J. Chem. Eng. Data **2002,** *47,* 1205−1212

The Dependence on Ionic Strength of Enthalpies of Protonation for Polyamines in $NaCl_{(aq)}$

Alessandro De Robertis, Claudia Foti, Ottavia Giuffrè, and Silvio Sammartano*

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina,
Salita Sperone 31, I-98166 Messina (Vill. S. Agata), Italy

Enthalpies of protonation of some polyamines [*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, bis(3-aminopropyl)amine, bis(6-aminohexyl)amine, 4-aminomethyl-1,8-octanediamine, 3,3′-diamino-*N*-methyldipropylamine, *N*,*N*,*N* ′,*N* ′,*N* ″-pentamethyldiethylenetriamine, 1,1,4,7,10,10-hexamethyltriethylenetetraamine, and tris-(2-aminoethyl)amine] were determined by calorimetric titrations in $NaCl_{(aq)}$ in the ionic strength range $0 < I/(\text{mol kg}^{-1}) \leq 3$ [$0 < I/(\text{mol kg}^{-1}) \leq 5$ for bis(6-aminohexyl)amine and tris(2-aminoethyl)amine] and at $t = 25$ °C. The dependence on ionic strength was considered by using two different models. Both ΔH^0 values and their dependence on *I* are affected by *N*-alkyl substitution. Parameters for the dependence on *I* are very similar for all unsubstituted or partially substituted polyamines, and common parameters are proposed. Analogously, for fully methyl-substituted polyamines, strong similarities were found in the dependence on *I*, and also in this case, common empirical parameters are given. Previous data from this laboratory for the protonation of some unsubstituted diamines were also considered in the analysis of the results. An attempt to calculate enthalpy changes for the interaction of Cl^- with polyammonium cations was made.

Introduction

Because of the importance of polyamines in natural and biological fluids,[1,2] it is necessary to investigate extensively their interactions with components of these fluids, in different ionic media and under different ionic strength and temperature conditions. The most important reaction of polyamines in aqueous media is protonation, and several investigations have been devoted to this matter, in particular by determining protonation constants and, to a lesser extent, by measuring enthalpies of protonation.

The protonation of low-molecular-weight polyamines has been studied extensively, and a great deal of data have been reported in several papers.[3−21] Nevertheless, only a few papers report other thermodynamic parameters at several values of the ionic strength. The parameters are always calculated at only one, generally low (0.1 mol dm^{-3}), value of ionic strength and often in KCl, KNO_3, or $NaClO_4$. Furthermore, most of the enthalpies of protonation are calculated from the “temperature dependence” of the formation constants, which often leads to less accurate values compared to those measured by direct calorimetry.

In this work, we report experimental data (from calorimetric measurements) on the enthalpies of protonation of some polyamines (Table 1) at different ionic strengths in the range $0 < I/\text{mol kg}^{-1} \leq 5$ and at $t = 25$ °C. The results are analyzed in terms of ionic strength dependence using different models. The influence of alkyl substitution on the enthalpy of protonation is considered in detail.

Experimental Section

Materials. Amines [*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1,2ds), bis(3-aminopropyl)amine (TR1), bis(6-aminohexyl)amine (TR2), 4-aminomethyl-1,8-octanediamine (TR3), 3,3′-diamino-*N*-methyldipropylamine (TR4), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (TR6), 1,1,4,7,10,10-hexamethyltriethylenetetraamine (TE1), and tris(2-aminoethyl)amine (TE2); Aldrich or Fluka products] were purified by transformation into the corresponding hydrochlorides and were used in this form. Sodium chloride (Fluka, puriss.) was prepared by weighing the pure salt after drying in an oven at 110 °C. Standard solutions of NaOH were prepared by diluting concentrated Fluka ampules and were standardized against potassium biphthalate. Grade A glassware and twice-distilled water were used for all solutions.

Calorimetric Measurements. Calorimetric measurements were performed by titrating 50 mL of the solution containing the amine hydrochloride under study and NaCl at variable ionic strength, at (25.000 ± 0.001) °C, using a Tronac isoperibolic titration calorimeter (model 450), coupled with a Keithley 196 system Dmm digital multimeter. The titrant NaOH was delivered by a 2.5-mL-capacity Hamilton syringe, model 1002TLL. A computer program was used for the acquisition of the calorimetric data. The accuracy was checked by titrating a TRIS [tris(hydroxymethyl)amino methane] buffer with HCl. The concentrations used in the experiments were $C_{H_nA} = 10$ mmol dm^{-3}, $C_{NaOH} = 1$ mol dm^{-3}, and $C_{NaCl} = 0.1{-}5$ mol dm^{-3} (H_nA = fully protonated amine). The enthalpy of dilution was measured before each experiment under the same ionic strength conditions as the measurements. The accuracy of the calorimetric apparatus was $Q \pm 0.008$ J, and the accuracy of the titrant volume was $v \pm 0.001$ cm^3.

Calculations. Calorimetric titration data were analyzed by the computer program ES5CM.[22] The LIANA program[23] was used to test the dependence of ΔH on ionic strength according to different equations. The enthalpies of proto-

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* Corresponding author. Fax: +39 090 392827. E-mail: sammartano@chem.unime.it.

10.1021/je020040d CCC: $22.00

Table 1. Amines Considered in this Work

amine	name	symbol	log *K* ref	Δ*H* ref
$H_2N-(CH_2)_2-NH_2$	ethylenediamine	1,2d	21	20
$H_2N-(CH_2)_6-NH_2$	1,6-diaminohexane	1,6d	21	20
$H_2N-(CH_2)_8-NH_2$	1,8-diaminooctane	1,8d	21	20
$H_2N-(CH_2)_{10}-NH_2$	1,10-diaminodecane	1,10d	21	20
$(CH_3)_2N-(CH_2)_2-N(CH_3)_2$	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine	1,2ds	21	*a*
$H_2N-(CH_2)_3-NH-(CH_2)_3-NH_2$	bis(3-aminopropyl)amine	TR1	21	*a*
$H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$	bis(6-aminohexyl)amine	TR2	21	*a*
$H_2N-(CH_2)_4-CH(CH_2-NH_2)-(CH_2)_3-NH_2$	4-aminomethyl-1,8-octanediamine	TR3	21	*a*
$H_2N-(CH_2)_3-N(CH_3)-(CH_2)_3-NH_2$	3,3′-diamino-*N*-methyldipropylamine	TR4	21	*a*
$(CH_3)_2N-(CH_2)_2-N(CH_3)-(CH_2)_2-N(CH_3)_2$	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine	TR6	21	*a*
$(CH_3)_2N-(CH_2)_2-[N(CH_3)-(CH_2)_2]_2-N(CH_3)_2$	1,1,4,7,10,10-hexamethyltriethylenetetraamine	TE1	21	*a*
$N(CH_2CH_2NH_2)_3$	tris(2-aminoethyl)amine	TE2	21	*a*

[a] This work.

nation refer to the reaction (A = amine)

$$iH^+ + A^0 = H_iA^{i+} \tag{1}$$

Thermodynamic protonation parameters are given on the molal scale [mol (kg of H_2O)$^{-1}$]. Enthalpy changes for the ionization of water at different ionic strengths used in the calculations were taken from ref 24.

Equations for the Dependence on Ionic Strength. The dependence on ionic strength of the enthalpy of protonation ΔH can be expressed by the simple polynomial equation

$$-\Delta H = -\Delta H^0 + CI + EI^2 \tag{2}$$

with

$$C = c_1 i(i-1) + c_2 i \tag{2a}$$

and

$$E = e_1 i(i-1) \tag{2b}$$

where ΔH^0 is the enthalpy change at $I \rightarrow 0$ and c_1, c_2, and e_1 are empirical parameters that can be obtained from experimental data by least-squares calculations.

The dependence on ionic strength can also be taken into account by using the Pitzer equations.[25] According to the Pitzer equations, for electrolytes 1−1, 1−2, and 2−1, the activity coefficients of cation M or anion X can be expressed by

$$\ln \gamma_M, \ln \gamma_X = f(I,\beta^{(0)},\beta^{(1)},C_{H,Cl}{}^{(\phi)},\Theta,\Psi) \tag{3}$$

and for neutral species

$$\ln \gamma_{MX^0} = 2\lambda I \tag{3a}$$

where I is the ionic strength on the molal scale; $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters between two ions of opposite signs; Θ represents interaction parameters between two ions of the same sign, Ψ represents triple interactions (+ − +, − + −), and λ is the interaction parameter for neutral species. At $I < 3$ mol (kg of H_2O)$^{-1}$, the Θ and Ψ parameters can generally be neglected.

If we consider the protonation reaction

$$H^+ + H_{i-1}A^{(i-1)+} = H_iA^{i+} \tag{4}$$

the thermodynamic constants in NaCl can be expressed by

$$\ln K_i{}^H = \ln {}^TK_i{}^H + \ln \gamma_H + \ln \gamma_{H_{i-1}A} - \ln \gamma_{H_iA} \tag{5}$$

and by combining eq 5 with the explicit form of eq 3, we obtain

$$\begin{aligned}\ln K_i{}^H = {} & \ln {}^TK_i{}^H + 2(1-i)f^{\gamma}A_{\phi} + 2I(\beta_{H,Cl}{}^{(0)} + \\ & \beta_{H_{i-1}A,Cl}{}^{(0)} - \beta_{H_iA,Cl}{}^{(0)} + \Theta_{H,Na} + \Theta_{H_{i-1}A,Na} - \Theta_{H_iA,Na}) + \\ & I^2\{C_{H,Cl}{}^{(\phi)} + C_{H_{i-1}A,Cl}{}^{(\phi)}/[2(i-1)^{1/2}] - C_{H_iA,Cl}{}^{(\phi)}/(2i^{1/2}) + \\ & \Psi_{H,Na,Cl} + \Psi_{H_{i-1}A,Na,Cl} - \Psi_{H_iA,Na,Cl}\} + (\beta_{H,Cl}{}^{(1)} + \\ & \beta_{H_{i-1}A,Cl}{}^{(1)} - \beta_{H_{i-}A,Cl}{}^{(1)})f_1 + (1-i)\beta_{Na,Cl}{}^{(1)}f_2\end{aligned} \tag{5a}$$

and for $i = 1$

$$\begin{aligned}\ln K_1{}^H = {} & \ln {}^TK_1{}^H + 2I(\beta_{H,Cl}{}^{(0)} + \lambda_A - \beta_{HA,Cl}{}^{(0)} + \Theta_{H,Na} - \\ & \Theta_{HA,Na}) + I^2(C_{H,Cl}{}^{(\phi)} - C_{HA,Cl}{}^{(\phi)}/(2i^{1/2}) + \Psi_{H,Na,Cl} - \\ & \Psi_{HA,Na,Cl}) + (\beta_{H,Cl}{}^{(1)} - \beta_{HA,Cl}{}^{(1)})f_1\end{aligned} \tag{5b}$$

with

$$A_{\phi} = -0.3912 + 6.636 \times 10^{-4}(t/°C - 25) + 3.562 \times 10^{-6}(t/°C - 25) \tag{5c}$$

$$f^{\gamma} = I^{1/2}(1 + 1.2I^{1/2})^{-1} + 1.667 \ln(1 + 1.2I^{1/2}) \tag{5d}$$

$$f_1 = 1 - (1 + 2I^{1/2}) \exp(-2I^{1/2}) \tag{5e}$$

$$f_2 = -1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2}) \tag{5f}$$

In this work, for the protonation constants at different ionic strengths we used the simplified version of eq 5a

$$\ln K_i{}^H = \ln {}^TK_i{}^H + 2(1-i)f^{\gamma}A_{\phi} + 2IP_1 + I^2P_2 + f_1P_3 + (1-i)f_2\beta_{Na,Cl}{}^{(1)} \tag{6}$$

where $\beta_{Na,Cl}{}^{(1)} = 0.2664$[25] and

$$P_i = \beta_{H,Cl}{}^{(0)} + \beta_{H_{i-1}A,Cl}{}^{(0)} - \beta_{H_iA,Cl}{}^{(0)} + \Theta_{H,Na} + \Theta_{H_{i-1}A,Na} - \Theta_{H_iA,Na} \tag{6a}$$

$$\begin{aligned}P_2 = {} & C_{H,Cl}{}^{(\phi)} + C_{H_{i-1}A,Cl}{}^{(\phi)}/[2(i-1)^{1/2}] - C_{H_iA,Cl}{}^{(\phi)}/(2i^{1/2}) + \\ & \Psi_{H,Na,Cl} + \Psi_{H_{i-1}A,Na,Cl} - \Psi_{H_iA,Na,Cl}\end{aligned} \tag{6b}$$

$$P_3 = \beta_{H,Cl}{}^{(1)} + \beta_{H_{i-1}A,Cl}{}^{(1)} - \beta_{H_iA,Cl}{}^{(1)} \tag{6c}$$

Using the known thermodynamic relation

$$\Delta H = RT^2(\partial \ln K/\partial T)_P \tag{7}$$

Table 2. Thermodynamic Parameters[a] for the Protonation of Triamines in NaCl at Different Ionic Strengths and at 25 °C

I[b]	$-\Delta G_1^0$	$-\Delta H_1^0$	$T\Delta S_1^0$	$-\Delta G_2^0$	$-\Delta H_2^0$	$T\Delta S_2^0$	$-\Delta G_3^0$	$-\Delta H_3^0$	$T\Delta S_3^0$
					TR1				
0	60.2[c]	51.4 ± 0.4[d]	8.8 ± 0.4[d]	113.4[c]	105.3 ± 0.6[d]	8.1 ± 0.6[d]	154.2[c]	151.0 ± 0.7[d]	3.2 ± 0.7[d]
0.1	60.5	51.7 ± 0.3	8.8 ± 0.3	115.1	105.7 ± 0.5	9.4 ± 0.5	158.7	151.4 ± 0.5	7.3 ± 0.5
0.5	61.4	52.5 ± 0.2	8.9 ± 0.3	117.2	106.9 ± 0.2	10.3 ± 0.3	162.9	153.2 ± 0.3	9.7 ± 0.3
1	62.4	53.5 ± 0.2	8.9 ± 0.2	119.1	108.3 ± 0.5	10.8 ± 0.5	166.1	155.3 ± 0.6	10.8 ± 0.6
2	64.2	55.2 ± 0.3	9.0 ± 0.3	122.5	110.9 ± 0.6	11.6 ± 0.6	171.5	159.5 ± 0.6	12.0 ± 0.6
3	66.0	56.4 ± 0.2	9.6 ± 0.2	126.2	113.2 ± 0.5	13.0 ± 0.5	176.8	163.5 ± 0.5	13.3 ± 0.5
ΔX[e]	63 ± 3	54 ± 2	9 ± 0.5	119 ± 7	109 ± 4	11 ± 3	165 ± 11	157 ± 6	8 ± 5
					TR2				
0	63.7	56.8 ± 0.2	6.9 ± 0.3	122.3	113.7 ± 0.2	8.6 ± 0.2	175.6	170.3 ± 0.6	5.3 ± 0.6
0.1	64.1	57.0 ± 0.2	7.1 ± 0.3	124.0	114.0 ± 0.2	10.0 ± 0.2	180.0	170.7 ± 0.5	9.3 ± 0.5
0.5	64.9	57.9 ± 0.2	7.0 ± 0.3	126.1	115.3 ± 0.2	10.8 ± 0.3	184.0	172.6 ± 0.1	11.4 ± 0.1
1	65.7	58.9 ± 0.2	6.8 ± 0.3	127.9	116.9 ± 0.2	11.0 ± 0.2	186.9	175.1 ± 0.4	11.8 ± 0.4
2	67.4	60.8 ± 0.2	6.6 ± 0.3	131.1	120.5 ± 0.4	10.6 ± 0.4	191.8	180.3 ± 0.9	11.5 ± 0.9
3	69.1	62.5 ± 0.2	6.6 ± 0.3	134.3	124.2 ± 0.4	10.1 ± 0.4	196.5	185.8 ± 0.9	10.7 ± 0.9
5	72.4	65.5 ± 0.2	6.9 ± 0.3	141.6	132.3 ± 0.2	9.3 ± 0.3	207.2	197.8 ± 0.4	9.4 ± 0.4
ΔX[e]	68 ± 4	61 ± 6	7 ± 0.5	132 ± 10	123 ± 9	10 ± 1	191 ± 16	184 ± 14	11 ± 6
					TR3				
0	62.2	57.3 ± 0.3	4.9 ± 0.3	119.1	114.7 ± 0.8	4.4 ± 0.8	169.4	170.6 ± 1.1	−1 ± 1.1
0.1	62.5	57.6 ± 0.2	4.9 ± 0.2	120.8	115.1 ± 0.6	5.7 ± 0.6	173.9	171.1 ± 0.8	2.8 ± 0.8
0.5	63.1	58.7 ± 0.2	4.4 ± 0.2	123.1	116.7 ± 0.3	6.4 ± 0.3	178.2	173.2 ± 0.2	5.0 ± 0.2
1	63.7	60.2 ± 0.5	3.5 ± 0.5	124.8	118.7 ± 1	6.1 ± 1.0	181.0	175.7 ± 1.1	5 ± 1.1
2	64.8	63.4 ± 0.6	1.4 ± 0.6	127.2	122.7 ± 1.2	4.5 ± 1.2	185.0	180.6 ± 1.3	4 ± 1.3
3	65.3	66.9 ± 0.2	−1.6 ± 0.2	129.1	126.5 ± 0.3	2.6 ± 0.3	186.7	185.2 ± 0.3	1.5 ± 0.3
ΔX[e]	64 ± 1	62 ± 5	2 ± 3	124 ± 5	121 ± 5.5	5 ± 2	178 ± 9	178 ± 7	2 ± 3
					TR4				
0	59.2	50.8 ± 0.3	8.4 ± 0.3	112.1	103.8 ± 0.2	8.3 ± 0.2	148.7	136.9 ± 0.2	11.8 ± 0.2
0.1	59.5	51.0 ± 0.2	8.5 ± 0.3	113.9	104.1 ± 0.2	9.8 ± 0.3	153.4	137.3 ± 0.1	16.1 ± 0.2
0.5	60.4	51.7 ± 0.2	8.7 ± 0.3	116.1	105.2 ± 0.2	10.9 ± 0.3	157.8	139.0 ± 0.2	18.8 ± 0.2
1	61.2	52.6 ± 0.2	8.6 ± 0.2	118.0	106.5 ± 0.2	11.5 ± 0.2	161.2	141.2 ± 0.4	20.0 ± 0.4
2	63.0	53.9 ± 0.3	9.1 ± 0.3	121.1	109.1 ± 0.2	12.0 ± 0.2	166.6	146.2 ± 0.5	20.4 ± 0.5
3	64.6	54.8 ± 0.2	9.8 ± 0.3	124.0	111.7 ± 0.2	12.3 ± 0.3	171.4	151.9 ± 0.2	19.5 ± 0.3
ΔX[e]	62 ± 3	52 ± 3	9 ± 1	118 ± 6	108 ± 4	10 ± 2	160 ± 11	144 ± 8	16 ± 4
					TE2				
0	57.9	47.1 ± 0.3	10.8 ± 0.3	110.4	101.1 ± 0.2	9.3 ± 0.3	155.5	153.7 ± 0.4	1.8 ± 0.4
0.1	58.1	47.3 ± 0.2	10.8 ± 0.2	112.0	101.3 ± 0.2	10.7 ± 0.3	159.8	154.1 ± 0.3	5.7 ± 0.3
0.5	58.7	48.1 ± 0.2	10.6 ± 0.2	114.1	102.5 ± 0.2	11.6 ± 0.3	163.9	155.5 ± 0.2	8.4 ± 0.3
1	59.5	49.1 ± 0.2	10.4 ± 0.3	116.0	104.0 ± 0.2	12.0 ± 0.3	167.0	157.5 ± 0.3	9.5 ± 0.3
2	61.0	50.9 ± 0.2	10.1 ± 0.2	119.2	107.1 ± 0.2	12.1 ± 0.3	171.9	161.7 ± 0.7	10.2 ± 0.7
3	62.5	52.7 ± 0.2	9.8 ± 0.3	122.1	110.4 ± 0.2	11.7 ± 0.3	176.4	166.3 ± 0.6	10.1 ± 0.6
5	65.3	55.8 ± 0.4	9.5 ± 0.4	127.8	117.4 ± 0.2	10.4 ± 0.3	185.5	176.9 ± 0.7	8.6 ± 0.7
ΔX[e]	62 ± 3	51 ± 5	10 ± 1	119 ± 9	109 ± 8	11 ± 1	170 ± 16	165 ± 12	6 ± 4
1,2d	59 ± 2	52 ± 2	7 ± 0.5	101 ± 6	98 ± 4	3 ± 2	–	–	–
1,6d	66 ± 4	61 ± 4	4 ± 1	127 ± 9	123 ± 9	4 ± 1	–	–	–
1,8d	65 ± 2	61 ± 3	4 ± 1	125 ± 5	122 ± 4	3 ± 1	–	–	–
1,10d	65 ± 2	62 ± 3	3 ± 1	125 ± 5	122 ± 5	4 ± 1	–	–	–
ΔY[f]	63 ± 4	58 ± 4	5 ± 3	121 ± 15	115 ± 10	6 ± 3	173 ± 15	166 ± 15	7 ± 5

[a] ΔG^0, ΔH^0, and $T\Delta S^0$ (in kJ mol^{-1}) refer to the reaction $i\mathrm{H}^+ + \mathrm{A}^0 = \mathrm{H}_i\mathrm{A}^{i+}$. [b] In mol kg^{-1}. [c] Protonation constants were reported in ref 21. [d] ≥95% confidence intervals. [e] Mean values of different thermodynamic parameters (approximately equal to the medians) ± range [(max − min)/2]. [f] Average value of all of the means.

and combining eqs 6 and 7, we obtain

$$\Delta H_i = \Delta H_i^{\,0} + RT^{\,2}[2(1-\mathrm{i})f^{\,\gamma}\,\partial A_\phi/\partial T + 2I\,\partial P_1/\partial T + I^{\,2}\,\partial P_2/\partial T + f_1\,\partial P_3/\partial T + (1-i)f_2\,\partial\beta_{\mathrm{Na,Cl}}^{(1)}/\partial T] \quad (8)$$

with $R = 8.3143$ J mol^{-1} K^{-1}, T = temperature in Kelvin, and $\partial\beta_{\mathrm{Na,Cl}}^{(1)}/\partial T = 7.005 \times 10^{-4}$ (ref 25).

Results and Discussion

General Features of Protonation Thermodynamic Parameters. Protonation constants of the various polyamines considered in this work have already been reported.[17−21] Enthalpies of protonation calculated from calorimetric measurements for each ionic strength value are reported in Table 2 (unsubstituted or partially substituted triamines) and Table 3 (fully substituted polyamines). Enthalpies of protonation of diamines $NH_2-(CH_2)_n-NH_2$ (n = 2, 6, 8, 10) have already reported,[20] and some of these data are given in Table 2. A semiqualitative inspection of the data reported in these tables leads to the following considerations: (a) Unsubstituted or partially substituted polyamines show exothermic protonation ΔH values (see also ref 20 for diamines), with ΔH/(kJ mol^{-1}) in the order $\Delta H_1 > \Delta H_2 > \Delta H_3$. (b) Enthalpy changes for the protonation of fully N-methyl-substituted polyamines are markedly less exothermic than those for unsubstituted or partially

Table 3. Thermodynamic Parameters[a] for the Protonation of Substituted Polyamines in NaCl at Different Ionic Strengths and at 25 °C

I[b]	$-\Delta G_1{}^0$	$-\Delta H_1{}^0$	$T\Delta S_1{}^0$	$-\Delta G_2{}^0$	$-\Delta H_2{}^0$	$T\Delta S_2{}^0$	$-\Delta G_3{}^0$	$-\Delta H_3{}^0$	$T\Delta S_3{}^0$	$-\Delta G_4{}^0$	$-\Delta H_4{}^0$	$T\Delta S_4{}^0$
1,2ds												
0	52.2[c]	29.2 ± 0.2[d]	23.0 ± 0.3[d]	84.4[c]	55.2 ± 0.2[d]	29.2 ± 0.3[d]	–	–	–	–	–	–
0.1	52.6	29.6 ± 0.2	23.0 ± 0.3	86.2	55.9 ± 0.1	30.3 ± 0.2	–	–	–	–	–	–
0.5	53.7	31.1 ± 0.2	22.6 ± 0.3	89.0	58.7 ± 0.1	30.3 ± 0.2	–	–	–	–	–	–
1	54.7	32.7 ± 0.2	22.0 ± 0.3	91.4	61.8 ± 0.3	29.6 ± 0.4	–	–	–	–	–	–
2	56.6	35.2 ± 0.3	21.4 ± 0.4	95.5	66.4 ± 0.3	29.1 ± 0.4	–	–	–	–	–	–
3	58.3	36.8 ± 0.5	21.5 ± 0.6	99.1	69.0 ± 0.5	30.1 ± 0.6	–	–	–	–	–	–
ΔX[e]	55 ± 3	33 ± 4	22 ± 1	92 ± 7	62 ± 7	30 ± 0.5						
TR6												
0	52.7	28.4 ± 0.2	24.3 ± 0.3	99.3	66.2 ± 0.4	33.1 ± 0.5	107.8	76.1 ± 0.3	31.7 ± 0.4	–	–	–
0.1	53.0	28.8 ± 0.2	24.2 ± 0.3	101.1	67.0 ± 0.3	34.1 ± 0.4	112.4	77.3 ± 0.2	35.1 ± 0.3	–	–	–
0.5	54.0	30.2 ± 0.2	23.8 ± 0.3	103.9	69.9 ± 0.4	34.0 ± 0.5	117.6	81.4 ± 0.4	36.2 ± 0.5	–	–	–
1	55.0	31.6 ± 0.2	23.4 ± 0.3	106.6	73.0 ± 0.8	33.6 ± 0.9	121.5	85.4 ± 0.4	36.1 ± 0.5	–	–	–
2	56.7	33.7 ± 0.2	23.0 ± 0.3	110.8	77.2 ± 0.8	33.6 ± 0.9	127.5	89.1 ± 0.5	38.4 ± 0.6	–	–	–
3	58.3	34.7 ± 0.5	23.6 ± 0.6	114.6	78.6 ± 0.8	36.0 ± 0.9	133.2	87.4 ± 0.5	45.8 ± 0.6	–	–	–
ΔX[e]	55 ± 3	32 ± 3	24 ± 0.5	107 ± 8	72 ± 5	35 ± 1	121 ± 12	82 ± 5	39 ± 7			
TE1												
0	52.6	27.8 ± 0.2	24.8 ± 0.3	99.1	57.7 ± 0.5	41.4 ± 0.6	126.0	83.1 ± 0.3	42.9 ± 0.4	129.2	98.1 ± 0.6	31.1 ± 0.7
0.1	52.9	28.2 ± 0.2	24.7 ± 0.3	100.9	58.5 ± 0.3	42.4 ± 0.4	130.7	84.4 ± 0.3	46.3 ± 0.4	137.8	99.3 ± 0.6	38.5 ± 0.7
0.5	53.9	29.5 ± 0.2	24.4 ± 0.3	103.7	61.8 ± 0.2	41.9 ± 0.3	136.0	88.9 ± 0.3	47.1 ± 0.4	146.2	102.7 ± 0.6	43.5 ± 0.7
1	54.9	31.0 ± 0.3	23.9 ± 0.4	106.1	65.1 ± 0.3	41.0 ± 0.4	140.1	93.3 ± 0.3	46.8 ± 0.4	151.6	104.2 ± 0.6	47.4 ± 0.7
ΔX[e]	54 ± 1	29 ± 2	24 ± 1	103 ± 3	61 ± 4	42 ± 0.5	133 ± 7	88 ± 5	45 ± 2	140 ± 12	101 ± 3	39 ± 8

[a] ΔG^0, ΔH^0, and $T\Delta S^0$ (in kJ mol^{-1}) refer to the reaction $i\mathrm{H}^+ + \mathrm{A}^0 = \mathrm{H}_i\mathrm{A}^{i+}$. [b] In mol kg^{-1}. [c] Protonation constants are reported in ref 21. [d] ≥95% confidence intervals. [e] Mean values of different thermodynamic parameters (approximately equal to the medians) ± range [(max − min)/2].

substituted polyamines. (c) The mean values, for the entire I/(mol kg^{-1}) range considered, are

for unsubstituted di- and triamines

$$-\overline{\Delta G_i} = 9 + 55i \tag{9}$$

$$-\overline{\Delta H_i} = 5 + 54i \tag{9a}$$

$$\overline{T\Delta S_i} = 4 + i \tag{9b}$$

and for fully substituted di-, tri-, and tetraamines

$$-\overline{\Delta G} = 160 - 100/i \tag{10}$$

$$-\overline{\Delta H} = 120 - 95/i \tag{10a}$$

$$\overline{T\Delta S} = 40 - 5/i \tag{10b}$$

(d) According to the different charge variations from reactants to products, the dependence on ionic strength can be expressed by the simple equations

$$\overline{\Delta H_i} = 54.9i + 2.2iI \tag{11}$$

$$\overline{\Delta H_i} = 58 - 39/i + 0.8i(i - 1)I + 12i \tag{11a}$$

for all unsubstituted and fully substituted polyamines, respectively.

Note that, in the rough approximate equations, the confidence intervals are quite large for ΔG and ΔH [approximately $\pm 5i$/(kJ mol^{-1})] and surprisingly small for $T\Delta S$ (approximately $\pm 2i$/(kJ mol^{-1})]. As expected, eqs 11 and 11a are affected by a smaller error [$\sim 2i$/(kJ mol^{-1})].

Dependence on Ionic Strength Using Polynomial Equation. Two examples of dependence on ionic strength are shown in Figure 1, where both ΔG and ΔH are plotted vs I/(mol kg^{-1}) for unsubstituted and fully substituted diamines. Remarkable features include (i) the quite different behaviors of substituted and unsubstituted diamines, as in the first case, the curvatures of ΔG and ΔH vs I are more marked than in the second, when the quadratic term (eq 2) should be very small (see also hereafter). (ii) In addition, the ΔG and ΔH curves are almost parallel, indicating that the dependence on I of the entropic term should be low. The trends shown in Figure 1 are very similar for the other amines and the protonation step.

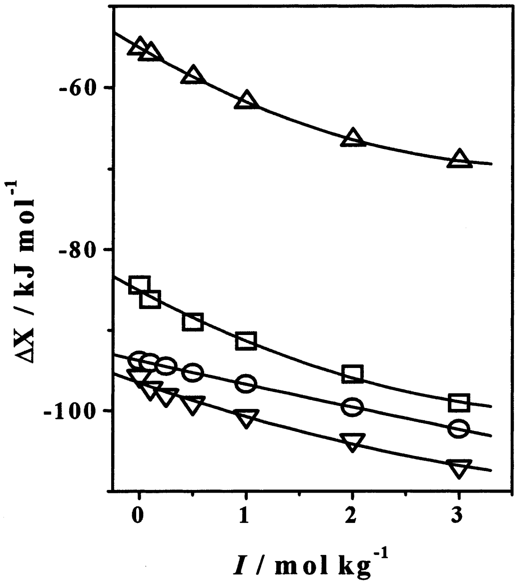

Figure 1. Dependence on ionic strength for the second protonation steps of 1,2d and 1,2ds of ΔG and ΔH (ΔX) at t = 25 °C. The symbols are Δ, ΔH_2 of 1,2ds; □, ΔG_2 of 1,2ds; O, ΔH_2 of 1,2d; and ∇, ΔG_2 of 1,2d.

The dependence on ionic strength of ΔG and ΔH of protonation can be expressed by eq 2, whose empirical parameters are reported in Table 4. In all cases, the values of E were constrained to be equal for homogeneous groups of amines for the same protonation step. As can be seen,

Table 4. Empirical Parameters *C* and *E* of Eq 2

amine	*i*	*C*	E^a	amine	*i*	*C*	E^a	amine	*i*	*C*	E^a	amine	*i*	*C*	E^a	amine	*i*	*C*	E^a	amine	*i*	*C*	E^a
1,2d	1	2.39	a	1,10d	1	3.18	a	TR2	1	2.09	c	TR4	1	1.58	c	1,2ds	1	4.16	f	TE1	1	3.70	f
	2	3.09	b		2	3.57	b		2	3.47	d		2	2.53	d		2	9.11	g		2	9.13	g
1,6d	1	2.87	a	TR1	1	1.97	c		3	4.74	e		3	4.51	e	TR6	1	3.67	f		3	12.63	g
	2	3.80	b		2	2.67	d	TR3	1	3.34	c	TE2	1	2.05	c		2	8.86	g		4	9.67	g
1,8d	1	2.83	a		3	3.84	e		2	3.84	d		2	3.00	d		3	11.12	g				
	2	3.40	b						3	4.50	e		3	3.80	e								

[a] Common parameters: (a) $E = -0.252$; (b) $E = -0.090$; (c) $E = -0.07$; (d) $E = 0.04$; (e) $E = 0.15$; (f) $E = -0.54$, $i = 1$; and (g) $E = -0.81i$, $i = 2-4$.

Table 5. Empirical Parameters of Eqs 2a and b for the Dependence of Enthalpies of Protonation in $NaCl_{(aq)}$ at 25 °C

	c_1	c_2	e_1	ϵ^a
diamines	−0.373	2.004	0.0106	0.42
triamines[b]	−0.213	1.791	0.0313	0.70
di- and triamines[c]	−0.258	1.816	0.0510	0.57
di- and triamines[d]	−0.27	1.86	0.025	0.8
(fully) substituted amines	0.119	3.215	−0.364	0.9

[a] Mean deviation. [b] Unsubstituted and partially substituted triamines. [c] Unsubstituted di- and triamines. [d] As before and partially unsubstituted triamines.

for the same protonation step, for similar amines, the values of *C* are quite similar. As observed in Figure 1, quadratic terms (empirical coefficients *E*) are quite low for unsubstituted amines. An attempt was made to rationalize the *I* dependence for homogeneous groups of amines using eqs 2a and 2b; numerical results are reported in Table 5. The mean deviation observed by considering several amines and protonation steps is quite low, particularly for unsubstituted di- and triamines, indicating the possibility of using a few empirical predictive equations for estimating the protonation thermodynamic parameters of many other amines. Within a single class of amines, other parameters can be taken into account to give general class empirical parameters; for example, for diamines $NH_2-(CH_2)_n-NH_2$, equations can be obtained as a function of *n*, as previously reported.[20]

Dependence on Ionic Strength According to Pitzer Equation. The dependence on ionic strength of the thermodynamic parameters can be taken into account using different models. The simplest equation is eq 2, i.e., a polynomial expression. Among others, the most popular equations are those related to the SIT (specific interaction theory), which has been used mostly for the dependence on ionic strength of protonation and metal complex formation constants, and the Pitzer equations, also widely used for other thermodynamic parameters (ΔH, ΔC_p, ΔV).

In the past two decades, many laboratories have contributed to the implementation of a large database of Pitzer interaction coefficients obtained from different experimental data.[26−32] The present calorimetric data were analyzed using eq 8, i.e., the derivative of simplified eq 6. Empirical parameters P_1, P_2, and P_3, obtained from potentiometric data, were already reported,[21] and their temperature gradients are given here in Tables 6−8. Calculations were performed in different ways: by considering that the gradients are fairly similar for homogeneous classes of amines, we tried, by successive constraints, to obtain parameters valid for all of the amines in a class. For example, for the second protonation step of unsubstituted or partially substituted triamines, we followed the procedure: (i) calculation of $\partial P_1/\partial T$, $\partial P_2/\partial T$, and $\partial P_3/\partial T$ separately for all of the triamines (mean deviation from experimental data $\epsilon = 0.08$); (ii) calculation of $\partial P_1/\partial T$ and $\partial P_3/\partial T$ for each amine and of $\partial P_2/\partial T$ constrained to be equal for all of the amines considered ($\epsilon = 0.10$); (iii) calculation of $\partial P_1/\partial T$ with constraints for $\partial P_2/\partial T$ and $\partial P_3/\partial T$ ($\epsilon = 0.18$); and (iv) calculation with all gradients constrained ($\epsilon = 0.34$). From Table 2, we see that errors in ΔH_2 range from 0.2 to 1.2 (≥95% confidence intervals), and therefore, even the last approximation obtained by constraining all temperature gradients can be considered satisfactory. In particular, we note that the very low mean deviation observed for separate calculations of the gradients ($\epsilon = 0.08$) can be attributed to overparametrization.

For the other amines studied in this work (diamines and fully substituted di-, tri-, and tetraamines) and for the other protonation steps, analogous considerations can be made. General equations can be implemented for a single class of amines by taking other parameters into account. As an example, for diamines $NH_2-(CH_2)_n-NH_2$, we can express $\partial P_1/\partial T$ as a function of *n* for both ΔH_1 and ΔH_2. In this case, we have, for ΔH_1, $\partial P_1/\partial T = 10^{-4}(4.65 + 0.59n)$ with $\epsilon = 0.25$ and, for ΔH_2, $\partial P_1/\partial T = 10^{-4}(1.62-0.23n)$ with $\epsilon = 0.15$. In turn, these equations give a relationship between the gradient and log *P* (*P* = partition coefficient octanole/water), because there is a perfect correlation between *n* and log *P*.

Enthalpy Changes for the Interaction of Cl^- with Polyammonium Cations. The dependence of ΔH of protonation on ionic strength can be interpreted in terms of enthalpy change contributions due to the binding of chloride anions by polyammonium cations. In a series of papers dealing with the dependence on ionic strength of protonation and metal complex formation constants, we tried to find the empirical parameters of a Debye−Hückel-type equation and, in some cases, their temperature gradients when the most significant interactions are taken into consideration. This means, for example, that, for O ligands alkali metal cation complexes must also be taken into account[33] and, for polyammonium cations, the formation of Cl^- (or other monoanion) complexes must be considered. In these studies,[18−21] we found that, for $I \leq 1$ mol dm^{-3}, the dependence on *I* of ΔH values is very low, and some empirical equations have been reported for both $\Delta H = f(I)$ and $\partial C/\partial T$ (*C* = parameter for the dependence on *I* of the formation constants). The *I* gradients for the protonation of amines in $NaCl_{(aq)}$ are significantly higher, and the differences can be interpreted in terms of chloride−polyammonium cation complex formation. Formation constants have been reported previously, and here, we calculate enthalpy changes for these weak complexes. In Table 9, we report ΔH values for the formation of $AClH_i^{(i-1)+}$, together with ΔG and $T\Delta S$, at infinite dilution. The values of ΔH and $T\Delta S$ are quite low and very similar for all of the amines here considered. In particular, the small differences observed in ΔG between substituted and unsubstituted amines[20] (in favor of substituted ones) are

Table 6. Parameters for the Dependence on Ionic Strength of Enthalpies of Protonation of Unsubstituted Diamines at 25 °C Using the Simplified Pitzer Equation (Eq 8)

amine	$\partial P_1/\partial T \times 10^4$	$\partial P_2/\partial T \times 10^4$	$\partial P_3/\partial T \times 10^3$	ϵ[a]	amine	$\partial P_1/\partial T \times 10^4$	$\partial P_2/\partial T \times 10^4$	$\partial P_3/\partial T \times 10^3$	ϵ[a]
		ΔH_1					ΔH_2		
1,2d	−8.64	–	−1.53	0.18	1,2d	3.89	−5.29	−7.01	0.10
1,6d	−7.66	–	−3.39		1,6d	−3.57	−3.00	−5.39	
1,8d	−8.57	–	−3.23		1,8d	5.68	−6.01	−7.04	
1,10d	−9.47	–	−4.01		1,10d	7.60	−6.44	−7.13	
1,2d	−6.11	–	−3.14[b]	0.22	1,2d	0.22	−3.74[b]	−6.07	0.11
1,6d	−7.93	–			1,6d	−1.19		−6.11	
1,8d	−8.73	–			1,8d	0.35		−5.64	
1,10d	−11.14	–			1,10d	1.40		−5.56	
A[c]	−8.01[b]	–	−3.31[b]	0.38	1,2d	−0.61	−3.49[b]	−0.574[b]	0.12
					1,6d	−2.10			
					1,8d	0.21			
					1,10d	1.40			
					A[c]	4.06	−5.6[b]	−6.80[b]	0.25

[a] Mean deviation on the fit of eq 8. [b] Common parameter for all the amines. [c] Calculations performed by considering the amines altogether.

Table 7. Parameters for the Dependence on Ionic Strength of Enthalpies of Protonation of Unsubstituted and Partially Substituted Triamines at 25 °C Using the Simplified Pitzer Equation (Eq 8)

amine	$\partial P_1/\partial T \times 10^3$	$\partial P_2/\partial T \times 10^4$	$\partial P_3/\partial T \times 10^3$	ϵ[a]	amine	$\partial P_1/\partial T \times 10^3$	$\partial P_2/\partial T \times 10^4$	$\partial P_3/\partial T \times 10^3$	ϵ[a]	amine	$\partial P_1/\partial T \times 10^3$	$\partial P_2/\partial T \times 10^4$	$\partial P_3/\partial T \times 10^3$	ϵ[a]
		ΔH_1					ΔH_2					ΔH_3		
TR1	−0.88	–	−1.83	0.075	TR1	0.44	−4.5	−7.24	0.084	TR1	0.32	−5.8	−12.0	0.16
TR2	−1.06	–	−1.36		TR2	−0.44	−3.4	−5.10		TR2	−0.42	−2.6	−10.7	
TR3	−2.34	–	1.24		TR3	−0.33	0.5	−6.00		TR3	0.74	−4.9	−13.1	
TR4	−0.65	–	−1.83		TR4	0.54	−6.6	−7.34		TR4	0.46	−10.1	−12.4	
TE2	−1.10	–	−0.92		TE2	−0.28	−2.8	−5.27		TE2	0.26	−3.9	−11.2	
TR1	−1.02	–	−1.05[b]	0.13	TR1	0.13	−3.1[b]	−6.48	0.10	TR1	−0.12	−3.9[b]	−10.9	0.18
TR2	−1.10	–			TR2	−0.54		−4.77		TR2	0.05		−12.3	
TR3	−1.93	–			TR3	0.50		−8.10		TR3	0.52		−12.6	
TR4	−0.79	–			TR4	−0.27		−5.19		TR4	−0.98		−8.7	
TE2	−1.08	–			TE2	−0.15		−5.66		TE2	0.22		−11.2	
A[c]	−1.07	–	−1.31	0.52	TR1	0.24	−3.9[b]	−6.54[b]	0.18	TR1	−0.14	−3.5[b]	−11.1[b]	0.24
					TR2	−0.17				TR2	−0.19			
					TR3	0.31				TR3	0.20			
					TR4	0.07				TR4	−0.61			
					TE2	0.12				TE2	0.13			
					A[c]	0.44	−5.5	−7.30	0.34	*A*[c]	−0.24	−2.8	−10.9	0.60

[a−c] See footnotes of Table 6.

Table 8. Parameters for the Dependence on Ionic Strength of Enthalpies of Protonation of Fully Substituted Amines at 25 °C Using the Simplified Pitzer Equation (Eq 8)

amine	$\partial P_1/\partial T \times 10^3$	$\partial P_2/\partial T \times 10^3$	$\partial P_3/\partial T \times 10^3$	ϵ[a]	amine	$\partial P_1/\partial T \times 10^3$	$\partial P_2/\partial T \times 10^3$	$\partial P_3/\partial T \times 10^3$	ϵ[a]
		ΔH_1					ΔH_3		
1,2ds	−1.16	–	−4.02	0.13	TR6	−0.96	1.26	−13.4	0.16
TR6	−0.78	–	−4.63		TE1	12.1	−10.5	−38.2	
TE1	−1.80	–	−1.23		TR6	−0.86	1.22	−13.7	0.20
1,2ds	−1.15	–	−4.12[b]	0.16	TE1	−0.05		−15.2	
TR6	−0.88	–			TR6	−0.66	1.13	−14.2	0.20
TE1	−0.89	–			TE1	−0.81			
A[c]	−1.14	–	−3.42	0.25	*A*[c]	−0.56	1.12	−14.8	0.21
		ΔH_2					ΔH_4		
1,2ds	−2.08	0.56	−5.40	0.07	TE1	7.83	0	−30.0	0.22
TR6	−2.72	0.97	−5.10						
TE1	−0.43	−0.77	−11.17						
1,2ds	−2.25	0.63	−4.97	0.08					
TR6	−1.92		−7.16						
TE1	−19.4		−8.44						
1,2ds	−1.69	0.48	−7.13	0.16					
TR6	−1.74								
TE1	−2.28								
A[c]	−1.47	0.44	−8.32	0.23					

[a−c] See footnotes of Table 6.

compensated by ΔH differences (in favor of unsubstituted ones), and the $T\Delta S$ values are pratically equal (within experimental errors) and linearly dependent on i (reaction $AH_i^{i+} + Cl^- = AClH_i^{(i-1)+}$), according to the relation

$$T\Delta S = -7.7 + 5.5i \tag{12}$$

Table 9. Thermodynamic Parameters for the Formation of $AClH_i^{(i-1)+}$ Species[a] at $I = 0$ mol kg^{-1} and $t = 25$ °C

amine	i	ΔG^b	$\Delta H \pm 3\sigma^{b,c}$	$T\Delta S^b$	amine	i	ΔG^b	$\Delta H \pm 3\sigma^{b,c}$	$T\Delta S^b$	amine	i	ΔG^b	$\Delta H \pm 3\sigma^{b,c}$	$T\Delta S^b$
1,2d	1	1.2	−1.0 ± 0.6	−2	TR1	1	0	−1.4 ± 0.3	−1	TR6	1	−0.5	−4 ± 1	−4
	2	−3.4	0.9 ± 0.3	4		2	−4.0	0.6 ± 0.2	5		2	−5.7	−3.7 ± 0.6	2
1,6d	1	1.2	−1.2 ± 0.6	−2		3	−8.0	1.0 ± 0.2	9		3	−9.4	−2.5 ± 0.6	7
	2	−4.0	0.4 ± 0.2	4	TR2	1	0.6	0 ± 1	0	TE1	1	−0.6	−2.5 ± 1.8	−2
1,8d	1	1.1	−1.8 ± 0.6	−3		2	−4.0	1.4 ± 0.3	5		2	−5.7	−3.3 ± 0.6	2
	2	−3.4	0.6 ± 0.3	4		3	−8.0	1.4 ± 0.3	9		3	−10.8	−2.8 ± 0.6	8
1,10d	1	1.4	−3 ± 1	−5	TR3	1	1.7	−0.6 ± 1	−2	TE2	1	1.7	−7.2 ± 0.6	−9
	2	−3.5	1.8 ± 0.6	5		2	−4.0	0.1 ± 0.3	4		2	−4.0	−1.6 ± 0.2	2
1,2ds	1	−1.1	−2.6 ± 0.3	−2		3	−8.5	0.7 ± 0.3	9		3	−7.7	−1.0 ± 0.2	7
	2	−5.7	−2.5 ± 0.2	3	TR4	1	0	−1.1 ± 0.9	−1					
						2	−4.6	1.5 ± 0.3	6					
						3	−8.0	1.0 ± 0.3	9					

[a] Reaction: $AH_i^{i+} + Cl^- = AClH_i^{(i-1)+}$. [b] Expressed in kJ mol^{-1}. [c] σ = standard deviation.

(linear correlation coefficient, $r = 0.93$), valid at $I = 0$ mol kg^{-1} and $t = 25$ °C.

Literature Comparisons. Few papers on the thermodynamic parameters (particularly from direct calorimetric measurements) for the protonation of amines can be found in the literature,[3−21] and to our knowledge, no systematic study at different ionic strengths over a wide NaCl concentration range has been reported. For example, Martell and Smith[4] reported enthalpies of protonation of linear diamines $NH_2-(CH_2)_n-NH_2$ ($n = 2-6$) and of *N*-alkyl-substituted di-, tri-, and tetraamines (1,2ds, TR6, and TE2), but the data often refer to a single ionic strength value. The agreement between our data and literature data is good. For example, we previously found[4] $\Delta H_1 = -30.0$ kJ mol^{-1} and $\Delta H_2 = -27.0$ kJ mol^{-1} for 1,2ds at $I = 0.5$ (our current values are −31.1 and −27.6 kJ mol^{-1}, respectively). Moreover, the values of ΔH reported in the literature follow the same trends described in the section describing general features of protonation thermodynamic parameters in this paper. For example, a marked effect can be observed for the *N*-alkyl substitution (ΔH substituted > ΔH unsubstituted) and a general decreasing effect on ΔH for increasing ionic strength.

Final Remarks

The findings of this work can be summarized as follows:

(a) Thermodynamic parameters for the protonation of polyamines are very similar for homogeneous classes (*N*-alkyl-substituted and unsubstituted), and rough equations can be written as a function of the protonation step (eqs 9 and 10) without taking into account the dependence on ionic strength or considering the *I* variation (eq 11).

(b) The shape of the function $\Delta H = f(I)$ is quite different for the protonation of substituted and unsubstituted amines (Figure 1).

(c) Two models have been used to express the function $\Delta H = f(I)$ for each amine and protonation step, namely, a simple polynomial equation (eq 2) and the Pitzer equation. In both cases, we found that empirical parameters are very similar for each class of amines, and we report common parameters (Tables 4−8).

(d) An attempt was made to calculate thermodynamic parameters for the binding of Cl^- by polyammonium cations (Table 9). The entropic term can be expressed for all of the amines by a simple linear function of the protonation step (eq 12).

Acknowledgment

We thank MIUR (Ministero dell'Istruzione, dell'Università e della Ricerca) for financial support.

Literature Cited

(1) Bremmer, J. M. In *Soil Biochemistry*; McLaren, A. D., Peterson, G. H., Eds.; Marcel Dekker: New York, 1967; Vol. 1, Chapter 2.

(2) Stevenson, F. J.; Bultler, J. H. A. In *Organic Geochemistry*; Eglinton, G., Murphy, M. T. J., Eds.; Springer-Verlag: Berlin, 1969; Chapter 22.

(3) Pettit, L.; Powell, K. *The IUPAC Stability Constants Data Base*; Academic Software: Lexington, KY, 1997.

(4) Martell, A. E.; Smith, R. M.; Motekaitis, R. J. *Critically Selected Stability Constants of Metal Complexes Database*, version 4.0; NIST: Gaithersburg, MD, 1997.

(5) Murray, K.; May, P. M. *Joint Expert Speciation System*; Jess Primer: Murdoch, Western Australia, 2000

(6) Christensen, J. J.; Hansen, L. D.; Izatt, R. M. *Handbook of Proton Ionization Heats*; Wiley: New York, 1976.

(7) Sóvágó, I.; Gergely, A. Effects of Steric Factors on the Equilibrium and Thermodynamic Conditions of Mixed Ligand Complexes of the Copper(II) Ion with Diamines. *Inorg. Chim. Acta* **1976**, *20*, 27−32.

(8) Yperman, J.; Mullens, J.; François, J.-P.; Van Poucke, L. C. Calorimetric and Potentiometric Investigation of Diethylenetriamine and Its *N*-Methyl-Substituted Derivatives in Aqueous Solution. *J. Phys. Chem.* **1982**, *86*, 238−303.

(9) Vacca, A.; Arenare, D.; Paoletti, P. Transition Metal Complexes of 3,3′-Diaminodipropylamine: Stability Constants. *Inorg. Chem.* **1966**, *5*, 1384−1389.

(10) Paoletti, P.; Nuzzi, F.; Vacca, A. Thermochemical Studies. Part XVII. Heats and Entropies of Reaction of 3,3′-Diaminodipropylamine with Protons and Bivalent Transition Metal Ions. *J. Chem. Soc. A* **1966**, 1385−1391.

(11) Dazzi, E.; Falqui, M. Equilibria in Solution between 3,3-diaminodipropylamine and Cd^{2+}, Zn^{2+}, Cu^{2+} and Ag^{2+} ions. *Gazz. Chim. Ital.* **1974**, *104*, 589−597.

(12) Goldberg, D.; Fernelius, W. Formation Constants of Methylbis-(3-aminopropyl)amine with Copper, Nickel, and Cadmium Ions. *J. Phys. Chem.* **1959**, *63*, 1328−1330.

(13) Bertsch, C.; Fernelius, W.; Block, B. A Thermodynamic Study of Some Complexes of Metal Ions with Polyamines. *J. Phys. Chem.* **1958**, *62*, 444−450.

(14) Christensen, J. J.; Izatt, R. M.; Wrathall, D. P.; Hansen, L. D. Thermodynamics of Proton Ionization in Dilute Aqueous Solution. Part XI. p*K*, $\Delta H°$, and $\Delta S°$ Values for Proton Ionization from Protonated Amines at 25°. *J. Chem. Soc. A* **1969**, 1212−1223.

(15) Hedwig, G.; Powell, H. K. J. Thermodynamics of Complex Formation of 1,5,8,12-Tetra-azadodecane with Copper(II) Ions and Protons in Aqueous Solution. *J. Chem. Soc., Dalton Trans.* **1973**, 793−797.

(16) Barbucci, R.; Fabbrizzi, L.; Paoletti, P. Thermodynamics of Complex Formation of Aliphatic Linear Tetra-amines. $\Delta H°$, and $\Delta S°$ for the Reactions of 1,5,9,13-Tetra-azatridecane with Protons and Some Bivalent Transition Metal Ions. *J. Chem. Soc., Dalton Trans.* **1972**, 745−749.

(17) Casale, A.; Foti, C.; Sammartano, S.; Signorino, G. Thermodynamic Parameters for the Protonation of Some Polyamines $C_{(2n-2)}N_nH_{(5n-2)}$ in NaCl Aqueous Solution at Different Ionic Strengths. *Ann. Chim. (Rome)* **1998**, *88*, 55−70.

(18) Cascio, S.; De Robertis, A.; Foti, C. Protonation of Diamines $H_2N-(CH_2)_n-NH_2$ ($n = 2-10$) in NaCl Aqueous Solution at Different Ionic Strengths. *J. Chem. Eng. Data* **1999**, *44* (4), 735−738.

(19) Cascio, S.; De Robertis, A.; Foti, C. Protonation of polyamines in NaCl aqueous solution and binding of Cl^- by polyammonium cations. *Fluid Phase Equilib.* **2000**, *170*, 167−181.

(20) De Stefano, C.; Foti, C.; Giuffrè, O. Medium effects on the protonation enthalpies of linear diamines in NaCl aqueous solutions at 25 °C. *Thermochim. Acta* **2000**, *363*, 29−35.

(21) De Robertis, A.; Foti, C.; Giuffrè, O.; Sammartano, S. Dependence on ionic strength of polyamine protonation in NaCl aqueous solution. *J. Chem. Eng. Data* **2001**, *46*, 1425−1435.

(22) De Robertis, A.; De Stefano, C.; Rigano, C. Computer Analysis of Equilibrium Data in Solution. ES5CM Fortran and Basic Programs for Computing Formation Enthalpies from Calorimetric Measurements. *Thermochim. Acta* **1989**, *138*, 141−146.

(23) De Stefano, C.; Sammartano, S.; Mineo, P.; Rigano, C. *Computer Tools for the Speciation of Natural Fluids. In Marine Chemistry—An Environmental Analytical Chemistry Approach*; Gianguzza, A., Pellizzetti, E., Sammartano, S., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997; pp 71−83.

(24) De Stefano, C.; Foti, C.; Giuffrè, O.; Sammartano, S. Dependence on ionic strength of protonation enthalpies of polycarboxylic anions in NaCl aqueous solution. *J. Chem. Eng. Data* **2001**, *46*, 1417−1424.

(25) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.

(26) Millero, F. J.; Hawke, D. J. Ionic interactions of divalent metals in natural waters. *Mar. Chem.* **1992**, *40*, 19−48 and references therein.

(27) Millero, F. J.; Roy, R. N. A chemical equilibrium model for the carbonate system, in natural waters. *Croat. Chem. Acta* **1997**, *70*, 1−38, and references therein.

(28) Alonso, P.; Barriada, J. L.; Rodríguez, P.; Brandariz, I.; Sastre de Vicente, M. E. Acid−Base Equilibrium Constants for Glycine in $NaClO_4$, KCl, and KBr at 298 K. Dependence on Ionic Strength. *J. Chem. Eng. Data* **1998**, *43*, 876−879 and references therein.

(29) Barriada, J. L.; Brandariz, I.; Sastre de Vicente, M. E. Acid−Base Equilibria of Monocarboxylic Acids in Various Saline Media: Analysis of Data Using Pitzer Equations. *J. Chem. Eng. Data* **2000**, *45*, 1173−1178 and references therein.

(30) De Robertis, A.; De Stefano, C.; Foti, C. Medium Effects on the Protonation of Carboxylic Acids at Different Temperatures. *J. Chem. Eng. Data* **1999**, *44*, 262−270 and references therein.

(31) Foti, C.; Gianguzza, A.; Piazzese, D.; Trifiletti, G. Inorganic speciation of organotin(IV) cations in natural waters with particular references to seawater. *Chem. Spec. Bioavail.* **2000**, *12*, 41−52 and references therein.

(32) De Stefano, C.; Foti, C.; Gianguzza, A.; Sammartano, S. The interaction of amino acids with the major constituents of natural waters at different ionic strengths. *Mar. Chem.* **2000**, *72*, 61−76 and references therein.

(33) Daniele, P. G.; De Stefano, C.; Prenesti, E. Sammartano, S. Weak Complex Formation in Aqueous Solution. *Curr. Top. Sol. Chem.* **1994**, *1*, 95−106 and references therein.

Received for review February 25, 2002. Accepted May 16, 2002.

JE020040D