J. Chem. Eng. Data **2001,** *46,* 1425−1435

Dependence on Ionic Strength of Polyamine Protonation in NaCl Aqueous Solution

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The protonation constants of several *N*-alkyl-substituted and unsubstituted polyamines (eight diamines, eight triamines, and four tetraamines) were determined at different ionic strengths in NaCl aqueous solutions and at 25 °C by potentiometric measurements. For the dependence on ionic strength of protonation constants two approaches were used: a Debye−Hückel type equation and Pitzer equations. The empirical parameters calculated for the two models are very similar for the same class of amines, that is, *N*-alkyl-substituted, partially substituted, and unsubstituted. Therefore, some general parameters and relationships that have quite good predictive value were obtained. A number of literature protonation constants were also examined in $NaClO_4$ at different ionic strengths using the same procedure and gave results similar to those obtained in this work. The general tertiary > secondary > primary amino group trend was observed for the dependence on ionic strength of protonation constants. The formation of polyammonium cation−Cl^- ion pairs was considered in the range $0 < I/\text{mol L}^{-1} \le 1$, and the relative formation constants are reported.

Introduction

The reason amines excite such interest is because of their importance in several fields:[1−4] medicine, biochemistry, food conservation, industrial applications, and speciation studies. In the medical field, an excess of amines in biological tissues and fluids can be an indicator of disease; in particular, measuring bioamine concentrations in extracellular fluids is a useful way of evaluating the efficacy of cancer therapies.[1] In biochemistry, polyamines are of primary importance because they are present in the cells of animal organisms and microorganisms and contribute to the stabilization of the structure and activity of tRNA and DNA.[2] The interaction of spermine and spermidine polyamines with DNA is demonstrated by the fact that they offer marked protection against the heat denaturation of DNA; the temperature at which DNA denaturation occurs is markedly increased by the addition of very low concentrations of amines.[3] In foodstuffs, bioamine concentrations are an indicator of freshness and efficient preservation, because bioamine synthesis is determined by the decarboxylation of either enzymatic or microbial amino acids.[4] Amines are employed industrially in the manufacture of corrosion inhibitors and scale removers, and aminic derivatives are widely used in pharmaceutics.

Amines are present as trace components in all biological fluids and natural waters, and for this reason the effect of salt on protonation constants is very important in speciation studies. Open-chain polyamines in particular have been widely studied owing to their ability (in their protonated form) to bind organic and inorganic polyanions.

Several authors have studied the dependence on ionic strength of the protonation constants of polyamines in different ionic media ($NaClO_4$, NaCl, $NaNO_3$, KNO_3, and KCl),[5−10] and in particular some Finnish authors have published extensive data on these compounds in aqueous solution, mainly in $NaClO_4$ medium, at different ionic strengths.[11−22] Other Finnish papers describe the protonation of aminoalkanols in $NaClO_4$ aqueous solution.[23−29] The protonation mechanism of polyamines has been described by some authors, in particular using NMR measurements.[30−32]

We have carried out a systematic investigation mainly of linear polyamines at different ionic strengths in NaCl medium because this salt is present in almost all natural and biological fluids.[33−41] In some of these papers,[40,41] the effect of *N*-alkyl substitution and the interactions of different protonated species with Cl^- were also studied.

Here we describe a potentiometric study (H^+-glass electrode) of the protonation of seven unsubstituted diamines, eight unsubstituted and partially substituted triamines, four tetraamines, and three fully substituted amines at 25 °C and $0 \le I \le 5$ mol L^{-1} in NaCl aqueous solutions. The amines were chosen to evaluate the influence of *N*-alkyl substitution and methylenic chain length on the basicity of amino groups. Table 1 shows formulas and abbreviations for the amines considered in this work. Several data from previous works[16,33−35,39,40] were used (in general at $I \le 1$ mol L^{-1}), and in this work new measurements ($I > 1$ mol L^{-1}) and new calculations were performed. Different models were used for dependence on medium (Debye−Hückel and Pitzer type equations), and our own and literature data were analyzed together for predictive purposes.

Experimental Section

Materials. Amine hydrochlorides (Fluka, Sigma, or Aldrich products) were used without further purification, and their purities, checked alkalimetrically, were found to be >99%. Sodium chloride solutions were prepared by weighing pure salt (Fluka, p.a.) previously dried in an oven

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10.1021/je010143g CCC: \$20.00

Table 1. Amines Considered in This Work

amine	name	symbol	I_{max}	ref
$H_2N-(CH_2)_2-NH_2$	ethylenediamine	*1,2d*	3	*33*, this work
$H_2N-(CH_2)_3-NH_2$	1,3-diaminopropane	*1,3d*	1	39, this work
$H_2N-(CH_2)_4-NH_2$	1,4-diaminobutane	*1,4d*	1	39, this work
$H_2N-(CH_2)_5-NH_2$	1,5-diaminopentane	*1,5d*	1	39, this work
$H_2N-(CH_2)_6-NH_2$	1,6-diaminohexane	*1,6d*	5	39, this work
$H_2N-(CH_2)_8-NH_2$	1,8-diaminooctane	*1,8d*	3	39, this work
$H_2N-(CH_2)_{10}-NH_2$	1,10-diaminodecane	*1,10d*	3	39, this work
$(CH_3)_2N-(CH_2)_2-N(CH_3)_2$	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine	*1,2ds*	3	16, 40, this work
$H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$	diethylenetriamine	*dien*	1	34, this work
$H_2N-(CH_2)_3-NH-(CH_2)_4-NH_2$	*N*-(3-aminopropyl)-1,4-diaminobutane	*spd*	4.5	this work
$H_2N-(CH_2)_3-NH-(CH_2)_3-NH_2$	bis(3-aminopropyl)amine	*TR1*	3	40, this work
$H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$	bis(6-aminohexyl)amine	*TR2*	5	40, this work
$H_2N-(CH_2)_4-CH(CH_2-NH_2)-(CH_2)_3-NH_2$	4-(aminomethyl)-1,8-diaminoctane	*TR3*	3	40, this work
$H_2N-(CH_2)_3-N(CH_3)-(CH_2)_3-NH_2$	3,3′-diamino-*N*-methyldipropylamine	*TR4*	3	40, this work
$(CH_3)NH-(CH_2)_6-N(CH_3)-(CH_2)_6-NH(CH_3)$	*N*,*N*′,*N*″-trimethylbis(hexamethylene)triamine	*TR5*	1	40, this work
$(CH_3)_2N-(CH_2)_2-N(CH_3)-(CH_2)_2-N(CH_3)_2$	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine	*TR6*	3	40, this work
$H_2N-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH_2$	triethylenetetramine	*trien*	1	35, this work
$H_2N-(CH_2)_3-NH-(CH_2)_4-NH-(CH_2)_3-NH_2$	*N*-(3-aminopropyl)-1,4-diaminobutane	*sper*	1	35, this work
$(CH_3)_2N-(CH_2)_2\text{-}[N(CH_3)-(CH_2)_2]_2-N(CH_3)_2$	1,1,4,7,10,10-hexamethyltriethylenetetramine	*TE1*	1	40, this work
$N(CH_2CH_2NH_2)_3$	tris(2-aminoethyl)amine	*TE2*	5	40, this work
$H_2N-CH_2-CH(NH_2)\text{-}CH_3$	1,2-diaminopropane	*D1*	1	15
$H_2N-(CH_2)_2-CH(NH_2)\text{-}CH_3$	1,3-diaminobutane	*D2*	2	20
$[(CH_3)_2CH]HN-CH_2-CH(CH_3)(NH_2)\text{-}CH_3$	*N*-isopropyl-2-methyl-1,2-propanediamine	*D3*	2	12
$(CH_3)HN-(CH_2)_3-NH(CH_3)$	*N*,*N*′-dimethyl-1,3-propanediamine	*D4*	2	13
$H_2N-(CH_2)_3-N[(CH_2)_3CH_3]_2$	*N*,*N*-dibutyl-1,3-propanediamine	*D5*	2	13
$(CH_3)HN-(CH_2)_2-N(CH_2-CH_3)_2$	*N*,*N*-diethyl-*N*′-methylethylenediamine	*D6*	2	16
$H_2N-(CH_2)_2-NH(CH_3)$	*N*-methylethylenediamine	*D7*	2	18
$H_2N-(CH_2)_2-NH(CH_2-CH_3)$	*N*-ethylethylenediamine	*D8*	2	17
$(CH_3)HN-(CH_2)_2-NH(CH_3)$	*N*,*N*′-dimethylethylenediamine	*D9*	2	19
$(H_3C-H_2C)HN-(CH_2)_2-NH(CH_2-CH_3)$	*N*,*N*′-diethylethylenediamine	*D10*	2	22
$H_2N-(CH_2)_2-N(CH_2-CH_3)_2$	*N*,*N*-diethylethylenediamine	*D11*	2	21
$(CH_3)_2N-(CH_2)_3-N(CH_3)_2$	*N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine	*D12*	2	14
$(CH_3-CH_2)_2N-(CH_2)_2-N(CH_2-CH_3)_2$	*N*,*N*,*N*′,*N*′-tetraethylenediamine	*D13*	2	11
$(CH_2-CH_2OH)_2N-(CH_2)_2-N(CH_2-CH_2OH)_2$	*N*,*N*,*N*′,*N*′-tetra(2-hydroxyethyl)ethylenediamine	*A1*	2	23
$H_2N-(CH_2)_3-N(CH_2-CH_2OH)_2$	*N*,*N*-di(2-hydroxyethyl)-1,3-propanediamine	*A2*	2	24
$H_2N-CH_2-CH(OH)\text{-}CH_2-NH_2$	2-hydroxy-1,3-propanediamine	*A3*	2	25
$H_2N-(CH_2)_3-NH(CH_2-CH_2OH)$	1,3-diamino-*N*-(*β*-hydroxyethyl)propane	*A4*	2	26
$H_2N-(CH_2)_2-NH(CH_2-CH_2OH)$	*N*-(2-hydroxyethyl)ethylenediamine	*A5*	2	27

at 110 °C. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated ampules (Fluka). Solutions of acid and hydroxide were standardized against dried sodium carbonate and potassium hydrogen phthalate, respectively. All solutions were prepared with analytical grade water, using grade A glassware.

Apparatus. Potentiometric measurements were made using an apparatus consisting of a Metrohm model 713 potentiometer equipped with an Orion combination glass electrode (Ross type 8102) and a Metrohm model 654 motorized buret. The estimated accuracies were ±0.15 mV and ±0.003 cm^3 for emf and titrant volume readings, respectively. The apparatus was connected to a personal computer, and automatic titrations were carried out using a suitable computer program (titrant delivery, data acquisition, check for emf stability). All titrations were carried out by stirring magnetically and by bubbling purified and presaturated N_2 through the solution, in order to exclude O_2 and CO_2. Measurements were performed in thermostated cells, at (25 ±0.1) °C.

Procedure. Twenty-five milliliters of the solution containing the amine under study (5−10 mmol L^{-1}), a small excess of HCl (10 mmol L^{-1}), and the background salt (NaCl: $0.1 \leq I \leq 5$ mol L^{-1}) was titrated with standard NaOH solution up to 80−90% neutralization. For each experiment, independent titration of a hydrochloric acid solution with standard NaOH under the same ionic strength conditions as the systems under investigation was carried out to determine electrode potential ($E°$).

Calculations. The following computer programs were used to perform calculations: ESAB2M, to calculate the purity of the reagents and to refine all of the parameters related to the calibration of the electrode system; BSTAC and STACO, to calculate protonation constants; LIANA, to test the dependence of log K on ionic strength using different equations; ES2WC, to calculate weak Cl$^-$ complex formation constants. Details of the computer programs have already been published.[42]

Models for Dependence on Ionic Strength. Amine protonation constants are expressed as K^H or β^H according to the reactions:

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

$$A^0 + iH^+ = H_iA^{i+} \qquad \beta_i^H = \prod_{i=1}^{n} K_i^H \tag{2}$$

The dependence on ionic strength of protonation constants was taken into account using a Debye−Hückel type equation (DHT) and Pitzer equations.

DHT Equation. Over the past decade we have made extensive studies of the dependence on ionic strength of protonation constants and of metal complex formation constants[43] using the DHT equation

$$\log K = \log {}^{T}K - z^*I^{1/2}(2 + 3I^{1/2})^{-1} + CI + DI^{3/2} + EI^2 \tag{3}$$

where

$$z^* = \Sigma\,(\text{charges})^2_{\text{reactants}} - \Sigma\,(\text{charges})^2_{\text{products}}$$

Table 2. Protonation Constants of Unsubstituted Diamines at Different Ionic Strengths (NaCl), at 25 °C

amine[a]	I/mol L^{-1}	log $\beta_1 \pm 3s^b$	log $\beta_2 \pm 3s^b$
1,2d	0	9.90 ± 0.02	16.77 ± 0.01
	0.1	9.94 ± 0.02	17.04 ± 0.01
	0.25	9.99 ± 0.01	17.19 ± 0.01
	0.50	10.06 ± 0.01	17.36 ± 0.01
	0.75	10.13 ± 0.01	17.51 ± 0.01
	1.00	10.20 ± 0.01	17.65 ± 0.01
	1.50	10.33 ± 0.01	17.91 ± 0.01
	2.00	10.45 ± 0.01	18.17 ± 0.01
	2.50	10.58 ± 0.01	18.45 ± 0.01
	3.00	10.71 ± 0.01	18.74 ± 0.01
1,3d	0	10.48 ± 0.02	18.91 ± 0.01
	0.1	10.53 ± 0.01	19.21 ± 0.01
	0.25	10.58 ± 0.01	19.40 ± 0.01
	0.50	10.66 ± 0.01	19.63 ± 0.01
	0.75	10.74 ± 0.01	19.83 ± 0.01
	1.00	10.82 ± 0.01	20.00 ± 0.01
1,4d	0	10.54 ± 0.01	19.64 ± 0.02
	0.10	10.58 ± 0.01	19.90 ± 0.01
	0.25	10.62 ± 0.01	20.05 ± 0.01
	0.50	10.68 ± 0.01	20.23 ± 0.01
	0.75	10.73 ± 0.01	20.39 ± 0.01
	1.00	10.78 ± 0.01	20.53 ± 0.01
1,5d	0	10.80 ± 0.02	20.34 ± 0.02
	0.10	10.84 ± 0.01	20.64 ± 0.01
	0.25	10.89 ± 0.01	20.82 ± 0.01
	0.50	10.97 ± 0.01	21.04 ± 0.01
	0.75	11.04 ± 0.01	21.22 ± 0.01
	1.00	11.12 ± 0.01	21.37 ± 0.01
1,6d	0	10.90 ± 0.02	20.70 ± 0.01
	0.10	10.94 ± 0.01	20.99 ± 0.01
1,6d	0.25	10.98 ± 0.01	21.16 ± 0.01
	0.50	11.05 ± 0.01	21.36 ± 0.01
	0.75	11.12 ± 0.01	21.53 ± 0.01
	1.00	11.19 ± 0.01	21.68 ± 0.01
	1.50	11.31 ± 0.01	21.94 ± 0.01
	2.00	11.44 ± 0.01	22.19 ± 0.01
	2.50	11.56 ± 0.01	22.43 ± 0.01
	3.00	11.69 ± 0.01	22.67 ± 0.01
	4.00	11.93 ± 0.01	23.17 ± 0.01
	4.50	12.05 ± 0.01	23.44 ± 0.01
	5.00	12.17 ± 0.01	23.73 ± 0.01
1,8d	0	10.94 ± 0.02	20.90 ± 0.01
	0.10	10.98 ± 0.02	21.18 ± 0.01
	0.25	11.03 ± 0.02	21.34 ± 0.01
	0.50	11.10 ± 0.02	21.53 ± 0.01
	0.75	11.16 ± 0.02	21.69 ± 0.01
	1.00	11.23 ± 0.02	21.83 ± 0.01
	1.50	11.36 ± 0.01	22.09 ± 0.01
	2.00	11.49 ± 0.01	22.34 ± 0.01
	2.50	11.61 ± 0.01	22.59 ± 0.01
	3.00	11.74 ± 0.01	22.85 ± 0.01
1,10d	0	10.94 ± 0.01	20.99 ± 0.01
	0.10	10.98 ± 0.01	21.27 ± 0.01
	0.25	11.02 ± 0.01	21.42 ± 0.01
	0.50	11.09 ± 0.01	21.61 ± 0.01
	0.75	11.16 ± 0.01	21.76 ± 0.01
	1.00	11.22 ± 0.01	21.89 ± 0.01
	1.50	11.34 ± 0.01	22.13 ± 0.01
	2.00	11.46 ± 0.01	22.37 ± 0.01
	2.50	11.58 ± 0.01	22.60 ± 0.01
	3.00	11.70 ± 0.01	22.85 ± 0.01

[a] For abbreviations, see Table 1. [b] s = standard deviation.

(K = formation constant; ^TK = formation constant at infinite dilution; C, D, and E = empirical parameters). At $I < 1$ mol L^{-1}, parameter E can be neglected, and, in some cases, for $I < 2$ mol L^{-1}, only term D or E can be used. When all of the interactions ($K > 0.2$ mol^{-1} L) are taken into account, we have[43]

$$C = 0.1p^* + 0.20z^* \tag{3a}$$

$$D = -0.075z^* \tag{3b}$$

where $p^* = \Sigma\,(\text{moles})_{\text{reactants}} - \Sigma\,(\text{moles})_{\text{products}}$ Equation 3, using parameters shown in eqs 3a and 3b, for $0 \le I \le 1$ mol L^{-1}, is independent of the reactants and depends only on the charges involved in the formation reaction.

Pitzer Equations. According to the Pitzer equations,[44,45] for electrolytes 1-1, 1-2, and 2-1, the activity coefficients of cation M or anion X can be expressed by

$$\begin{aligned}\ln \gamma_{\text{M}} = {} & z_{\text{M}}^2 f^{\gamma} + 2\Sigma_{\text{a}}\, m_{\text{a}}(B_{\text{Ma}} + EC_{\text{Ma}}) + \\ & \Sigma_{\text{a}}\,\Sigma_{\text{c}}\, m_{\text{c}} m_{\text{a}}(z_{\text{M}}^2 B'_{\text{ca}} + z_{\text{M}} C_{\text{ca}}) + \\ & \Sigma_{\text{c}}\, m_{\text{c}}(2\Theta_{\text{Mc}} + \Sigma_{\text{a}}\, m_{\text{a}}\Psi_{\text{Mca}}) + \Sigma_{\text{a}}\,\Sigma_{\text{a}'}\, m_{\text{a}} m_{\text{a}'}\,\Psi_{\text{Maa}'}\end{aligned} \tag{4}$$

$$\begin{aligned}\ln \gamma_{\text{X}} = {} & z_{\text{X}}^2 f^{\gamma} + 2\Sigma_{\text{c}}\, m_{\text{c}}(B_{\text{Xc}} + EC_{\text{Xc}}) + \\ & \Sigma_{\text{a}}\,\Sigma_{\text{c}}\, m_{\text{c}} m_{\text{a}}(z_{\text{X}}^2 B'_{\text{ca}} + z_{\text{X}} C_{\text{ca}}) + \\ & \Sigma_{\text{a}}\, m_{\text{a}}(2\Theta_{\text{Xa}} + \Sigma_{\text{c}}\, m_{\text{c}}\Psi_{\text{Xca}}) + \Sigma_{\text{c}}\,\Sigma_{\text{c}'}\, m_{\text{c}} m_{\text{c}'}\Psi_{\text{Xaa}'}\end{aligned} \tag{4a}$$

and for neutral species

$$\ln \gamma_{\text{MX}^0} = 2\lambda I \tag{4b}$$

where m_i is the molality of the cation (c) and anion (a) in the solution, z the charge, E the equivalent molality ($E = {}^1\!/_2\Sigma_i\, m_i|z_i|$), I the ionic strength in molal scale, and

$$B_{\text{MX}} = \beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)}(2I)^{-1}f_1 \tag{5}$$

$$B'_{\text{MX}} = \beta_{\text{MX}}^{(1)}(2I^2)^{-1}f_2 \tag{5a}$$

$$C_{\text{MX}} = C_{\text{MX}}^{(\phi)}(2|z_{\text{M}}z_{\text{X}}|^{1/2})^{-1} \tag{5b}$$

$$f^{\gamma} = -0.392[I^{1/2}(1 + 1.2I^{1/2})^{-1} + 1.667\ \ln(1 + 1.2I^{1/2})] \tag{5c}$$

$$f_1 = 1 - (1 + 2I^{1/2})\exp(-2I^{1/2}) \quad (0 \le f_1 \le 1) \tag{5d}$$

$$f_2 = -1 + (1 + 2I^{1/2} + 2I)\exp(-2I^{1/2}) \quad (-1 \le f_2 \le 0) \tag{5e}$$

$\beta^{(0)}$, $\beta^{(1)}$, 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 interaction parameters (+ − +, − + −), and λ represents the interaction parameter for neutral species. At $I < 3$ mol (kg of H$_2$O)$^{-1}$, Θ and Ψ parameters can generally be neglected.

If we consider the protonation reactions (1), the thermodynamic protonation constants in NaCl can be expressed by

$$\ln K_i^{\text{H}} = \ln {}^TK_i^{\text{H}} + \ln \gamma_{\text{H}} + \ln \gamma_{\text{H}i-1\text{A}} - \ln \gamma_{\text{HA}} \tag{6}$$

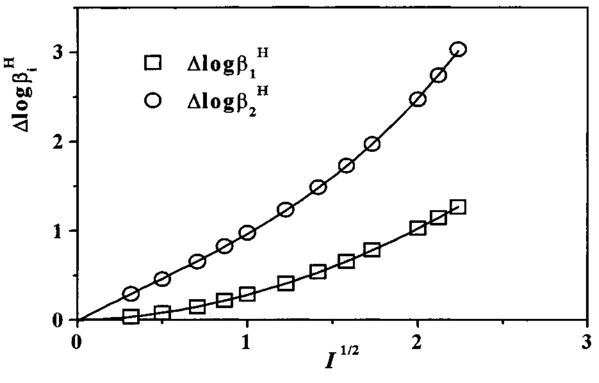

Figure 1. $\Delta \log \beta_i^H$ values ($\Delta \log \beta_i^H = \log {}^T\beta_i^H - \log \beta_i^H$) vs I, for *1,6d* at 25 °C.

and, by combining eqs 4−6, we obtain

$$\ln K_i^H = \ln {}^TK_i^H + 2(1 - i)f^{\gamma} + 2I(\beta_{H,Cl}^{(0)} + \beta_{Hi-1A,Cl}^{(0)} - \beta_{HiA,Cl}^{(0)} + \Theta_{H,Na} + \Theta_{Hi-1A,Na} - \Theta_{HiA,Na}) + I^2\,(C_{H,Cl}^{(\phi)} + C_{Hi-1A,Cl}^{(\phi)}/(2(i-1)^{1/2}) - C_{HiA,Cl}^{(\phi)}/(2i^{1/2}) + \Psi_{H,Na,Cl} + \Psi_{Hi-1A,Na,Cl} - \Psi_{HiA,Na,Cl}) + (\beta_{H,Cl}^{(1)} + \beta_{Hi-1A,Cl}^{(1)} - \beta_{HiA,Cl}^{(1)})f_1 + (1-i)\beta_{Na,Cl}^{(1)}f_2 \quad (7)$$

Results

Unsubstituted Diamines. The protonation constants of unsubstituted diamines at different ionic strengths are reported in Table 2. The dependence of $\log \beta_i^H$ on I is shown in Figure 1, where the difference $\Delta \log \beta_i^H = \log {}^T\beta_i^H - \log \beta_i^H$ is reported for *1,6d*. Both the first and second protonation constants are strongly dependent on I (particularly the second one); for example, for $I = 5$ mol L^{-1}, $\Delta \log \beta_2^H = 3.03$. Parameters for dependence on I using the DHT equation are shown in Table 3. As can be seen, parameters C and E are fairly constant (parameter D was always considered the common parameter for all of the diamines). When E is considered a common parameter, the fit for $\log \beta_1^H$ remains unaltered and worsens slightly for $\log \beta_2^H$. [In these and subsequent calculations we applied some constraints; that is, we kept equal some parameters for different amines. This was done for several reasons: (i) to avoid overparametrization (e.g., when $I \leq 1$ mol L^{-1}, values of protonation constants at only five ionic strengths are reported, and the calculation of the $\log \beta_i^H$ at infinite dilution and three empirical parameters to one degree of freedom of the system); (ii) to reduce to minimum the correlation between linear parameters; and (iii) to have a better understanding of the similarities of different amines.] When constants C, D, and E are maintained for all of the diamines, the fit remains good for the first protonation constant and acceptable for the second protonation step. This is consistent with previous results on the protonation of diamines at $I < 1$ mol L^{-1} (NaCl).[38,39]

Table 3. Parameters for the Dependence on Ionic Strength of Protonation Constants of Unsubstituted Diamines, in NaCl and at 25 °C, Using the DHT Equation (Equation 3)

amine	$C \pm s^a$	$D \pm s^a$	$E \pm s^a$	ϵ^b
		$\log \beta_1^H$		
1,2d	0.382 ± 0.004		0.0250 ± 0.0023	
1,3d	0.446 ± 0.006		–	
1,4d	0.350 ± 0.006		–	
1,5d	0.421 ± 0.006	−0.107 ± 0.009[c]	–	0.0034
1,6d	0.374 ± 0.005		0.0250 ± 0.0017	
1,8d	0.372 ± 0.005		0.0275 ± 0.0022	
1,10d	0.362 ± 0.004		0.0263 ± 0.0022	
	0.39 ± 0.04[d]		0.026 ± 0.002[d]	
1,2d	0.380 ± 0.002			
1,3d	0.423 ± 0.002			
1,4d	0.328 ± 0.003			
1,5d	0.402 ± 0.003	−0.107 ± 0.003[c]	0.0245 ± 0.010[c]	0.0037
1,6d	0.372 ± 0.002			
1,8d	0.376 ± 0.003			
1,10d	0.364 ± 0.002			
	0.38 ± 0.03[d]			
A[e]	0.383 ± 0.010	−0.115 ± 0.013	0.0259 ± 0.0039	0.012
		$\log \beta_2^H$		
1,2d	0.667 ± 0.006		0.1210 ± 0.0032	
1,3d	0.991 ± 0.007		–	
1,4d	0.766 ± 0.009		–	
1,5d	0.937 ± 0.008	−0.3075 ± 0.0085[c]	–	0.0055
1,6d	0.797 ± 0.007		0.0782 ± 0.0024	
1,8d	0.744 ± 0.006		0.0924 ± 0.0034	
1,10d	0.714 ± 0.006		0.0923 ± 0.0035	
	0.80 ± 0.14[d]		0.10 ± 0.03[d]	
1,2d	0.703 ± 0.014			
1,3d	0.880 ± 0.013			
1,4d	0.658 ± 0.012			
1,5d	0.827 ± 0.014	−0.239 ± 0.016[c]	0.0625 ± 0.0046[c]	0.013
1,6d	0.726 ± 0.013			
1,8d	0.711 ± 0.013			
1,10d	0.680 ± 0.013			
	0.74 ± 0.09[d]			
A[e]	0.759 ± 0.004	−0.31 ± 0.02	0.0877 ± 0.0011	0.038

[a] s = standard deviation. [b] Mean deviation on the fit of eq 3. [c] Common parameter for all of the diamines. [d] Mean value ± 95% confidence interval. [e] Calculations performed by considering all of the polyamines in this class together.

Unsubstituted and Partially Substituted Triamines. Protonation constants for unsubstituted and partially substituted triamines are shown in Table 4. As expected [because of the interaction between the tricharged amines and the anion of background salt (see ref 35)], we observe a strong dependence on ionic strength for triamines: at $I = 5$ mol L^{-1}, for *TR2*, the difference $\Delta \log \beta_3^H = \log \beta_3^H - \log {}^T\beta_3^H = 5.43$. Parameters for dependence on I using the DHT equation are reported in Table 5. The procedure followed for these amines is the same as for diamines, and here again the use of common parameters gives acceptable results. When N-alkyl substitution is partial, the effect on I dependence is slight.

Tetramines. Protonation constants for tetramines are reported in Table 6. Parameters for dependence on ionic strength, using the DHT equation, are reported in Table 7. The parameter C is quite different for the various amines and, in particular, we note that parameter C for *TE1* (fully substituted tetraamine) is significantly higher than that of unsubstituted amines (see below). In this case only parameters D and E can be kept equal for all of the amines.

Fully Substituted Amines. The protonation constants of fully substituted amines are reported in Table 8, and the parameters for dependence on I using the DHT equation are reported in Table 9. This is a very homogeneous class of amines, and all of the parameters for dependence on I can, as a first approximation, be considered equal and dependent only on the stoichiometry of the protonation reaction (z^*). With regard to the tetramine *TE1*, measurements were made twice using different apparatus to check protonation data that are quite important in determining the different behavior of fully substituted polyamines. Experimental data reported in Tables 6 and 8 are quite close, and therefore the check is confirmatory. Nevertheless, there is an apparent inconsistency in the values of C,

Table 4. Protonation Constants of Unsubstituted and Partially Substituted Triamines at Different Ionic Strengths (NaCl), at 25 °C

amine^a	I/mol L^{-1}	log $\beta_1 \pm 3s^b$	log $\beta_2 \pm 3s^b$	log $\beta_3 \pm 3s^b$
dien	0	9.79 ± 0.01	18.54 ± 0.01	22.20 ± 0.01
	0.1	9.84 ± 0.01	18.84 ± 0.01	23.04 ± 0.02
	0.25	9.88 ± 0.01	19.00 ± 0.01	23.44 ± 0.01
	0.5	9.94 ± 0.01	19.18 ± 0.01	23.82 ± 0.02
	0.75	9.99 ± 0.01	19.31 ± 0.01	24.05 ± 0.01
	1	10.04 ± 0.01	19.41 ± 0.01	24.19 ± 0.01
spd	0	10.80 ± 0.01	20.38 ± 0.02	28.20 ± 0.05
	0.1	10.85 ± 0.01	20.68 ± 0.03	28.98 ± 0.07
	0.25	10.89 ± 0.01	20.83 ± 0.02	29.32 ± 0.05
	0.5	10.95 ± 0.01	21.02 ± 0.01	29.66 ± 0.02
	0.75	11.00 ± 0.01	21.16 ± 0.01	29.93 ± 0.01
	1	11.05 ± 0.01	21.29 ± 0.01	30.15 ± 0.01
	1.5	11.14 ± 0.01	21.52 ± 0.01	30.55 ± 0.02
	2	11.24 ± 0.01	21.73 ± 0.01	30.92 ± 0.02
	2.5	11.33 ± 0.01	21.95 ± 0.01	31.27 ± 0.01
	3	11.42 ± 0.01	22.16 ± 0.01	31.63 ± 0.01
	3.5	11.52 ± 0.01	22.38 ± 0.01	32.00 ± 0.01
	4	11.61 ± 0.01	22.62 ± 0.01	32.38 ± 0.01
	4.5	11.70 ± 0.01	22.86 ± 0.01	32.79 ± 0.01
TR1	0	10.54 ± 0.02	19.86 ± 0.01	27.01 ± 0.01
	0.1	10.60 ± 0.01	20.16 ± 0.01	27.80 ± 0.03
	0.25	10.66 ± 0.01	20.32 ± 0.01	28.15 ± 0.02
	0.5	10.75 ± 0.01	20.52 ± 0.01	28.53 ± 0.01
	0.75	10.84 ± 0.01	20.69 ± 0.01	28.82 ± 0.01
	1	10.92 ± 0.01	20.85 ± 0.01	29.09 ± 0.01
	1.5	11.09 ± 0.01	21.15 ± 0.01	29.57 ± 0.01
	2	11.25 ± 0.01	21.46 ± 0.01	30.03 ± 0.01
	2.5	11.41 ± 0.01	21.77 ± 0.01	30.49 ± 0.01
	3	11.56 ± 0.01	22.10 ± 0.01	30.97 ± 0.01
TR2	0	11.16 ± 0.02	21.41 ± 0.01	30.76 ± 0.01
	0.1	11.22 ± 0.01	21.71 ± 0.01	31.53 ± 0.02
	0.25	11.28 ± 0.01	21.88 ± 0.01	31.87 ± 0.01
	0.5	11.36 ± 0.01	22.08 ± 0.01	32.23 ± 0.01
	0.75	11.44 ± 0.01	22.25 ± 0.01	32.50 ± 0.01
TR2	1	11.51 ± 0.01	22.40 ± 0.01	32.74 ± 0.02
	1.5	11.66 ± 0.01	22.69 ± 0.01	33.18 ± 0.01
	2	11.81 ± 0.01	22.96 ± 0.01	33.59 ± 0.01
	3	12.10 ± 0.01	23.52 ± 0.01	34.42 ± 0.02
	4	12.39 ± 0.01	24.13 ± 0.01	35.31 ± 0.01
	5	12.68 ± 0.01	24.80 ± 0.01	36.29 ± 0.04
TR3	0	10.90 ± 0.01	20.86 ± 0.02	29.67 ± 0.02
	0.1	10.95 ± 0.01	21.17 ± 0.01	30.46 ± 0.01
	0.25	10.99 ± 0.01	21.35 ± 0.01	30.82 ± 0.01
	0.5	11.05 ± 0.01	21.56 ± 0.01	31.20 ± 0.01
	0.75	11.10 ± 0.01	21.72 ± 0.01	31.47 ± 0.01
	1	11.16 ± 0.01	21.86 ± 0.01	31.70 ± 0.01
	1.5	11.25 ± 0.01	22.09 ± 0.01	32.08 ± 0.01
	2	11.35 ± 0.01	22.28 ± 0.01	32.40 ± 0.01
	2.5	11.44 ± 0.01	22.45 ± 0.01	32.69 ± 0.01
	3	11.54 ± 0.01	22.61 ± 0.01	32.97 ± 0.01
TR4	0	10.36 ± 0.01	19.64 ± 0.01	26.05 ± 0.01
	0.1	10.42 ± 0.01	19.95 ± 0.01	26.86 ± 0.03
	0.25	10.48 ± 0.01	20.13 ± 0.01	27.23 ± 0.02
	0.5	10.57 ± 0.01	20.34 ± 0.01	27.64 ± 0.01
	0.75	10.65 ± 0.01	20.52 ± 0.01	27.96 ± 0.01
	1	10.72 ± 0.01	20.67 ± 0.01	28.23 ± 0.01
	1.5	10.88 ± 0.01	20.95 ± 0.01	28.72 ± 0.01
	2	11.03 ± 0.01	21.21 ± 0.01	29.17 ± 0.01
	2.5	11.18 ± 0.01	21.46 ± 0.01	29.60 ± 0.01
	3	11.32 ± 0.01	21.71 ± 0.01	30.02 ± 0.01
TR5	0	11.18 ± 0.02	21.49 ± 0.01	30.65 ± 0.02
	0.1	11.24 ± 0.01	21.80 ± 0.01	31.44 ± 0.01
	0.25	11.30 ± 0.01	21.97 ± 0.01	31.81 ± 0.01
	0.5	11.38 ± 0.01	22.18 ± 0.01	32.19 ± 0.01
	0.75	11.46 ± 0.01	22.37 ± 0.01	32.48 ± 0.01
	1	11.54 ± 0.01	22.54 ± 0.01	32.73 ± 0.01

[a,b] See footnotes to Table 2.

D, and *E* reported in Tables 7 and 9, due to the strong correlation in these parameters: if we consider altogether data of Tables 6 and 8, we have the values reported in parentheses in Table 9, with a quite good fit ($\epsilon = 0.003-0.014$).

General DHT Equation Parameters. DHT parameters for the protonation constants of unsubstituted diamines and triamines are very similar and, for $I \leq 0.5$ mol L^{-1}, can be kept constant, according to the equations

$$C = 0.39 - 0.12z^* \tag{8}$$

$$D = -0.071 + 0.047z^* \tag{9}$$

Values of log β^{H} calculated using eqs 3 with parameter values of eqs 8 and 9 are in excellent agreement with experimental ones, and differences are $\Delta = |\log \beta_{\mathrm{exp}}{}^{\mathrm{H}} - \log \beta_{\mathrm{calcd}}{}^{\mathrm{H}}| \leq 0.012iI$.

For fully substituted amines, the following empirical relationships are valid over the whole ionic strength range considered:

$$C_i = (0.070 \pm 0.005)i(i-1) + (0.545 \pm 0.006)i \tag{10a}$$

$$D_i = (-0.144 \pm 0.008)i(i-1) + (-0.106 \pm 0.004)i \tag{10b}$$

$$E_i = (0.0556 \pm 0.0034)i(i-1) \tag{10c}$$

Protonation constants calculated using eqs 10a−c show very little deviation from the experimental ones, that is, $\epsilon = 0.022$.

Literature Data Analysis. Finnish authors have published extensive data on the protonation of amines at different ionic strengths, in particular, in $\mathrm{NaClO_4}$ medium.[11−22] We examined some of these data both to compare dependence on ionic strength in NaCl with that in $\mathrm{NaClO_4}$ and to find out more about the effect of substitution on the function log $K_i{}^{\mathrm{H}} = f(I)$. The amines taken into consideration in this work (all diamines) are reported in Table 1. For the diamines containing an −OH group, *A1*−*A5*, the ionic strength dependence parameters (DHT equation) are reported in Table 10 ($I \leq 2$ mol L^{-1}). The behavior is the same as that shown by the different set of diamines studied in this work. There is little difference between *I* dependence in $\mathrm{NaClO_4}$ and in NaCl for $I \leq 2$ mol L^{-1}. Also, the trend in magnitude of ionic strength effect, tertiary > secondary > primary, is the same as that observed for diamines containing −OH groups. The second group of diamines, *D1*−*D13* (see Table 1), contains primary, secondary, and tertiary amino groups, and the protonation of these was considered separately, as reported in Table 11. For these amines, too, there is a very regular trend in *I* dependence as a function of *N*-alkyl substitution, and general equations were found

for log $K_1{}^{\mathrm{H}}$:

$$C = 0.281\ (\pm\ 0.003) + 0.018\ (\pm\ 0.001)(x_1{}^2 + x_2{}^2)$$

$$E = -0.020\ (\pm\ 0.006) \tag{10d}$$

Table 5. Parameters for the Dependence on Ionic Strength of Protonation Constants of Unsubstituted and Partially Substituted Triamines, in NaCl and at 25 °C, Using the DHT Equation (Equation 3)

amine	$C \pm s^a$	$D \pm s^a$	$E \pm s^a$	ϵ^b
		$\log \beta_1^H$		
dien	0.449 ± 0.015		−	
spd	0.408 ± 0.013		0.0497 ± 0.0045	
TR1	0.538 ± 0.012		0.0512 ± 0.0060	
TR2	0.515 ± 0.013	−0.203 ± 0.015^{c}	0.0486 ± 0.0044	0.0061
TR3	0.408 ± 0.012		0.0517 ± 0.0060	
TR4	0.523 ± 0.012		0.0494 ± 0.0060	
TR5	0.557 ± 0.015		−	
	0.49 ± 0.07^{d}		0.050 ± 0.002^{d}	
dien	0.405 ± 0.006			
spd	0.407 ± 0.005			
TR1	0.541 ± 0.006			
TR2	0.511 ± 0.005	−0.200 ± 0.007^{c}	0.0487 ± 0.0022	0.0064
TR3	0.411 ± 0.005			
TR4	0.521 ± 0.006			
TR5	0.513 ± 0.005			
	0.47 ± 0.07^{d}			
A^{e}	0.473 ± 0.023	−0.20 ± 0.01	0.049 ± 0.004	0.075
		$\log \beta_2^H$		
dien	0.880 ± 0.017		−	
spd	0.809 ± 0.014		0.1103 ± 0.0051	
TR1	0.854 ± 0.013		0.1470 ± 0.0068	
TR2	0.886 ± 0.014	−0.408 ± 0.017^{c}	0.1208 ± 0.0049	0.0066
TR3	0.946 ± 0.013		0.0604 ± 0.0068	
TR4	0.944 ± 0.013		0.0973 ± 0.0068	
TR5	1.036 ± 0.017		−	
	0.91 ± 0.08^{d}		0.11 ± 0.04^{d}	
dien	0.852 ± 0.016			
spd	0.874 ± 0.013			
TR1	1.010 ± 0.015			
TR2	0.989 ± 0.013	−0.505 ± 0.018^{c}	0.143 ± 0.006^{c}	0.021
TR3	0.898 ± 0.015			
TR4	0.983 ± 0.014			
TR5	1.004 ± 0.018			
	0.94 ± 0.08^{d}			
A^{e}	0.944 ± 0.025	−0.51 ± 0.03	0.15 ± 0.01	0.074
		$\log \beta_3$		
dien	2.313 ± 0.049	−1.711 ± 0.054		
spd	1.225 ± 0.006	−0.645 ± 0.009		
TR1	1.258 ± 0.004	−0.561 ± 0.011		
TR2	1.205 ± 0.009	−0.591 ± 0.010	0.1836 ± 0.0029^{c}	0.010
TR3	1.444 ± 0.012	−0.795 ± 0.010		
TR4	1.501 ± 0.008	−0.705 ± 0.009		
TR5	1.555 ± 0.055	−0.864 ± 0.060		
dien	1.48 ± 0.04			
spd	1.35 ± 0.04			
TR1	1.51 ± 0.04			
TR2	1.43 ± 0.03	−0.82 ± 0.04^{c}	0.239 ± 0.013^{c}	0.033
TR3	1.35 ± 0.04			
TR4	1.55 ± 0.04			
TR5	1.46 ± 0.03			
	1.45 ± 0.09^{d}			
A^{e}	1.52 ± 0.06	−0.90 ± 0.10	0.25 ± 0.03	0.10

[a−e] See footnotes to Table 3.

for log K_2^H:

$$C = 0.214\ (\pm 0.004) + 0.018\ (\pm 0.001)(x_1^2 + 1.5x_2^2)$$

$$E = -0.017\ (\pm 0.012) \tag{10e}$$

where $x = 1$, 2, or 3 for primary, secondary, or tertiary amines, respectively (x_1 refers to the first protonable N and x_2 to the second) with a mean deviation $\epsilon = 0.016$.

Table 6. Protonation Constants of Tetramines at Different Ionic Strengths (NaCl), at 25 °C

amine^{a}	I/mol L^{-1}	$\log \beta_1^H \pm 3s^b$	$\log \beta_2^H \pm 3s^b$	$\log \beta_3^H \pm 3s^b$	$\log \beta_4^H \pm 3s^b$
trien	0	9.67 ± 0.01	18.54 ± 0.01	24.65 ± 0.02	27.03 ± 0.02
	0.1	9.69 ± 0.01	18.79 ± 0.01	25.38 ± 0.02	28.43 ± 0.02
	0.25	9.72 ± 0.01	18.92 ± 0.01	25.70 ± 0.02	29.05 ± 0.02
	0.5	9.78 ± 0.01	19.08 ± 0.01	26.03 ± 0.02	29.67 ± 0.01
	0.75	9.83 ± 0.01	19.23 ± 0.01	26.29 ± 0.01	30.08 ± 0.02
	1	9.88 ± 0.01	19.37 ± 0.01	26.50 ± 0.02	30.39 ± 0.02
sper	0	10.70 ± 0.01	20.40 ± 0.01	28.71 ± 0.02	35.89 ± 0.05
	0.1	10.73 ± 0.01	20.67 ± 0.01	29.44 ± 0.03	37.28 ± 0.04
	0.25	10.78 ± 0.01	20.82 ± 0.01	29.76 ± 0.02	37.87 ± 0.04
	0.5	10.86 ± 0.01	21.02 ± 0.01	30.11 ± 0.02	38.44 ± 0.02
	0.75	10.94 ± 0.01	21.20 ± 0.01	30.38 ± 0.01	38.81 ± 0.01
	1	11.02 ± 0.01	21.38 ± 0.01	30.61 ± 0.02	39.08 ± 0.03
TE2	0	10.14 ± 0.01	19.33 ± 0.01	27.24 ± 0.04	27.28 ± 0.05
	0.1	10.17 ± 0.01	19.61 ± 0.01	27.98 ± 0.02	28.70 ± 0.04
	0.25	10.21 ± 0.01	19.78 ± 0.01	28.33 ± 0.02	29.34 ± 0.03
	0.5	10.28 ± 0.01	19.98 ± 0.01	28.70 ± 0.01	30.00 ± 0.02
	0.75	10.35 ± 0.01	20.15 ± 0.01	29.00 ± 0.01	30.47 ± 0.01
	1	10.42 ± 0.01	20.31 ± 0.01	29.25 ± 0.01	30.82 ± 0.01
	1.5	10.56 ± 0.01	20.60 ± 0.01	29.70 ± 0.01	−
	2	10.69 ± 0.01	20.87 ± 0.01	30.11 ± 0.01	−
	2.5	10.82 ± 0.01	21.13 ± 0.01	30.50 ± 0.01	−
	3	10.95 ± 0.01	21.38 ± 0.01	30.89 ± 0.01	−
	4.5	11.31 ± 0.01	22.14 ± 0.01	32.07 ± 0.01	−
	5	11.43 ± 0.01	22.39 ± 0.01	32.49 ± 0.01	−
TE1	0	9.22 ± 0.01	17.36 ± 0.01	22.10 ± 0.03	22.67 ± 0.04
	0.1	9.26 ± 0.01	17.68 ± 0.01	22.89 ± 0.02	24.13 ± 0.03
	0.25	9.33 ± 0.01	17.88 ± 0.01	23.31 ± 0.01	24.84 ± 0.02
	0.5	9.44 ± 0.01	18.15 ± 0.01	23.81 ± 0.01	25.60 ± 0.01
	0.75	9.55 ± 0.01	18.39 ± 0.01	24.23 ± 0.01	26.16 ± 0.02
	1	9.66 ± 0.01	18.61 ± 0.01	24.61 ± 0.01	26.61 ± 0.02

[a,b] See footnotes to Table 2.

Table 7. Parameters for the Dependence on Ionic Strength of Protonation Constants of Tetramines, in NaCl and at 25 °C, Using the DHT Equation (Equation 3)

amine	$C \pm s^a$	$D \pm s^a$	$E \pm s^a$	ϵ^b
		$\log \beta_1^H$		
trien	0.211 ± 0.002 (0.217)^{d}			
sper	0.319 ± 0.002 (0.325)			
TE2	0.279 ± 0.002 (0.287)	−0.0084 ± 0.0008 (0)	0.0092 ± 0.0026 (−0.0058 ± 0.0002)	0.0013 (0.0016)
TE1	0.438 ± 0.002 (0.445)			
		$\log \beta_2^H$		
trien	0.533 ± 0.014			
sper	0.683 ± 0.015			
TE2	0.704 ± 0.017	−0.159 ± 0.020^{c}	0.0323 ± 0.0055^{c}	0.008
TE1	0.984 ± 0.014			
		$\log \beta_3^H$		
trien	0.914 ± 0.004			
sper	0.959 ± 0.004			
TE2	1.073 ± 0.004	−0.356 ± 0.005^{c}	0.093 ± 0.002^{c}	0.0024
TE1	1.572 ± 0.004			
		$\log \beta_4^H$		
trien	1.11 ± 0.04			
sper	0.94 ± 0.04			
TE2	1.29 ± 0.04	−0.71 ± 0.05^{c}	0.56 ± 0.09^{c}	0.004
TE1	1.69 ± 0.04			

[a−c] See footnotes to Table 3. [d] Values calculated by keeping $D = 0$ in parentheses.

Pitzer Parameters for the Dependence on Media of Protonation Constants. A particularly interesting model for the dependence on ionic strength of activity coefficients was proposed by Pitzer in 1973.[44] Since then, the interaction coefficients of Pitzer equations have been calculated using a variety of experimental data, and an extensive database has been built up.[45] Several (potentiometric) equilibrium data have been used to obtain $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ parameters[46−52] and, in some cases, modified Pitzer equations have been used.[50] In this work, for protonation

Table 8. Protonation Constants of Fully Substituted Di-, Tri-, and Tetraamines at Different Ionic Strengths (NaCl), at 25 °C

amine[a]	I/mol L^{-1}	log β_1 ± 3s[b]	log β_2 ± 3s[b]	log β_3 ± 3s[b]	log β_4 ± 3s[b]
1,2ds	0	9.15 ± 0.01	14.78 ± 0.01		
	0.1	9.21 ± 0.01	15.10 ± 0.01		
	0.25	9.28 ± 0.01	15.32 ± 0.01		
	0.5	9.40 ± 0.01	15.59 ± 0.01		
	0.75	9.50 ± 0.01	15.82 ± 0.01		
	1	9.59 ± 0.01	16.02 ± 0.01		
	1.5	9.76 ± 0.01	16.40 ± 0.02		
	2	9.92 ± 0.01	16.73 ± 0.02		
	2.5	10.08 ± 0.01	17.05 ± 0.01		
	3	10.22 ± 0.01	17.37 ± 0.02		
TR6	0	9.23 ± 0.01	17.39 ± 0.01	18.88 ± 0.01	
	0.1	9.28 ± 0.01	17.71 ± 0.01	19.69 ± 0.01	
	0.25	9.35 ± 0.01	17.93 ± 0.01	20.12 ± 0.01	
	0.5	9.46 ± 0.01	18.21 ± 0.01	20.60 ± 0.01	
	0.75	9.55 ± 0.01	18.45 ± 0.01	20.97 ± 0.01	
	1	9.64 ± 0.01	18.67 ± 0.01	21.28 ± 0.01	
	1.5	9.80 ± 0.01	19.06 ± 0.02	21.83 ± 0.01	
	2	9.94 ± 0.01	19.41 ± 0.02	22.33 ± 0.01	
	2.5	10.08 ± 0.01	19.75 ± 0.01	22.82 ± 0.01	
	3	10.21 ± 0.01	20.08 ± 0.02	23.34 ± 0.01	
TE1	0	9.22 ± 0.01	17.36 ± 0.01	22.07 ± 0.01	22.63 ± 0.01
	0.1	9.27 ± 0.01	17.68 ± 0.01	22.89 ± 0.01	24.15 ± 0.01
	0.25	9.34 ± 0.01	17.89 ± 0.01	23.33 ± 0.01	24.87 ± 0.01
	0.5	9.44 ± 0.01	18.16 ± 0.01	23.83 ± 0.01	25.61 ± 0.01
	0.75	9.53 ± 0.01	18.38 ± 0.01	24.21 ± 0.01	26.13 ± 0.01
	1	9.62 ± 0.01	18.58 ± 0.01	24.55 ± 0.01	26.56 ± 0.01

[a,b] See footnotes to Table 2.

Table 9. Parameters for the Dependence on Ionic Strength of Protonation Constants of Fully Substituted Amines, in NaCl and at 25 °C, Using the DHT Equation (Equation 3)

amine	C ± s[a]	D ± s[a]	E ± s[a]	ϵ[b]
		log β_1^{H}		
1,2ds	0.643 ± 0.001			
TR6	0.613 ± 0.001	−0.254 ± 0.002[c]	0.0517 ± 0.003[c]	0.002
TE1	0.603 ± 0.001			
	0.62 ± 0.01[d]			
TE1	(0.49 ± 0.01)[e]	(−0.07 ± 0.01)[e]	(0)	0.003
		log β_2^{H}		
1,2ds	1.220 ± 0.004			
TR6	1.258 ± 0.004	−0.481 ± 0.005[c]	0.0528 ± 0.0014 ($-z^*$)[c]	0.003
TE1	1.195 ± 0.003			
	1.22 ± 0.03[d]			
TE1	(1.08 ± 0.01)[e]	(−0.25 ± 0.01)[e]	(0)[e]	0.004
		log β_3^{H}		
TR6	2.005 ± 0.009			
TE1	2.088 ± 0.010	−1.13 ± 0.02[c]	0.0528 ± 0.0014 ($-z^*$)[c]	0.004
	2.05 ± 0.05[d]			
TE1	(1.68 ± 0.02)[e]	(−0.39 ± 0.02)[e]	(0)[e]	0.006
		log β_4^{H}		
TE1	3.00 ± 0.02	−2.10 ± 0.04	0.0528 ± 0.0014 ($-z^*$)	0.012
TE1	(2.41 ± 0.03)[e]	(−0.87 ± 0.06)[e]	(0)[e]	0.014

[a−d] See footnotes to Table 3. [e] Calculations performed by considering data from Tables 6 and 8 altogether.

Table 10. Parameters for the Dependence on Ionic Strength (NaClO₄) of Protonation Constants of Some Diamino Alkanols (Literature Data, Refs 23−27), at 25 °C, Using the DHT Equation (Equation 3)

amine	C±s[a]	E±s[a]
	log K_1^{H}	
A1	0.404 ± 0.008	−0.0065 ± 0.0028[b]
A2	0.314 ± 0.006	
A3	0.289 ± 0.006	
A4	0.341 ± 0.007	
A5	0.325 ± 0.007	
A[d]	0.335 ± 0.05[c]	
A2−A5	0.317 ± 0.03	
	log K_2^{H}	
A1	0.324 ± 0.008	−0.019 ± 0.004[b]
A2	0.441 ± 0.008	
A3	0.246 ± 0.009	
A4	0.347 ± 0.008	
A5	0.304 ± 0.009	
A[d]	0.33 ± 0.08[c]	

[a] s = standard deviation. [b] Common parameter for all of the diamines. [c] Mean value ± 95% confidence interval. [d] Calculations performed by considering all the diamines together.

Table 11. Dependence on Ionic Strength (NaClO₄) of Protonation Constants of Some Diamines (See Table 1, *D1*−*D13*) at 25 °C, $I \le 2$ mol L^{-1}

C	E	ϵ	N(1)[a]	N(2)[a]
	log K_1^{H}			
0.315 ± 0.007	−0.023 ± 0.004	0.017	P	P
0.389 ± 0.008			P	S
0.476 ± 0.008			P	T
0.438 ± 0.013	−0.032 ± 0.006	0.010	S	S
0.465 ± 0.015			S	T
0.606 ± 0.008	−0.059 ± 0.004	0.012	T	T
	log K_2^{H}			
0.277 ± 0.013	−0.014 ± 0.007	0.014	P	P
0.278 ± 0.007	−0.023 ± 0.003	0.014	P	S
0.393 ± 0.006			S	S
0.490 ± 0.009	−0.073 ± 0.004	0.015	P	T
0.528 ± 0.010			S	T
0.619 ± 0.008			T	T

[a] N(1) and N(2) refer to the first and second protonable amino groups, respectively: P = primary, S = secondary, T = tertiary.

constants at different ionic strengths we used the simplified version of eq 7

$$\ln K_i^{\mathrm{H}} = \ln {}^{T}K_i^{\mathrm{H}} + 2(1-i)f^{\gamma} + 2IP_1 + I^2P_2 + f_1P_3 + (1-i)\beta_{\mathrm{Na,Cl}}^{(1)}f_2 \quad (7a)$$

where

$$P_1 = \beta_{\mathrm{H,Cl}}^{(0)} + \beta_{\mathrm{H}i-1\mathrm{A,Cl}}^{(0)} - \beta_{\mathrm{H}i\mathrm{A,Cl}}^{(0)} + \Theta_{\mathrm{H,Na}} + \Theta_{\mathrm{H}i-1\mathrm{A,Na}} - \Theta_{\mathrm{H}i\mathrm{A,Na}} \quad (8a)$$

$$P_2 = C_{\mathrm{H,Cl}}^{(\phi)} + C_{\mathrm{H}i-1\mathrm{A,Cl}}^{(\phi)}/(2(i-1)^{1/2}) - C_{\mathrm{H}i\mathrm{A,Cl}}^{(\phi)}/(2i^{1/2}) + \Psi_{\mathrm{H,Na,Cl}} + \Psi_{\mathrm{H}i-1\mathrm{A,Na,Cl}} - \Psi_{\mathrm{H}i\mathrm{A,Na,Cl}} \quad (8b)$$

$$P_3 = \beta_{\mathrm{H,Cl}}^{(1)} + \beta_{\mathrm{H}i-1\mathrm{A,Cl}}^{(1)} - \beta_{\mathrm{H}i\mathrm{A,Cl}}^{(1)} \quad (8c)$$

and $\beta_{\mathrm{Na,Cl}}^{(1)} = 0.2664$.[45] The parameters of eq 7a, calculated using the protonation constants of amines converted in the molal concentration scale, are reported in Tables 12−15. As can be seen, four groups of amines were considered (unsubstituted diamines, unsubstituted and partially substituted triamines, tetraamines, and fully substituted amines), and the procedure followed to perform calculations was the same as for the DHT equation. Here again, parameters are fairly constant for amines belonging to the same group, and the use of common parameters gives acceptable results.

Discussion

Dependence on Ionic Strength and Speciation. As observed in the preceding sections, amine protonation

Table 12. Parameters for the Dependence on Ionic Strength of Protonation Constants of Unsubstituted Diamines, in NaCl and at 25 °C, Using a Simplified Pitzer Equation [Equation 7A)

amine	P_1 (±0.001−0.01)	P_2 (±0.002−0.004)	P_3 (±0.005−0.06)	ϵ^a
		log K_1^H		
1,2d	0.242		0.285	0.0030
1,3d	0.279		0.312	
1,4d	0.139		0.414	
1,5d	0.284		0.224	
1,6d	0.227		0.309	
1,8d	0.242		0.263	
1,10d	0.228		0.265	
1,2d	0.242		0.288[b]	0.0036
1,3d	0.287			
1,4d	0.179			
1,5d	0.260			
1,6d	0.229			
1,8d	0.237			
1,10d	0.224			
A[c]	0.228[b]		0.321[b]	0.012
A[d]	0.226[b]		0.313[b]	0.011
		log K_2^H		
1,2d	0.062	0.060	−0.605	0.0047
1,3d	0.231		−0.393	
1,4d	0.320		−1.089	
1,5d	0.116		−0.152	
1,6d	0.036	0.035	−0.047	
1,8d	0.088	0.024	−0.413	
1,10d	0.037	0.038	−0.325	
1,2d	0.115	0.036[b]	−0.737	0.0052
1,3d	0.231		−0.394	
1,4d	0.320		−1.089	
1,5d	0.116		−0.152	
1,6d	0.031		−0.033	
1,8d	0.059		−0.332	
1,10d	0.041		−0.338	
1,2d	0.107	0.0102[b]	−0.506[b]	0.015
1,3d	0.271			
1,4d	0.130			
1,5d	0.239			
1,6d	0.143			
1,8d	0.122			
1,10d	0.102			
A[c]	0.048[b]	0.037[b]	−0.265[b]	0.032
A[d]	0.176[b]		−0.565[b]	0.031

[a] Mean deviation on the fit of equations (7a). [b] Common parameter for all of the amines. [c] Calculations performed by considering all of the diamines together. [d] Calculations performed by considering all of the diamines together at $I < 1$ mol L^{-1}.

Table 13. Parameters for the Dependence on Ionic Strength of Protonation Constants of Unsubtituted and Partially Substituted Triamines, in NaCl and at 25 °C, Using a Simplified Pitzer Equation [Equation 7A)

amine	P_1 (±0.002−0.03)	P_2 (±0.002−0.005)	P_3 (±0.005−0.07)	ϵ^a
		log K_1^H		
dien	0.106		0.556	0.0045
spd	0.163		0.379	
TR1	0.302		0.419	
TR2	0.267		0.435	
TR3	0.164		0.398	
TR4	0.275		0.415	
TR5	0.228		0.557	
dien	0.151		0.418[b]	0.0051
spd	0.158			
TR1	0.302			
TR2	0.269			
TR3	0.161			
TR4	0.281			
TR5	0.273			
A[c]	0.208[b]		0.531[b]	0.077
A[d]	0.179[b]		0.587[b]	0.028
		log K_2^H		
dien	0.002		−0.114	0.0044
spd	0.055	0.033	−0.233	
TR1	0.036	0.076	−0.445	
TR2	0.049	0.047	−0.320	
TR3	0.149	−0.051	−0.086	
TR4	0.084	0.0048	−0.266	
TR5	0.233		−0.646	
dien	−0.035	0.036[b]	−0.049	0.0074
spd	0.044		−0.498	
TR1	0.122		−0.659	
TR2	0.088		−0.444	
TR3	−0.048		0.422	
TR4	0.008		−0.056	
TR5	0.194		−0.577	
dien	−0.004	0.046[b]	−0.147[b]	0.022
spd	0.017			
TR1	0.020			
TR2	0.030			
TR3	0.037			
TR4	0.011			
TR5	0.050			
A[c]	0.007	0.052[b]	−0.106[b]	0.025
A[d]	0.142		−0.446[b]	0.020
		log K_3^H		
dien	−0.514		1.087	0.0040
spd	−0.017	0.042	−0.975	
TR1	−0.046	0.056	−0.731	
TR2	−0.026	0.040	−1.151	
TR3	−0.094	0.053	−0.788	
TR4	0.051	0.042	−0.798	
TR5	−0.156		−0.497	
dien	−0.514	0.043[b]	1.087	0.0043
spd	−0.019		−0.966	
TR1	−0.015		−0.813	
TR2	−0.036		−1.119	
TR3	−0.070		−0.853	
TR4	0.049		−0.792	
TR5	−0.156		−0.497	
dien	0.107	0.063[b]	−0.747[b]	0.013
spd	−0.085			
TR1	−0.051			
TR2	−0.122			
TR3	−0.113			
TR4	0.018			
TR5	−0.076			
A[c]	0.002	0.025[b]	−0.882[b]	0.053
A[d]	−0.105		−0.558[b]	0.035

[a−d] See footnotes to Table 12.

constants are strongly dependent on ionic strength. As a result, the speciation of these compounds varies significantly with ionic strength. Figure 2, for example, shows speciation diagrams of *TR2* at $I = 0.01$ mol L^{-1} and $I = 5$ mol L^{-1}. The profile at $I = 5$ mol L^{-1} is shifted, with respect to that at $I = 0.01$ mol L^{-1}, by ~2 pH units. This (overall) effect is due to changes in free ion activity and to the formation of polyammonium cation−chloride ion pairs.

Effect of N-Alkyl Substitution on I Dependence. As observed both for the results of this investigation and for literature data, *N*-alkyl substitution significantly affects the dependence on ionic strength of protonation constants. Comparing diamines and their *N*-alkyl homologues, at $I = 3$ mol L^{-1}, we have $\Delta \log \beta_2^H = 2.0$ (*1,2d*) and 2.6 (*1,2ds*) and for triamines $\Delta \log \beta_3^H = 3.4$ (*spd*) and 4.5 (*TR6*). Even at low ionic strength values these dependencies must be taken into account. This effect is largely due to the reduction in hydrogen bonding.

Polyammonium Cation—Cl$^-$ Ion Pairs. Assuming that eq 3 together with empirical parameters 3a and 3b, in the range $0 < I/\text{mol L}^{-1} \le 1$, is a valid means of taking into account the *I* dependence of free ions, the formation constants of ion pairs can be calculated as already

Table 14. Parameters for the Dependence on Ionic Strength of Protonation Constants of Tetramines, in NaCl and at 25 °C, Using a Simplified Pitzer Equation (Equation 7a)

amine	P_1 (±0.002−0.02)	P_2 (±0.002−0.006)	P_3 (±0.015−0.060)	ϵ^a
		log K_1^H		
trien	0.222		0.025	0.0072
sper	0.245		0.289	
TE1	0.479		0.024	
TE2	0.234		0.463	
trien	0.140		0.270^b	0.0097
sper	0.308			
TE1	0.397			
TE2	0.236			
A^c	0.225^b		0.383^b	0.034
A^d	0.312^b		0.131^b	0.0052
		log K_2^H		
trien	0.261		−1.019	0.0024
sper	0.278		−0.924	
TE1	0.245		−0.231	
TE2	0.135	0.0087	−0.307	
trien	0.052	0.0024^b	−0.402^b	0.0096
sper	0.100			
TE1	0.304			
TE2	0.160			
A^c	0.165^b	0.0015^b	−0.429^b	0.033
A^d	0.237^b		−0.639^b	0.041
		log K_3^H		
trien	−0.135		−0.593	0.0038
sper	−0.169		−0.865	
TE1	0.362		−1.371	
TE2	−0.019	0.038	−1.034	
trien	0.004	0.040^b	−1.000^b	0.0075
sper	−0.119			
TE1	0.237			
TE2	−0.028			
A^c	−0.078	0.050^b	−0.754^b	0.038
A^d	−0.016		−0.930^b	0.045
		log K_4^H		
trien	−0.077		−1.337	0.020
sper	−0.380		−1.157	
TE1	−0.206		−1.203	
TE2	−0.036		−1.394	
trien	−0.097		−1.276^b	0.020
sper	−0.341			
TE1	−0.182			
TE2	−0.076			
A^c	−0.130^b		−1.363^b	0.046
A^d	−0.130^b		−1.363^b	0.046

[a−d] See footnotes to Table 12.

described.[33−35,38−40] Table 16 reports the equilibrium constants relative to the reaction

$$H_iA^{i+} + pCl^- = H_iACl_p^{(i-p)} \qquad K_{ip} \qquad (11)$$

K_{ip} values show that the stability of $AH_i^{i+}-Cl^-$ ion pairs depends strictly on polyammonium cation charge. This is evidenced in the last column of Table 16, where mean log K_{ip} values for each equilibrium are reported: the behavior of log K_{ip} versus i is shown in Figure 3. A linear plot is obtained with two straight lines for unsubstituted (or partially substituted) and totally substituted amines having the same slope, 0.754 ± 0.025, and different intercepts, −0.91 ± 0.06 and −0.56 ± 0.08, respectively, with a mean deviation on the fit ϵ = 0.07 for both plots. As also evidenced in a previous work,[40] substituted amines form stronger ion pairs with Cl^- than unsubstituted ones, and this may be due to their different *N*-alkyl substitution-related lipophilicities. The influence of *N*-alkyl substitution on the basicity of amines, as well as on the dependence on ionic strength (and, as a consequence on the stability of ion pairs), has been widely discussed in several papers of

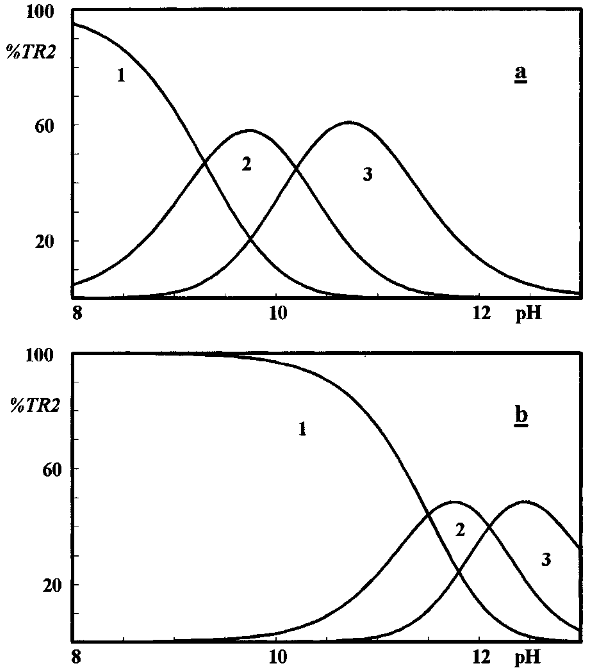

Figure 2. Speciation diagrams versus pH of *TR2*, at 25 °C. Analytical conditions: C_A = 0.1 mmol L^{-1}; (a) I = 0.01 and (b) I = 5 (NaCl) mol L^{-1}. Species: 1, H_3A^{3+}; 2, H_2A^{2+}; 3, HA^+.

Table 15. Parameters for the Dependence on Ionic Strength of Protonation Constants of Fully Substituted Amines, in NaCl and at 25 °C, Using a Simplified Pitzer Equation (Equation 7a)

amine	P_1 (±0.007−0.02)	P_2 (±0.004−0.009)	P_3 (±0.02−0.07)	ϵ^a
		log K_1^H		
1,2ds	0.288		0.675	0.0048
TR6	0.260		0.638	
TE1	0.323		0.404	
1,2ds	0.293		0.648	0.0063
TR6	0.258			
TE1	0.239			
A^c	0.288		0.563	0.019
A^d	0.321		0.467	0.10
		log K_2^H		
1,2ds	0.256	−0.008	−0.294	0.0041
TR6	0.358	−0.023	−0.366	
TE1	0.269		−0.264	
1,2ds	0.274	−0.016	−0.340	0.0043
TR6	0.342		−0.324	
TE1	0.269		−0.264	
1,2ds	0.268	−0.014	−0.318	0.0043
TR6	0.338			
TE1	0.287			
A^c				
A^d	0.305		−0.356	0.013
		log K_3^H		
TR6	0.248	0.137	−0.077	0.0042
TE1	0.134		−0.599	
TR6	−0.165	0.104	−0.312	0.0082
TE1	0.035			
A^c	0.0101	0.0025	−0.566	0.037
A^d	0.062		−0.605	0.033
		log K_4^H		
TE1	−0.252		−1.010	

[a−d] See footnotes to Table 12.

Table 16. Equilibrium Constants for the Formation of Polyammonium Cation−Cl⁻ Ion Pairs, at 25 °C and $I = 0$ mol L^{-1}

		log *K*							
equilibrium		*1,2d*	*1,3d*	*1,4d*	*1,5d*	*1,6d*	*1,8d*	*1,10d*	mean
$HA^+ + Cl^-$	(±0.2)[a]	−0.2	−0.1	−0.4	−0.1	−0.2	−0.2	−0.25	−0.2 ± 0.2[b]
$H_2A^{2+} + Cl^-$	(±0.1)	0.6	0.8	0.6	0.8	0.7	0.6	0.6	0.7 ± 0.1

		log *K*							
equilibrium		*dien*	*spd*	*TR1*	*TR2*	*TR3*	*TR4*	*TR5*	mean
$HA^+ + Cl^-$	(±0.2)	−0.3	−0.3	0	−0.1	−0.3	0	0	−0.1 ± 0.2
$H_2A^{2+} + Cl^-$	(±0.1)	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.7 ± 001
$H_3A^{3+} + Cl^-$	(±0.1)	1.5	1.3	1.4	1.4	1.5	1.4	1.5	1.4 ± 0.1
$H_3ACl^{2+} + Cl^-$	(±0.2)	−0.4	−0.1	0	−0.2	−0.3	0.2	−0.2	−0.2 ± 0.2

		log *K*			
equilibrium		*trien*	*sper*	*TE2*	mean
$HA^+ + Cl^-$	(±0.2)	−0.5	−0.2	−0.3	−0.3 ± 0.3
$H_2A^{2+} + Cl^-$	(±0.1)	0.5	0.7	0.7	0.6 ± 0.1
$H_3A^{3+} + Cl^-$	(±0.1)	1.3	1.3	1.35	1.3 ± 0.1
$H_4A^{4+} + Cl^-$	(±0.1)	2.0	2.0	1.9	2.0 ± 0.1
$H_3ACl^{2+} + Cl^-$	(±0.3)	−0.6	−0.45	−0.1	−0.4 ± 0.3
$H_4ACl^{3+} + Cl^-$	(±0.2)	0.7	0.3	1.0	0.7 ± 0.3

		log *K*			
equilibrium		*1,2ds*	*TR6*	*TE1*	mean
$HA^+ + Cl^-$	(±0.2)	0.2	0.1	0.1	0.1 ± 0.1
$H_2A^{2+} + Cl^-$	(±0.1)	1.0	1.0	1.0	1.0 ± 0.0
$H_3A^{3+} + Cl^-$	(±0.1)		1.65	1.9	−1.8 ± 0.2
$H_4A^{4+} + Cl^-$	(±0.1)			2.4	
$H_3ACl^{2+} + Cl^-$	(±0.3)		0.1	−0.4	−0.1 ± 0.3
$H_4ACl^{3+} + Cl^-$	(±0.2)			0.7	

[a] ± 3 standard deviations. [b] ± maximum deviation.

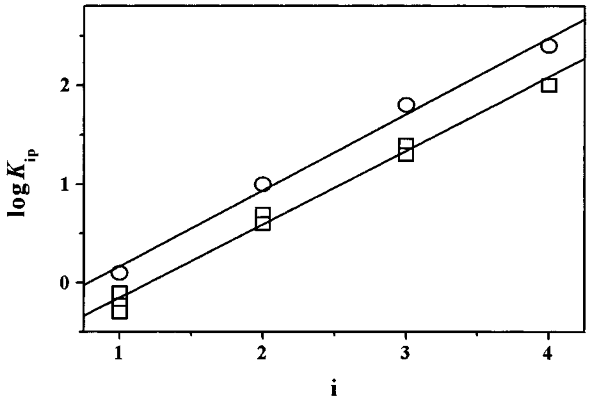

Figure 3. Formation constants of Cl⁻−polyammonium cation ion pairs (equilibrium 11) versus charge: □, unsubstituted and partially substituted amines; ○, totally substituted amines.

the Finnish school, cited in the Introduction (see, e.g., ref 23).

Final Remarks

In this work we determined protonation constants for several unsubstituted and *N*-alkyl-substituted amines, in NaCl aqueous solution at different ionic strengths. We focused our attention on the *I* dependence of protonation constants of some amines: the effect on thermodynamic parameters of electronic properties and molecular topology of polyamines has been discussed in a recent review by Bencini et al.[53]

The main conclusions may be summarized as follows:

(i) The dependence on ionic strength of amine protonation constants is very strong and is significantly affected by *N*-alkyl substitution.

(ii) For each group of amines (unsubstituted diamines, unsubstituted and partially substituted triamines, tetraamines, and fully substituted amines) dependence on ionic strength is very similar.

(iii) DHT (eq 3) and Pitzer (eq 7) parameters are fairly constant for amines belonging to the same group, and the use of common parameters gave acceptable results.

(iv) The *I* dependence of free ions can be interpreted in terms of the formation of $AH_i^{i+}-Cl^-$ ion pairs, the formation constants of which depend strictly on polyammonium cation charge and on *N*-alkyl substitution: stability is higher for substituted than for unsubstituted amines (Table 16; Figure 3).

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Received for review May 2, 2001. Accepted July 10, 2001. We thank MURST for financial support.

JE010143G