658 *J. Chem. Eng. Data* **2004,** *49,* 658−663

Thermodynamic Parameters for the Protonation of Poly(allylamine) in Concentrated LiCl(aq) and NaCl(aq)

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The acid−base properties of poly(allylamine) (MW = 15 kDa) were determined by potentiometry and calorimetry in aqueous solutions at $t = 25$ °C. Potentiometric measurements were carried out in a wide range of ionic strengths ($0.1 \leq I/\text{mol}\cdot\text{L}^{-1} \leq 5.0$) in NaCl(aq) and LiCl(aq), while enthalpy changes for the protonation of poly(allylamine) were determined by calorimetry in the same ionic strength range but only in NaCl(aq). Analysis of the experimental data was carried out using two different models: the first based on a modified Henderson−Hasselbalch two parameter equation and the second on the three parameter equation proposed by Högfeldt. Protonation constants are given for both models and ionic media at $t = 25$ °C, while ΔG, ΔH, and $T\Delta S$ values were determined using the three parameter model alone. The dependence on ionic strength of protonation constants was determined by the SIT model (Specific ion Interaction Theory), while the parameters for the dependence on ionic strength of ΔH and $T\Delta S$ were determined by a simple empirical equation. Comparison is also made of the protonation constants of poly(allylamine) and some low molecular weight polyamines. Thermodynamic parameters for the protonation of poly(allylamine) are very close to those of low molecular weight polyamines, which are included for purposes of comparison.

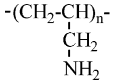
Introduction

Polyelectrolytes play an important role in industry and in natural fluids due to their many important properties, not the least of which is their sequestering ability toward cationic and anionic organic and inorganic species in different pH ranges. Like many other polyelectrolyte gels, poly(allylamine) (PAAm) gels obtained by several cross-linking agents are used as superabsorbent materials in separation processes and in controlling drug delivery. An important characteristic of these gels is discrete volume transition with small variations in pH, temperature, and solvent compositions.[1] Moreover, one of the most widely studied polyelectrolyte combinations for multilayer thin films is poly(allylamine hydrochloride) (PAAm−HCl) and poly(acrylic acid). Recently, multilayer thin films of weak polyacrylates have become increasingly important because their physical properties are strongly dependent on pH and on the ionic strength of the solution and these characteristics make them useful for many potential applications, such as drug capsules and templates for nanoparticle growth.[2]

Our research group has long been involved in the study of the acid−base behavior of polyacrylate and polymethacrylate (with different molecular weights) and of the dependence of their thermodynamic protonation parameters (ΔG, ΔH, and $T\Delta S$) on ionic media and ionic strengths.[3−7] We used two models to interpret experimental data: a modified Henderson−Hasselbalch two parameter equation[8] and the three parameter equation proposed by Högfeldt.[9] Useful relationships between protonation parameters and ionic strength or log N (N = number of functional groups in the polymers) were found.[3−7] The choice of these models is dictated by the high charge of the polyions and, therefore, the high values assumed by the electrostatic potential of the whole molecule, which makes the study of ion charge interaction more complicated. A high charge weighs on the conformation of polyelectrolytes, as is demonstrated by variations in the specific viscosity of PAAm depending on the pH in the solution; specific viscosity does not change at pH ≤ 7 and decreases with increasing pH (pH ≥ 7). In fact, at pH < 7 polymer chains are stretched due to the repulsion charge of ammonium groups, while, when pH is increased, this kind of repulsion is reduced.[10] This charge variation becomes less relevant when the polyelectrolyte solution is diluted, in particular for polymers with low molecular weights. The decrease of the charge density of the polyanion when the solution is diluted causes an increase of the activity coefficient of the counterion with dilution, as reported in a study on the counterion binding to poly(allylamonium) cation.[11]

Very few papers exist in the literature that investigate the protonation constants of PAAm in aqueous solution,[2,10] and none of these deal with the dependence of this parameter on ionic strength. Moreover, there are no reports of calorimetric investigations on the contribution of ΔH and ΔS to protonation ΔG.

This paper describes a potentiometric (ISE-H$^+$, glass electrode) and calorimetric study of the protonation of PAAm−HCl with an average molecular weight of 15 kDa (corresponding to about 162 monomers) and a monomer structure:



$$-(\mathrm{CH_2}\text{-}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{NH_2}}}{\mathrm{CH}})_n-$$

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10.1021/je0342264 CCC: \$27.50

We used the above cited models to assess the effects of electrostatic interactions on protonation parameters. Investigations were carried out in NaCl and LiCl aqueous ionic media in a wide range of ionic strengths ($0.1 \leq I/\mathrm{mol \cdot L^{-1}} \leq 5$). The aims of this paper are to test the applicability of the two models to weak polyelectrolytes and to contribute to the understanding of the acid–base properties of the more complicated macromolecules, such as humic acids, present in aquatic environments.

Experimental Section

Materials. All reagents were of analytical grade. A solution of PAAm–HCl (MW = 15 kDa) was prepared from a commercial product by Aldrich. Its purity was checked by potentiometric titration. Sodium and lithium chloride (Fluka, purissimum) were used without further purification. Sodium chloride was used after drying in a stove at 140 °C, while lithium chloride was vacuum-dried before use. Hydrochloric acid and sodium or lithium hydroxide solutions were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All the solutions were prepared using freshly prepared, twice distilled CO_2 free water ($R = 18\ \mathrm{M\Omega\ cm^{-1}}$), and grade A glassware was employed.

Apparatus. Potentiometric measurements were carried out using a potentiometric apparatus consisting of an automatic titrant dispenser (Methrom Dosimat model 665) coupled with a potentiometer (Methrom model E605) and a combination Orion-Ross 8172 glass electrode. The buret and potentiometer were connected through a personal computer, and suitable software was employed to control titrations. Measurement cells were thermostated at $t = (25 \pm 0.2)$ °C. The estimated accuracy of these systems was ±0.15 mV and ±0.003 $\mathrm{cm^3}$ for emf and titrant volume readings, respectively. In titration cells pure nitrogen was bubbled through the solutions in order to avoid O_2 and CO_2 inside, and the solutions were magnetically stirred.

Calorimetric measurements were carried out using a model 450 Tronac isoperibolic titration calorimeter, coupled with a Keithley 196 system Dmm digital multimeter. The titrant was delivered with a 2.5 mL capacity Hamilton syringe, model 1002TLL. A computer program was used for the acquisition of calorimetric data. Accuracy was checked by titrating a THAM (tris(hydroxymethyl)aminomethane) buffer with HCl. The accuracy of the calorimetric apparatus was ($Q \pm 0.008$) J and ($v \pm 0.001$) $\mathrm{cm^3}$.

Procedure. For the potentiometric measurements, a volume of 25 mL of solution containing the PAAm–HCl (MW = 15 kDa) ligand and the background salt (NaCl or LiCl) used to adjust the ionic strength to different values ($0.1 \leq I/\mathrm{mol \cdot L^{-1}} \leq 5$) was titrated with hydroxide solutions (NaOH or LiOH). For each experiment, independent titrations of HCl with NaOH or LiOH solutions were performed, under the same experimental conditions of ionic strength and temperature as those for the systems under study, to determine the formal electrode potential. Proton concentrations were given as $\mathrm{pH} = -\log [\mathrm{H^+}]$; that is, the free hydrogen ion concentration scale was used. The reliability of the calibration in the alkaline range was checked by calculating $\mathrm{p}K_{\mathrm{w}}$ values.

For the calorimetric measurements, a volume of 50 mL of solution containing PAAm–HCl (MW = 15 kDa) and the background salt (NaCl) used to adjust the ionic strength to different values ($0.1 \leq I/\mathrm{mol \cdot L^{-1}} \leq 5$) was titrated with a NaOH solution at (25.000 ± 0.001) °C. The heat of dilution was measured before each experiment.

Calculation. The nonlinear least squares computer program ESAB2M[12] was used to determine all the parameters of an acid–base potentiometric titration (acid–base concentrations, formal potential of electrode couple, and coefficient j_{a} for junction potential $E_j = j_{\mathrm{a}}[\mathrm{H^+}]$). Calorimetric titration data were analyzed by the computer program ES5CM,[13] which was modified to analyze protonation data for polyelectrolytes. The general computer program LIANA[14] was used for the calculation of thermodynamic protonation parameters and parameters for dependence on ionic strength. Errors are given as standard deviations.

Models for the Dependence of Protonation Constants on α and *I*

Protonation constants, K^{H}, defined according to the equilibrium

$$\mathrm{H^+} + \mathrm{A^0} = \mathrm{HA^+}$$

($\mathrm{A^0}$ = monomer unit of poly(allylamine)) can be calculated for each α value (α = dissociation degree, $\alpha = [\mathrm{A^0}]/[\mathrm{A}]_{\mathrm{tot}}$). The dependence of $\log K^{\mathrm{H}}$ on α can be expressed using two different models. The first is represented by a two parameter Henderson–Hasselbalch type equation, as proposed by Katchalsky[8]

$$\mathrm{pH} = \log K_n^{\mathrm{H}} - n \log[(1 - \alpha)/\alpha] \tag{1}$$

$$\log K^{\mathrm{H}} = \log K_n^{\mathrm{H}} - (n - 1) \log[(1 - \alpha)/\alpha] \tag{2}$$

where n is an empirical parameter and K_n^{H} is the protonation constant at α = 0.5, which can be approximated as the intrinsic constant, $K_{\mathrm{int}}^{\mathrm{H}}$; that is, $K_n^{\mathrm{H}} = K_{\mathrm{int}}^{\mathrm{H}}$. In fact, considering that the protonation constants of polyelectrolytes are dependent on the effective charge of the polyanion, we have

$$\log K^{\mathrm{H}} = \log K_{\mathrm{int}}^{\mathrm{H}} + (-\Delta G_{\mathrm{e}})/(RT \ln 10)$$

where ΔG_{e} is the free energy change for removing the proton against the negative charges of the polyelectrolyte and $K_{\mathrm{int}}^{\mathrm{H}}$ is the intrinsic protonation constant. The term $(\Delta G_{\mathrm{e}})/(RT \ln 10)$ can be approximated as $\log(z)^{n-1}$ (z is the degree of charging of the polyelectrolyte), and in turn, we can write $z = (1 - \alpha)/\alpha$ and, therefore,

$$\log K^{\mathrm{H}} = \log K_{\mathrm{int}}^{\mathrm{H}} - (n - 1) \log[(1 - \alpha)/\alpha]$$

which is identical to eq 2, with $\log K_{\mathrm{int}}^{\mathrm{H}} = \log K_n^{\mathrm{H}}$.

The second model is represented by a three parameter equation, as proposed by Högfeldt[9] on the basis of the Guggenheim zeroth approximation

$$\log K^{\mathrm{H}} = \alpha^2 \log K_1^{\mathrm{H}} + (1 - \alpha)^2 \log K_0^{\mathrm{H}} + 2\alpha(1 - \alpha) \log K_m^{\mathrm{H}} \tag{3}$$

In eq 3 the parameters K_1^{H} and K_0^{H} represent the protonation constants at $\alpha \rightarrow 1$ and $\alpha \rightarrow 0$, respectively, and K_m^{H} is an intermediate value which accounts for the nonlinearity of the function $\log K^{\mathrm{H}}$ versus α. Another important parameter is the true protonation constant, $\log \bar{K}^{\mathrm{H}}$, defined as

$$\log \bar{K}^{\mathrm{H}} = \int_0^1 \log K^{\mathrm{H}}\, \mathrm{d}\alpha$$

and by integrating eq 3 we have

$$\log \bar{K}^{\mathrm{H}} = (\log K_1^{\mathrm{H}} + \log K_0^{\mathrm{H}} + \log K_m^{\mathrm{H}})/3 \tag{4}$$

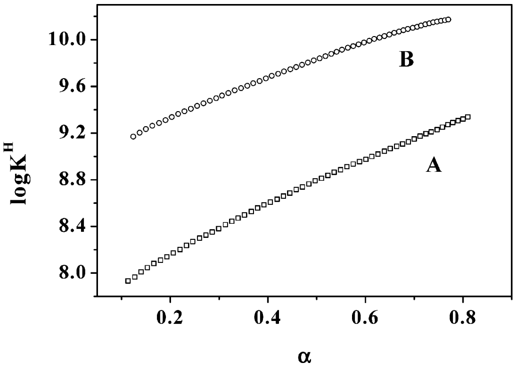

Figure 1. Protonation constants of PAAm vs α, at $t = 25$ °C: A, 0.1 mol·L^{-1} LiCl; B, 1 mol·L^{-1} NaCl.

We applied both eqs 2 and 3 to the protonation of some carboxylic polyelectrolytes studied in several ionic media.[4−7] As expected, the three parameter equation gave better results in terms of goodness of fit; moreover, this equation contains parameters with clear physical significance. In particular, log K_1^H and log K_0^H can be used for solutions in which the polyelectrolytes are almost completely dissociated or protonated. On the other hand, the two parameter model gives an important parameter, log K_{int}^H, which is indicative of the acid−base properties of polyelectrolytes. In our experience eq 3 is more appropriate for the protonation of polyelectrolytes, especially when apparent protonation constants are used to calculate the formation constants of weak or stable complexes. On the basis of residual plots, we showed, for polyacrylates and polymethacrylates,[6] that, at the extremes of the $0 \le \alpha \le 1$ interval, residuals for the two parameter model may be relevant, while, at $\alpha \approx 1/3$ and $\alpha \approx 2/3$, the two models can be considered equivalent. Moreover, eq 3 can be applied to the dependence of other parameters, such as ΔH and $T\Delta S$, on the degree of dissociation; that is

$$\Delta X = \alpha^2 \Delta X_1 + (1 - \alpha)^2 \Delta X_0 + 2\alpha(1 - \alpha)\Delta X_m \qquad (5)$$

where $\Delta X = \Delta H$ or $T\Delta S$.

All protonation parameters are also dependent on ionic strength according to the simple polynomial equation

$$P = P° + \sum_i a_i(\sqrt{I})^i \qquad (6)$$

In general, one or two a_i empirical parameters are sufficient and therefore eq 6 assumes the form

$$P = P° + a\sqrt{I} + bI \qquad (6a)$$

($P°$ is the thermodynamic value at infinite dilution).

Results and Discussion

Protonation Constants. Protonation constants in both LiCl and NaCl ionic media are a continuous increasing function of α, as shown in Figure 1, where log K^H versus α is plotted for two different experimental conditions (experimental protonation constants as a function of α, in LiCl and NaCl, are reported as Supporting Information in Tables S1 and S2). Using eqs 2 and 3, we calculated the protonation parameters relative to the two and three parameter models, and smoothed results are reported in Tables 1 and 2 (original values are reported as Supporting Information in Tables S3 and S4). These parameters are in good agreement with the values found in the literature, where, using the Henderson−Hasselbalch equation, the authors obtained log $K_{int}^H = 9.67$ and $n = 1.85$ for $0.1 \le \alpha \le 0.7$ at $I = 1$ mol·L^{-1} in KCl and at $t = 25$ °C for PAAm (MW = 10 kDa).[10] As expected for protonated cationic species, all the protonation parameters increase with increasing ionic strength due to the stabilization of the cation by the counterion. Small differences are observed between values in LiCl and NaCl (in particular for K_1^H) with LiCl > NaCl. The standard deviation on the fit, σ_{fit}, is fairly similar for both models for potentiometric data in both NaCl and LiCl, but the three parameter model was observed to be slightly more efficient. In fact, the mean values of the standard deviations on the fit are 0.022 and 0.039 (three parameter model) and 0.034 and 0.048 (two parameter model) for LiCl and NaCl, respectively. This indicates, once again (see also ref 6), that the Högfeldt model is slightly better at fitting log K^H versus α data, but the difference between this and the Henderson−Hasselbalch type model is quite low. Therefore, in some cases the latter model can be used without significantly sacrificing accuracy.

Table 1. Protonation Parameters of PAAm[a] According to Different Models, at $t = 25$ °C, in LiCl Aqueous Solutions, at Different Ionic Strengths

Three Parameter Model (Eq 3)

I/mol·L^{-1}	log K_1^H	log K_0^H	log K_m^H	log $\bar{K}^H$
0.1	9.70 ± 0.07[b]	7.776 ± 0.007[b]	9.06 ± 0.04[b]	8.84
0.5	10.10 ± 0.05	8.231 ± 0.006	9.30 ± 0.03	9.21
1	10.41 ± 0.05	8.571 ± 0.008	9.47 ± 0.02	9.48
3	11.20 ± 0.06	9.42 ± 0.02	9.91 ± 0.02	10.18
5	11.77 ± 0.08	10.01 ± 0.02	10.21 ± 0.03	10.66

Two Parameter Model (Eq 2)

I/mol·L^{-1}	log K_{int}^H	n
0.1	8.86 ± 0.02[b]	1.97 ± 0.03[b]
0.5	9.21 ± 0.02	1.92 ± 0.02
1	9.48 ± 0.02	1.87 ± 0.03
3	10.14 ± 0.03	1.76 ± 0.03
5	10.59 ± 0.04	1.70 ± 0.04

[a] Smoothed values. [b] ± standard deviation on the parameters.

Table 2. Protonation Parameters of PAAm[a] According to Different Models, at $t = 25$ °C, in NaCl Aqueous Solutions, at Different Ionic Strengths

Three Parameter Model (Eq 3)

I/mol·L^{-1}	log K_1^H	log K_0^H	log K_m^H	log $\bar{K}^H$
0.1	9.62 ± 0.08[b]	7.764 ± 0.009[b]	9.15 ± 0.03[b]	8.84
0.5	9.93 ± 0.04	8.20 ± 0.01	9.49 ± 0.03	9.21
1	10.17 ± 0.04	8.53 ± 0.01	9.74 ± 0.02	9.48
3	10.79 ± 0.03	9.36 ± 0.02	10.38 ± 0.03	10.18
5	11.24 ± 0.06	9.92 ± 0.03	10.81 ± 0.05	10.66

Two Parameter Model (Eq 2)

I/mol·L^{-1}	log K_{int}^H	n
0.1	8.88 ± 0.02[b]	1.99 ± 0.03[b]
0.5	9.25 ± 0.01	1.93 ± 0.02
1	9.52 ± 0.01	1.88 ± 0.02
3	10.22 ± 0.02	1.77 ± 0.02
5	10.70 ± 0.03	1.71 ± 0.03

[a] Smoothed values. [b] ± standard deviation on the parameters.

The parameter n (eq 2) decreases with increasing ionic strength due to the interaction of protonated amino groups with Cl$^-$: when this interaction is very strong, at very high ionic strength, the protonation of each amino group becomes independent of the protonation of the other amino groups, and then $n = 1$ and log K^H is independent of α. This trend is the same as that indicated by the protonation

Table 3. Δ*G*, Δ*H*, and *T*Δ*S* Values for the Protonation of PAAm at *t* = 25 °C, at Different Ionic Strengths in Aqueous NaCl Solutions, According to the Three Parameter Model (Eq 3)

I	$-\Delta G_1$	$-\Delta G_0$	$-\Delta G_m$	$-\overline{\Delta G}$
mol·L^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
0.1	54.9 ± 0.4[a]	44.3 ± 0.1[a]	52.2 ± 0.2[a]	50.5
0.5	56.7 ± 0.2	46.8 ± 0.1	54.2 ± 0.2	52.6
1	58.0 ± 0.2	48.7 ± 0.1	55.6 ± 0.1	54.1
3	61.6 ± 0.2	53.4 ± 0.1	59.2 ± 0.2	58.1
5	64.2 ± 0.3	56.6 ± 0.2	61.7 ± 0.3	61.0

I	ΔH_1	ΔH_0	ΔH_m	$\overline{\Delta H}$
mol|L^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
0.1	−57.9 ± 0.4[a]	−53.3 ± 0.3[a]	−55.3 ± 0.2[a]	−55.5
0.5	−58.1 ± 0.4	−53.3 ± 0.3	−55.4 ± 0.2	−55.6
1	−58.4 ± 0.3	−53.3 ± 0.3	−55.6 ± 0.2	−55.8
3	−59.6 ± 0.4	−53.4 ± 0.3	−56.2 ± 0.3	−56.4
5	−60.9 ± 0.5	−53.6 ± 0.3	−56.8 ± 0.4	−57.1

I	$T\Delta S_1$	$T\Delta S_0$	$T\Delta S_m$	$\overline{T\Delta S}$
mol·L^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
0.1	−3 ± 0.6[a]	−9 ± 0.4[a]	−3.1 ± 0.3[a]	−5.0
0.5	−1.4 ± 0.6	−6.5 ± 0.4	−1.2 ± 0.3	−3.0
1	−0.4 ± 0.4	−4.6 ± 0.4	0 ± 0.3	−1.6
3	2 ± 0.6	0 ± 0.4	3 ± 0.4	1.7
5	3.3 ± 0.7	3 ± 0.4	4.9 ± 0.6	3.7

[a] Standard deviation on the parameters.

Table 4. Thermodynamic Protonation Parameters for PAAm (Pure Solvent Values) and Parameters for the Dependence on Ionic Strength, at *t* = 25 °C, in Aqueous LiCl and NaCl Solutions (Eq 6)

	medium	$\log {}^{T}K_x^{H}$	a	b
$\log K_1^H$	NaCl	9.4 ± 0.1[a]	0.7 ± 0.2[b]	0.03 ± 0.08[b]
	LiCl		1.0 ± 0.2	0.03 ± 0.08
$\log K_0^H$	NaCl	7.41 ± 0.01	1.12 ± 0.01	
	LiCl		1.16 ± 0.01	
$\log K_m^H$	NaCl	8.87 ± 0.04	0.87 ± 0.04	
	LiCl		0.60 ± 0.03	
$\log K_{int}^H$	NaCl	8.58 ± 0.03	0.95 ± 0.02	
	LiCl		0.90 ± 0.02	
$\log \bar{K}^H$	NaCl	8.539 ± 0.009	0.948 ± 0.006	
	LiCl		0.948 ± 0.006	

[a] Standard deviation on the fit. [b] ± standard deviation on the parameters.

Table 5. Thermodynamic Protonation Parameters for PAAm (Pure Solvent Values) and Parameters for the Dependence on Ionic Strength, at *t* = 25 °C, in Aqueous NaCl Solutions (Eq 6)

parameter	value at $I \rightarrow 0$ mol·L^{-1}	A
ΔH_1/kJ·mol^{-1}	−57.0 ± 0.2[b]	−1.61 ± 0.1[a]
ΔH_0/kJ·mol^{-1}	−53.2 ± 0.2	−0.15 ± 0.06
ΔH_m/kJ·mol^{-1}	−54.9 ± 0.2	−0.81 ± 0.09
$T\Delta S_1$/kJ·mol^{-1}	−3.3 ± 0.2	3.2 ± 0.1
$T\Delta S_0$/kJ·mol^{-1}	−10.9 ± 0.1	6.27 ± 0.07
$T\Delta S_m$/kJ·mol^{-1}	−4.3 ± 0.1	4.2 ± 0.1

[a] Standard deviation on the parameters.

range observed in the three parameter model ($\log K_1^H - \log K_0^H$), or in other words, we have $n \propto (\log K_1^H - \log K_0^H)$.

The dependence of n on I can be expressed by the equation

$$n = 1 + p_1/(I + 1)^{p_2} \qquad (7)$$

with $p_2 = 0.19$ and $p_1 = 0.99$ and 1.00 for LiCl and NaCl, respectively. The proportionality between n and the range ($\log K_1^H - \log K_0^H$) is represented by the simple linear equation

$$n = 1 + \frac{1}{2}(\log K_1^H - \log K_0^H) \qquad (8)$$

for both supporting electrolytes with a mean deviation in the fit $\epsilon = 0.06$. A very similar relationship was found for polyacrylates [$(n - 1) = (\log K_1^H - \log K_0^H)/(6 \log 2)$].[6]

Protonation ΔH and TΔS. The parameters of eq 5 for protonation, Δ*G*, Δ*H*, and *T*Δ*S*, are reported in Table 3. Some remarks can be made about the values reported in this table: (a) enthalpic values are quite high, as they are for low molecular weight polyamines;[15−18] (b) the contribution of *T*Δ*S*, however, is very low with a mean value $T\Delta S \sim 0$ kJ·mol^{-1}; (c) the dependence on ionic strength (decreasing and increasing functions for Δ*H* and *T*Δ*S*, respectively) is almost not significant for ΔH_0 and is very small for ΔH_1, while for *T*Δ*S* it is more considerable for the three parameters of eq 5. Moreover, the $\Delta H_0 - \Delta H_1$ range is very small, particularly at low ionic strengths. No comparison can be made with the literature, since no other data have yet been published.

Dependence on Ionic Strength of Protonation Thermodynamic Parameters. By using the simple eq 6, we calculated parameters for the dependence on ionic strength of the different protonation parameters, as reported in Tables 4 and 5. The value of $\log K_{int}^H = 8.58 \pm 0.03$ ($I = 0$ mol·L^{-1}) reported in Table 4 is in agreement with what we found in the literature at $I = 0.001$ mol·L^{-1} in NaCl at the same temperature as that for PAAm (MW = 60 kDa).[2] The dependence of $\log K^H$ on I is about the same for the two supporting electrolytes and increases significantly with 1/α due to the polyelectrolyte charge density. As already observed, the dependence of Δ*H* on *I* is very low.

According to the SIT (Specific ion Interaction Theory)[19] model, the dependence on *I* of protonation constants for a polyamine can be written (at *t* = 25 °C)

$$\log K^H = \log {}^{T}K^H + \frac{2z(0.51\sqrt{I})}{1 + 1.5\sqrt{I}} + \Delta\epsilon I \qquad (9)$$

where *z* is the charge of the polycation and Δϵ is the difference in specific interaction coefficients:

$$\Delta\epsilon = \epsilon(H^+,Cl^-) + \epsilon(AH_x^{z+},Cl^-) - \epsilon(AH_{x+1}^{(z+1)+},Cl^-)$$

with *x* depending on the degree of polyamine protonation. Moreover, it is necessary in the case of poly(allylamine) to determine the value of the charge *z*. As an example we applied eq 9 to $\log \bar{K}^H$ and, by simultaneously refining $\log {}^{T}\bar{K}^H$, *z*, and Δϵ, we obtained

$$\log {}^{T}\bar{K}^H = 8.35 \pm 0.15$$

$$z = 2.25 \pm 0.07$$

$$\Delta\epsilon = 0.209 \pm 0.016 \text{ (LiCl)}$$

$$\Delta\epsilon = 0.200 \pm 0.011 \text{ (NaCl)}$$

(to apply the SIT model, the molal concentration scale must be used ($\log \bar{K}^H$), and *I* values were converted to this scale and are reported as Supporting Information (Table S5). The value of $\log \bar{K}^H$ at infinite dilution, though affected by a fairly large error, is in agreement with that reported in Table 4 ($\Delta \ll 3\sigma$), and the charge value indicates ap-

Table 6. Protonation Parameters (ΔH and log K^{H}) of Some Low Molecular Weight Polyamines, at $I = 0$ mol·L^{-1} and $t = 25$ °C

amine	log K_i^{H} [a]	ΔH_i [b]/kJ·mol^{-1}
$NH_2-(CH_2)_2-NH_2$	9.91, 6.86	−49.1, −44.8
$NH_2-(CH_2)_4-NH_2$	10.54, 9.04	−50.5, −50.0
$NH_2-(CH_2)_{10}-NH_2$	10.94, 10.05	−58.1, −58.9
$NH_2-(CH_2)_2-NH-(CH_2)_2-NH_2$	9.79, 8.75, 3.66	−49.2, −49.5, −31.5
$NH_2-(CH_2)_3-NH-(CH_2)_4-NH_2$	10.80, 9.58, 7.82	−56.5, −53.0, −48.9
$NH_2-(CH_2)_4-[CH-CH_2-NH_2]-(CH_2)_3-NH_2$	10.90, 9.96, 8.81	−57.3, −57.4, −55.9

[a] Reference 21. [b] References 15−18.

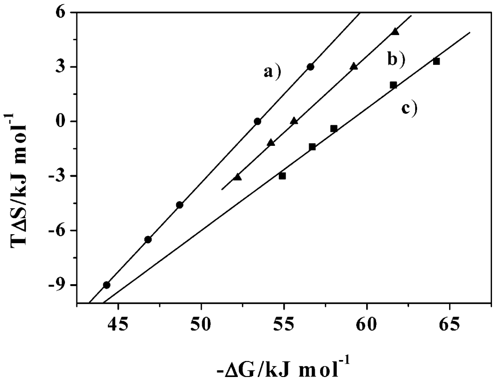

Figure 2. $T\Delta S$ vs ΔG for the three protonation parameters of PAAm according to the Högfeldt model, at different ionic strengths, in NaCl aqueous solution, at $t = 25$ °C: a, $T\Delta S_0$ vs ΔG_0; b, $T\Delta S_m$ vs ΔG_m; c, $T\Delta S_1$ vs ΔG_1.

proximately that this aminic polyelectrolyte behaves like a di−tri polyammonium cation in the middle of the α range. The parameter $\Delta\epsilon$ is the same for the two supporting electrolytes (the difference is statistically not significant) and indicates that the difference in specific interaction coefficients between two successive protonation steps is quite low. In fact, by using the value $\epsilon(H^+,Cl^-) = 0.12$,[20] we have

$$\epsilon(AH_x^{z+},Cl^-) - \epsilon(AH_{x+1}^{(z+1)+},Cl^-) = 0.08 \pm 0.02$$

By plotting $T\Delta S$ versus ΔG, we observed very good linearity, as shown in Figure 2. For the three parameters of eq 5, we have (r = linear correlation coefficient)

$$T\Delta S_1 = 39.6 + 0.6724\Delta G, \quad r = 0.9952$$

$$T\Delta S_0 = 52.2 + 0.9765\Delta G, \quad r = 0.9999$$

$$T\Delta S_m = 46.7 + 0.8386\Delta G, \quad r = 0.9993$$

These linear relationships are very useful, since they suggest it might be possible to considerably reduce the number of experiments needed to obtain information on thermodynamic protonation parameters in a wide ionic strength range.

Comparison with Low Molecular Weight Polyamines. Thermodynamic parameters for the protonation of poly(allylamine) are very close to those relative to low molecular weight polyamines.[15−18,21] A brief comparison is given in Table 6. To understand the significance of the differences or similarities, we must consider the following points: (a) successive protonation constants follow the general trend log K_1^{H} > log K_2^{H} > log K_i^{H} > log K_m^{H} (m = total number of amino groups); (b) Δ log K_i^{H} = log K_i^{H} − log K_{i-1}^{H} is a decreasing function of the length of the alkyl chain; (c) Δ log K_m^{H} = log K_1^{H} − log K_m^{H} increases with m; (d) both protonation constants and their dependence on ionic strength are dependent on N-alkyl substitution; (e) ΔH values are quite high and the $\Delta H_1 - \Delta H_m$ range is very small. Table 6 shows some thermodynamic parameters for the protonation of low molecular weight polyamines. By comparing data in this table with the values in Tables 4 and 5, we can observe the close similarity between low and high molecular weight polyamines, especially those whose primary amino groups are separated by more than two methylenic groups.

Final Remarks

The extensive data reported here and derived from both potentiometry and calorimetry in a wide ionic strength range give a complete picture of the thermodynamics of protonation at 25 °C. The results can be summarized as follows.

(i) The protonation constants of PAAm as a function of α range from 7.4 to 9.9 ($I = 0$ mol·L^{-1}) and from 9.9 to 11.8 ($I = 5$ mol·L^{-1}).

(ii) Protonation data in NaCl and LiCl are very similar, and the dependence on ionic strength is very similar to that shown by low molecular weight polyamines.

(iii) Experimental data are satisfactorily explained by both the two and three parameter models, but the standard deviation in the fit is significantly better for the second one (see Tables S3 and S4 of the Supporting Information).

(iv) Protonation enthalpies also follow the same trend as that for low molecular weight polyamines.

(v) A linear relationship was found between ΔG and $T\Delta S$, which considerably reduces the need for experimental data at different ionic strengths.

(vi) By applying the SIT model for dependence on ionic strength, it was possible to find a mean effective charge value.

Future developments of this work include potentiometric and calorimetric measurements at different temperatures and the use of poly(allylamine)s at different molecular weights. Density measurements will be considered too, in order to obtain partial molal and apparent molal volumes.

Supporting Information Available:

Additional tables of data: protonation constants and parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review November 10, 2003. Accepted January 22, 2004. We thank the University of Messina for financial support.

JE0342264