Colloid Polym Sci 275:938–945 (1997)

ORIGINAL CONTRIBUTION

H. Kodama
T. Miyajima
M. Mori
M. Takahashi
H. Nishimura
S. Ishiguro

A unified analytical treatment of the acid-dissociation equilibria of weakly acidic linear polyelectrolytes and the conjugate acids of weakly basic linear polyelectrolytes

Received: 4 February 1997
Accepted: 26 May 1997

H. Kodama · Dr. T. Miyajima (✉) · M. Mori
M. Takahashi · H. Nishimura · S. Ishiguro
Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki Higashi-ku, Fukuoka, Japan

Abstract The influence of added sodium chloride concentration levels on the acid-dissociation equilibria of a weakly acidic linear polyelectrolyte and a conjugate acid of weakly basic linear polyelectrolyte has been investigated potentiometrically by use of polyacrylic acid (PAA) and poly(N-vinylimidazole) (PVIm) as examples of polyelectrolytes. Both equilibria are strongly influenced by the degree of dissociation of the polyacids as well as the concentration levels of sodium chloride due to an electrostatic effect originating from the negatively or positively charged polymer surfaces. These have been analyzed in a unified manner by taking accounts of two-phase properties of the charged linear polyions. Distribution of counterions and coions between a polyelectrolyte phase formed around the polymer skeleton and a bulk solution phase has been rationalized by a Donnan's relation. Introduction of a volume term for the polyelectrolyte phase permits definition of averaged concentrations of mobile ions in the vicinity of the polyion molecules, which enables us to define hypothetical intrinsic acid-dissociation constants in the polyion domain. The intrinsic constants estimated by extrapolation of apparent acid-dissociation constants at zero-charge state are in good agreement with the acid-dissociation constants of the monomer analogs of the polymers, i.e., acetic acid for PAA and imidazole for PVIm, respectively. The difference between the apparent and intrinsic acid-dissociation constants for PVIm was much higher than that for PAA at defined degree of dissociation of the polyacids, even though the separations of the functionalities fixed on the linear polymers are approximately equal to each other.

Key words Donnan model – ion-exchange – polyacrylic acid – poly(N-vinylimidazole) – acid-dissociation equilibria

Introduction

Due to its primary importance in the characterization of ion binding in polyion systems, thermodynamic analyses of acid-dissociation equilibria of linear polyelectrolytes with weakly acidic or weakly basic functionalities have been made extensively in various disciplines of chemistry. One of the main objectives of these studies is the evaluation of an electrostatic effect (polyelectrolytic effect) on the ion-binding equilibria inherent in all the highly charged macromolecules. A large number of theoretical approaches to the modeling of the polyelectrolytic proposed up to the present time can be classified into two categories, i.e., (1) approaches based on the Poisson–Boltzmann (P–B) equation [1, 2], and (2) Manning's counterion-condensation (C–C) theory [3]. According to the P–B equation, the electrostatic surface potential of polyions can directly be calculated, where most of the linear polyacids are approximated as rod-like molecules [1, 2]. The potentiometric titration behaviors obtained experimentally have been explained by computing the electrostatic non-ideality terms with two arbitrary parameters, i.e., the closest approach of the counterions to the polyion surface and the linear charge separation of the polyions. Compared with the P–B equation, only one adjustable parameter, ξ, is needed for the C–C theory, ξ being related to the structure of the polyion and is defined as $\xi = 7.14/b$, where b indicates the averaged linear charge separation of a rigid and infinitely long linear polyion, whose skeletal volume is neglected [3]. It is anticipated for all the linear polyions with $\xi > 1$, that univalent counterions such as H^+ ions are "condensed" or "accumulated" in the vicinity of the polyion molecules until the ξ value is reduced to unity. According to this model, discontinuity is predicted to appear in the polyion-titration curve at $\xi = 1$, however, such a peculiar phenomenon has not clearly been observed in their thermodynamic properties [3], which has been a matter of debate [4]. Ambiguities in the geometrical parameters, such as the "closest approach" and the "linear charge separation" needed for the computations by the theoretical approaches become serious, when they are applied to predict the equilibria encountered in the polyion systems with heterogeneous functionalities fixed on flexible polymer backbones, such as naturally occurring polyions.

With regard to the state of counterions "bound" to polyions, it is generally accepted that some fraction of counterions "bound" in a thermodynamic sense, can move freely in a "bound region" formed in the vicinity of the polyion skeleton [5, 6]. This "naive" picture of the "purely electrostatic binding" in polyion systems, has been conceptualized as "counterion-condensation" by Manning [5, 6], and such a counterion binding is termed as "territorial" binding. In the C–C theory, the "bound region" is defined explicitly as a "polyelectrolyte phase", which is separated from the bulk solution phase [5, 6]. Due to this simplification, the model does not give concentration gradients of the mobile small ions from the polyion surface to the bulk solution, but gives the averaged concentrations of counterions and coions in both the polyelectrolyte and bulk solution phases. It has been proven in most cases, however, that the averaged concentrations calculated by the C–C theory are in good agreement with those calculated by the P–B equation [7, 8].

Due to the essential equality of the "two phase" approach in the treatment of ion-binding equilibria of linear polyion systems to the water insoluble cross-linked linear polyion systems, i.e., ion-exchangers, Marinsky has analyzed the ion-binding equilibria of water soluble linear polyions based on a Gibbs–Donnan concept, even though no phase boundary is observable visually between the two phases [9, 10]. The ion-exchange equilibria of counterions between the two phases is quantified according to the Gibbs–Donnan equilibrium. No geometrical parameter is needed for this approach; it only uses the logic of "two phase" in a polyelectrolyte/excess inert salt system. A "polyelectrolyte phase volume", V_p, is defined and the distribution of counterions and coions between the polyelectrolyte phase and the bulk solution phase is described by the Gibbs–Donnan equation. Even though this concept has originally been proposed by Katchalsky [11] and Oosawa [12], its applicability to the analysis of various categories of ionic reactions in polyion systems, has recently been verified by several research groups including the present authors [13] mainly by the use of negatively charged polymers as examples. The theoretical computations by the "P–B equation" or "C–C theory" require hypothetical molecular geometries of polyions as well as ambiguous parameters, however, the Gibbs–Donnan approach determines the electrostatic non-ideality terms directly by the use of ion-binding equilibria as a probe [13], which is experimentally available. In order to examine the validity and the limitation of this semi-empirical model to the thermodynamic analyses of ionic reactions in polyion systems, it is of special interest to examine the ion-binding equilibria of positively charged polyions by this approach. The polyelectrolytic nature of positively charged polyions is compared with that of negatively charged polyions as well.

Since quite a limited number of studies have been carried out on the influences of the magnitudes of added salt concentration on the ion-binding equilibria of weakly basic polyelectrolytes, the present authors have investigated the acid-dissociation equilibria of the conjugate acids of weakly basic linear polymers (positively charged polyions) at 25 °C potentiometrically by the use of a glass electrode in the presence of sodium chloride of a wide concentration range. They are analyzed in a similar manner as weakly acidic linear polymers (negatively charged polymers). The influence of the concentration levels of an excess salt on the equilibria has been examined based on the Gibbs–Donnan logic. PVIm was chosen as an example of the linear polymers. Acid dissociation equilibria of weakly acidic linear polymer, PAA have been examined for comparison. The acid dissociation equilibria of PAA and the conjugate acids of PVIm, $PVImH^+$, have particularly been investigated in detail, because the whole pH region needed for both titration systems, i.e., $3 < pH < 8$, is well suited for the potentiometric pH measurement by the use of a glass electrode. The electrostatic non-ideality terms observed in both polyions of PVIm and PAA at defined degree of charging were compared with each other due to similar linear separation of the functionalities. It is concluded that the influence of excess salt on the ion-binding equilibria of both negatively and positively charged polymers can equally be analyzed based on the Gibbs–Donnan concept as predicted [9], even though an additional non-ideality term, originating probably from the preferential binding of Cl^- ions to the positively charged imidazolium groups is appreciable in the PVIm system.

Theoretical

Acid-dissociation equilibria of the monomeric functionalities of weakly acidic polyelectrolyte, $(HA)_n$, and the conjugate acid of weakly basic polyelectrolyte, $(HB^+)_n$, respectively, can generally be expressed as follows:

$$HA \rightleftarrows H^+ + A^- , \qquad HB^+ \rightleftarrows H^+ + B .$$

Both equilibria may be quantified in a unified manner by defining an apparent acid dissociation constants of the polyelectrolytes, pK_{app}, which is calculated as follows by the use of the pH value and the degree of dissociation of the polyacids, α, which are measured at equilibrium.

$$pK_{app} = pH - \log\{\alpha/(1-\alpha)\} , \tag{1}$$

pK_{app} indicates a macroscopic or overall constant, which is greatly influenced by α, i.e., the electric potential at the surface of the polyion, as well as by the added salt concentration level, C_s, through a Debye–Hückel-type screening effect. We can define a hypothetical equilibrium constant, i.e., an intrinsic acid dissociation constant, pK_0, which corresponds to a microscopic equilibrium constant for respective functionalities. By its definition, pK_0 is free from the electrostatic effect and is constant irrespective of the change in α and C_s. Based on the Donnan's logic, pK_0 can be defined as follows [13] by the use of the averaged pH value in the polyelectrolyte phase, $(pH)_p$.

$$pK_0 = (pH)_p - \log\{\alpha/(1-\alpha)\} , \tag{2}$$

where the subscript p indicates the polyelectrolyte phase. The pK_0 value must be equal to or close to the pKa value of the monomeric acid analog of the polymer functionality. Combining Eqs. (1) and (2), pK_{app} at a defined α value can be related to pK_0 as

$$pK_{app} = pK_0 + \log\{(a_H)_p/a_H\} . \tag{3}$$

In the presence of an excess inert salt, i.e., sodium chloride in the present case, the following relationship is anticipated [13] by equating the activities of NaCl in both the polyelectrolyte and the bulk solution phases:

$$(a_{Na})_p(a_{Cl})_p = a_{Na}a_{Cl} . \tag{4}$$

Similarly, by equating the activities of HCl in both phases, the following equation is obtained:

$$(a_H)_p(a_{Cl})_p = a_H a_{Cl} . \tag{5}$$

Due to the strong electric surface potential formed at the polyion surface, counterions, i.e., Na^+ ions for PAA anions and Cl^- ions for PVIm H^+ cations are highly accumulated in the polyion domain. The activity ratios of the counterions between the two phases, $(a_{Na})_p/a_{Na}$ and $(a_{Cl})_p/a_{Cl}$, can be related to the H^+ ion activity ratio by the use of Eqs. (4) and (5), respectively as

$$(a_{Na})_p/a_{Na} = (a_H)_p/a_H \tag{6}$$

and

$$(a_{Cl})_p/a_{Cl} = a_H/(a_H)_p . \tag{7}$$

Since the $(a_H)_p/a_H$ term in Eq. (3) can be replaced by the counterion activity ratios expressed by Eqs. (6) and (7), the effect of counterion concentration level on the acid-dissociation equilibria of a polyacid, $(HA)_n$, and the conjugate acids of a polybase, $(HB^+)_n$, can be expressed, respectively, as,

$$pK_{app} = pK_0 + \log(a_{Na})_p - \log a_{Na} \tag{8}$$

and

$$pK_{app} = pK_0 - \log(a_{Cl})_p + \log a_{Cl} . \tag{9}$$

It has already been indicated by our previous works [14, 15] that the activities of counterions in the polyelectrolyte phase can be calculated as follows by the use of the specific polyelectrolyte phase volume V_p/n_p, where n_p indicates the amount of the functional groups fixed on the polyelectrolytes. For the $(HA)_n$ system, for example, $(a_{Na})_p$ can be expressed as the product of the activity coefficient of Na^+ ion in the polyelectrolyte phase, $(y_{Na})_p$, and the free Na^+ ion concentration in the polyelectrolyte phase, $[Na]_p$ as $(a_{Na})_p = (y_{Na})_p[Na]_p$. $[Na]_p$ is due to the sum of the two concentration terms, i.e., (1) Na^+ ions present in the polyelectrolyte phase to neutralize the free A^- groups and (2) Na^+ ions imbibed in the polyion domain in the form of Na^+Cl^-. Escape of Na^+ ions from the polyion domain due to their thermal motion produces site vacancy of the polyion which also should be taken into account. This fraction of site vacancy is experimentally available as a practical osmotic coefficient, $\phi_{p,Na}$, which can simply be related to the linear charge separation of the polyion, α/b. It has been revealed experimentally that $\phi_{p,Na}$ is not affected by the change in the polyion concentration level or C_s, which is known as an additivity rule [16, 17]. Since the $\phi_{p,Na}$ values determined in the salt-free system can be substituted for those for the excess-salt system, $(a_{\mathrm{Na}})_{\mathrm{p}}$ in Eq. (8) can finally be expressed as

$$(a_{\mathrm{Na}})_{\mathrm{p}} = (y_{\mathrm{Na}})_{\mathrm{p}} \{(1 - \phi_{\mathrm{p,Na}}) \alpha n_{\mathrm{p}}/V_{\mathrm{p}} + (C_{\mathrm{NaCl}})_{\mathrm{p}}\} . \qquad (10)$$

The $\phi_{\mathrm{p,Na}}$ values for PAA, for example, have been summarized by Katchalsky and the relationship between $\phi_{\mathrm{p,Na}}$ and the linear charge separation of polyions, α/b, has been reviewed in the literature [18].

At sufficiently low concentrations of the added salt, the $(C_{\mathrm{NaCl}})_{\mathrm{p}}$ term in Eq. (10) can be neglected and $\mathrm{p}K_{\mathrm{app}}$ for $(\mathrm{HA})_n$ can be expressed as

$$\mathrm{p}K_{\mathrm{app}} = \mathrm{p}K_0 + \log\{(y_{\mathrm{Na}})_{\mathrm{p}}(1 - \phi_{\mathrm{p,Na}}) \alpha n_{\mathrm{p}}/V_{\mathrm{p}}\} - \log a_{\mathrm{Na}} . \qquad (11)$$

Since the volume term in Eq. (11), $(n_{\mathrm{p}}/V_{\mathrm{p}})$, can be regarded constant at a specified α value when α is close to unity [13], the second term in Eq. (11) is expected to remain unvaried irrespective of the change in the concentrations of the added salt at sufficiently low C_{s}, which results in a straight line whose slope is exactly "-1" when $\mathrm{p}K_{\mathrm{app}}$ is plotted against $\log a_{\mathrm{Na}}$. With an increase in C_{s}, the salt imbibement effect on the $[\mathrm{Na}]_{\mathrm{p}}$ term cannot be neglected and at the higher salt concentration levels, the $(C_{\mathrm{NaCl}})_{\mathrm{p}}$ term becomes predominant over the $\{(1 - \phi_{\mathrm{p,Na}})\alpha n_{\mathrm{p}}/V_{\mathrm{p}}\}$ term. At the extreme condition, where $(a_{\mathrm{Na}})_{\mathrm{p}}$ can be approximated to a_{Na}, it is anticipated from Eq. (8) that $\mathrm{p}K_{\mathrm{app}}$ becomes equal to $\mathrm{p}K_0$. This extreme condition can also be fulfilled by lowering the charge density of the polyions, i.e., at α value close to zero, where the polyelectrolytic nature of $(\mathrm{HA})_n$ diminishes.

For $(\mathrm{HB}^+)_n$, on the other hand, the counter-anion activity in the polyelectrolyte phase, $(a_{\mathrm{Cl}})_{\mathrm{p}}$, can be expressed in the similar manner with Eq. (10) as

$$(a_{\mathrm{Cl}})_{\mathrm{p}} = (y_{\mathrm{Cl}})_{\mathrm{p}} \{(1 - \phi_{\mathrm{p,Cl}})(1 - \alpha) n_{\mathrm{p}}/V_{\mathrm{p}} + (C_{\mathrm{NaCl}})_{\mathrm{p}}\} , \qquad (12)$$

where $(y_{\mathrm{Cl}})_{\mathrm{p}}$ represents the activity coefficient of Cl^- ion in the polyelectrolyte phase and $\phi_{\mathrm{p,Cl}}$ is the practical osmotic coefficient of the chloride solution of $(\mathrm{HB}^+)_n$. Similarly as with the $(\mathrm{HA})_n$ system, it is anticipated that the $\phi_{\mathrm{p,Cl}}$ value is just dependent on the linear charge separation of the polyions, i.e., at a specified α value of nearly zero, the $\phi_{\mathrm{p,Cl}}$ value is not influenced by the polyion concentration level or C_{s}. Combination of Eqs. (9) and (12) gives the following equation:

$$\mathrm{p}K_{\mathrm{app}} = \mathrm{p}K_0 - \log\{(y_{\mathrm{Cl}})_{\mathrm{p}}(1 - \phi_{\mathrm{p,Cl}})(1 - \alpha) n_{\mathrm{p}}/V_{\mathrm{p}}\} + \log a_{\mathrm{Cl}} . \qquad (13)$$

Based on the discussion similar to that mentioned above for the salt concentration dependence of the acid-dissociation equilibria of $(\mathrm{HA})_n$, the following relationship is anticipated for $(\mathrm{HB}^+)_n$; at sufficiently low C_{s}, $\mathrm{p}K_{\mathrm{app}}$ at low degree of dissociation can simply be expressed as a linear function of $\log a_{\mathrm{Cl}}$, whose slope being exactly equal to "$+1$". With an increase in C_{s}, the slope is expected to decrease to approach 0. At ultimately high concentration of added salt, where the $(a_{\mathrm{Cl}})_{\mathrm{p}}$ term becomes equal to a_{Cl}, $\mathrm{p}K_{\mathrm{app}}$ approaches $\mathrm{p}K_0$. At sufficiently high α region, where the charge density of the positively charged polyions decreased remarkably, the polyelectrolyte nature of $(\mathrm{HB}^+)_n$ disappears, and $\mathrm{p}K_{\mathrm{app}}$ values obtained at various C_{s} converge to a constant value of $\mathrm{p}K_0$.

Experimental

Chemicals

The polyacrylic acid sample was prepared by polymerization of acrylic acid monomers with $(\mathrm{NH_4})_2\mathrm{S_2O_8}$ followed by dialysis with cellulose tube against distilled water. The PAA sample thus prepared was freeze-dried and stored at room temperature. The degree of polymerization of the PAA sample was determined by viscosity measurement to be *ca* 2.5×10^3. Poly(N-vinylimidazole) was prepared by free-radical polymerization of N-vinylimidazole in water–methanol mixture (50% v/v) with AIBN as an initiator. PVIm thus prepared was dialyzed by cellulose tube against distilled water. The dialyzed solution was then concentrated by evaporator and then dissolved in methanol. The PVIm was precipitated from ethylacetate, dried in vacua at 80 °C for 24 h and stored at room temperature. The degree of polymerization of the PVIm sample was determined by viscosity measurement to be *ca* 1.0×10^3. All other chemicals used in this investigation were of analytical grade.

Potentiometric titration

Acid form PAA solutions were titrated a standard sodium hydroxide solution ($C_{\mathrm{NaOH}}\ \mathrm{mol\,dm^{-3}}$), whereas neutral PVIm solutions were titrated with a standard hydrochloric acid solution ($C_{\mathrm{HCl}}\ \mathrm{mol\,dm^{-3}}$) at 25 °C. All the sample solutions contained sodium chloride of $C_{\mathrm{s}}\ \mathrm{mol\,dm^{-3}}$. The pH values of the equilibrium solutions were measured under $\mathrm{N_2}$ atmosphere with an Orion 91-01 glass electrode and an Orion 90-01 single-junction reference electrode equipped with an Orion research Ionalyzer 701A. The electrochemical cell for the pH measurement was calibrated by Gran's procedure [19]. The titration procedures were carried out automatically with an Auto-Buret (APB-118, Kyoto Electronics Manufacturing Co. Ltd., Tokyo), controlled by a personal computer.

Colloid & Polymer Science, Vol. 275, No. 10 (1997)

The α value of PAA solution has been calculated by the following equation:

$$\alpha = \{C_{\mathrm{NaOH}} V_{\mathrm{NaOH}} + [\mathrm{H}^+](V_0 + V_{\mathrm{NaOH}})\}/(C_p V_0) ,$$

whereas the α value for the conjugate acid of PVIm has been calculated as

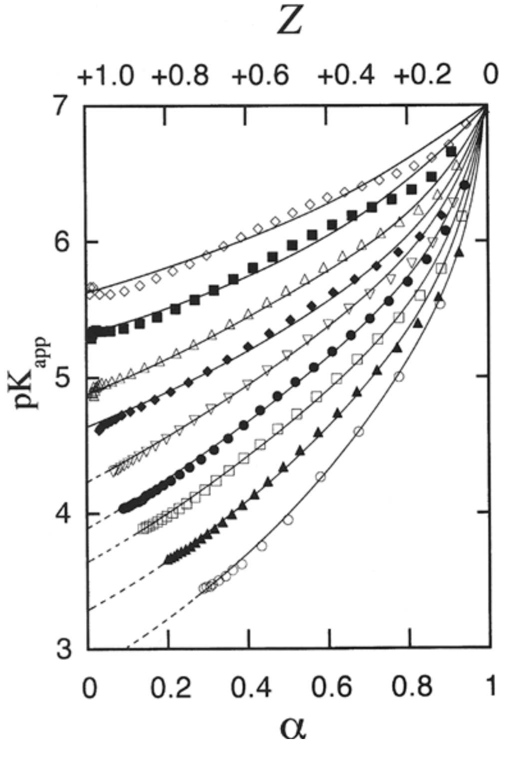
$$\alpha = \{C_p V_0 - C_{\mathrm{HCl}} V_{\mathrm{HCl}} + [\mathrm{H}^+](V_0 + V_{\mathrm{HCl}})\}/(C_p V_0) ,$$

where V_0, V_{NaOH}, and V_{HCl} indicate the initial volume of the polyion solutions, the volume of the added NaOH solution, and the volume of the added HCl solution, respectively. The initial concentration of the polyions, C_p, was kept constant at 2×10^{-3} monomol dm^{-3}.

Results and discussion

The plots of pK_{app} vs α for PVIm and PAA are shown in Figs. 1 and 2, respectively. In these figures, the average charge per one functional group, Z, is shown in the upper abscissa, i.e., $Z = 1 - \alpha$ for the PVIm system and $Z = -\alpha$ of the PAA system, respectively. The pK_{app} value increases with α in both titration systems, whereas the effect of C_s is completely opposite to each other. Depression of pK_{app} with increasing C_s is remarkable in the PAA system, whereas the substantial increase in pK_{app} with the addition of salt is observed for the PVIm system. It should be pointed out that the pK_{app} vs α curves determined under various C_s's converge to specific values of pK_0 for both systems at $Z = 0$, where the surface charge is completely diminished, i.e., at the complete neutral condition. The pK_0 values thus estimated for PVIm and PAA are *ca* 7.0 and *ca* 4.3, respectively, being quite close to the p*K*a values of the monomer analogs of the polymer functionalities, i.e., imidazole (p*K*a = 6.99) [20] for PVIm and acetic acid (p*K*a = 4.56) [21] for PAA.

Fig. 1 Salt concentration effect on pK_{app} vs α plots of PVIm. (○) $C_s = 0.01$ mol dm^{-3}; (▲) $C_s = 0.02$ mol dm^{-3}; (□) $C_s = 0.05$ mol dm^{-3}; (●) $C_s = 0.10$ mol dm^{-3}; (▽) $C_s = 0.20$ mol dm^{-3}; (◆) $C_s = 0.50$ mol dm^{-3}; (△) $C_s = 1.00$ mol dm^{-3}; (■) $C_s = 2.00$ mol dm^{-3}; (◇) $C_s = 3.00$ mol dm^{-3}



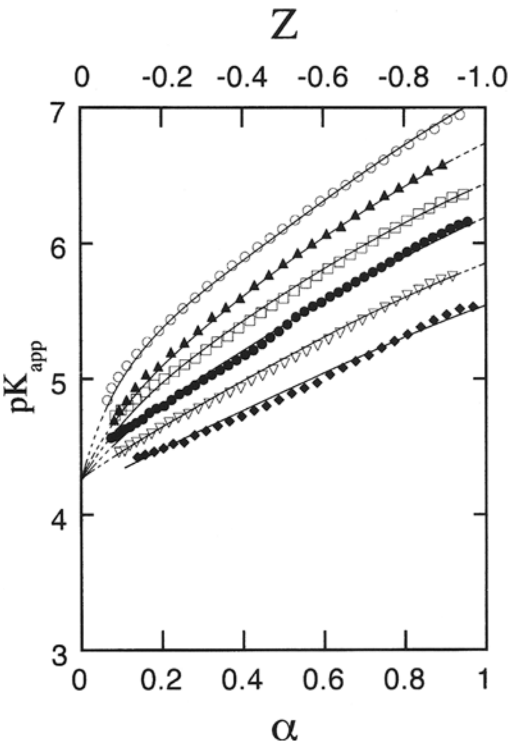


Fig. 2 Salt concentration effect on pK_{app} vs α plots of PAA. (○) $C_s = 0.01$ mol dm^{-3}; (▲) $C_s = 0.02$ mol dm^{-3}; (□) $C_s = 0.05$ mol dm^{-3}; (●) $C_s = 0.10$ mol dm^{-3}; (▽) $C_s = 0.20$ mol dm^{-3}; (◆) $C_s = 0.50$ mol dm^{-3}

The pK_{app} change upon neutralization of the polyacids as well as the effect of the salt concentration level can be rationalized qualitatively by taking into account the repulsion or attraction between H^+ ions and the charged polyions. Due to the crowded positive charges formed at the PVImH^+ polymer surface, the concentration of the free H^+ ions in the vicinity of the polymer molecules is diluted compared with the bulk solution, which results in the decrease of pK_{app} than pK_0 (= 7.0). This electrostatic

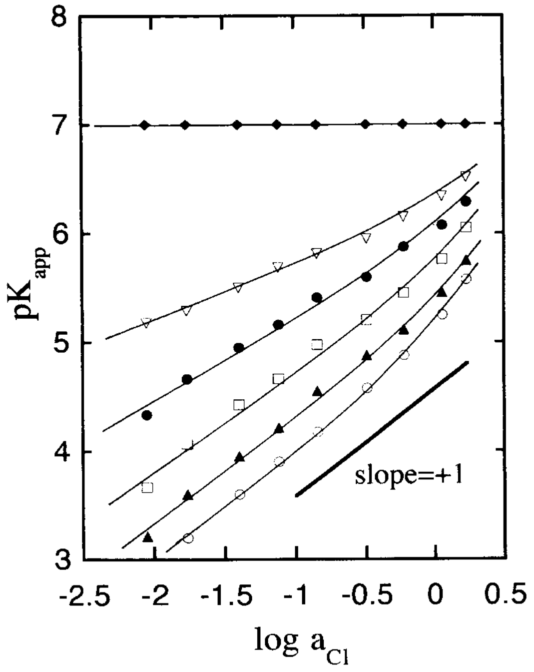


Fig. 3 pK_{app} of PVIm as a function of $\log a_{Cl}$. (○) $\alpha = 0$; (▲) $\alpha = 0.2$; (□) $\alpha = 0.4$; (●) $\alpha = 0.6$; (▽) $\alpha = 0.8$; (◆) $\alpha = 1.0$

repulsion between the positively charged polyion surface and H^+ ions is reduced by the presence of excess salt as shown in Fig. 1 through the Debye–Hückel-type screening effect, which is most pronounced at the highest salt concentration level, i.e., at $C_s = 3.00\,\mathrm{mol\,dm^{-3}}$ examined in the present study. With decreasing C_s, the repulsion effect becomes appreciable and the discrepancy between pK_{app} and pK_0 is enhanced. Contrary to the PVIm system, H^+ ions are strongly attracted to the surface of the negatively charged PAA molecules, and the increased concentration of the mobile H^+ ions in the vicinity of the fixed carboxylate groups of PAA molecules leads to the increase in pK_{app} than pK_0. The ion-screening effect due to the added inert salt is most effective at the highest C_s as well, i.e., at $C_s = 0.50\,\mathrm{mol\,dm^{-3}}$ in the present study, as shown in Fig. 2.

In the present study, the effect of salt concentration levels on the pK_{app}–α curve has been examined in the wide range 0.01–3.00 $\mathrm{mol\,dm^{-3}}$, in order to examine the applicability of the Gibbs–Donnan-based concept to the interpretation of the acid-dissociation properties of the weakly basic polyelectrolytes. The pK_{app} values determined at specified α values are plotted against $\log a_{Cl}$ in Fig. 3 as suggested by Eq. (13). Approximately good linearities are obtained at relatively low region for any combinations of the pK_{app} values determined at specified α values. It is notable that the slope of the straight line of the linear portion is quite close to "+ 1" at $\alpha = 0$, where all the functionalities are completely charged, which is indeed expected by the Gibbs–Donnan's concept. With decreasing Z to 0, the slope decreases to reach 0, where no salt concentration dependence is observed, which is also in accord with the prediction due to Eq. (13). These relationships found in the pK_{app} vs $\log a_{Cl}$ plots, clearly indicate the phase-separation property of PVIm molecules dissolved in aqueous solution, even though the polymer solution appears homogeneous and no boundary between the two-phases is observable visually. The fixed imidazole groups on the linear polymers were endowed with positive charges by H^+ ion binding, and Cl^- ions must be accumulated in the vicinity of the polymer skeleton due to the strong attraction between the positively charged polyion surface and Cl^- ions. Even though the mobile H^+ ion concentration in the vicinity of the positively charged polyion molecules must be much lower than the bulk solution due to electrostatic repulsion between H^+ ion and the polyion surface, the magnitude of the dilution of the free H^+ ions is reduced by the Cl^- ion binding to the polyion surface, which is controlled directly by the concentration of Cl^- ions in the bulk solution. The correlation between H^+ and Cl^- ion activities between the polyelectrolyte domain (or polyelectrolyte phase) and the bulk solution phase is characterized by the Donnan's law, which can be expressed by Eq. (5).

Validity of the Gibbs–Donnan approach must be confirmed by analyzing the acid-dissociation equilibria of weakly acidic polymers based on the same concept as well. The acid-dissociation equilibria of PAA were examined for this purpose at various salt concentration levels, i.e., $C_s = 0.01$–$0.50\,\mathrm{mol\,dm^{-3}}$; the PAA sample used in this study formed precipitation at high salt concentration level as $1.0\,\mathrm{mol\,dm^{-3}}$, which prevented precise pH determination at the higher C_s region than $0.5\,\mathrm{mol\,dm^{-3}}$. The pK_{app} values determined at specified α are plotted against $\log a_{Na}$ as shown in Fig. 4. It is notable that all the plots form approximately straight lines at any α values when C_s is sufficiently low; in particular, at $\alpha = 1$, i.e., $Z = -1$, the slope of the linear plots is quite close to "-1", as expected by Eq. (11). On the contrary, at $Z = 0$, the slope becomes equal to 0, due to the invasion effect of the inert salt to the polyelectrolyte phase.

In order to compare the magnitude of the non-ideality terms observed in both PVIm and PAA systems directly, the absolute value of ΔpK, $|\Delta pK|$, is plotted in Figs. 5 and 6 against Z, respectively, for PVIm and PAA. Discrepancy is appreciated between the $|\Delta pK|$ vs Z plots obtained for both systems, i.e., much higher $|\Delta pK|$ values are given for the PVIm system, even though it has been revealed that the ΔpK term can be related to the electrostatic effect straightforwardly in the case of PAA [2, 13]. This

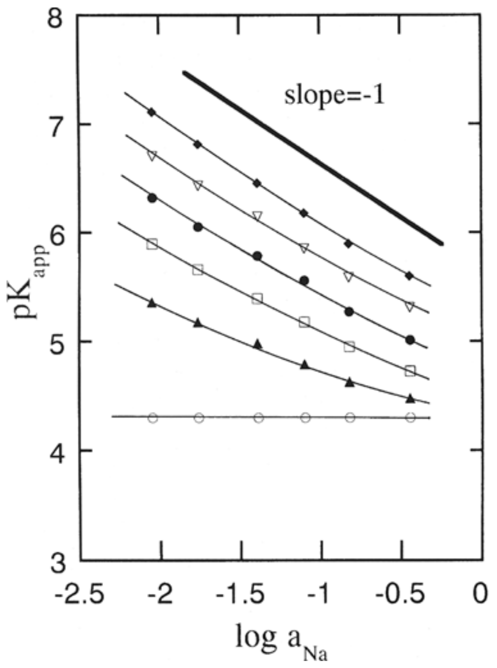


Fig. 4 pK_{app} of PAA as a function of log a_{Na}. (○) α = 0; (▲) α = 0.2; (□) α = 0.4; (●) α = 0.6; (▽) α = 0.8; (◆) α = 1.0

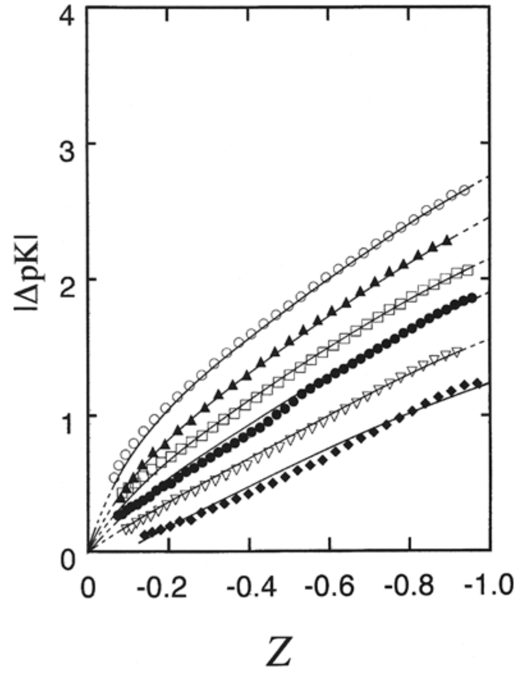


Fig. 5 |ΔpK| as a function of Z for PAA. (○) C_s = 0.01 mol dm^{-3}; (▲) C_s = 0.02 mol dm^{-3}; (□) C_s = 0.05 mol dm^{-3}; (●) C_s = 0.10 mol dm^{-3}; (▽) C_s = 0.20 mol dm^{-3}; (◆) C_s = 0.50 mol dm^{-3}

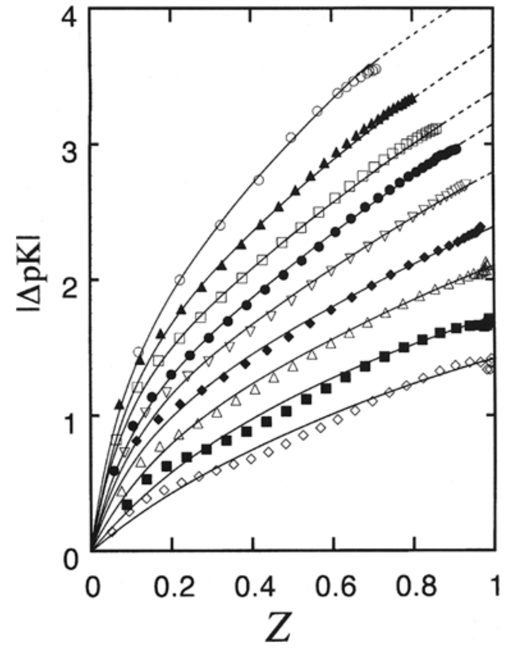


Fig. 6 |ΔpK| as a function of Z for PVIm. (○) C_s = 0.01 mol dm^{-3}; (▲) C_s = 0.02 mol dm^{-3}; (□) C_s = 0.05 mol dm^{-3}; (●) C_s = 0.10 mol dm^{-3}; (▽) C_s = 0.20 mol dm^{-3}; (◆) C_s = 0.50 mol dm^{-3}; (△) C_s = 1.00 mol dm^{-3}; (■) C_s = 2.00 mol dm^{-3}; (◇) C_s = 3.00 mol dm^{-3}

discrepancy observed between the two polymer systems is attributable to a preferential binding of Cl$^-$ ions to the positively charged imidazolium groups, even though the binding of Na$^+$ ions to the carboxylate groups of PAA molecules is estimated to be purely electrostatic in nature. This additional interaction between the charged polymer surface and the supporting anions must play an important role in the positively charged polymer systems, which may be categorized as hydrophobic interaction originating from the low degree of hydration of imidazolium groups and Cl$^-$ ions. Further systematic investigation is needed on the effect of the nature of the counter anions on the potentiometric titration of positively charged polymers [22–24].

Conclusions

Polyelectrolytic nature observed in the potentiometric titrations of linear polyions with weakly acidic or weakly basic functionalities can be rationalized in a unified manner with a Gibbs–Donnan concept by assuming a two-phase property of aqueous polyion solutions. Acid-dissociation equilibria of both polyacrylic acid and the conjugate acid of poly(N-vinylimidazole) have been quantified by an apparent acid-dissociation constant, which is strongly dependent on the degree of neutralization of the functionalities and the added salt concentration level. The apparent acid-dissociation constants at completely neutralized condition determined by extrapolation are quite close to those of the monomer functionalities resembling the functionalities fixed on the polymer backbone. It has been verified by this procedure that the effective polyelectrolyte phase volume becomes calculable by the use of the electrochemical measurement data, even though an additional non-ideality term must be taken into account for the poly(N-vinylimidazole) system due to specific interactions of supporting anions to the surface of the positively charged polymers.

References

1. Nagasawa M, Murase T, Kondo K (1965) J Phys Chem 69:4005
2. Nagasawa M (1971) Pure and Appl Chem 26:519
3. Manning GS, Holtzer A (1973) J Phys Chem 73:2206
4. Manning GS (1988) J Chem Phys 89:3772
5. Manning GS (1979) Acc Chem Res 12:443
6. Manning GS (1978) Q Rev Biophys 2:179
7. Fixman M (1979) J Chem Phys 70:4995
8. Anderson CF, Record Jr MT (1982) Ann Rev Phys Chem 33:191
9. Marinsky JA (1992) J Phys Chem 96:6484
10. Marinsky JA (1996) J Phys Chem 100:1858
11. Alexandrowicz Z, Katchalsky A (1963) J Polym Sci Pt A 1:3231
12. Oosawa F (1971) Polyelectrolytes. Marcel Dekker, New York
13. Miyajima T (1995) In: Marinsky JA, Marcus Y (Eds) Ion Exchange and Solvent Extraction – A Series of Advances, Vol 12. p 275, Marcel Dekker, New York
14. Marinsky JA, Miyajima T, Högfeldt E, Muhammed M (1989) React Polym 11:279
15. Marinsky JA, Miyajima T, Högfeldt E, Muhammed M (1989) React Polym 11:291
16. Katchalsky A, Alexandrowitcz Z (1963) J Polym Sci A1 2093
17. Kotin L, Nagasawa M (1962) J Chem Phys 36:873
18. Katchalsky A, Alexandrowicz Z, Kedem O (1966) In: Conway BE, Barradas RG (Eds) Chemical Physics of Ionic Solutions, p 295, Wiley, New York
19. Gran G (1951) Analyst 77:661
20. Datta SP, Grybowski AK (1966) J Chem Soc (B) 136
21. Portnanova R, DiBernade P, Cassol A, Tondello E, Magon L (1974) Inorg Chim Acta 8:233
22. Gold DH, Gregor HP (1958) Z Phys Chem (Frankfurt) 15:93
23. Gold DH, Gregor HP (1960) J Phys Chem 64:1461, 1464
24. Liu K, Gregor HP (1965) J Phys Chem 69:1252