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ORIGINAL CONTRIBUTION

H. Kodama
T. Miyajima
H. Tabuchi
S. Ishiguro

A calorimetric study of the acid dissociation of the conjugate acids of poly(*N*-vinylimidazole) and polyallylamine

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H. Kodama
Department of Biological Resource
Chemistry, Faculty of Agriculture
Kyoto Prefectural University
Kyoto 606-8201, Japan

T. Miyajima (✉)
Department of Chemistry
Faculty of Science and Engineering
Saga University, Saga 840-8502, Japan
e-mail: t-miyaji@cc.saga-u.ac.jp
Fax: +81-952-288548

H. Tabuchi · S. Ishiguro
Department of Chemistry and Physics
Graduate School of Science
Kyushu University
Fukuoka 812-8581, Japan

Abstract Thermodynamic parameters for acid dissociation of the conjugate acids of poly(*N*-vinylimidazole) and polyallylamine have been determined in the presence of sodium chloride and sodium nitrate. Even though the plots of ΔG^0 against the degree of dissociation, α, are highly dependent on the added salt concentration levels, the concentration effect has never been observed for the corresponding ΔH^0 versus α plots. The effect on the ΔG^0 versus α plots has been attributed to the entropy change of the counterions between a polyelectrolyte phase and a bulk solution phase. The α dependency of ΔH^0 is affected remarkably by the kinds of cationic polymers and counter-anions. Each ΔH^0 value at completely neutralized conditions is quite close to the corresponding ΔH^0 value of the monomer analog. The difference in the ΔH^0 values at fully charged conditions has been explained by the heats due to

1. Contact ion-pair formation of counter-anions to singly charged sites of the polymer.
2. Hydration of counter-anion and polymer charged sites.

The ion-pair formation of chloride anion to the conjugate acids of poly(*N*-vinylimidazole) and polyallylamine has been supported by ^{35}Cl NMR measurement. It has also been suggested that chloride anions bind the basic polymer molecules even at fully neutralized conditions.

Key words Poly(*N*-vinylimidazole) · Polyallylamine · Acid-dissociation equilibria · Calorimetric titration · ^{35}Cl nuclear magnetic resonance

Introduction

Compared with weak acidic linear polyelectrolytes, such as polycarboxylic acids, quite a limited number of thermodynamic parameters have so far been reported for the acid-dissociation equilibria of the conjugate acids of weak basic polyelectrolytes [1–3]. Quite recently, a precise potentiometric titration study was performed by us [4] on the conjugate acid of poly(*N*-vinylimidazole), PVIm, in the presence of NaCl at various concentration levels, C_s, at 25 °C. Even though the skeletal structure as well as the formal distance between adjacent functionalities of PVImH$^+$ molecules are almost same as for poly(acrylic acid), PAA, the magnitude of nonideality observed in the acid-dissociation equilibria of PVImH$^+$ is always much larger than for PAA. A much larger difference between an apparent acid-dissociation constant, pK_{app}, and the intrinsic acid-dissociation constant of PVImH$^+$ molecules, i.e., the p*K*a value of imidazole (7.0) [5], has been observed than for PAA at any specified α or C_s. Since the nonideality term calculated for PAA molecules has been rationalized by a purely electrostatic attraction [6–9] between the negatively charged polymer surface and positively charged counterions, i.e., H$^+$ ions and supporting cations, the unexpectedly high deviation observed in the PVImH$^+$

system has been attributed to specific interaction between chloride anions and positively charged $PVImH^+$ molecules [2].

Counter-anion binding to strong basic linear polymers has frequently been investigated potentiometrically by the use of the respective anion-selective electrode [10–13]. In most cases, appreciable ion-specificity has been observed in the bindings of polycations to halogen ions, thiocyanate, and perchlorate ions. Inconsistency between experimental results and theoretical predictions due to Manning's ion-condensation theory has often been reported for combinations of hydrophobic anions and hydrophobic polycations [13].

In order to clarify the nature of the specific interaction between cationic polymers and counteranions in general, and to correlate the acid-dissociation behavior of the conjugate acids of weak basic polyelectrolytes to the nature of the supporting anions, a calorimetric titration technique was applied in this work. The enthalpy change upon acid dissociation of the conjugate acids of PVIm and polyallylamine, PAAm, has been determined in the presence of various concentrations of NaCl and $NaNO_3$. It has been revealed that the nature of the functionalities of the polymer as well as supporting anions considerably affect the enthalpy change upon acid dissociation of the polyacids. In addition, ^{35}Cl NMR spectra have been measured for the mixture solutions of chloride ions and $PVImH^+$ or $PAAmH^+$ polymers with various α in order to get microscopic information on the binding of chloride ions to these cationic polymers. It has been clarified by the present study that chloride anions interact even with neutral PVIm molecules, which verifies the fact that chloride ions bind positively charged $PVImH^+$ sites.

Experimental

Chemicals

PVIm was prepared by free-radical polymerization of *N*-vinylimidazole in water–methanol (50% v/v) with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator under deoxygenated conditions at 60 °C for 6 h. The *N*-vinylimidazole used for this polymerization was distilled under reduced pressure (85 °C, 18 mmHg) just before use, and AIBN was recrystallized from methanol. The polymer material thus prepared was then dialyzed using a cellulose tube (8000 molecular weight cutoff) against distilled water for 5 days. The dialyzed solution was concentrated using a rotating evaporator, and was then dissolved in methanol. PVIm was precipitated from ethyl acetate, dried in vacuo at 80 °C for 24 h, and was stored at room temperature. The molecular weight of the polymer determined by viscosity measurement using the Mark–Houwink–Sakurada relation was about 10^5, i.e., an average degree of polymerization of about 1.0×10^3 [4]. The ^1H NMR spectrum of the PVIm sample dissolved in a D_2O solution was the same as the literature spectrum [14]. Elemental analysis of the *N*-vinylimidazole sample used in the present study is as follows:

Calculated for $C_5H_6N_2$:C, 63.9%; H, 7.3%; N, 28.8%. Found: C, 63.7%; H, 7.2%; N, 29.5%. $PAAmH^+Cl^-$ with a nominal degree of polymerization of 2×10^2, purchased from Nittobo Co., Tokyo, was used as received. All other chemicals used in this study were of reagent grade.

Calorimetric titration

Neutral basic linear polymer solutions of PVIm and PAAm were titrated with a standardized acidic solution, HX (X = Cl^- or NO_3^-) in the presence of a Na^+X^- salt of various concentration levels. Calorimetric titrations were performed using a twin-type isoperibal calorimeter (Tokyo Riko Co., Tokyo) regulated at a constant temperature (298 K) with baseline fluctuations of ±0.0001 K [15]. An autoburette (APB-118, Kyoto Electronics Manufacturing Co., Tokyo) was placed in a thermostatically controlled room at 298 K and connected to the outlet through a 15-m long Teflon tube, which was cooled round an aluminium block inside the calorimeter. Blank titration and gravimetric calibration assured that the temperature difference between the titrant and titrate was negligible at a slow titration speed. The heat of dilution measured by titrating a polymer-free solution with the titrant was small (below 0.1 J) and was used for correction of the reaction heats. All the solutions were prepared in a glove box under a nitrogen atmosphere at 298 K.

Potentiometric titration

Neutralized polymer solutions were titrated with HX in the presence of NaX under a nitrogen atmosphere. The pH values of the equilibrated solutions were measured potentiometrically with an Orion 91-01 glass electrode together with an Orion 90-01 single-junction reference electrode, both being connected with an Orion Research Ionalyzer 720A under a nitrogen atmosphere. The electrochemical cell was standardized using a Gran plot [16] performed just before and after the sample titration procedures. The α values of the polyacids, i.e., $PVImH^+$ and $PAAmH^+$, were calculated using the following equation:

$$\alpha = 1 - \{C_H V_{HX} - ([H^+] - K_w/[H^+])(V_0 + V_x)\}/n_p \ , \tag{1}$$

where C_H and [H] indicate total HX concentration in the titrant solution and the free H^+ ion concentration measured at each titration point, respectively. V_0 and V_{HX} represent the volumes of the initial and the added HX solutions, respectively. n_p corresponds to the total number of functionalities of the polyacids. K_w indicates the ion product.

^{35}Cl NMR

NMR spectra of $^{35}Cl(I = 3/2)$ nuclei were measured at $22 \pm 2\,°C$ with a JEOL GX 400 NMR spectrometer operating at 39.17 MHz. The reference used for the chemical-shift measurement was a solution of 0.1 mol dm^{-3} NaCl. All the sample solutions together with the reference solution contained 10% D_2O for field-frequency lock. The ^{35}Cl NMR titration was carried out as follows.

Polybase sample (PVIm and PAAm) solutions of 1.0 monomol dm^{-3} were acidified completely by the addition of an appropriate volume of aqueous solution of 1.0 mol dm^{-3} HCl. To those $PVImH^+Cl^-$ and $PAAmH^+Cl^-$ solutions, a portion of a concentrated NaOH solution was added stepwise to neutralize the conjugate acids of the weak basic polymers. The α value at each titration point was calculated as follows:

$$\alpha = \{C_{NaOH} V_{NaOH} + ([H^+] - K_w/[H^+])(V_0 + V_{NaOH})\}/n_p \ , \tag{2}$$

where C_{NaOH} and V_{NaOH} indicate the concentration of the NaOH solution added, i.e., 2.0 mol dm^{-3}, and the volume, respectively. The $[H^+]$ values in the mixture solutions of the acidified polybase and NaOH solution were measured by the use of a combination electrode (Horiba 6069-10C) connected with a Horiba pH meter (model F-14). V_0 and n_p in Eq. (2) indicate the initial sample solution volume of 3.3 cm^3 and the total number of functionalities of the polybase, i.e., about 3 meq, respectively.

Results and discussion

ΔH^0 change upon acid dissociation of $PVImH^+$ and $PAAmH^+$

According to our previous work [4, 17], the nonideality term in the acid-dissociation equilibria of a polyacid can be expressed as the difference between an apparent acid-dissociation constant, pK_{app}, and an intrinsic constant, pK_0. pK_{app} is defined by Eq. (3) and is usually dependent on both α and C_s. In contrast, pK_0 is constant irrespective of the change in α or C_s and should be equal or quite close to the pK_a value of the monomer analog of the polyacid.

$$pK_{app} = pH - \log\{\alpha/(1-\alpha)\} \tag{3}$$

The nonideality term defined as the difference between pK_{app} and pK_0 is indicated as ΔpK.

$$\Delta pK = pK_{app} - pK_0 \tag{4}$$

The standard Gibbs free-energy change, ΔG^0, of acid dissociation of $PVImH^+$ was calculated to be 5.71 pK_{app} (kJ monomol^{-1}) by the use of the pK_{app} values previously determined [4]. The ΔG^0 values are plotted in Fig. 1 against α at various C_s. The ΔG^0 values for the acid-dissociation reaction of the conjugate acids of imidazole and methylimidazole, the monomer analogs of $PVImH^+$ molecules, are 39.94 kJ mol^{-1} [5] and 39.98 kJ mol^{-1} [18], respectively, which are almost equal to the ΔG^0 value, 40 kJ monomol^{-1}, obtained for $PVImH^+$ at $\alpha = 1$.

In the present study, the enthalpy change (ΔH^0) upon acid dissociation of $PVImH^+$ was measured as a function of α and C_s. The heat produced by protonation, q, of a portion of the imidazole group, n_{HB}(monomol), upon addition of a HX standard solution, can be related to ΔH^0 by the following equation.

$$\Delta H^0 = -(-q/n_{HB}) \tag{5}$$

Note that the sign"−" is placed on the right-hand side of Eq. (5) in order to correlate the q value obtained by the present experiment, i.e., protonation of the polybase, to the ΔH^0 value defined for acid dissociation of the conjugate acid of the polybase. At each titration point, the differential heat, Δq, produced by the differential amount of dissociated HB^+ groups is

$$\Delta H^0 = \Delta q/\Delta n_{HB} \ . \tag{6}$$

The Δn_{HB} value at each titration point was calculated by measuring the pH of the equilibrium solution,

$$\Delta n_{HB} = C_H \Delta V_x - \Delta[H^+](V_0 + V_x) \ , \tag{7}$$

where ΔV_x and $\Delta[H^+]$ represent the small changes in the volume of titrant and the free H^+ ion concentration, respectively, upon addition of HX solution. The ΔH^0 values thus determined for PVIm plotted against α are shown in Fig. 2. It is apparent that ΔH^0 is not influenced by C_s at all. For comparison, the ΔH^0 values of imidazole, the monomer analog of PVIm, are plotted

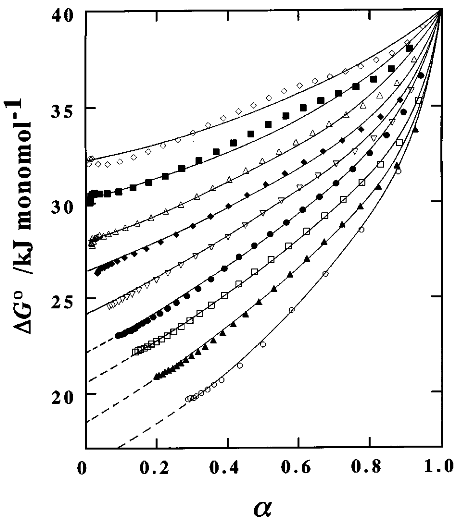


Fig. 1 ΔG^0 change with degree of acid dissociation, α, of the poly(*N*-vinylimidazolium) cation ($PVImH^+$) in the presence of NaCl. Calculated from Fig. 1 in Ref. 4. C_s/mol dm^{-3}: 0.01 (○); 0.02 (▲); 0.05 (□); 0.10 (●); 0.20 (▽); 0.50 (◆); 1.00 (△); 2.00 (■); 3.00 (◇)

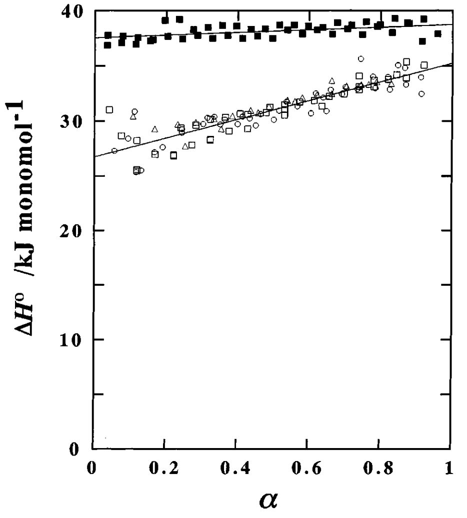


Fig. 2 ΔH^0 change with α of $PVImH^+$ (*open symbols*) and the imidazolium cation (*filled squares*) in the presence of NaCl. $C_p = 0.05$ monomol dm^{-3}. C_s/mol dm^{-3}: 0.01 (○); 0.10 (△); 1.00 (□, ■). The solid lines were calculated using a linear least-squares method

against α in order to compare them with the α dependency of the ΔH^0 value of the polymer system. As shown in Fig. 1, since the ΔG^0 versus α plots are strongly affected by C_s, it is apparent that the C_s effect is just due to the entropy change, i.e., the free H^+ ion distribution between a bulk solution phase and a polyelectrolyte phase at a defined α value is absolutely controlled by the entropy change of the reaction.

Our previous insight into the effect of the nature of the counterions, X^- , on the acid-dissociation equilibria of $PVImH^+$ revealed that X^- ions bind the positively charged imidazolium groups fixed on the polymer backbone in a specified manner [4]. It is of special interest to compare the ΔH^0 versus α plots obtained with different HX solutions in the presence of an excess of NaX salt. Unfortunately, the addition of Na^+ salts with hydrophobic anions, such as perchlorate, thiocyanate, and iodide ions produced appreciable amounts of precipitation with $PVImH^+$ molecules, which prevented precise titration measurements [1, 4]. This phenomenon may be supportive evidence for the strong and specific (hydrophobic) interaction of X^- ions with the positively charged sites of $PVImH^+$ molecules. Only the $NO_3^-/PVImH^+$ system allowed us to measure the ΔH^0 change upon acid dissociation in the whole α and C_s regions as for the $Cl^-/PVImH^+$ system. As shown in Fig. 3, the ΔH^0 versus α plots of the $NO_3^-/PVImH^+$ system are independent of C_s, even though the change in ΔH^0 with α for the $NO_3^-/PVImH^+$ system is much smaller than that for the $Cl^-/PVImH^+$ system.

In order to examine further the effect of the nature of the functionalities of polyelectrolyte, the ΔH^0 change with α was determined for $PAAmH^+$ in the presence of NaCl or $NaNO_3$. The polymer backbone structure of polybasic PAAm is the same as that of PVIm, but the functionalities are more hydrophilic. Since the ΔH^0 values for the acid dissociation of the monomer analogs of $PAAmH^+$, i.e., the conjugate acids of methylamine, ethylamine, *n*-propylamine, and isopropylamine, are about 55.29, 57.44, 57.99, and 58.53 kJ mol^{-1}, respectively [19], being much higher in value than for the imidazolium ion, the ΔH^0 values for $PAAmH^+$ are much larger than for $PVImH^+$ as shown in Fig. 4. The effect of the counterion, X^-, on the ΔH^0 values was also examined in the presence of NaCl or $NaNO_3$. It is again notable that the nature of the X^- ions is appreciable in the ΔH^0 versus α plots, and that the direction and the magnitude of the change in ΔH^0 with α is not the same as for the more hydrophobic $PVImH^+$ molecules.

In all the ΔH^0 versus α plots, it is obvious that the ΔH^0 values at completely neutralized conditions ($\alpha = 1$) are almost equal to the corresponding values of the conjugate acids of the monomer analogs, whereas for a completely protonated state ($\alpha = 0$), the ΔH^0 values are usually different from those of the monomer systems. Since ΔH^0 seems to change linearly with α for all the systems examined in the present study, the α dependence of ΔH^0 upon acid dissociation of the conjugate acids of weak basic polymers can be rationalized in the following way.

The observed ΔH^0 term can be divided into two portions.

1. The enthalpy change corresponding to the intrinsic acid-dissociation reaction of BH^+ sites, i.e., $BH^+ \rightarrow B + H^+$, $(\Delta H^0_{BH^+})$

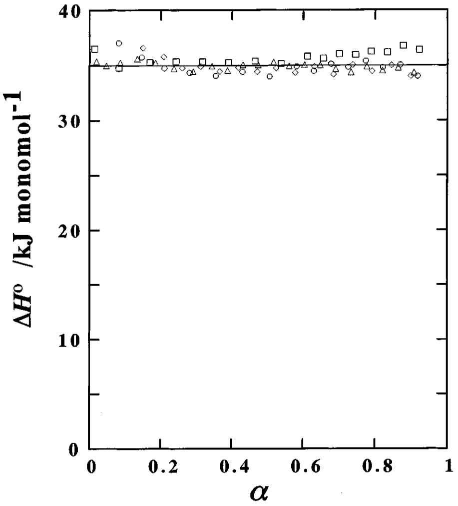


Fig. 3 ΔH^0 change with α of $PVImH^+$ in the presence of $NaNO_3$. $C_p = 0.05$ monomol dm^{-3}. C_s/mol dm^{-3}: 0.01 (○); 0.05 (◇); 0.10 (△); 1.00 (□). The solid line was calculated using a linear least-squares method

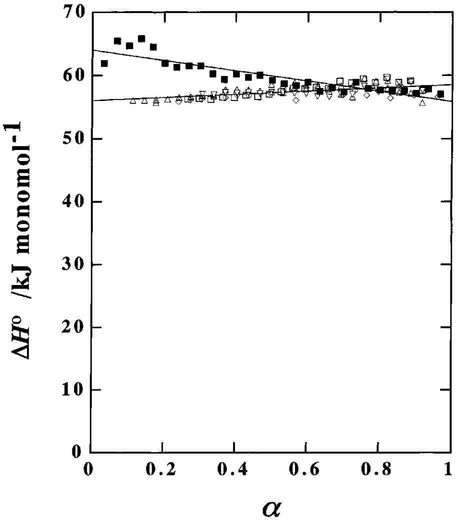


Fig. 4 ΔH^0 change with α of the polyallylammonium cation (*$PAAmH^+$*) in the presence of NaCl (*open symbols*) or $NaNO_3$ (*filled squares*). $C_p = 0.05$ monomol dm^{-3}. c_s/mol dm^{-3}: 0.05 (◇); 0.10 (△); 0.50 (▽); 1.0 (□, ■). The solid lines were calculated using a linear least-squares method

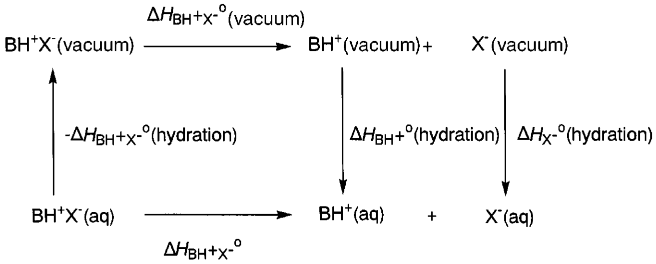
2. The enthalpy change accompanied with counterion dissociation from the positively charged site, BH^+X^-, i.e., $BH^+X^- \rightarrow BH^+ + X^-$, $(\Delta H^0_{BH^+X^-})$.

Thus the overall ΔH^0 term can be expressed as follows:

$$\Delta H^0 = \Delta H^0_{BH^+} + (1-\alpha) f_{BH^+X^-} \Delta H^0_{BH^+X^-}, \quad (f_{BH^+X^-} = 0 \sim 1) \tag{8}$$

where $f_{BH^+X^-}$ represents the fraction of contact ion-pairs. The $\Delta H^0_{BH^+X^-}$ term originates from the assembled positive charges fixed on the polymer backbone. Indeed, singly charged positive groups due to the monomer base cannot produce such a strong ion-specificity. The linearity observed in all the ΔH^0 versus α plots indicates the constancy of the $f_{BH^+X^-}$ term irrespective of the change in X^- concentrations. It can be elucidated that some fraction of X^- ions, which are electrostatically concentrated in the polymer domain, are bound to the positively charged sites to form contact ion-pairs.

According to the Born-Haber cyclic process (Scheme 1), the release of X^- ions from BH^+ sites involves the following four steps Eqs. (9–12) with respective ΔH^0 values.



Scheme 1 Born-Haber cyclic process for dissociation of X^- from BH^+X^-

$$1.\ BH^+X^-(\text{vacuum}) \rightarrow BH^+X^-(\text{aq});\ \Delta H^0_{BH^+X^-}(\text{hydration})\ . \tag{9}$$

$$2.\ BH^+(\text{vacuum}) \rightarrow BH^+(\text{aq});\ \Delta H^0_{BH^+}(\text{hydration})\ . \tag{10}$$

$$3.\ X^-(\text{vacuum}) \rightarrow X^-(\text{aq});\ \Delta H^0_{X^-}(\text{hydration})\ . \tag{11}$$

$$4.\ BH^+X^-(\text{vacuum}) \rightarrow BH^+(\text{vacuum}) + X^-(\text{vacuum});\ \Delta H^0_{BH^+X^-}(\text{vacuum})\ . \tag{12}$$

Consequently, the $\Delta H^0_{BH^+X^-}$ term can be expressed as the following additive form.

$$\Delta H^0_{BH^+X^-} = \Delta H^0_{BH^+X^-}(\text{vacuum}) - \Delta H^0_{BH^+X^-}(\text{hydration}) + \Delta H^0_{BH^+}(\text{hydration}) + \Delta H^0_{X^-}(\text{hydration})\ . \tag{13}$$

According to Eq. (8), the product $f_{BH^+X^-}\Delta H^0_{BH^+X^-}$ can be calculated as $\Delta H^0(\alpha = 0) - \Delta H^0(\alpha = 1)$, and the values are listed in Table 1. Though the exact $f_{BH^+X^-}$ values are not available for the present study, it may be worthwhile elucidating whether the dissociation of BH^+X^- into BH^+ and X^- is endothermic or exothermic by examining the sign of the $\Delta H^0_{BH^+X^-}$ values for various combinations of cationic polymers and X^- ions. As indicated by Eq. (13), $\Delta H^0_{BH^+X^-}$ is determined by the balance among the four terms, where $\Delta H^0_{BH^+X^-}(\text{vacuum})$ should be positive, and $\Delta H^0_{BH^+X^-}(\text{hydration})$, $\Delta H_{B^+}(\text{hydration})$ and $\Delta H^0_{X^-}(\text{hydration})$ should be negative. The fact that the $\Delta H^0_{BH^+X^-}$ values obtained for the NO_3^- system are always more endothermic than for the Cl^- system for both polymers can be explained by assuming that the term $\Delta H^0_{BH^+X^-}(\text{vacuum}) - \Delta H^0_{BH^+X^-}(\text{hydration})$ in the NO_3^- system is much larger in value than in the Cl^- system. The change in $\Delta H^0_{BH^+X^-}$ observed for the $PVImH^+$ system is much more negative than for the $PAAmH^+$ system for both counteranions, which seems to reflect the difference in the hydration state change around the imidazolium and methylammonium groups accompanied with dissociation of X^- from BH^+.

Table 1 $f_{BH^+X^-}\Delta H_{BH^+X^-}[=\Delta H^0(\alpha = 0) - \Delta H^0(\alpha = 1)]$ values (/kJ monomol^{-1})

Conjugate acid	Cl^-	NO_3^-
Poly(*N*-vinylimidazolium)	−8.5	−0.1
Polyallylammonium	−2.5	+8.2

It should again be noted that the linear ΔH^0 change with α reflects a contact ion-pair formation of X^- anions and positively charged sites of the polymers. In order to obtain much more microscopic information on the specific binding of X^- anions to the positively charged polymers, a ^{35}Cl NMR study was conducted on the Cl^- ion binding.

Line broadening of $^{35}Cl^-$ ions due to binding to cationic polymers

Representative ^{35}Cl NMR spectra of $PAAmH^+Cl^-$ and $PVImH^+Cl^-$ are shown in Fig. 5a and b, respectively. For comparison, the spectrum obtained for the reference NaCl solution is shown in the same figure. It is obvious that all the ^{35}Cl NMR spectra obtained with the cationic polymers are appreciably broadened compared with the reference, mainly due to a quadrupolar relaxation effect. Nuclei with a spin quantum number (I) higher than 1 possess nuclear quadrupolar moments and are relaxed by interactions between the quadrupolar moment (eq) and electric field gradients (eQ) arising from asymmetry in the surrounding electric charge distribution [20]. The relaxation time (T_2) of these nuclei can be related to the width of the half height, $\Delta\nu_{1/2}$, as expressed by the following equation [21–23].

$$\Delta\nu_{1/2} = 1/(\pi T_2) \\ = (3/40\pi)\{(2I+3)/[I^2(2I-1)]\}(e^2qQ/h)\tau_c \ , \quad (14)$$

where τ_c is the rotational correlation time of the chemical bond. In the present study, all the spectra obtained were analyzed using a Lorentzian-curve-fitting method.

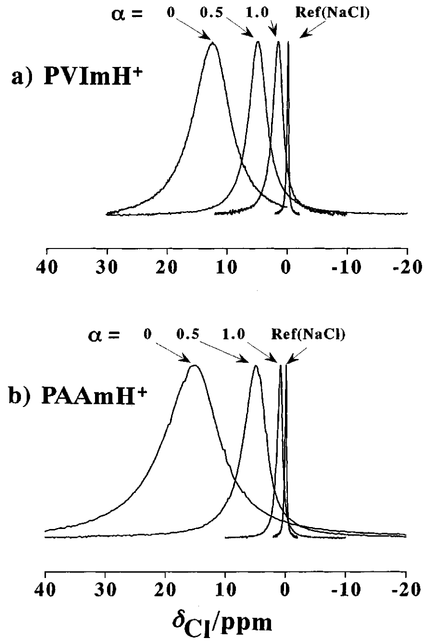


Fig. 5a, b ^{35}Cl NMR spectra of PVImH$^+$Cl$^-$ and PAAmH$^+$Cl$^-$ with different α. **a** PVImH$^+$Cl$^-$, **b** PAAmH$^+$Cl$^-$

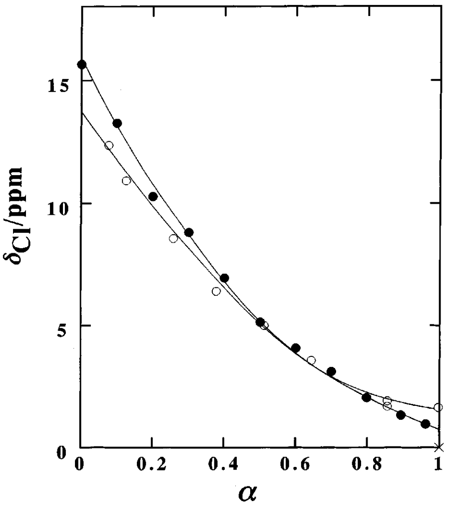


Fig. 6 δ_{Cl} against α for PVImH$^+$Cl$^-$ and PAAmH$^+$Cl$^-$. PVImH$^+$Cl$^-$ (○), PAAmH$^+$Cl$^-$ (●), NaCl (×)

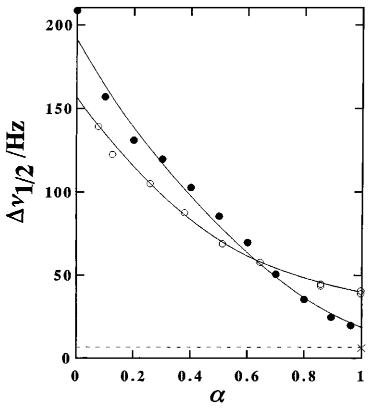


Fig. 7 $\Delta\nu_{1/2}$ against α for PVImH$^+$Cl$^-$ and PAAmH$^+$Cl$^-$. PVImH$^+$Cl$^-$(○), PAAmH$^+$Cl$^-$ (●), NaCl (×)

The δ_{Cl} and $\Delta\nu_{1/2}$ values calculated by the peak analyses are expressed as a function of α in Figs. 6 and 7, respectively. It is obvious that δ_{Cl} shifts downfield upon Cl$^-$ ion binding to cationic polymers, i.e., with an α decrease. Due to a symmetrical electric field gradient around the free ions of Cl$^-$, the ^{35}Cl NMR spectrum of the NaCl solution is quite sharp, i.e., the $\Delta\nu_{1/2}$ value is 6.2 Hz; however, when Cl$^-$ nuclei are placed in the vicinity of the cationic polymer skeletons, where an unsymmetrical field gradient is generated mainly due to the strong electric field, the peak is broadened remarkably. Because of rapid chemical exchange, the magnitude of the peak-broadening can be expressed by the fraction of bound counterions and the intrinsic peak width of the bound ions:

$$(\Delta\nu_{1/2}) = (\Delta\nu_{1/2})_f p_f + (\Delta\nu_{1/2})_b p_b \quad (p_f + p_b = 1) \ , \quad (15)$$

where the suffixes “f” and “b” denote “free” and “bound”, respectively, and “p” indicates the fraction. $(\Delta\nu_{1/2})_b$ corresponds to the intrinsic peak width of the ions located in the sheath of the polyion skeleton. Since p_f can be directly related to α in the present study, it can be expected that the plots of observed $\Delta\nu_{1/2}$ against α give straight lines, once $(\Delta\nu_{1/2})_b$ is a unique value. It is apparent, however, that the plots do not give straight lines, which indicates the presence of different binding modes of Cl$^-$ ions to the polymers. For a completely neutralized condition, it is expected that $p_b = 0$, i.e., $(\Delta\nu_{1/2}) = (\Delta\nu_{1/2})_f$; however, even at $\alpha = 1$, $\Delta\nu_{1/2}$ values for both polymers are apparently larger than for free Cl$^-$ ions, showing that Cl$^-$ ions interact with the polymer molecules under completely neutralized conditions. This result is consistent with the reports by Oh et al. [24] and Song et al. [25], who studied the halogen ion binding to neutral polymers using halogen NMR. They determined binding constants of halogen anions to neutral polymers, such as poly(vinylpyrrolidone) and poly(ethylene oxide). Our results show that the magnitude of deviation observed between the mixture solutions of NaCl and neutral polymers from free Cl^- ions is much larger for PVIm than for PAAm, which is in accord with the order of the hydrophobicity of the polymer functionalities [24, 25].

In contrast to the peak-broadening under neutral conditions, the limiting $\Delta v_{1/2}$ values in the completely charged state ($\alpha = 0$) for $PVImH^+$ and $PAAmH^+$ are 150 Hz and 200 Hz, respectively. The smaller value obtained for $PVImH^+$ may be due to delocalization of the unit positive charge (+1) per functionality distributed over the imidazole rings, which is not the case for the ammonium ions fixed on the $PAAmH^+$ molecules. In accord with the order found in the $\Delta v_{1/2}$ versus α plots, the ultimate order of the δ_{Cl} values at $\alpha = 1$ for all the series of polybases, i.e., 0.73 ppm for PAAm < 1.69 ppm for PVIm, is again consistent with the order of the hydrophobicity.

Since ^{35}Cl NMR of Cl^- ions in the presence of monomeric ligand, imidazole, gives δ_{Cl} and $\Delta v_{1/2}$ values equal or quite close to the values of NaCl, suggesting no interaction between Cl^- and imidazole, it should be pointed out again that fixation of week basic functionalities in a limited volume element around the polymer skeleton is essentially responsible for giving rise to the specific interaction between anions and the polymers.

Conclusions

The exceptionally high nonideality term observed in the acid-dissociation equilibria of the conjugate acid of PVIm compared with PAA at specified α or c_s can be attributed to specific interaction between positively charged sites fixed on PVIm molecules and supporting anions, but not to the change in the intrinsic acid-dissociation property of the conjugate polyacid. Calorimetric titration measurement reveals that ΔH^0 is not influenced by the added salt concentration levels at all; on the other hand, ΔG^0 is highly sensitive to the added salt concentration levels. The ΔH^0 change upon acid dissociation of the conjugate acids of PVIm and PAAm is highly affected by the hydrophobicity/hydrophilicity of the polymers as well as the counter-anions, even though the ΔH^0 value of the respective polymer molecules at a neutralized condition becomes quite close to the ΔH^0 value of the corresponding monomer analogs. The difference in the ΔH^0 values of the polymer and the corresponding monomer analog becomes largest at the fully charged state of the weak basic polymers, and is strong proof for the specific interaction. The change in δ and $\Delta v_{1/2}$ values of the ^{35}Cl NMR spectra of poly(*N*-vinylimidazolium) chloride and polyallylammonium chloride solutions supports the contact ion-pair formation of counter-anions to positively charged sites of the polymer molecules.

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