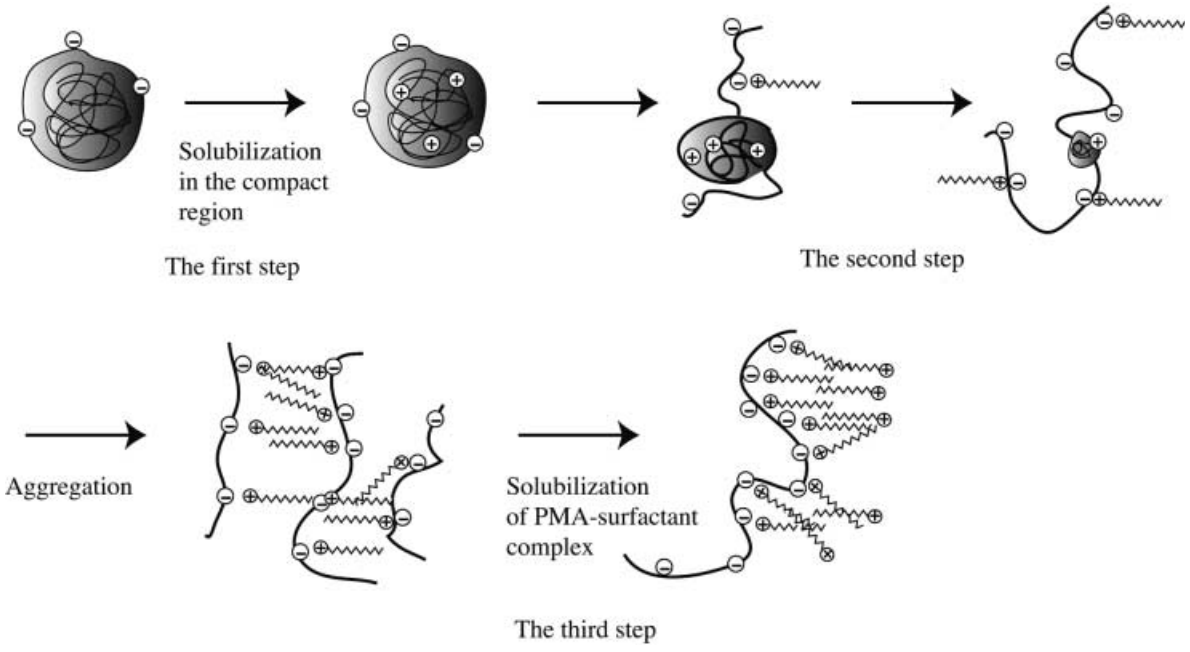

Fig. 4 A schematic illustration of the binding model of surfactant ion with PMA

Binding isotherms (curve a) at pH values lower than 3.2 in buffer solutions and the binding isotherm in unbuffered NaCl solution (curve b taken from Fig. 2) for the purpose of comparison are shown in Fig. 6. As shown in Fig. 6, the binding isotherms at pH 2.8 and 3.0 were almost identical. This is simply because the charge densities of PMA at these two low pH values are nearly equal. The binding isotherms in buffer solutions consisted of two steps in contrast to the three steps in the unbuffered solution. The two steps are considered to correspond to the first and the third steps of curve b. The absence of the second step in the binding isotherm shown by curve a may be explained as follows. The compact region of PMA will grow as the pH decreases and the amount of solubilization of the surfactant in the region will increase accordingly. The hydrophobicity of the PMA–C12Py complex at the final stage of the first step is expected to be large enough to form the second layer of bound surfactant and hence the binding process

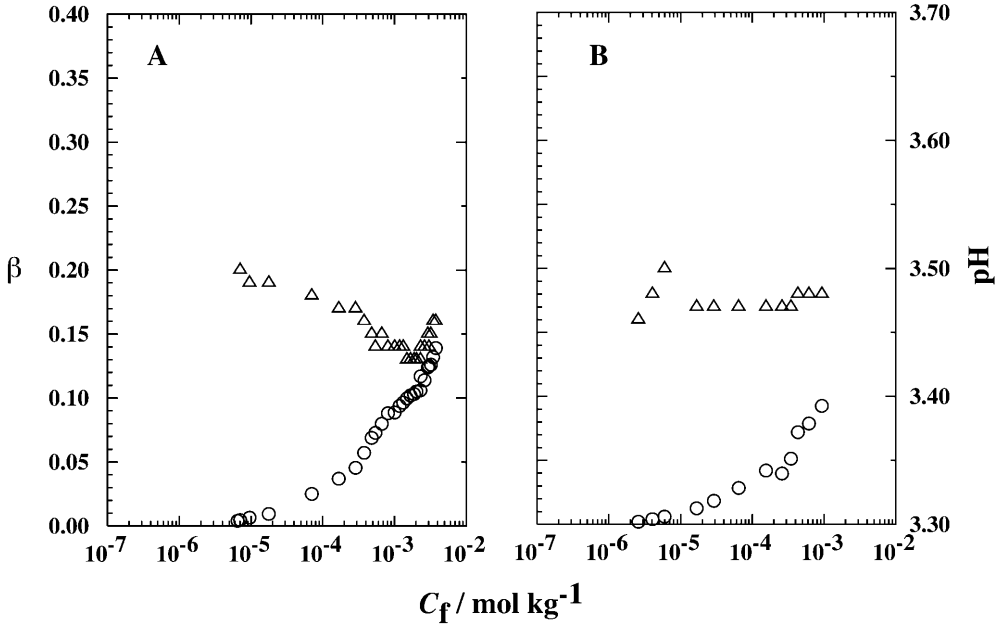

Fig. 5A, B An example of the constant pH values during the $C12Py^{+}$ binding process in 0.05 $molkg^{-1}$ buffer solution at 25 °C. **A** $c_p = 9 \times 10^{-3}$ $molkg^{-1}$ and **B** $c_p = 1 \times 10^{-3}$ $molkg^{-1}$. β (○) and pH (△)

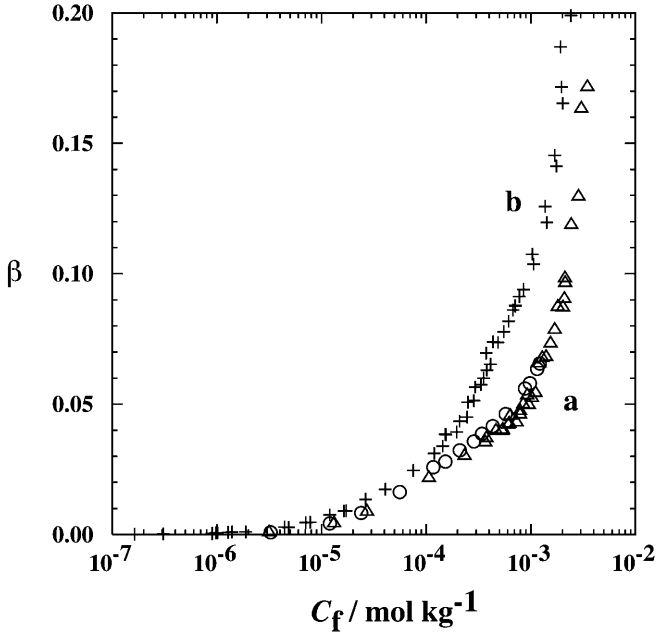

Fig. 6 Binding isotherms of C12Py$^+$ in buffer solutions and unbuffered 0.1 molkg^{-1} NaCl solution at $c_p = 9 \times 10^{-3}$ molkg^{-1} and 25 °C. unbuffered NaCl solution (+), pH 2.8 (○), and pH 3.0 (△)

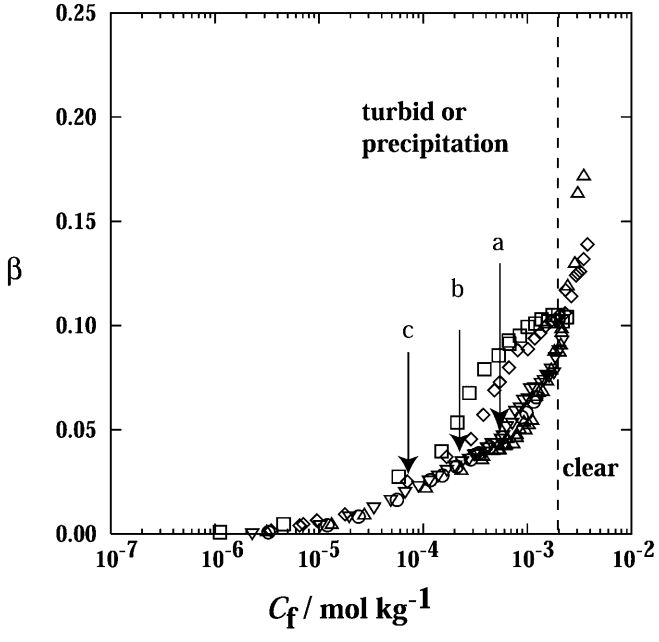

Fig. 7 Binding isotherms of C12Py$^+$ in buffer solutions at $c_p = 9 \times 10^{-3}$ molkg^{-1} and 25 °C. The *arrows* indicate the lowest concentrations where the turbidity of the solution or the formation of precipitation was first observed. pH 2.8 (○), pH 3.0 (△), pH 3.3 (▽, *a*), pH 3.5 (◇, *b*), and pH 3.8 (□, *c*)

directly shifts to the third step. That all solutions at pH values lower than 3.2 were transparent is consistent with the picture. Figure 6 also indicates that binding isotherms in buffer solution agree with that in unbuffered NaCl solution in the first step or the solubilization in the compact region.

We tried to analyze the binding isotherms in buffer solutions by the same approach as applied to PAA in the previous study [13]. In the approach, three kinds of site are considered, COO^-, COOH and COO*R* (*R* denoting the surfactant ion) on a one-dimensional lattice and only the interactions between the nearest-neighbor sites are taken into account. Poor agreement with experimental data was found in the case of PMA, however, probably because of the existence of the first step. The binding isotherms obtained at five pH values in buffer solutions are shown in Fig. 7. The binding isotherms at pH higher than 3.2 are clearly different from those at pH lower than 3.2, and they consisted of three steps, similar to that in the unbuffered NaCl solution. All five isotherms coincide with each other in the first step. This pH-independent nature of the first step strongly supports the validity of our binding model that surfactant counterions dissolve in compact regions of PMA through hydrophobic interaction.

At pH values higher than 3.2, the concentration of the onset of the second step (c_f^*) decreases and β increases with the increase in pH. This is because the compact region of PMA and the amount of solubilization in the region will decrease as the pH increases. On the other hand, the number of binding site of PMA increases with increasing pH. Increased values of β will result in increased hydrophobicity of the complex. Precipitates were then formed in the second step. A sharp increase in β in the third step took place when β exceeded about 0.1. This implies that the critical extent of the hydrophobicity of the PMA–C12Py complex that allows the second layer of bound surfactant to be formed is about 0.1. Dissolution in the third step of the precipitates formed in the second step strongly supports our model; however, no dissolution of precipitates was observed at pH 3.8.

Discussion

Existence of the compact form of PMA at low charge density

The compact form of low-charge-density PMA has been investigated in detail using various techniques: potentiometry, spectrophotemeric titration, fluorescence [14–19]. In the present study, the surfactant ion binding took place in three steps. The initial step that was independent of pH is characteristic to PMA and it is absent in the case of PAA. This first step was reasonably interpreted as a kind of dissolution of the hydrocarbon chain of the surfactant into the nonpolar domain of the compact form of PMA. The existence of the compact form of

PMA at low charge densities is thus shown from the binding isotherm for the first time.

The solubilization of the PAA–C12Py complex

In the present study, the solubilization of a PMA–C12Py complex was observed as shown in Fig. 2 in the third step where the β value exceeded about 0.1. The number of hydrocarbon chains of the bound surfactants at $\beta > 0.1$ is sufficient enough to allow further binding of the surfactants through hydrophobic interactions. This can be regarded as the solubilization of the complex. On the other hand, no solubilization of the PAA–C12Py complex was observed even in the range of β larger than 0.15. The insolubility may arise from the lower nonpolar nature of the PAA–C12Py complex. The solubilization of the PAA–C12Py complex may be observed at higher β values expected at significantly high c_f. Actually, Kogej and Skerjanc [12] have reported the solubilization of the PAA–C16Py complex, which is more hydrophobic than the PAA–C12Py complex. However, the c_f which is required to solubilize the PAA–C12Py complex is likely to be higher than the critical micelle concentration of C12Py and hence the solubilization of the PAA–C12Py complex was not observed.

The linear relationship between β and pH

Linear relationships between β and pH values were found in the present study in the first step for PAA and in the second step for PMA. In both steps, the surfactant ion is considered to bind to the ionized site COO^- by electrostatic interaction. On binding, a fraction of the COOH groups will dissociate. Hence, we can write the binding reaction as follows in terms of a parameter f,

$$COO^- + R^+ + f\,COOH \leftrightarrow COOR + f\,COO^- + f\,H^+ \ , \tag{5}$$

where R^+ denotes a $C12Py^+$ ion. The concentration of COOR, [COOR], is equal to βc_p. The increment of the hydrogen ion concentration, $[H^+]_r$, is given by Eq. (6) as follows,

$$[H^+]_r = f[COOR] = f\beta c_p \ . \tag{6}$$

In terms of $[H^+]$, the activity (a_H) and the activity coefficient (γ_H), the pH can be described as follows,

$$pH = -\log a_H = -\log \gamma_H - \log([H^+]_r + [H^+]_0) \ , \tag{7}$$

where $[H^+]_0$ denotes the hydrogen ion concentration either at the cac in the case of PAA or at c_f^* in the case of PMA. Here c_f^* is defined as the onset concentration of the second step. We denote the pH at either the cac or at c_f^* as $pH_0 = -\log(\gamma_H[H^+]_0)$. Then, assuming a negligible change of γ_H for a change of pH, we have

$$pH = pH_0 - \log[1 + ([H^+]_r/[H^+]_0)] \ . \tag{8}$$

Since the change in pH was small, $[H^+]_r/[H^+]_0 \ll 1$, we obtain Eq. (9) after the expansion of $\log[1 + ([H^+]_r/[H^+]_0)]$.

$$\begin{aligned} pH &\sim pH_0 - 0.434\{[H^+]_r/[H^+]_0 \\ &\quad + (1/2)([H^+]_r/[H^+]_0)^2 - \} \\ &\sim pH_0 - 0.434\, f\, c_p\, \beta/[H^+]_0 \end{aligned} \tag{9}$$

According to Eq. (9) from the values of the slope of the straight lines in Fig. 3, we have 0.21 and 0.33 for the f values for PAA in 0.1 and 0.01 $molkg^{-1}$ unbuffered NaCl solutions, respectively. The f value for PMA was 0.26 in 0.1 $molkg^{-1}$ unbuffered NaCl solution. These f values suggest that new binding sites corresponding to one-fifth to one-third of the bound sites are regenerated by proton dissociation. According to the present analysis, a shift of the protonation equilibrium significantly occurs together with the surfactant ion binding.

The low cooperativity of the binding

As shown in Fig. 7, the cooperativity in the second step of binding isotherms of C12Py at constant pH with PMA is significantly smaller than that with PAA in our previous study [13]. Kiefer et al. [10] have shown that the binding of C12Py with fully ionized PMA ($i = 1.0$) takes place with high cooperatively and the binding isotherm is similar to that of PAA. The significantly smaller cooperativity of the binding isotherm observed in the present study is characteristic of low-charge-density PMA. We consider that a part of the compact form still remains in the second step and that the surfactant binding proceeds in parallel with the destruction of the compact form. On account of the resisting interaction, the cooperativity of the binding with PMA is considered to be significantly smaller than that of PAA.

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