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Thermodynamics of Proton Ionization from Poly(vinylammonium salts)

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ABSTRACT: The thermodynamic parameters ΔG, ΔH, and ΔS for proton ionization from the hydrochloride, hydrobromide, hydroiodide, and hydroperchlorate salts of poly(vinylamine) (PVA) have been determined by calorimetric and potentiometric titration. The thermodynamic data are reported as a function of the fraction of sites protonated (α), polymer concentration, electrolyte concentration, counterion type, and temperature. The ΔH and ΔS curves are much more sensitive than the corresponding ΔG curve to temperature, concentration, salt, and counterion effects. The largest anomalies in all of the curves are observed to occur at α values between 0.5 and 1. The counterion dependence is indicative of ion pairing between the polyion and the counterion with the association constant decreasing in the order $Cl^- > Br^- > I^- > ClO_4^-$. The enthalpy and the entropy changes show a strong dependence on temperature, characterized by a large positive ΔC_p for all charge states with the maximum in ΔC_p occurring at $\alpha = 1$. Current polyelectrolyte theories, including those allowing for counterion condensation, fail to predict these titration data.

Introduction

We propose here that the difference in the apparent pK_a values at the extremes of the titration curve for a polyacid or polybase defines the "polyelectrolyte effect". In other words, a polymer exhibiting a strong polyelectrolyte effect shows a large change in pK_a on going from the uncharged state to the charged state.

The polyelectrolyte nature of poly(vinylamine) (PVA) was first examined by Katchalsky and co-workers.[1] They reported that PVA was unique in showing a stronger than usual dependence of the apparent pK_a on the charge state of the polymer, α. The fully charged polymer ($\alpha = 1$) was a stronger acid than the uncharged polymer ($\alpha = 0$) by about 5 orders of magnitude. Katchalsky explained this unusual behavior by postulating that there were two different ammonium groups. One group was hydrogen bonded while the other was not and each type had a unique intrinsic pK_a.

Recently, the acid–base behavior of PVA has been reexamined by Bloys van Treslong[2] and Lewis et al.[3] Bloys van Treslong has concentrated his efforts on obtaining precise pK_a and $dpK_a/d\alpha$ data. In our preliminary report on the calorimetric and potentiometric study of proton ionization from PVA-HCl and poly(iminoethylene hydrochloride), we showed that the changes in the enthalpy and entropy for ionization are more sensitive functions of polymer charge state than is the free energy change, pK_a, or ΔG.[3]

In this paper, we explore the effects of polymer concentration, the nature of the counterion, supporting electrolyte concentration, and temperature on the titration behavior of PVA.

Experimental Section

Polymer Synthesis. Poly(vinylamine) (PVA) was synthesized by the procedure reported by Hughes and St. Pierre.[4] By this procedure, acrylic acid was converted to *tert*-butyl vinylcarbamate and then polymerized with azobis(isobutyronitrile). The *tert*-butoxycarbonyl group was removed by acid hydrolysis. NMR and IR analyses indicated complete hydrolysis. The polymer was isolated as the hydrochloride salt and characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy, and specific viscosity measurements.

PVA in the free base form was prepared from the hydrochloride salt by neutralization with a 10% excess of NaOH and exhaustive dialysis against water. The PVA free base was isolated by lyophilization and characterized by elemental analysis.

PVA–HX, where X = Br, I, or ClO_4, was prepared in two ways. Procedure I involved exhaustive dialysis of a PVA–HCl solution against first a solution of HX, then water, and finally isolation of the PVA–HX salt by lyophilization. The PVA–HCl starting solution had a nominal concentration of 0.1 monomolar and the HX solutions nominal concentrations of 0.15 M. The dialysis against either HX or water was done with three changes of the dialyzing solution at 4-h intervals to give a final dilution factor

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[†] Contribution no. 340.

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for the dialyzate of 6.4×10^4. Polymer recovery after lyophilization was better than 90% in all cases. Procedure II, the eventual method of choice, simply involved preparation of PVA–HX solutions by adding a slight (known) excess of HX to a solution of PVA prepared by weight from the PVA free base described above. The solutions prepared by this method were indistinguishable in their titration behavior from solutions prepared by dissolving weighed samples of PVA–HX isolated by the first procedure.

Solutions. The PVA–HX solutions were prepared by using distilled/deionized, CO_2-free water. To ensure complete protonation of the PVA, these solutions were adjusted to contain a slight known excess of HX. In some instances Baker reagent NaCl, NaBr, NaI, or $NaClO_4$ was added as a supporting electrolyte. The PVA–HCl solutions had nominal concentrations of 0.001, 0.01, or 0.1 monomolar, while the other poly(vinylammonium salt) solutions were nominally 0.01 monomolar. The concentration of the supporting electrolyte ranged from 0.0 to 0.9 M in NaX with the salt anion matched to the PVA–HX used. The PVA–HX solutions were titrated with either 0.1 or 1.0 M NaOH. The base titrant solutions were shown to be carbonate free by calorimetric titration with HCl and were standardized against dry Baker Analyzed potassium hydrogen phthalate to a visual end point using phenolphthalein as the indicator.

Titrations. The titrations were done with a Tronac 450 calorimeter equipped with either a 3-mL or a 50-mL Dewar as the reaction vessel (Tronac Inc., Orem, UT 84057). Both calorimeters incorporated miniature glass and Ag/AgCl reference electrodes, allowing for simultaneous collection of the calorimetric and potentiometric data.

Calorimetric titrations done in the 3-mL Dewar employed a charge of 2 mL of the PVA–HX solution while those done in the 50-mL vessel used a charge of 40 mL. After thermal equilibration, titrant was introduced at a rate of approximately 0.02 mL min^{-1} to the smaller calorimeter and at a rate of approximately 0.04 mL min^{-1} to the large calorimeter. The titrant concentration for experiments done in the 3-mL Dewar was nominally 10 times the PVA–HX titrate concentration while experiments in the 50-mL Dewar required a ratio of titrant to titrate concentrations of approximately 100. A typical experiment involved collection of temperature data at 10-s intervals for approximately 5 min in the lead region, 10 min in the reaction region, and 5 min in the trail region of the thermogram. The titrant was delivered with a Tronac high-precision motorized buret, and the total volume change during the titration was kept below 10% of the charging volume. Titrations were done at two temperatures, either 298 or 323 ± 0.1 K.

Potentiometric data were collected with a Beckman 4500 digital pH meter and Model MI-405 glass and MI-402 reference electrodes from Microelectrodes, Inc. The pH meter and electrodes were calibrated immediately before each titration with pH 6.682 phosphate and pH 4.008 potassium acid phthalate buffers prepared according to NBS instructions. The calibration was routinely checked following each titration. The pH was recorded simultaneously with the calorimetric temperature data at 10-s intervals.

As stated above, a typical titration was complete in about 10 min. However, to check for electrode response and chemical equilibrium, a few titrations were done more slowly, taking from 30 min to 1 h to complete. No significant differences in either the heat or pH data were seen in comparing the fast and slow titration curves.

Calculations. The method used to calculate the heat change value, Q, from the temperature–time data in the reaction region has been described previously.[5,6] The heat change to each point in the thermogram reaction region was calculated by the RENPLT computer program in use at the Thermochemical Institute, B.Y.U., Provo, Utah. These data were corrected for the heat of dilution of the strong base titrant and for the heat of formation of water by use of data taken from ref 7. The ΔH values were calculated from the slope of a tangent to the enthalpogram at the various values of α, where α is the mole fraction of protonated amino groups in the polymer. The ΔG values, for these same values of α, were calculated from the pH data as described previously.[3] The thermodynamic parameters, ΔG and ΔH, are reported at the ionic strength at which they were measured with no attempt made to make activity corrections or extrapolate the data to infinite dilution. The α values were calculated from the PVA–HX solution concentration, the concentration of any excess HX, the Dewar charge volume, and the volume and concentration of added NaOH titrant. The end points observed in the enthalpogram were used to check the titrate concentrations. With some care taken to locate the end points in the calorimetric titration data, the agreement between the titrate concentration by weight and from the titration was always within ±5% and usually within ±2%. The calculation of the α, ΔH, ΔG, and $T\Delta S$ values throughout the titration was accomplished by the PHPLOT program in use at the Thermochemical Institute. All calculations were done on a VAX/780 computer.

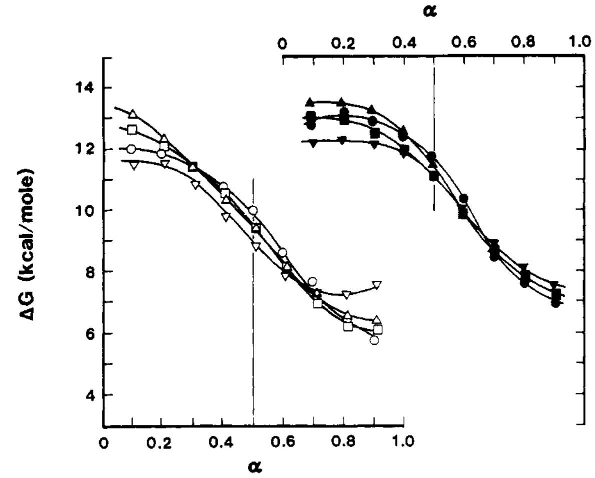

Figure 1. Free energy change for proton ionization from PVA–HCl, ΔG, as a function of charge state, α, at $M_s = 0.0$ M: (△) $M_p = 0.01$ M, $T = 323$ K; (○) $M_p = 0.1$ M, $T = 298$ K; (□) $M_p = 0.01$ M, $T = 298$ K; (▽) $M_p = 0.001$ M, $T = 298$ K; shaded symbols are for the same M_p and T but with $M_s = 0.9$ M NaCl.

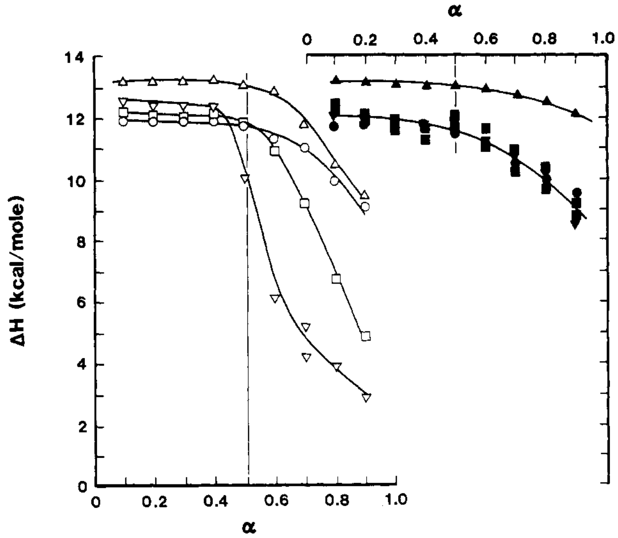

Figure 2. Enthalpy change for proton ionization from PVA–HCl, ΔH, as a function of charge state, α. The symbols are the same as in Figure 1.

Results and Discussion

Aqueous solutions of the polymer in the fully charged state ($\alpha = 1$) were titrated under a variety of conditions. The hydrochloride salt, PVA–HCl, was titrated at three polymer concentrations ($M_p = 0.001$, 0.01, and 0.1 monomolar) in the absence or presence of added NaCl ($M_s = 0.0$, 0.5, and 0.9 M), and at two temperatures ($T = 298$ and 323 K). These results (except for $M_s = 0.5$) are summarized in Figures 1–3. The hydrobromide, PVA–HBr, hydroiodide, PVA–HI, and hydroperchlorate, PVA–$HClO_4$, salts of PVA were titrated at one polymer concentration ($M_p = 0.01$ monomolar), at one temperature ($T = 298$ K),

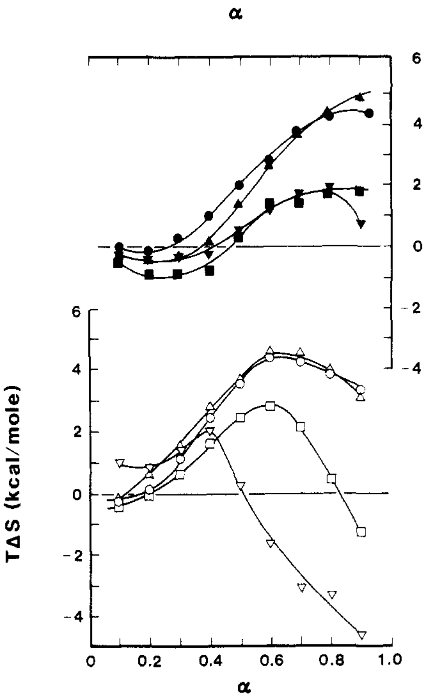

Figure 3. Entropy change data for proton ionization from PVA-HCl, $T\Delta S$, as a function of the charge state, α. The symbols are the same as in Figure 1.

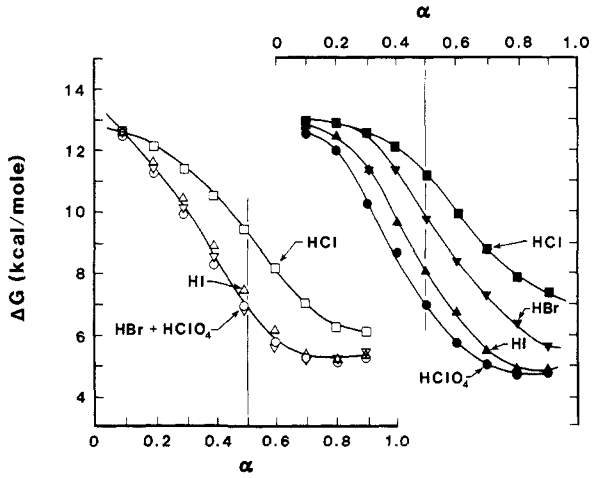

Figure 4. Free energy change for proton ionization from PVA-HX, ΔG, as a function of charge state, α, at 298 K, for M_p = 0.01 M and M_s = 0.0 M: (□) X = Cl; (▽) X = Br; (◇) X = I; (○) X = ClO_4; shaded symbols are for the same polymers and conditions but with M_s = 0.9 M NaX.

and at a minimum of two sodium salt concentrations (M_s = 0.0 and 0.9 M NaX). These results are reported in Figures 4–6. Each data set plotted in Figures 1–6 represents an average for at least three individual titration experiments. The charge-state parameter, α, was calculated from the polymer concentration by weight and the titrant concentration and volume. Although data were collected continuously throughout a titration, only the average parameters at α values of 0.1–0.9 at intervals of approximately 0.1 are shown in these figures. The smooth curves were drawn by eye to be a reasonable fit of the average parameter data. The ΔG, ΔH, and $T\Delta S$ values given in the figures are for the ionization reaction

$$\text{PVA-H}^+ \rightarrow \text{PVA} + \text{H}^+ \qquad (1)$$

The estimated uncertainty in ΔG or ΔH, calculated as the standard deviation of the mean for at least three determinations, is ±0.3 kcal/mol with a corresponding uncertainty of ±0.4 kcal/mol in $T\Delta S$. The thermodynamic parameters ΔG, ΔH, and $T\Delta S$ will be discussed in turn, first for PVA-HCl and then for the other salts.

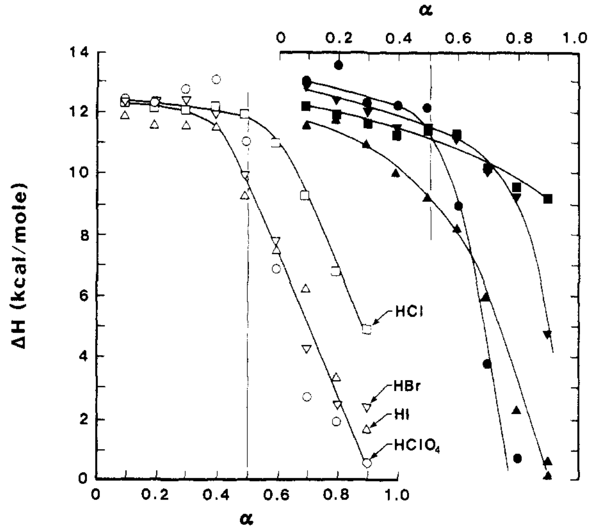

Figure 5. Enthalpy change for proton ionization from PVA-HX, ΔH, as a function of charge state, α. The symbols are the same as in Figure 4.

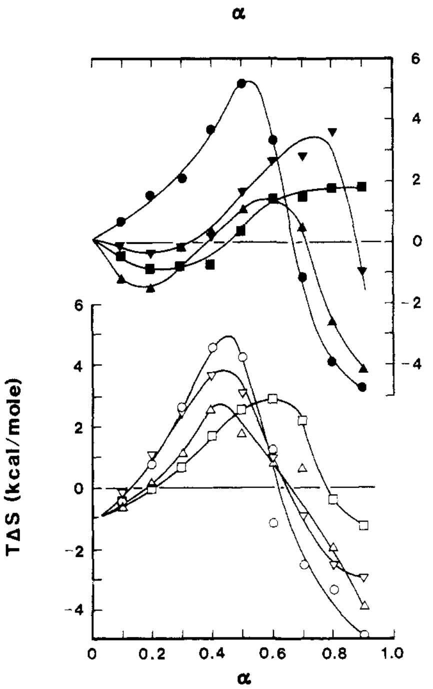

Figure 6. Entropy change data for proton ionization from PVA-HX, $T\Delta S$, as a function of charge state, α. The symbols are the same as in Figure 4.

Free Energy Change. Modern polyelectrolyte theory has been developed almost entirely from the standpoint of predicting the free energy changes for ionization of polymeric acids.[8] There exists a rather extensive literature dealing with the potentiometric titration of polyelectrolytes, including a number of previous studies on poly(vinylamine).[1,2] Our ΔG data for ionization of PVA-HCl are given in Figure 1, and in Figure 4 we report our results for PVA-HBr, PVA-HI, and PVA-$HClO_4$. In comparing our ΔG data at low polymer concentration (M_p = 0.01 and M_p = 0.001) with the data published previously for PVA-HCl at higher concentration (M_p = 0.1 monomolar),[3] it became apparent that the earlier values were in error by as much as 2 kcal/mol at α values less than 0.3 or greater than 0.7.

The problem with the earlier ΔG results[3] was traced to an error in calculating the polymer concentration in the 0.1 M solutions, and these high concentration experiments were repeated in this work. In all other cases, the present data are in agreement with the earlier results where the titration conditions are comparable.

The ΔG data shown in both Figures 1 and 4 exhibit a strong polyelectrolyte effect as their most striking feature. For example, the difference in ΔG exhibited at the extremes of the curves for PVA–HCl is 5–6 kcal/mol. This difference appears to be unaffected by changes in polymer concentration, NaCl concentration, or temperature. The data in Figure 4 show the change in ΔG between $\alpha = 0$ and $\alpha = 1$ to be reasonably insensitive to the nature of the counterion. The change in ΔG at $M_s = 0$ for the counterion ClO_4^-, I^-, or Br^- is about 7 kcal/mol and about 6 kcal/mol for Cl^-. At $M_s = 0.9$, the change in ΔG ranges from about 5 to 7 kcal/mol. The effect of the added salt decreases in the order $Cl^- > Br^- > I^- > ClO_4^-$. It should also be noted that at $\alpha = 0$, the uncharged polymer exhibits a ΔG value for ionization that closely resembles values in the literature for both monomeric amines and low molecular weight model polyamines like *cis,cis*-1,3,5-triaminocyclohexane.[9]

The large polyelectrolyte effect for PVA, twice that of poly(acrylic acid) (PAA),[10,11] seems reasonable on the basis of charge separation arguments alone. A comparison of PVA where the localized charges are separated by four bonds with PAA where the charges are delocalized and separated by six bonds has already been made.[11] One of the few points on which all of the polyelectrolyte theories agree and one which is consistent with all of the data is that the polyelectrolyte effect, $\mathrm{d}pK_a/\mathrm{d}\alpha$, must be a function of charge density or spacing.

The popular theories for polyelectrolyte behavior fall into two categories. Those theories which are based on a lattice model form one group, while the other is made up of theories which are based on an electrostatic model. The counterion condensation theory of Manning[12] is one theory from the second group and the theories of Marcus[10] and of Lifson and Katchalsky[13] are examples from the first group. Our view is that none of these theories are very accurate as judged by their ability to predict the titration behavior of poly(vinylamine) under the conditions examined in this study.

The counterion condensation approach predicts a change in slope in the ΔG curve at the critical charge density, calculated to occur at $\alpha = 0.35$ for PVA. The predicted critical charge density would be independent of the counterion type. At high salt concentration some of the ΔG curves, e.g., the hydrochloride data, do suggest a rough approximation to the condensed counterion prediction. However, it does not seem appropriate to extend the Manning analysis developed for dilute polyelectrolyte at low ionic strength to these solutions. In general, neither the break in the ΔG curve at $\alpha = 0.35$ nor the independence of $\mathrm{d}\Delta G/\mathrm{d}\alpha$ on counterion type is observed here. In addition, a reduced dependence of ΔG on α at α values greater than the critical value would be predicted. Instead, for PVA–HX at $M_s = 0.9$, ΔG shows a small dependence on α at α less than 0.35 and for PVA–$HClO_4$ at $M_s = 0$, ΔG shows a small dependence on α at α greater than 0.65. Also, Olofsson has recently reported that the counterion condensation theory fails to predict the sodium ion activities in poly(acrylic acid) solution.[14]

The lattice model, even when three-body interactions are considered,[15] does not predict the observed changes in curve shape with changes in polymer or salt concentration and cannot account for differences in counterions.

A careful look at the PVA–HCl data in Figure 1 reveals small but regular trends in ΔG with changes in polymer or salt concentration and temperature. The polyelectrolyte effect on ΔG diminishes as the polymer concentration, salt concentration, and temperature increase. All of these trends are predictable on the basis of diminished electrostatic effects due to ion screening or changes in solvent structure (lowered dielectric constant). The ΔG values for proton ionization from PVA–HX presented in Figure 4 show that counterion effects can be very large. For example, the difference in ΔG at $\alpha = 0.5$ is approximately 2.5 kcal/mol between the hydrochloride and hydroperchlorate salts at $M_s = 0$ and 4 kcal/mol at $M_s = 0.9$. In effect, the hydroperchlorate salt of poly(vinylamine) is a stronger acid than the hydrochloride by almost 2–3 pK_a units, depending on the amount of added salt. The only explanation seems to be that the effective charge on the protonated polyamine is reduced in the presence of Cl^- counterions but not by Br^-, I^-, or ClO_4^- at 0.01 monomolar polymer and in the absence of added electrolyte. At high salt concentration the screening effect of X^- decreases in the order $Cl^- > Br^- > I^- > ClO_4^-$. These data indicate that ion–pair formation between counterions and the polyion reduces the effective charge on the polyelectrolyte.

The data in Figure 4 are consistent with the formation of significant numbers of ion pairs by chloride even in the absence of added salt and of no ion pairs formed by the perchlorate ion even in 0.9 M sodium perchlorate. Obviously, we cannot learn anything about this ion-pairing process by looking at low molecular weight ammonium salt behavior since it has long been known that monovalent atomic and small molecular ions behave as strong electrolytes in media with dielectric constants greater than 40.[16] However, ammonium salts immobilized on silica gel have been shown to bind chloride ion in preference to bromide, iodide, or perchlorate ion.[17]

Strauss has shown a similar specific binding phenomenon for the association of Li^+ with maleic acid copolymers. The binding of the Li^+ to the polyion was found to disrupt the *electrostriction of water by the polyion*.[18] Some evidence for the cooperative solvation of polyelectrolytes has been reported by Boyd.[19] The heats of dilution and partial molar volumes for these cooperatively solvated polyelectrolytes could not be predicted by an *infinite line charge* theory like that of Manning. Our results show that the solvent structure in the vicinity of the polyion must yield a sufficiently low dielectric constant or high enough charge density for specific counterion association to occur. It is apparent that the effects due to altered solvent structure in the vicinity of the polyion, which allow for counterion binding, have been underestimated by all previous theories.

Enthalpy Change. There have been only a few reports published previously on calorimetric studies of polyelectrolyte ionization[20] and, with the exception of our earlier report on PVA and PIE, poly(iminoethylene),[3] none directly comparable to the work presented here. This is unfortunate since the published work of Crescenzi,[21] Barbucci,[22] and Strauss,[18] as well as our own work, has clearly shown the advantage of considering ΔH, along with ΔG, when attempting to probe such complex as proton ionization from polyelectrolytes.

The ΔH data are reported in Figure 2 for PVA–HCl and in Figure 5 for the other salts. It is apparent from Figure 2 that ΔH increases slightly, if at all, from $\alpha = 0$ to $\alpha = 0.5$ and thereafter decreases, with the amount of the decrease depending on M_p and M_s. The decrease in ΔH is most pronounced at low polymer concentration and is diminished as the polymer concentration is increased. At

Table I
Equilibrium Constants for Formation of $PVAH^+$-X^- Ion Pairs at $\alpha = 0.9$

anion	M_p	M_s	$\delta\Delta H^a$	X_c^b	K_c^c
Cl^-	0.001	0.0	1.8 ± 0.3	0.21	340 ± 90
	0.001	0.9	8.5	1.0	
Cl^-	0.01	0.0	4.4 ± 0.3	0.52	230 ± 60
	0.01	0.9	8.5	1.0	
Cl^-	0.10	0.0	8.5	1.0	
Br^-	0.01	0.0	1.9 ± 0.3	0.22	36 ± 9
	0.01	0.9	4.0 ± 0.3	0.47	(1.0)
I^-	0.01	0.0	1.1 ± 0.3	0.13	17 ± 7
	0.01	0.9	1.7 ± 0.3	0.20	(0.3)

[a] $\delta\Delta H = \Delta H(\text{PVA-HX}) - \Delta H(\text{PVA-HClO}_4)$ at $\alpha = 0.9$; data taken from Figure 5. [b] X_c is the fraction of ammonium groups to which anions are bound, calculated on the basis of the assumptions given in the text above. [c] K_c is the concentration product equilibrium constant at $\alpha = 0.9$ for the reaction $PVAH^+ + X^- \rightarrow$ PVAH-X(ion pair).

Table II
Heat Capacity Changes for Proton Ionization from Poly(vinylamine hydrochloride) at 310.5 K[a]

	$\Delta C_p{}^b$	
α	$M_s = 0.0$ M	$M_s = 0.9$ M
0.1	40	44
0.2	44	48
0.3	48	48
0.4	48	52
0.5	48	56
0.6	76	68
0.7	112	84
0.8	152	104
0.9	184	124

[a] Polymer concentration = 0.01 monomolar; ΔH data taken from Figure 2. [b] Units are cal/(monomol K).

high added salt concentrations (at least for NaCl), the polymer concentration dependence of ΔH is completely masked.

An examination of the data in Figure 5 reveals that ΔH is sensitive to the nature of the counterion. In the case of no added salt, the ΔH data fall on two lines, one for the hydrochloride and one for the other salts. The change in ΔH at $0.5 < \alpha < 1.0$ for the hydrochloride polymer calculated from the extremes of the curve is about 7 kcal/mol while the changes for the other salts range from about 10 to 12 kcal/mol. The changes in ΔH are about twice the corresponding changes in ΔG. As salt is added, the HBr, HI, and $HClO_4$ salts are differentiated, with Br^- and I^- salts being intermediate between the behavior of the Cl^- and ClO_4^- salts.

Association constants for formation of the various $PVAH^+$-X^- ion pairs can be estimated from the difference in the enthalpy change for ionization of PVA-HX and PVA-$HClO_4$ by assuming (1) ClO_4^- ion is completely dissociated under all conditions in these experiments, (2) the fraction of ammonium groups complexed with Cl^- is 1.0 under conditions of $M_p = 0.001$ and $M_s = 0.9$, (3) the change in ΔH for ionization at $\alpha = 0.9$ is proportional to the fraction of ammonium groups associated with a counterion, and (4) the change in ΔH on binding a counterion is independent of the counterion type. The values calculated for the formation constants, K_c, and the fraction of ion-paired ammonium groups, X_c, are listed in Table I. The relationships used to calculate K_c from the assumptions listed above are $[M_p] = [P] + [PH^+] + [PHX]$, $[X^-] = [Ms] + [PH^+]$, $\alpha = ([PH^+] + [PHX])/[M_p]$, $X_c = [PHX]/([PH^+] + [PHX]) = \delta\Delta H/8.5$, and $K_c = [PHX]/([PH^+][X^-]$, where the terms $[P]$, $[PH^+]$, $[PHX]$, and $[X^-]$ represent the concentrations of amine, ammonium, and ion-paired ammonium groups, and of free counterion, respectively. Even though the calculated formation constants have large uncertainties, the agreement between the two K values calculated for chloride binding is convincing, and the trend in the constants for Cl^-, Br^-, and I^- appears reasonable. This interpretation of the enthalpy change data in Figure 5 in terms of ion-pair formation agrees with the ΔG data and a previous study of immobilized ammonium salts.[17]

In discussing the ΔH data in general it is important to offer an explanation for the sharp break in the curves around $\alpha = 0.4$–0.6. The value of ΔH is nearly constant at $0 < \alpha < 0.5$, and ΔG or pK_a would be constant were it not for a change in $T\Delta S$ in this part of the titration curve. The effect of α on ΔH at $\alpha > 0.5$ is large or small depending on how effectively the charges are screened by counterion binding. For the counterion which shows no apparent binding, i.e., ClO_4^-, the maximum polyelectrolyte effect on ΔH is observed. The Cl^- counterion, which binds the most strongly, defines the minimum polyelectrolyte effect.

Because ΔH does not change significantly below $\alpha = 0.5$, the electrostatic contribution to ΔH for dissociation must be a short-range effect which may be rationalized in terms of nearest-neighbor effects as was suggested in our earlier work[3] and the work of Barbucci et al.[22] Solvation may provide the mechanism for this effect. It has previously been reported that the solvation shell around an ammonium ion extends for approximately 5 Å.[23] This distance has also been found to account for the alkyl chain length effect on the thermodynamics for ionization from simple protonated alkylamines.[24] In our previous report we noted that the electrostatic contribution to ΔH was incalculable since neither the dielectric constant nor its temperature derivative was known or could be effectively modeled for solvent in the vicinity of the polyion. Thermodynamic data on monoamines and low molecular weight polyamines are also of little help here. The electrostatic contributions in the case of monoamines are small due to the isoionic nature of the ionization.[24] In those cases where data exist for ionization of low molecular weight model polyamines, the charge densities are too low and the chain configuration too flexible for the cooperative solvation effects seen in PVA ionization to exist. We propose that the break in the ΔH curve occurs at the point where the solvation shells of the protonated amine groups begin to overlap and the solvation becomes cooperative. In effect, at high α there would be little or no change in solvation of the polyion with a change in α since the solvent shells of protonated groups neighboring the dissociating group would still overlap. The ionization process would thus proceed with a net increase in solvation due to solvation of the leaving proton and an exothermic contribution would be made to the overall enthalpy change. The increased solvation of the ionization products at high α is not only consistent with the decrease in ΔH at high α but is also consistent with the large positive ΔC_p at high α as discussed below. The break in the curve also occurs at the point where a stiff hydrogen-bonded structure between alternating protonated and unprotonated amine groups is known to prevail.[3,25] However, it is unlikely that the influence of hydrogen bonding on the enthalpy would be as great as the 7–12 kcal/mol change that is observed here. Also, hydrogen bonding would be expected to go through a maximum at $\alpha = 0.5$ and not vary monotonically to $\alpha = 1.0$. This brings us back to solvation effects as being the most likely origin of the large changes in ΔH with α.

Figure 2 illustrates the variation in ΔH with temperature. The ΔH data at the two temperatures can be used with eq 2 to estimate the change in heat capacity on dissociation, ΔC_p.

$$\Delta C_p = \mathrm{d}\Delta H/\mathrm{d}T = (\Delta H_{323} - \Delta H_{298})/(323 - 298) \quad (2)$$

The ΔC_p data are presented in Table II. The ΔC_p values calculated by eq 2 apply at the mean temperature and thus are reported at $T = 310.5$ K in the table.

One possibility that must be considered whenever ΔC_p data are derived from the temperature dependence of the enthalpy change is that the reaction might also be changed on changing the temperature. For example in the case of ionization of PVA–HCl, the extent of chloride ion binding might vary with temperature and thus change the overall ΔH at each temperature. We cannot rule out this possibility entirely with the present data set. However, the high salt data seem to suggest that any changes in counterion binding with temperature are not significant over the observed range of temperatures. We feel that the best explanation for the large positive ΔC_p values observed in PVA–HCl ionization comes from a discussion of solvation change and the hydrophobic effect.[26]

The denaturation of globular proteins has been sufficiently studied so that the thermodynamics of the hydrophobic effect are well-known.[27] The characteristic features are a positive free energy change and a positive change in heat capacity on hydration of a hydrophobic group. On ionization (loss of a proton or charge from PVA) the hydrocarbon backbone of the polyamine is exposed to solvent and the process proceeds with a positive change in heat capacity. The real surprise in Table II is the magnitude of the change, ranging from approximately 40 cal/(mol K) at low α to over 180 cal/(mol K) at $\alpha = 1.0$. In comparison, the ΔC_p reported for the transfer of a leucine side chain (4 carbons) from ethanol to water ranges from 30 cal/(mol K) at 273 K to about 90 cal/(mol K) at 353 K.[27] Strauss calculated the thermodynamic parameters for unfolding the uncharged copolymer of maleic acid and butyl vinyl ether and derived a ΔC_p for the transition of 22 cal/(monomol K) at 298 K.[18] Thus the ΔC_p values observed here seem inordinately large, particularly at high α values. In the presence of 0.9 M salt, the ΔC_p values are depressed somewhat at high α but remain unchanged for the uncharged polyamine. The large ΔC_p values seem to clearly indicate that the water structure in the vicinity of the protonated or deprotonated polyamine must be quite anomalous.

Entropy Change. The entropy change data are reported in Figure 3 for PVA–HCl and in Figure 6 for the PVA–HX experiments.

Although the $T\Delta S$ values are inherently more uncertain than the ΔG and ΔH data from which they were calculated, the trends in $T\Delta S$ with polymer or salt concentration and temperature in Figure 3 or with counterion type and salt concentration in Figure 6 are significant. The data in both figures show that the $T\Delta S$ value for proton ionization from the uncharged polymer ($\alpha = 0$) is independent of salt and polymer concentration. The $T\Delta S$ parameter, like ΔG and ΔH, approaches a value typical of monoamines[24] as α approaches zero. However, all of the curves show $T\Delta S$ to depend strongly on α throughout the range $0 < \alpha < 1.0$. The $T\Delta S$ curves may be characterized by two features: (1) the α value at which the maximum in $T\Delta S$ is observed, and (2) the value of $T\Delta S$ at $\alpha = 1$. The PVA–HCl data in Figure 3 show that the maximum in $T\Delta S$ moves regularly toward higher α values and the $T\Delta S$ value at $\alpha = 1$ becomes more positive as the polymer concentration is increased. An increase in temperature or polymer concentration produces the same effects as does an increase in salt concentration. The data in Figure 6 for no added salt show the behavior of the HBr, HI, and $HClO_4$ salts to be similar to each other but different from the hydrochloride. The HBr, HI, and $HClO_4$ salts of PVA all show a maximum in $T\Delta S$ at an α value of 0.4. In the presence of 0.9 M added salt, the HBr and HI data shift away from the curve for the hydroperchlorate salt and exhibit maximum $T\Delta S$ values at α values of 0.7 and 0.6, respectively. The $T\Delta S$ values at $\alpha = 1$ are also more positive than that observed for PVA–$HClO_4$. The results for the perchlorate salt of PVA are unaffected by added salt.

In order to understand the $T\Delta S$ data, at least three factors must be considered: (1) proton or charge distribution along the chain, (2) polymer conformation, and (3) solvation, including counterion effects. Estimates of these three contributions should at least allow the general shape of the $T\Delta S$ vs. α curve to be predicted qualitatively.

The first effect, that of proton distribution, is in principle calculable from the probabilities for finding distinguishable arrangements of n protons on m sites, and the relationship between probability and entropy given in eq 3 where σ is the symmetry number before (σ_{reac}) and after (σ_{prod}) removal of a proton.[28]

$$\Delta S_{\mathrm{sym}} = -R \ln (\sigma_{\mathrm{prod}})/(\sigma_{\mathrm{reac}}) \quad (3)$$

Statistical contributions to the entropy change for known random or nonrandom proton distributions can be estimated by using this approach. In any case, the change in $T\Delta S$ becomes more positive with increasing α. The curve is symmetrically sigmoidal for the case where all bound protons have the same energy, i.e., a nonrandom distribution. The proton distribution term would not be expected to vary significantly with concentration of polymer or salt or temperature. The ΔG and $T\Delta S$ values shown in Figures 1, 3, 4, and 6 do contain the symmetry contribution since the manner in which these parameters were calculated gives the excess or intrinsic values.

The second effect, that due to polymer conformation, cannot be calculated quantitatively at present but the qualitative shape of the $T\Delta S$ vs. α curve may be obtained from hydrodynamic data and NMR results published previously.[3,25] Viscosity and sedimentation data collected on PVA–HCl as a function of charge state indicate that the polymer has the maximum hydrodynamic volume and is rodlike at $\alpha = 0.5$. ^{15}N NMR results have been interpreted in terms of a maximum in hydrogen bonding between the polymer amine groups occurring at $\alpha = 0.5$. The fully charged polymer is either an extended or slightly relaxed coil, depending on whether the viscosity or sedimentation data are the more accurate. A reasonable estimate for the maximal contribution to the entropy can be made from knowledge of the entropy of fusion for crystalline polymers. Tonelli has published extensively on this subject,[29] and it seems unlikely that changes in the entropy due to changes in the polymer conformation accompanying dissociation could exceed R per monomol ($T\Delta S < +0.6$ kcal/monomol). The effect is positive at high α and zero at $\alpha = 0$. The conformational effect in $T\Delta S$ probably is sigmoidal with a rapid rise just prior to $\alpha = 0.5$. The conformational contribution to the entropy change is expected to decrease with increased polymer or salt concentration or increased temperature.

The solvation effect is in principle calculable from the electrostatic equation for proton dissociation from the charged polymer.[16]

$$\Delta S_{\mathrm{solv}} = -(Neq/Dr)(\mathrm{d} \ln D/\mathrm{d}T) \quad (4)$$

The difficulties in using eq 4 arise from the uncertainty in a choice for q, the charge on the polyion visible to the

Table III
Electrostatic and Symmetry Contributions to ΔH and $T\Delta S$ for Dissociation of PVA–$HClO_4$ at 298 K (kcal/mol)

α	$\delta\Delta H$	ΔH_{elec}	RPE[a]
0.0	−1.4	0.0	−1.4
0.33	−1.8	−0.1	−1.7
0.50	−4.2	−1.0	−3.2
1.00	−13.8	−4.1	−9.7
α	$\delta T\Delta S$	$T\Delta S_{elec}$	RPE[a]
0.0	+1.0	0.0	+1.0
0.33	+4.2	+0.5	+3.7
0.50	+6.8	+1.3	+5.5
1.00	−2.5	+4.2	−6.7

[a] Residual polyelectrolyte effect.

leaving proton, and the unknown values for the dielectric constant, D, and its temperature derivative. However, since the ($d \ln D/dT$) term is always negative, this part of the $T\Delta S$ term for proton ionization will be large and positive for the highly charged polymer and zero for the uncharged polymer. The electrostatic effect on $T\Delta S$ is probably sigmoidal with a rapid rise between $\alpha = 0.3$ and $\alpha = 0.5$. Again the effect would be expected to decrease with increased polymer concentration or salt concentration or increased temperature.

Summing the three effects considered so far, i.e., charge symmetry, polymer conformation, and solvation, qualitatively leads to a sigmoid curve of $T\Delta S$ vs. α which has a negative value at $\alpha = 0$, a larger positive value at $\alpha = 1$, and is steepest near $\alpha = 0.5$. The curve for $T\Delta S$ for PVA–$HClO_4$ in Figure 6 follows this prediction up to $\alpha = 0.4$, but then the experimental $T\Delta S$ values decrease whereas the theory above predicts further increase. Since the three factors presented above are sufficient to predict $T\Delta S$ quite well for proton ionization from small molecules,[24] the decrease in $T\Delta S$ above $\alpha = 0.4$ must be a polyelectrolyte effect.

Polyelectrolyte Effect on ΔH and $T\Delta S$. In an effort to quantitate the magnitude of the polyelectrolyte effect on the values of ΔH and $T\Delta S$ for dissociation of the ammonium groups of PVA, we have subtracted the electrostatic and alkyl group contributions to ΔH and $T\Delta S$ for proton ionization as are observed in model amines. The data are given in Table III along with the residual or unexplained polymer effect at the four most useful α values.

The $\delta\Delta H$ and $\delta T\Delta S$ terms in the second column of Table III are obtained by subtraction of the ΔH and $T\Delta S$ values for dissociation of *n*-propylammonium ion[24] from the measured ΔH and $T\Delta S$ values for proton dissociation from PVA–$HClO_4$. The ΔH and $T\Delta S$ values for dissociation of *n*-propylammonium ion were chosen because of the resemblance to the monomeric unit of PVA; however, the ΔH and $T\Delta S$ values for *n*-alkylamines change very little as the alkyl chain gets longer. Also, for our purpose here, the ΔH and $T\Delta S$ values for ionization of primary ammonium ions with secondary alkyl groups are not significantly different from those for ammonium ion with primary alkyl groups. A significant nonzero value of $\delta\Delta H$ or $\delta T\Delta S$ at $\alpha = 0$ thus represents the polyelectrolyte effect caused by the presence of the uncharged polymer attached to the ionizing group.

At $\alpha \geq 0.33$ electrostatic interactions between protonated amino groups will become significant.[24] The electrostatic contributions to ΔH and $T\Delta S$ for nearest-neighbor, nn, groups are calculated by subtracting the values of ΔH and $T\Delta S$ for the dissociation of 1-aminobutane from the ΔH and $T\Delta S$ terms for the first dissociation of diprotonated 1,3-diaminoprpane. The value of $T\Delta S$ for dissociation of the α,ω diamine must be corrected by $RT \ln 2$ to eliminate the symmetry factor and obtain only the electrostatic effect of the second ammonium group.[28] For example, the difference in ΔH for a 1–3 interaction estimated in this fashion is −1.54 kcal/mol and the difference in $T\Delta S$ is +1.40–0.41 kcal/mol. The effects of next-nearest neighbors, nnn, and of next-next-nearest neighbors, nnnn, were calculated from data for 1,5-diaminopentane and *n*-hexylamine and from 1,7-diaminoheptane and *n*-octylamine, respectively. These data were taken from or estimated from data in ref 24. In calculating the effects due to charge–charge interactions, a nonrandom proton distribution is assumed with only ...+00+00+00... and ...+0+0+0... sequences existing at $\alpha = 0.33$ and $\alpha = 0.50$, respectively. This assumed distribution is consistent with the ^{15}N NMR study by Rinaldi et al.[25] and is in agreement with our analysis of the enthalpy and hydrodynamic data in our earlier report.[3] We have also assumed for this discussion that contributions from charged neighbors are additive in both ΔH and $T\Delta S$. In order to account for the presence of neighbor groups on both sides of the group undergoing dissociation in the polymer, the model electrostatic contributions were simply doubled.

The fourth column of Table III, labeled "residual polyelectrolyte effect", is obtained by subtracting the third column from the second column. The residual polyelectrolyte effect in Table III is thus the excess enthalpy or entropy effect seen when the polymer is compared to small molecules.

From the magnitude of the polyelectrolyte effect, after taking into account nn, nnn, and nnnn effects, it seems that neither ΔH nor $T\Delta S$ is predictable from short-range interactions alone. This is especially true at high α, where the polyelectrolyte effect in ΔH and $T\Delta S$ is 5–10 kcal/mol. However, it appears that the results presented here justify speculation about polymer solvation as a major contributor to the polyelectrolyte effect.

If it is assumed that the amino groups in the polymer are either closer together, or that the dielectric constant between the groups is lower than in the small model molecules chosen, then the polyelectrolyte effect on ΔH for $0 < \alpha < 1$ and on $T\Delta S$ for $0 < \alpha < 0.5$ can be explained. For example, if ethylenediamine instead of 1,3-propanediamine, 1,3-propanediamine instead of 1,5-pentanediamine, etc., are chosen as monomeric models, the polyelectrolyte effect on ΔH given in Table III becomes nearly constant. The polyelectroltye effect on $T\Delta S$ in Table III also goes to near zero for $0 < \alpha < 0.5$. Coiling of the polymer backbone into a helix would both shorten the distance and reduce the dielectric constant between amino groups. We thus hypothesize that at $\alpha = 0.5$ the polymer is tightly coiled (rodlike) and the polyelectrolyte effect is primarily due to electrostatic effects.

As protons are added to the polymer in the range $0.5 < \alpha < 1$, the polyelectrolyte effect on $T\Delta S$ changes direction so that $T\Delta S$ for ionization becomes very negative at $\alpha = 1$. This enormous effect on the entropy of ionization (more than 50 cal/(mol K)) has no parallel in small molecules and must be due to a cooperative solvation phenomenon on the charged polymer. If this effect did not occur and the trend in $T\Delta S$ at $0 < \alpha < 0.5$ continued upward to $\alpha = 1$ (see Figure 6), then fully protonated PVA would be an extremely strong acid, i.e., $\Delta G \sim -6$ kcal/mol. The origin of this effect is of interest because of what could be learned concerning the hydration of other highly charged species in aqueous solution, e.g., ionic surfactant micelles, histones, and other proteins.

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Mechanisms of Polymer-Supported Catalysis. 7. Carbon-13 NMR Relaxation of Toluene in Cross-Linked Polystyrene Phase-Transfer Catalyst Gels

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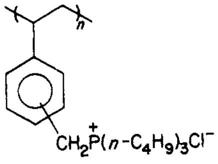
ABSTRACT: Carbon-13 spin–lattice relaxation times (T_1) and nuclear Overhauser effects have been determined for toluene in cross-linked polystyrene gel beads 16–18% ring substituted with benzyltri-*n*-butylphosphonium chloride groups. Toluene inside the beads and toluene outside the beads gave separate ^{13}C peaks for each carbon atom. The T_1 values and rate constants for exchange of toluene between the sites were measured by selective T_1 experiments with concurrent relaxation and exchange. The T_1 values of all protonated carbon atoms of toluene inside the beads were reduced to 0.05–0.33 times their values in low-viscosity toluene solutions. The T_1 values of aromatic carbon atoms of toluene outside the beads were reduced to 0.25–0.5 times their values in low-viscosity toluene solutions. The T_1 results are explained by slower rotational diffusion of toluene in the cross-linked polystyrene gels. The self-diffusion coefficient of toluene in the gel is estimated from the exchange rate constants to be 0.02 times that in liquid toluene.

In ^{13}C nuclear magnetic resonance spectra of cross-linked polystyrene gels in toluene,[1] the solvent peaks appear as doublets instead of proton-decoupled singlets. Since the NMR samples consist of toluene-swollen beads 0.1–0.3 mm in diameter immersed in toluene, the two peaks of each doublet were assigned to toluene inside the beads and toluene in the interstices. Similar doublets have been reported for organic solvents,[2,3] counterions,[2,4,5] and water[3,6–10] in ion-exchange resins. The polystyrenes in this investigation were 16–18% ring substituted with benzyltri-*n*-butylphosphonium ions (1). They have been used extensively as phase-transfer catalysts for reactions such as that of aqueous sodium cyanide with 1-bromooctane in toluene.[11–14] This paper reports the spin–lattice relaxation times of the toluene doublets in the ^{13}C NMR spectra and the rate constants for exchange between the two environments.



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NMR relaxation of small organic molecules has been studied in a variety of synthetic and naturally occurring heterogeneous systems, chiefly using ^1H, ^2H, ^{13}C, and ^{19}F nuclei.[15] The ^{13}C spin–lattice relaxation time (T_1) is particularly useful because its measurement requires no isotopic labeling and relaxation by the direct dipolar mechanism is intramolecular, allowing interpretation in

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