for poly(vinyl acetate) it increases linearly with temperature according to the relation

$$\alpha(T) = \alpha(T_g) + (7.7 \times 10^{-4})(T - T_g) \qquad (7)$$

We now apply this method to the PVDC–HMPA system at 40 °C. Retaining eq 7 for PVDC, which has a recorded glass temperature of 255 K, we obtain $\alpha = 0.078$. For the solvent, $\beta(T)$ should be proportional to the reduced temperature, and from Mashimo's figure of 0.308 for toluene at 40 °C and the normal boiling temperatures of 382 and 504 K for toluene and HMPA, respectively, we obtain $\beta = 0.233$ for HMPA, leading to $\sigma(T) = 0.204$. Now for the 24.8% (w/w) solution the solvent volume fraction is 0.816, and at 40 °C the harmonic mean correlation time τ_h is close to 0.3 ns and thus τ_a is about 1 ns. Taking a time intermediate to these, from eq 5 we find $B(T) \simeq 10^{-11}$ μs at this temperature, and then from the same equation we obtain $\tau \simeq 10$ μs for 100% PVDC. Of course, this refers to the amorphous material.

Dielectric relaxation measurements on pure PVDC were made long ago by Saito and Nakajima,[25] from whose curves we find $f_{max} \simeq 7$ kHz at 40 °C. This corresponds to a dielectric relaxation time of about 20 μs. Since this should be about 2–3 times that for the magnetic relaxation, the agreement between the dielectric and NMR results is highly gratifying and attests to the usefulness of the Mashimo treatment.

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Calorimetric Titration of Poly(vinylamine) and Poly(iminoethylene)[1]

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ABSTRACT: The thermodynamic parameters ΔG, ΔH, and ΔS for proton ionization of the hydrochloride salts of poly(vinylamine) at 298 K and of poly(iminoethylene) at 298 and 323 K have been measured by calorimetric and potentiometric titrations. These data are reported for both polymeric amines as a function of charge state and for three ionic strengths. The dependence of the hydrodynamic volume of poly(vinylamine) on charge state was determined by analytical ultracentrifugation measurements and is also reported. The titration data appear anomalous in comparison to most polymeric acids and bases studied previously in that the changes in ΔG with charge state are not predictable on the basis of electrostatic arguments alone. Simple theory also fails to predict the changes in ΔH and ΔS, for which there is little basis for comparison. An explanation of these results based on nearest-neighbor effects and on structural features of the polymers at intermediate degrees of protonation is presented. The data obtained in calorimetric experiments, like those reported here, will be important in the development or refinement of polyelectrolyte theories.

The acid–base properties of polyelectrolytes have been studied extensively by potentiometric titration.[2] The general theory of polyelectrolyte behavior is based on this body of knowledge: i.e., K_a or ΔG as a function of charge state, counterions, and ionic strength. However, until very recently,[3] there have been few reports of calorimetric titration of synthetic polyelectrolytes. As part of a comprehensive thermodynamic study of proton ionization from polymeric amines and amino acids we report now the calorimetric and potentiometric titrations of the hydrochloride salts of poly(vinylamine) (PVA) and linear poly(iminoethylene) (PIE).[1] The ΔG, ΔH, and $T\Delta S$ values

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have been calculated for the acid dissociation of these polyelectrolytes as a function of charge state.

Experimental Section

Polymer Synthesis. PVA was synthesized by a procedure adapted from Hart.[4,5] By this procedure acrylic acid was converted to *tert*-butyl vinylcarbamate, which was then polymerized by using 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. Proton NMR (D_2O) shows two broad-peaks at δ 2.35 (2 H) and 3.90 (1 H). The specific viscosity (1 g/dL, 1 M KCl, 25 °C) is 0.33 dL/g. Anal. Calcd for $C_2H_5N\cdot HCl\cdot {}^1/_2H_2O$: C, 27.13; H, 7.97; N, 15.82; Cl, 40.04. Found: C, 27.04; H, 8.05; N, 14.79; Cl, 39.88.

PIE was synthesized by the general method of Saegusa.[6] Freshly distilled 2-ethyl-2-oxazoline (a sample from Dow Chemical Co.) was combined with methyl iodide in a mole ratio of 100:1 in a polymerization tube. The tube was purged with nitrogen, sealed, and immersed in a 100 °C oil bath for 24 h. The amber solid plug, poly(*N*-propionylethylenimine), was dissolved in ten times its weight of water. To that solution an equal amount by volume of concentrated HCl was added. The final solution, 5% polymer in 6 N HCl, was refluxed for 24 h under a continuous stream of nitrogen. PIE·HCl, which precipitated during hydrolysis, was isolated in 98% yield after decanting the 6 N HCl, dissolving the precipitate in water, reprecipitating in acetone, and filtering under vacuum. The ^1H NMR spectra indicated less than 2% propionyl residues in the polymer. Proton NMR (D_2O) shows a single sharp peak, δ 3.6 (CH_2). The specific viscosity (1 g/dL, 1 M KCl, 30 °C) is 0.20 dL/g. Anal. Calcd for $C_2H_5N\cdot HCl\cdot {}^1/_2H_2O$: C, 27.13; H, 7.97; N, 15.82; Cl, 40.04. Found: C, 27.90; H, 8.02; N, 16.24; Cl, 40.60.[7]

Solutions. The polymeric amine solutions were prepared by dissolving weighed amounts of the hydrochloride salts in distilled/deionized, CO_2-free water. In some instances Baker reagent grade NaCl or KCl was added as a supporting electrolyte. The 0.1 or 0.01 monomolar poly(amine hydrochloride) solutions were titrated with 1.0 M solutions of NaOH or KOH. The base solutions were shown to be carbonate free by calorimetric titration with HCl and were standardized against dry Baker Analyzed potassium hydrogen phthalate.

Calorimetric Titrations. The calorimetric titrations were typically done with a Tronac 550 calorimeter operated in the isoperibol mode with a 3-mL Dewar reaction vessel. Some combined calorimetric–potentiometric titrations were done with a large Tronac insert incorporating miniature glass and Ag/AgCl reference electrodes and a 50-mL Dewar.

The small Dewar was charged with 2 mL of the poly(amine hydrochloride) solution and, after thermal equilibration, 0.2 mL of titrant was added at a rate of approximately 0.02 mL min^{-1}. All titrations were done at 298 or 323 ± 0.1 K. A typical experiment involved collecting 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. The sensitivity limit of our calorimeter is approximately 0.5 mcal (bridge output of 10 μV). A typical poly(amine hydrochloride) titration gave an energy change of 0.5 cal.

Potentiometric Titrations. The potentiometric titrations were done with a Beckman 4500 digital research pH meter and either a Fisher microcombination 13-639-92 glass electrode with Ag/AgCl reference or MI 405 glass and MI 402 Ag/AgCl microelectrodes in the 50-mL Dewar insert. All titrations were done at 298 or 323 ± 0.1 K. The pH meter and electrodes were calibrated by using pH 6.862 phosphate and pH 4.008 potassium acid phthalate buffers, both prepared with NBS materials according to NBS instructions. The titrant was delivered with a Tronac high-precision motorized buret. The pH was recorded throughout the titration. The titration was completed in 10 min for the combined calorimetric experiments; otherwise in 30 min.

Polymer Fractionation and Sedimentation Measurements. A sample of PVA·HCl was fractionated by gel permeation chromatography, using a 2 × 30 cm column packed with Bio-Gel P-60 (100–200 mesh). The column was loaded with 1.02 g of PVA·HCl as an 8% solution in 0.01 M HCl. The fractions eluting near the void volume and with concentrations greater than 10 mg/mL, as determined by refractive index, were pooled to have an adequate homogeneous sample for measuring the sedimentation coefficient at several pH values. The pH of small aliquots, transferred from the pooled material to 12 × 75 mm test tubes, was adjusted with 1 M NaOH and measured with miniature glass and reference electrodes.

The sedimentation velocity determinations were carried out at 20 °C with a Beckman Model E analytical centrifuge using an AnD rotor operating at 60000 rpm. A charcoal-filled Epon double-sector centerpiece, sandwiched between quartz windows, was loaded on one side with polymer solution and on the other with 0.01 M HCl. A schlieren optical system was used and the boundary position was determined by measurement on the projected (10×) plate image.

Calculations. The method used to calculate the heat change values, *Q*, from the temperature–time data in the reaction region has been previously described.[8] The heat change to each point was calculated by the CALTOC program (available from Dr. L. D. Hansen, Thermochemical Institute, B.Y.U., Provo, Utah). These *Q* values were corrected for the heat of formation of water and the heat of dilution of the strong base titrant. The ΔH values were calculated from the slope of a tangent to the enthalpogram at the various α values, where α is the mole fraction of protonated amine groups. These ΔH values are valid for the ionic strength at which they were measured and have not been corrected to infinite dilution. Calculations were done on a Univac 1110 computer.

The ΔG values were calculated from the potentiometric titration data according to eq 1. No attempt was made to correct the

$$\Delta G = 2.303RT(\mathrm{pH} + \log \{\alpha/(1 - \alpha)\}) \qquad (1)$$

reported ΔG values to zero ionic strength or to apply activity coefficient corrections, since under our solution conditions the ionic strengths were quite high. In order to make these corrections, data must be presented at a variety of low concentrations of both polyelectrolyte and supporting electrolyte.

The sedimentation coefficients were calculated from the least-squares slopes of the logarithm of the boundary midpoint position plotted against sedimentation time.

Results and Discussion

The thermodynamic parameters for acid dissociation of PVA·HCl and PIE·HCl are reported in Tables I–III and a comparison of the two polymers is given in Figure 1. In each case the thermodynamic parameters are reported for several values of α (fraction of charged amines) and at three ionic strengths for one polymer concentration. The ionic strength effects observed in this work are typical for polyelectrolytes. Increasing ionic strength diminishes, if only slightly, the dependence of ΔG and ΔH on α.

Poly(vinylamine hydrochloride). The potentiometric titration of PVA·HCl was first reported by Katachalsky et al.[9] and more recently by Bloys van Treslong.[10] Our $\Delta G(\mathrm{p}K_a)$ results are consistent with these earlier studies. There has been some speculation that PVA (and poly(ethylenimine)) occupies a special place among polyelectrolytes in that it shows a stronger than usual dependence of $\mathrm{p}K_a$ on α. To account for this, Katchalsky proposed two types of dissociating units, a hydrogen-bonded ammonium unit and an ammonium unit not involved in hydrogen bonding. Compared to poly(acrylic acid), PVA does show a much stronger dependence of $\mathrm{p}K_a$ on α. This is not unreasonable since the intercharge distance is shorter for the amino polymer. The same general effect is seen in the comparison of *cis*-1,2-cyclohexanedicarboxylic acid and *cis*-1,2-diaminocyclohexane.[11] The difference in the two $\mathrm{p}K_a$'s of the former is 2.4 compared to 3.7 for the latter. This suggests that PVA should be more susceptible to nearest-neighbor charge effects than most polyelectrolytes.

The results in Table I show that while ΔG changes continuously with α, ΔH does not. Starting with the fully charged polymer, α = 1.0, ΔH increases sharply with decreasing α but levels off near α = 0.5 and remains constant

Table I
Thermodynamic Parameters for Dissociation of Poly(vinylamine hydrochloride) at 298 K[a]

	C_s = 0.1 M			C_s = 0.5 M			C_s = 1.0 M		
α[b]	ΔG[c]	ΔH[d]	$T\Delta S$	ΔG[c]	ΔH[d]	$T\Delta S$	ΔG[c]	ΔH[d]	$T\Delta S$
0.9	3.06	9.10	6.04	4.06	9.43	5.37	4.47	9.60	5.13
0.8	4.19	9.97	5.78	5.23	10.09	4.86	5.53	10.00	4.47
0.7	5.57	11.02	5.45	6.60	10.43	3.38	6.84	10.53	3.69
0.6	6.86	11.33	4.47	7.99	11.08	3.09	8.15	10.96	2.81
0.5	8.17	11.72	3.55	9.10	11.58	2.48	9.34	11.37	2.03
0.4	9.47	11.89	2.42	10.47	11.75	1.28	10.67	11.74	1.07
0.3	10.74	11.89	1.15	11.76	11.75	−0.01	12.00	11.74	−0.26
0.2	12.12	11.89	−0.23	13.02	11.75	−1.27	13.20	11.74	−1.46
0.1	13.39	11.89	−1.50	14.27	11.75	−2.52	14.45	11.74	−2.71

[a] Reaction: $PVA{\cdot}H^+ \rightarrow PVA + H^+$. [PVA·HCl] = 0.1 M; supporting electrolyte, KCl; titrant, 1.0 M KOH. All thermodynamic parameters are given in kcal/mol. Analytical concentrations reported on the basis of $^1/_2$ mol of H_2O per repeat unit. In all cases the standard deviation from the mean is less than 0.3 kcal/mol for three determinations. [b] α is the fraction of amine groups in the protonated form. [c] $\Delta G = 2.30RT(\mathrm{pH} + \log\{\alpha/(1-\alpha)\})$. [d] $\Delta H = \Delta H_{\mathrm{measd}} - \Delta H_{H_2O} - \Delta H_{\mathrm{dil}}$.

Table II
Thermodynamic Parameters for Dissociation of Poly(iminoethylene hydrochloride) at 298 K[a]

	C_s = 0.1 M			C_s = 0.5 M			C_s = 0.9 M		
α[b]	ΔG[c]	ΔH[d]	$T\Delta S$	ΔG[c]	ΔH[d]	$T\Delta S$	ΔG[c]	ΔH[d]	$T\Delta S$
0.9	5.64	2.97	−2.67	5.72	2.59	−3.12	5.78	3.05	−2.73
0.8	5.62	3.74	−1.88	5.89	4.37	−1.52	6.04	4.17	−1.87
0.7	6.12	5.42	−0.70	6.67	6.04	−0.63	6.87	5.27	−1.60
0.6	7.16	6.62	−0.54	8.13	7.90	−0.23	8.61	7.32	−1.28
0.5	9.50	8.24	−1.26	10.54	9.46	−1.09	10.91	9.43	−1.47
0.4	10.79	9.60	−1.19	11.58	9.23	−2.35	11.72	9.39	−2.32
0.3	11.42	9.58	−1.85	12.00	9.23	−2.77			

[a] Reaction: $PIE{\cdot}H^+ \rightarrow PIE + H^+$. [PIE] = 0.01 M; supporting electrolyte, NaCl; titrant, 0.10 M NaOH. All thermodynamic parameters are given in kcal/mol. Analytical concentrations reported on the basis of $^1/_2$ mol of H_2O per repeat unit. [b-d] See Table I.

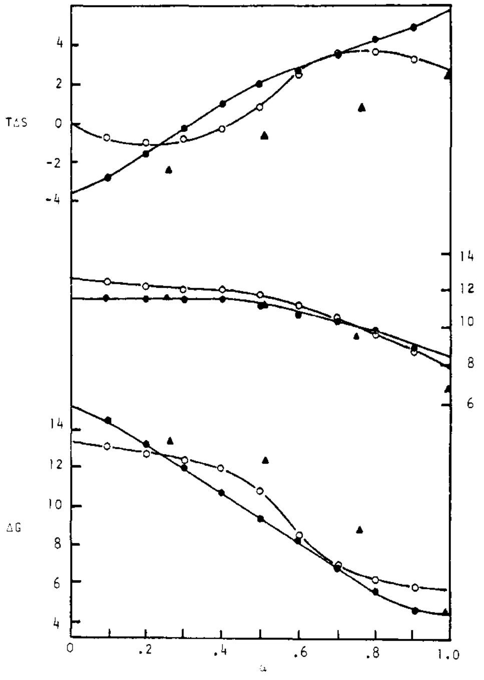

Figure 1. Thermodynamic parameters (kcal/mol) for dissociation of PVA·HCl (●) and PIE·HCl (○) at 298 and 323 K, respectively. PVA·HCl at 0.1 M in 1.0 M KCl was titrated with 1.0 M KOH and PIE·HCl at 0.01 M in 0.9 M NaCl was titrated with 0.10 M NaOH. For purposes of comparison, the titration of triethylenetetramine tetrahydrochloride[11] (▲) is included.

in the region α = 0.5–0. The change in $T\Delta S$ with α makes a significant contribution to the change in ΔG for all stages of dissociation and is solely responsible for changes in ΔG in the range α = 0.5–0. All the thermodynamic parameters for the uncharged polymer are rather typical for the dissociation of simple primary amines.[11] The depressed values for the charged polymer merely reflect the strongly enhanced acidity of the ammonium ion closely flanked by positively charged groups.

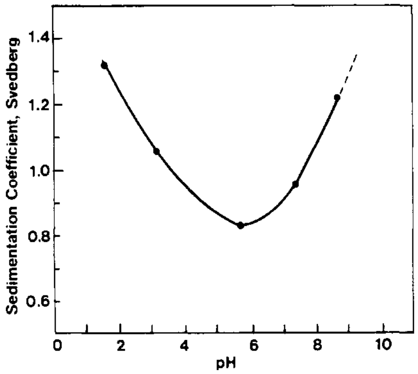

Figure 2. Sedimentation coefficient (S) for PVA·HCl fractionated by gel permeation chromatography, using Bio-Gel P-60 and 0.01 M HCl as the eluent. The PVA·HCl concentration for the sedimentation experiment was 0.01 g/mL and the temperature was 273 K.

The dissociation data for model amines such as 2,4-diaminopentane dihydrochloride or 2,4,6-triaminoheptane trihydrochloride, where similar charge effects might be observed, are not available. However, the dissociation of *cis,cis*-1,3,5-triaminocyclohexane trihydrochloride has been reported.[12] The thermodynamic parameters ΔG, ΔH, and $T\Delta S$ at 298 K in kcal/mol are 9.78, 11.02, and 1.25 for the +3 state, 11.80, 11.69, and −0.12 for the +2 state, and 13.86, 12.44, and −1.40 for the +1 state. Both polymer and model compounds show the same trends in ΔG, ΔH, and $T\Delta S$ with charge state. Only at the low charge state do the thermodynamic parameter values converge.

The influence of pH (charge state) over the solution conformation of PVA is illustrated in Figure 2. The sedimentation data show the PVA molecule to be most

Table III
Thermodynamic Parameters for Dissociation of Poly(iminoethylene hydrochloride) at 323 K[a]

	C_s = 0.1 M			C_s = 0.5 M			C_s = 0.9 M		
α[b]	ΔG[c]	ΔH[d]	$T\Delta S$	ΔG[c]	ΔH[d]	$T\Delta S$	ΔG[c]	ΔH[d]	$T\Delta S$
0.9	5.80	8.95	3.15	5.84	9.31	3.47	5.98	9.34	3.36
0.8	5.74	9.27	3.53	5.96	10.11	4.16	6.21	9.85	3.64
0.7	6.21	10.51	4.30	6.63	10.98	4.36	7.00	10.75	3.75
0.6	7.59	11.24	3.66	8.20	11.70	3.51	8.74	11.15	2.91
0.5	10.13	12.08	1.94	10.73	12.27	1.54	11.22	12.08	0.87
0.4	11.49	12.30	0.80	11.88	12.18	0.30	12.29	12.15	−0.14
0.3	12.21	12.18	−0.03	12.48	12.24	−0.25	12.78	12.17	−0.61
0.2	12.73	12.21	−0.52	12.88	12.36	−0.52	13.07	12.33	−0.74
0.1	13.19	12.41	−0.78	13.05	12.91	−0.14	13.20	12.73	−0.48

[a] Reaction: $\text{PIE}\cdot\text{H}^+ \rightarrow \text{PIE} + \text{H}^+$. [PIE] = 0.01 M; supporting electrolyte, NaCl; titrant, 0.10 M NaOH. All thermodynamic parameters are given in kcal/mol. Analytical concentrations reported on the basis of $^1/_2$ mol of H_2O per repeat unit. [b-d] See Table I.

extended at neutral pH and partially collapsed in either acid or base. These results agree with the trends in viscosity as a function of charge reported by Bloys van Treslong.[13] This seemingly anomalous behavior is explainable if we assume a very stiff structure at the intermediate pH being stabilized by H bonding between neighbor ammonium and amine groups. This extended conformation may be visualized as a series of six-membered rings along the polymer backbone. We believe this model should exhibit a high proton mobility, which on a time-averaged scale accounts for the observed data. Hydrogen bonding between these groups is also indicated by the ^{15}N NMR study reported by Rinaldi, Yu, and Levy in the following paper.[14]

Poly(iminoethylene hydrochloride). There are several reports in the literature on the potentiometric titration of poly(ethylenimine) (PEI). The latest of these is the study of Bloys van Treslong.[10] In every case the polymer investigated was the branched polymer prepared from the ring-opening polymerization of aziridine. The branched polymer contains three types of amine functions, primary, secondary, and tertiary in the approximate ratio 1:2:1. This feature complicates the interpretation of the titration results, especially since the titration of this polymer is restricted to α = 0–0.75. A study of PIE, the linear analogue of PEI, offers some distinct advantages since it contains only one amine function and may be titrated to α = 1.0.

The titration data for PIE·HCl are reported in Tables II and III. The polymer in the basic form is not soluble in water at 298 K and precipitates at $\alpha < 0.3$. At 323 K the polymer is soluble for all charge states. The unusual solubility behavior of this polymer, i.e., strong dependence of solubility on temperature and tendency to crystallize, has previously been reported by Saegusa.[6]

The trends in ΔG, ΔH, and $T\Delta S$ for the dissociation of PIE·HCl as a function of α are similar to the trends observed for PVA·HCl. This comparison is given in Figure 1. The similarity is most striking in ΔH. Enthalpy favors dissociation of the fully charged polymer, drops off with α up to half-neutralization, and thereafter shows little dependence on charge state. This behavior is reflected in ΔG. The acidity of PIE·HCl decreases with decreasing α, but unlike PVA·HCl, ΔG vs. α for PIE·HCl is distinctly sigmoidal. The inflection in this curve, where ΔG is most sensitive to α, comes near $\alpha \simeq 0.5$. This is usually taken as evidence for a change in polymer conformation. The plot of $T\Delta S$ vs. α suggests that this is the case for PIE·HCl. Possibly at temperatures higher than 323 K polymer–polymer interactions, which produce precipitation at 298 K, might disappear and the changes in ΔG, ΔH, and $T\Delta S$ with α might more closely resemble the trends observed in the PVA·HCl titration curves.

For purposes of comparison, ΔG, ΔH, and $T\Delta S$ in kcal/mol for the acid dissociation of triethylenetetramine[11] at 298 K are 4.42, 6.83, and 2.41 for the +4 state, 8.92, 9.53, and 0.60 for the +3 state, 12.35, 11.27, and −1.20 for the +2 state, and 13.30, 11.01, and −2.32 for the +1 state. There is a similarity between the tetramine and PIE·HCl with respect to ΔH, but not for ΔG and $T\Delta S$. This compound should exhibit the same short-range effects but not the long-range effects of the polymer. The model data are incorporated in Figure 1 for purposes of comparison.

Titration Curve Analysis. The dependence of the changes in ΔG, ΔH, and $T\Delta S$ on α seen here for both PVA and PIE will be analyzed in terms of the simple Kirkwood–Westheimer[15] treatment and the more sophisticated Manning[16] treatment. Other theoretical approaches have recently been reviewed by Fenyo et al.[17] They have applied a Lifson–Katchalsky and an extended Mandel treatment to the analysis of the titration of poly(carboxylic acids). The charge–charge interactions of neighboring groups for the polymeric ammonium salts presented in this study are stronger than those found in the poly(carboxylic acid) salts. The Kirkwood–Westheimer analysis best describes the former polyelectrolytes.

We will first discuss the Manning equations, which are based on the polyion being described as a linear lattice of univalent point charges with site spacing b. The charge density parameter, ξ, is given by

$$\xi = e^2/DkTb \tag{2}$$

where e is the charge on the proton, D is the bulk dielectric constant of the solvent, k is Boltzmann's constant, T is the absolute temperature, and b is the average distance between charged sites for the maximally extended polyelectrolyte chain and therefore a function of α. In the Manning theory the polyion is charged to a critical charge density, at which point counterion condensation minimizes further increases in ξ. The critical value of α for any polyelectrolyte (where $\xi = 1$) may be calculated from the chemical structural dimensions and eq 2. The critical α values for PVA and PIE are 0.35 and 0.52, respectively. According to the most recent work of Manning[16b] the apparent pK as a function of α is given by eq 3 for α values above the critical value and by eq 4 for α values below the critical value, where pK_0 is the intrinsic pK of the ionizing

$$\mathrm{p}K = \mathrm{p}K_0 + 0.434 - \log A^2 + 2 \log (\alpha\bar{\xi}) - 0.434(\alpha\bar{\xi})^{-1} - \log C_s \tag{3}$$

$$\mathrm{p}K = \mathrm{p}K_0 - 0.434\{2\alpha\bar{\xi} \ln [1 - \exp(-A\alpha^{-1}\bar{\xi}^{-1}C_s^{1/2})] - AC_s^{1/2}[\exp(A\alpha^{-1}\bar{\xi}^{-1}C_s^{1/2}) - 1]^{-1}\} \tag{4}$$

group (independent of α), A^2 is a constant defined by eq 5, ξ is the charge density of the fully charged polyion, α

$$A^2 = (8\pi) \times 10^{-3} N(e^2/DkT)^3 \tag{5}$$

is the charge fraction, and C_s is the supporting electrolyte concentration. These equations are free of adjustable parameters and appear reasonable for polyelectrolytes, where protons may be described as site bound but where the counterions are territorially bound. Equations 3 and 4 have been quite successful in predicting pK as a function of α for poly(DL-glutamic acid), with the difference in predicted and measured pK values being less than 0.5 at all α values. At the polyelectrolyte and salt concentrations reported here, a limiting law is not strictly applicable; however, the general character of the dependence of the thermodynamic parameters on α should still apply. According to counterion condensation theory, the greatest changes in ΔG (and/or ΔH and ΔS) ought to occur in the region between $\alpha = 0$ and $\alpha = 0.35$ for PVA and between $\alpha = 0$ and $\alpha = 0.52$ for PIE. The data presented earlier in Tables I and III and summarized in Figure 1 show this prediction to be in rather poor agreement with the experimental facts. The change in ΔG (or pK) with α for PVA is continuously linear without the predicted break in slope at $\alpha = 0.35$. The change in ΔG with α for PIE is even more contradictory, no change from $\alpha = 0$ to $\alpha = 0.3$ and then a continuous change to $\alpha = 1.0$. Schultz and Strauss[18] published titration curves for two maleic acid copolymers which deviated strikingly from the predictions of the Manning counterion condensation theory or the earlier Poisson–Boltzmann treatments.[9] They suggest that the assumption of independent proton binding, i.e., a random distribution of protons on ionizing groups, inherent in the development of the theories was invalid for their polymers. The calorimetric data, sedimentation coefficient results, and NMR data in the following paper[14] strongly suggest a nonstatistical arrangement of protons for PVA at intermediate values of α. The calorimetric data also indicate a nonstatistical proton distribution for PIE.

An alternative approach to polymers where the charged group interactions are significant is the Kirkwood–Westheimer[15] treatment. This model applies to polyions where the electrostatic influence extends over some limited distance, perhaps only as far as nearest neighbors. According to the Kirkwood–Westheimer theory, the change in pK with α can be calculated by eq 6, where r is the

$$\mathrm{p}K = \mathrm{p}K_0 - e^2/2.303kTrD \tag{6}$$

distance between charges and D is the "effective" rather than the bulk solvent dielectric constant. The differences between this simplisitic approach and the counterion condensation model are as follows: (1) the effective charge density on the polymer is not limited to some critical value, (2) no statistical term for proton distribution is used, and (3) the electrical work term is calculated for the transfer of a proton from a charged microscopic environment to a noninteracting distance, with the intervening dielectric being some weighted average between the dielectric constant of the polymer and the surrounding solvent. If no limits are placed on the interacting distances, then pK should change continuously with α, but if only nearest neighbors can influence the energetics then the pK (or other thermodynamic parameter) would change only from $\alpha = 0.5$ to $\alpha = 1.0$. This discontinuous trend in ΔpK is not really seen for either polymer but is somewhat in agreement with the ΔG vs. α data for PIE (see Figure 1). Both PVA and PIE show large changes in pK with α. This is indicative of a low effective dielectric constant. The results suggest that the more significant terms in the prediction of the changes in the various thermodynamic parameters for these polymers must arise from the interaction of nearest neighbors through low dielectric media.

According to the Kirkwood–Westheimer theory, the electrostatic contribution to ΔH may be calculated from molecular parameters and physical constants by eq 7.[15]

$$\Delta H_{\mathrm{elec}} = \frac{-Ne^2}{rD}\left(1 + T\left(\frac{\partial \ln D}{\partial T}\right)_p\right) \tag{7}$$

The term $1 + T(\partial \ln D/\partial T)_p$ normally takes on small positive values (0.4–0.7) and e^2/r decreases with decreasing α. Substitution of any reasonable values for r and D into eq 7 shows that typically ΔH_{elec} must be small for all values of α. This theory predicts a small electrostatic contribution to ΔH. This contribution is continuous and becomes more negative as the charge density of the polymer increases. It is discontinuous at $\alpha = 0.5$ for molecules showing only nearest-neighbor interactions. For PVA·HCl and PIE·HCl the data show the largest change in ΔH for $\alpha = 1.0$–0.5.

This behavior can be rationalized on the basis of nearest-neighbor effects.[19] The simplest model would require three dissociating species, symbolized by +++ (K_a^2), ++0 or 0++ (K_a^1), and 0+0 (K_a^0), where + respresents an ammonium group and 0 represents an amine group. For each of these triads the dissociating species is the central ammonium group. At the beginning of the titration ($\alpha = 1$) there is but one unit, +++. The fraction of this unit decreases rapidly with decreasing α, The next unit, ++0, increases through a maximum and then decreases with decreasing α. The enthalpy data strongly suggest that there is but one dissociating species from $\alpha = 0.5$ to $\alpha = 0$. This 0+0 triad would account for the constant ΔH in this region of the titration curve.

The change in $T\Delta S$ with α makes a significant contribution to the change in ΔG for all stages of dissociation for both polymers. It is mainly responsible for the changes in ΔG in the region $\alpha = 0.5$–0. The electrostatic contribution to the entropy change can be calculated from molecular parameters and physical constants by eq 8.[15] Since

$$\Delta S_{\mathrm{elec}} = \frac{-Ne^2}{rD}\left(\frac{\partial \ln D}{\partial T}\right)_p \tag{8}$$

the $(\partial \ln D/\partial T)_p$ term is always negative, the electrostatic contribution to the entropy change will be large and positive for the highly charged polymer and will be reduced to zero as α approaches zero. Of course, the same discontinuity at $\alpha = 0.5$ would be observed for the nearest-neighbor case. This predicted trend is qualitatively consistent with our data. A more detailed or quantitative analysis is difficult since there are at least three other factors that must be considered in the entropy of dissociation of the poly(amine hydrochlorides): (1) proton distribution along the polymer chain, (2) polymer conformation and the implicit effects of hydrogen bonding, and (3) solvation, including counterion effects. At this point we are not prepared to speculate on the direction or relative contribution that each of these will make on the net ΔS and the change in ΔS with α.

The Kirkwood–Westheimer treatment, developed for small charged acids and bases, makes no allowances for changes in dielectric constant during the course of titration. If D is not constant and is instead a function of polymer conformation, i.e., α, this would allow for ΔH_{elec} and ΔS_{elec} to change more drastically than predicted by eq 7 and 8. This is more consistent with the changes observed in this study, and the findings of Strauss.[3d]

The contribution of polymer conformation to the acid dissociation of PIE·HCl is best illustrated in the comparison of Tables II and III. The titration behavior of this polymer in terms of ΔH and $T\Delta S$ is very sensitive to temperature, much more sensitive than would be indicated by potentiometric titration alone. For a given ionic strength and charge state, ΔG is not very different for the two temperatures. The differences in ΔH and $T\Delta S$, however, are quite dramatic. The available polyelectrolyte theories cannot quantitatively explain this effect. Qualitatively, the origin of the temperature effect must come from changes in polymer conformation that are dependent on charge state and temperature. Conformational changes directly influence ΔS and indirectly effect ΔH through a change in heat capacity. The latter is a reasonable explanation for the change in ΔH with temperature at constant α.

In summary, the various thermodynamic parameters as a function of α for both polymers are shown in Figure 1. The electrostatic and counterion condensation models failed to accurately predict the changes in ΔH and $T\Delta S$ for both PVA and PIE, especially in the region $\alpha = 0$–0.5. The nearest-neighbor model mentioned above, which allows for the assignment of a separate ΔH for each triad and a change in triad distribution with α, is being explored. However, a complete description must take into consideration the changes in polymer conformation and all of their ramifications. The $T\Delta S$ term is apparently most sensitive to these effects. Calorimetric and NMR data should make an important contribution to our understanding of polyelectrolyte behavior.

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References and Notes

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Carbon-13 and Nitrogen-15 Spin–Lattice Relaxation Studies of Poly(vinylamine) and Poly(iminoethylene)

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ABSTRACT: ^{13}C and ^{15}N dipolar relaxation rates of poly(vinylamine) and poly(iminoethylene) were measured. Relaxation in poly(vinylamine) is consistent with relatively unhindered rotation of the NH_3^+ group. At neutral pH, the rotation rate is slowed, consistent with hydrogen bonding between alternate NH_3^+ and NH_2 groups. Rotational jump rates and barriers are reported. The motion of the NH groups of poly(iminoethylene) is more restricted relative to the polymer backbone CH_2 groups. This is reflected by the $^{15}N/^{13}C$ NT_1 ratios.

Introduction

In order to identify the segmental and group internal motions of poly(vinylamine) and, in particular, to determine whether ^{13}C and ^{15}N relaxation data were consistent with a proposed model where rapid NH_3^+ group rotation occurs up to a pH where alternate NH_2 and NH_3^+ groups interact to quench this motion, we studied the ^{13}C and ^{15}N relaxation properties of this polymer.

In general, relaxation of a given nucleus has a variety of mechanisms which all contribute to its total relaxation time, T_1^{total} (eq 1). These include, in the order shown in

$$\frac{1}{T_1^{\text{total}}} = \frac{1}{T_1^{\text{DD}}} + \frac{1}{T_1^{\text{CSA}}} + \frac{1}{T_1^{\text{SR}}} + \frac{1}{T_1^{\text{Q}}} + \frac{1}{T_1^{\text{SC}}} \quad (1)$$

eq 1, dipolar, chemical shift anisotropy, spin rotation, quadrupolar, and scalar mechanisms for relaxation.

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