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ORIGINAL CONTRIBUTION

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Interaction of partially ionized poly(acrylic acid) with a surfactant counterion at constant pH values

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Abstract Binding of a cationic surfactant ion, dodecylpyridinium ion, to poly(acrylic acids) of low charge densities was examined by potentiometry using surfactant-selective electrodes in the solutions, where the pH was kept constant by employing a pH buffering system. The binding of the surfactant counterions was thus able to be studied at a constant pH during the binding process. The binding took place in two steps, the first cooperative binding step and the second gradual binding step. The critical association concentration decreased as the pH increased, indicating the predominant role of the electric interaction in the binding. The binding isotherms obtained at different but constant pH values were analyzed by the matrix method, taking into account the nearest-neighbor interactions among three different kinds of sites on the polymer: ionized, protonated, and surfactant-bound. The theoretical analysis could describe only the first step but could not explain the second step. A relatively large cooperativity parameter, *u*, was found for the first step and it can be between 3×10^3 and 1×10^4. When the ionic strength was decreased tenfold, the cooperativity of the binding decreased ($u \sim 1 \times 10^3$). The binding constants of the isolated site were $5.5–6.0 \times 10^4$ kg mol^{-1} and slightly increased to 6.5×10^4 kg mol^{-1} as the ionic strength decreased. The deviation of the second step from the theoretical analysis was supposed to arise from a change of proton dissociation constant in the nonpolar space formed by the bound surfactants.

Key words Surfactant-ion binding · Surfactant–polymer interaction · Surfactant-specific electrode · Poly(acrylic acid)

Introduction

Interaction between ionic polymers and surfactant counterions has been studied for many years [1–5]. This interaction has many similarities with the micelle formation of surfactant ions in aqueous solutions. The interaction has been investigated on the basis of the binding isotherm [6–8]. Potentiometry using surfactant-sensitive membrane electrodes is the most direct method to determine the binding isotherm since the pioneering work of Satake and Yang [9]. The binding generally takes place cooperatively at a well-defined concentration, the critical association concentration (cac), just like micellization at a critical micelle concentration. The electrostatic interaction is of primary importance to determine the binding isotherm. The effect of the charge density of polyions on the interaction is interesting and it has been studied by Hayakawa and Kwak [6] by comparing the binding isotherms of a cationic surfactant with various polyanions of different linear charge densities or Manning's parameter, ξ. Different polyions differ not only in the linear charge density ξ but also in other properties and, hence, it was not easy to observe a strong correlation between ξ values and the binding curves [6].

Another way to change the charge density is to use poly(weak acids) or poly(weak bases). Shimizu and coworkers [10–12] first compared the binding isotherms of dodecylpyridinium (C12Py) ions with copolymers of maleic acid (MA) with styrene and of MA with ethylene. The different results observed with the two copolymers of MA were considered to arise from different nonpolar properties of the two comonomers. Binding of dodecyltrimethylammonium counterions to the copolymers of MA with methyl vinyl ether and with butyl vinyl ether were also studied. The cac decreased as the pH or α_0 (the initial values of the degree of ionization) increased in water but the dependence became less significant in 20 mM NaCl [13].

Interactions of poly(acrylic acid) (PAA) and/or poly(methacrylic acid) with surfactant counterions have been studied [11, 14, 15]. According to the results of Shimizu and Kwak [11], the cac of the C12Py–PAA complex slightly increased with α_0 in the range between 0.1 and 0.4 but the cac at $\alpha_0 = 0$ was larger than that at $\alpha_0 = 0.1$. The cac values scarcely depended on α_0 for $\xi > 0.5$. Kiefer et al. [14] observed the constant cac values for the range of α_0 greater than a critical value, α_c, that corresponded to the region when the counterion condensation took place, i.e., $\xi = 1$ ($\alpha_0 = \alpha_c$). However, they observed that the cac decreased with α_0 for the range of α_0 smaller than α_c. This result is inconsistent with the results obtained by others [11, 13]. A recent study on the binding of the hexadecylpyridinium counterion with PAA reported that the cac was the same irrespective of whether α_0 was between 0 and 1 [15]. In all these studies, changes in pH in the course of binding of surfactant counterions were observed [12–14] or expected [15]. This indicates that the binding of counterions couples with the proton dissociation reaction and, hence, the theoretical analysis on the basis of the constant number of total binding sites cannot be applied. The effect of the charge density on the interaction was monitored by cac values or structural parameters directly accessible from spectroscopic measurements. The diverse and mutually inconsistent (in part) results among the previous studies concerning the dependence of the cac on pH are probably due to complex events coupled with the binding. If the binding isotherms are determined under constant pH values in the presence of a buffer, the binding isotherms are expected to be analyzed to provide useful information such as the binding constant and the cooperativity.

Experimental

Materials

PAA was purchased from Aldrich (molecular weight 450,000). The polymer was purified by dialyzing against pure water and was then freeze-dried. Polymer stock solutions were prepared by dissolving the polymer in NaCl solutions. The concentrations of the stock solutions were determined by potentiometric titration with NaOH in the presence of 1 mol/kg NaCl. Glycine + HCl buffer solutions (pH = 2.9, 3.0, 3.1, 3.2, 3.4) were prepared in the presence of 50 mmol/kg NaCl and the concentration of glycine was 50 mmol/kg. Glycine + HCl buffer solutions of tenfold dilution were also employed.

Dodecylpyridinium chloride (C12PyCl) was purchased from Tokyo Kasei Kogyo and was purified by recrystallized four times from acetone. Surfactant stock solutions were prepared by dissolving C12PyCl in buffer solutions. All samples were prepared by mixing polymer stock solution, buffer solution, and surfactant solution in this sequence. The polymer concentration ($c_p = 9.0 \pm 0.2$ and 1.0 ± 0.02 mmol/kg) referred to residue. Deionized and distilled water was used in all the experiments.

Measurements

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. [16]. The following cell was used for the binding measurements

$$\text{Ag/AgCl|sample solution||internal solution|Ag/AgCl} \quad (1)$$

where || denotes the cationic surfactant-selective membrane. The internal solution was prepared by mixing with surfactant solution and the buffer solution having the same pH value as the sample solutions. In order to obtain calibration curves, a series of C12Py solutions of the same pH values as the sample solutions but containing no polymer were used. In the case of the calibration curves, the relationships between the electromotive force (emf) obtained and log c_f showed very good linearity and the typical slope was between 56.0 and 58.0 mV/decade. The emf of the cell was measured with an Advantest TR8652 or a R8240 digital electrometer with a stability of ±0.02 mV. The emf values were recorded more than 30 min after the electrodes had been immersed in the sample solution. A series of sample solutions of nearly identical polymer concentrations and different C12Py concentrations were prepared for the binding measurements.

The pH values of the sample solutions were measured with an Orion Research EA920 ion analyzer. All measurements were performed at 25 ± 1 °C.

Results

Analysis

In order to analyze the cooperative binding isotherms, we adopt the matrix method of the Zimm–Bragg theory applied for the helix–coil transition of polypeptides [17] and later extended to binding phenomena [9, 18].

There are three sites on the linear polymer chain in the present system. We represent the unoccupied site or the COO$^-$ group with 1, the site occupied by the H$^+$ ion or the COOH group with 2, and the site occupied by surfactant ion or COOD with 3. Then, any state of a polymer chain in the course of the binding process is easily expressed by a sequence of three numbers as follows: 12122121333333322112321. ….

The statistical weights for site 1 and site 2 are taken as 1 and *t*, irrespective of the state of the neighboring sites. The statistical weight t is related to the proton dissociation equilibrium between site 1 and site 2 and, hence, it is also related to the pH of the solution. The statistical weight for site 3 that follows 1 or 2 is taken as σs. The statistical weight for the site 3 that follows 3 is taken as s, since we take into account the hydrophobic interaction between hydrocarbon tails of surfactants bound on two neighboring sites.

Since we take into account only one nearest-neighbor interaction between adjacent sites on the polymer, the partition function of a polymer chain, $Z(T, N, c_f)$, can be calculated as follows using the statistical weight matrix, $\mathbf{M}$, and a column vector $(1, 0, 0)^+$.

$$Z = (1, 1, 1)\mathbf{M}^N(1, 0, 0)^+ \ , \tag{2}$$

$$\mathbf{M} = \begin{pmatrix} w11 & w21 & w31 \\ w12 & w22 & w32 \\ w13 & w23 & w33 \end{pmatrix} \ , \tag{3}$$

where w_{ij} stands for the statistical weight of site j neighboring site i.

$$\mathbf{M} = \begin{pmatrix} 1 & 1 & 1 \\ t & t & t \\ \sigma s & \sigma s & s \end{pmatrix}$$

In order to estimate Z, we must calculate eigenvalues of the matrix $\mathbf{M}$. Although the matrix $\mathbf{M}$ is of order 3×3, the characteristic equation can be reduced to quadratic because one of the three eigenvalues of matrix $\mathbf{M}$ is equal to zero.

According to the Zimm–Bragg theory, the degree of binding, β, becomes

$$\beta = \mathrm{d}\ln\lambda_0/\mathrm{d}\ln s \ , \tag{5}$$

where λ_0 represents the largest eigenvalues for the matrix and is given by

$$\lambda_0 = \{(s + t + 1) + [(s - t - 1)^2 + 4\sigma s(1 + t)]^{1/2}\}/2 \ . \tag{6}$$

So, the degree of binding is given by

$$\beta = 1/2 + 1/2\{(s - t - 1)/[(s - t - 1)^2 + 4\sigma s(1 + t)]^{1/2}\} \ . \tag{7}$$

We define β as the number of site 3s per number of total sites as follows: $\beta = [\mathrm{COOD}]/([\mathrm{COO}^-] + [\mathrm{COOH}] + [\mathrm{COOD}])$. This definition differs from those employed by others [12]. Our definition is more suitable in this system because the number of site 2s changes with the binding of surfactant.

At this stage, we relate the statistical weights with thermodynamic quantities including the equilibrium constants. The binding equilibria between the polyanion and the surfactant cation, D^+, can be expressed as follows:

$$\begin{aligned} &(11) + \mathrm{D}^+ \longleftrightarrow (13) \quad \{[13] + [23]\}/[1] = Kc_f = \sigma s, \\ &(21) + \mathrm{D}^+ \longleftrightarrow (23), \\ &(31) + \mathrm{D}^+ \longleftrightarrow (33) \quad [33]/[31] = Kuc_f = s, \end{aligned} \tag{8}$$

where K is the binding equilibrium constant of a surfactant ion to the site 1 which follows a site 1 or a site 2 and Ku is that to the site 1 which follows a site 3. Square brackets denote the concentrations of one of three states and/or dyads.

In the present study, the range of pH examined was below 3.4 and the intrinsic dissociation exponent, $\mathrm{p}K_0$, of PAA was reported to be 4.40 [19]. Hence, the fraction of charged sites is expected to be less than about 0.15. We approximate in the present study that t is given by the relation valid for monobasic acids. In terms of the degree of dissociation (α) t is expressed as follows

$$t = [2]/[1] = (1 - \alpha)/\alpha = \alpha_\mathrm{H}/K_0 \ , \tag{9}$$

since we have for a monobasic acid

$$K_0 = \alpha_\mathrm{H}\alpha/(1 - \alpha) \ , \tag{10}$$

where α_H represents the activity of a proton.

By combining Eqs. (7), (8), and (9), we obtain the final expression for β in terms of K, u, c_f, and α.

$$\beta = 1/2 + (1/2)(\alpha Kuc_f - 1)/[\alpha Kuc_f - 1)^2 + 4\alpha Kc_f]^{1/2} \tag{11}$$

The equation is equal to one that Schwarz had developed in treating noncooperative competitive binding [18].

Binding isotherms at constant pH values in 50 mmol/kg NaCl + 50 mmol/kg glycine/HCl buffer

The binding curves of C12Py ions with PAA at different pH values in 50 mmol/kg buffer (glycine + HCl) at 25 °C are shown in Fig. 1. The curves obtained at different pH values had similar shapes. The binding takes place cooperatively at a well-defined concentration for each pH examined. This concentration is referred to as the cac. The binding became less steep after the initial cooperative step. We call this second step the gradual binding step. Clearly, the cac values decreased as the pH or the charge density increased. The present result is partly consistent with the results of Anthony and Zana [13] with respect to the correlation, but they reported at the same time very weak correlation at 20 mM ionic strength, while we observed clear correlation in the 50 mmol/kg NaCl + 50 mmol/kg buffer. We have thus shown unambiguously that the correlation between the cac and the charge density is not masked even in media of ionic strength 50–100 mmol/kg. The diverse and mutually inconsistent results in the previous study

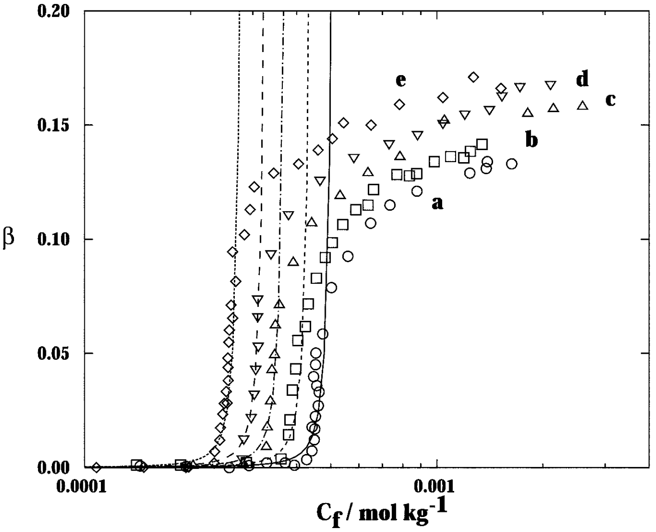

Fig. 1 Binding isotherms of dodecylpyridinium ion (*C12Py*$^+$) in 50 mmol/kg buffer at $c_P = 9 \times 10^{-3}$ mol/kg and 25 °C and theoretical curves calculated from Eq. (11) using $u = 3 \times 10^3$. pH 2.9 (*a*, ○), pH 3.0 (*b*, □), pH 3.1 (*c*, △), pH 3.2 (*d*, ▽), and pH 3.4 (*e*, ◇)

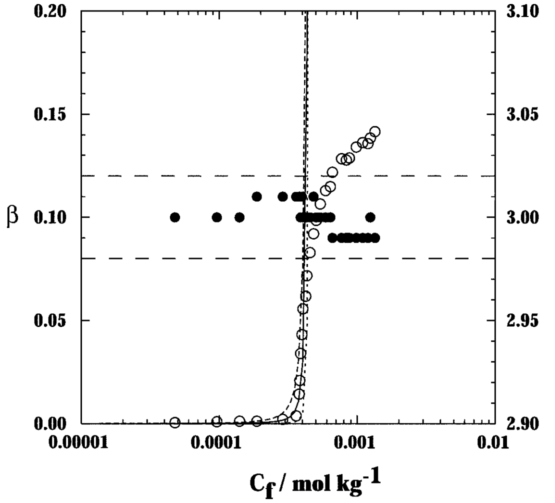

Fig. 2 An example of constant pH values during the C12Py$^+$ ion binding process in 50 mmol/kg buffer. β (○), pH (●). The values of the pH are within the experimental error (± 0.02) indicated by two *dashed lines*. Theoretical binding curves of u ≈ 1×10^3, 3×10^3, and 20×10^3 (from *left* to *right*) at $Ku = 5.9 \times 10^4$ are also shown for comparison

[11–15], which also differ from the present result, possibly originated from different modes of pH changes caused by the binding of surfactant counterions. In the present study, the pH of the solution practically remained constant during the binding process, as shown in Fig. 2 for the case of pH 3.00 ± 0.02. The solution became turbid when c_f exceeded the cac and then white, sticky sediments were formed. To examine the effect of polymer concentration, the binding curves were also determined at $c_p = 1$ mmol/kg for pH 3.0. The solution became slightly turbid and then a minuscule amount of white, sticky sediment was formed. As shown in Fig. 3, the binding curves obtained at two different c_p values differ only slightly, but it is suggested that the binding is smaller at high c_p.

Analysis of the binding isotherms

We fitted Eq. (11) to the isotherms obtained at five different pH values. For the initial cooperative binding step, we found it impossible to fit all the data with a single set of K and u values. We could not determine the u value accurately, simply because it turned out to be large compared with previously reported values for polyion–surfactant counterion pairs. As shown in Fig. 2, any value smaller than 1×10^3 and greater than 2×10^4 is not acceptable as a proper value of u. The data could be fitted well with u values in a range 3×10^3–10×10^3. Tentatively, we employed $u = 3 \times 10^3$ and determined the best fit to the cooperative binding region by adjusting the Ku values. The calculated isotherms are also shown in Fig. 1 with lines. The Ku values obtained shown in Table 1 tend to decrease as the pH increases. This result seems inconsistent with the correlation between the cac and the pH but should not be taken literally. It is to be noted that the quantity obtained from the fitting is αKu instead of Ku itself. Values of αKu increased with pH as shown in Table 1.

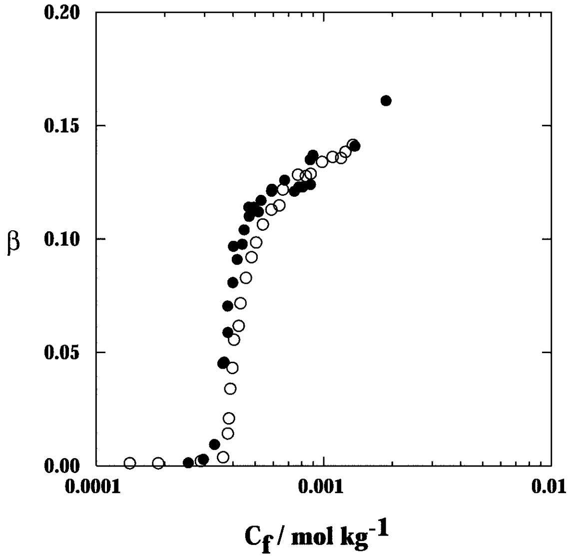

Fig. 3 The effect of poly(acrylic acid) concentration on the binding isotherms at pH 3.0 in 50 mmol/kg buffer. *Open* and *closed* circles represent the results obtained at $c_P = 9.0 \times 10^{-3}$ mol/kg and $c_P = 1.0 \times 10^{-3}$ mol/kg, respectively

Table 1 Values of α, the critical association concentration (*cac*), β_c, and the binding parameters for various pH values in 50 mmol/kg buffer

pH (± 0.03)	α (± 0.2)	cac (mol kg^{-1}) ($\pm 0.3 \times 10^{-4}$)	β_c ($\pm 0.3 \times 10^{-2}$)	αKu (kg mol^{-1}) ($\pm 0.3 \times 10^3$)	Ku (kg mol^{-1}) ($\pm 0.5 \times 10^4$)	u ($\pm 2 \times 10^3$)
2.94	3.4×10^{-2}	4.5×10^{-4}	7.0×10^{-2}	1.9×10^3	5.7×10^4	3×10^3
3.00	3.8×10^{-2}	3.9×10^{-4}	6.0×10^{-2}	2.2×10^3	5.9×10^4	
3.11	4.9×10^{-2}	3.5×10^{-4}	7.5×10^{-2}	2.6×10^3	5.4×10^4	
3.20	5.9×10^{-2}	3.3×10^{-4}	8.0×10^{-2}	3.0×10^3	5.1×10^4	
3.35	8.2×10^{-2}	2.6×10^{-4}	9.5×10^{-2}	3.5×10^3	4.3×10^4	

The Ku value was calculated from αKu and the α value and, hence, was influenced by the accuracy of the latter. In the present study, we approximately evaluated α by assuming monobasic acid behavior. This way of evaluation tends to overestimate α values as the pH increases. We believe the observed anomalous dependence of Ku on pH comes from this source of error. Accordingly, we can conclude that a constant Ku value of 5.5×10^4–6.0×10^4 kg mol^{-1} was obtained in 50 mmol/kg buffer solutions.

It is clear from Fig. 1 that the present theoretical analysis can describe only the initial cooperative binding step of the isotherms. At all pH values examined, the theory cannot describe the second gradual binding step. In the previous study, where the pH was not kept constant, the binding curves exhibited the second plateau region after the cooperative binding step [6, 13, 14]. It was expected that the failure of Eq. (11) to describe the second gradual binding step might originate from the neglected nearest-neighbor interactions. We took into account the interaction between site 1 and site 3 in such a way to introduce a different statistical weight γS for site 3 neighboring site 2, while keeping σS for site 3 neighboring site 1. The statistical-weight matrix, $\mathbf{M}$, is now modified as $\mathbf{M}'$.

$$\mathbf{M}' = \begin{pmatrix} 1 & 1 & 1 \\ t & t & t \\ \sigma s & \gamma s & s \end{pmatrix} .$$

In terms of the binding constant, $\gamma s = Ku' c_f$. It is expected that $\gamma > \sigma$ and hence $u' > 1$. With the values of Ku, u, and three different u' values, agreement between the calculated and the observed binding isotherms was not improved significantly by the incorporation of this nearest-neighbor interaction (not shown). For the moment, we assume that the failure of the present theory arises from neglecting a kind of three-site interaction rather than from neglecting some nearest-neighbour interactions.

We tentatively tried to fit the isotherms by varying the pK_0 values. The result is shown in Fig. 4. We determined the critical values of β and β_c, to define the onset of the deviation. The values of β_c are shown in Table 1 together with the α values. It is found that $\beta_c \geq \alpha$. In the range of β greater than β_c, pK_0 increases with β. This can be ascribed to difficult ionization in the space of a low dielectric constant. We have previously shown that the pK_0 of acrylic acid in the shrunken state of *N*-isopropylacrylamide-*co*-acrylic acid gels is higher than normal values around 5.0 [20]. For $\beta_c = 0.1$ and $\alpha = 0.1$, one ionized carboxylate group is surrounded by, on the average and approximately, one dodecyl tail and eight CO_2H groups. If this mechanism is to be the case, the present result suggests this extent of the nonpolar environment is sufficient to affect pK_0.

Binding isotherms in 5 mmol/kg NaCl + 5 mmol/kg glycine/HCl buffer

To suppress the aggregation of the polymer–surfactant complex, we examined the binding in a medium of low ionic strength of 5 mmol/kg NaCl + 5 mmol/kg glycine/HCl buffer. We examined three pH values of 2.9, 3.0 and

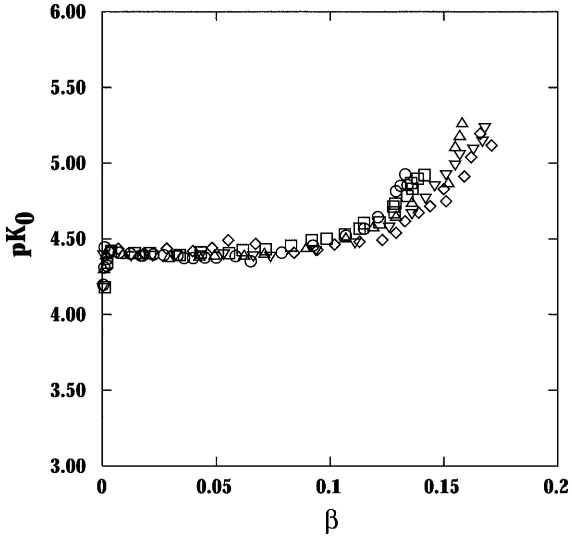

Fig. 4 Calculated values of pK_0 of the carboxyl group as a function of the degree of binding, β. Values of pH: 2.9 (○), 3.0 (□), 3.1 (△), 3.2 (▽), and 3.4 (◇)

3.1. At pH 3.1, the pH began to drop as a deviation from the initial cooperative binding started. Hence, we determined the isotherm in the range $\beta < 0.07$, where the pH drop was smaller than 0.05. For higher initial pH values, we could not keep the pH constant within 0.05 units when the binding proceeded and hence the results are not discussed here. The binding curves also showed two steps, as seen in Fig. 5. The results are summarized in Table 2. In spite of the low ionic strength, the solutions became turbid when c_f exceeded the cac value, but a much smaller amount of white, sticky sediment was formed than encountered in 50 mmol/kg buffer solutions. Hence, the solubility of the complex was improved but not enough to prevent precipitates. The dependence of the cac on the pH was similar to that found in 50 mmol/kg buffer solutions. As seen in Fig. 5, the cooperativity decreased (u was about 1000) in the low ionic strength medium compared with the data in Fig. 1. This is consistent with the previous result on C12Py–dextran sulfate [6, 8]. The values of Ku were approximately constant in the pH range examined, which was lower than that examined in 50 mmol/kg buffer solutions.

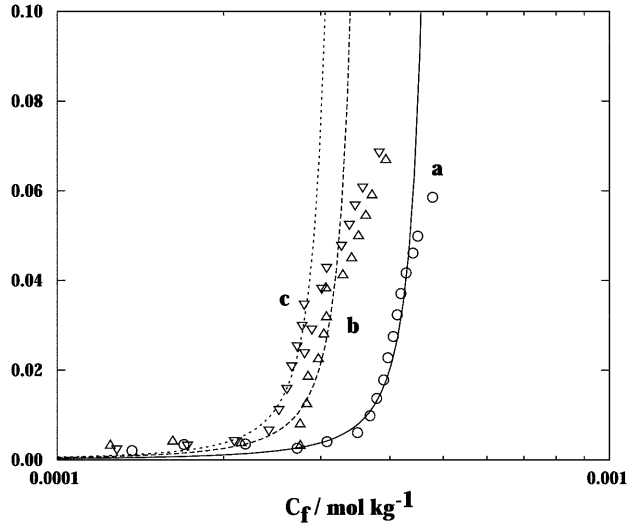

Fig. 5 Binding isotherms of the C12Py$^+$ ion in 5 mmol/kg buffer at $c_p = 9 \times 10^{-3}$ mol/kg and 25 °C and theoretical curves calculated from Eq. (11) using $u = 1 \times 10^3$. pH 2.9 (*a*, ○), pH 3.0 (*b*, △), and pH 3.1 (*c*, ▽)

The value of Ku of 6.5×10^4 kg mol^{-1} was significantly greater than that obtained in 50 mmol/kg buffer solutions. This is reasonable since the major contribution to Ku comes from the electric interaction.

Discussion

In the present study, the binding of C12PyCl to PAA was found to take place in a highly cooperative manner ($u = 3 \times 10^3$), more cooperative than those found on other polyanions of higher charge densities ($u \sim 100$). Although a convincing mechanism for this unexpected high cooperative binding mode is not found at present, it is pertinent to discuss two features characteristic to the present system: the coiled conformation of PAA at low α and the dynamic nature of the unbound sites. In the coiled conformations, two- or three-dimensional interaction among the hydrocarbon chains of bound surfactants becomes possible. In the analysis of the present study, a linear lattice model is employed where one-dimensional interaction between the two neighboring hydrocarbon chains is assumed. The cooperativity may be enhanced by this increased dimensionality in the interaction space. The unbound sites are either ionized (site 1) or protonated (site 2). For a given unbound site, a large fraction of time it is occupied by a proton, but the rate of dissociation and the association of a proton is very rapid compared with the binding/escaping of the surfactant counterions. Owing to the dynamic nature of the unbound sites, the small average fraction of binding sites is expected to scarcely interfere with developing the cooperativity among bound sites. These two factors undoubtedly contribute to the unexpectedly high cooperativity observed in the present study.

The high cooperativity may be related to the precipitation of PAA–C12Py complexes that takes place essentially cooperatively owing to the nature of the phase transition.

If this mechanism is dominant, we should observe more cooperative binding at high PAA concentrations. This expectation is, however, inconsistent with the finding shown in Fig. 3. Although the precipitation of the complex is certainly one of the important mechanisms for the observed unexpectedly high cooperativity, its dominant role cannot be concluded.

Table 2 Values of α, the cac, β_c, and binding parameters for various pH values in 5 mmol/kg buffer

pH (± 0.03)	α (± 0.1)	cac (mol kg^{-1}) ($\pm 0.3 \times 10^{-4}$)	β_c ($\pm 0.3 \times 10^{-2}$)	αKu (kg mol^{-1}) ($\pm 0.3 \times 10^3$)	Ku (kg mol^{-1}) ($\pm 0.5 \times 10^4$)	u ($\pm 2 \times 10^2$)
2.91	3.1×10^{-2}	3.2×10^{-4}	4.8×10^{-2}	2.0×10^3	6.5×10^4	1×10^3
3.03	4.1×10^{-2}	2.9×10^{-4}	4.2×10^{-2}	2.7×10^3	6.6×10^4	
3.09	4.7×10^{-2}	2.0×10^{-4}	3.9×10^{-2}	3.0×10^3	6.4×10^4	

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