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Ionic Strength Dependence of Protonation Constants of *N*-Alkyl Substituted Open Chain Diamines in $NaCl_{aq}$

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The protonation of nine *N*-alkyl substitited diamines was studied in $NaCl_{aq}$ in the ionic strength range $0.1 < I/\text{mol}\cdot\text{L}^{-1} < 5$, at $t = 25$ °C. The dependence on ionic strength of protonation constants was taken into account by using two different models, namely a Debye−Hückel type equation and a simplified version of Pitzer equations. The dependence on *N*-alkyl substitution of both protonation constants and their parameters for the medium effects is discussed, and empirical relationships are reported.

Introduction

Amines are part of the basic building block of life, amino acids, and are widely found in nature. They are present in all biological fluids as trace components and in natural waters; in marine environment they can also be sequestered by living organisms such as bacteria. Moreover, amines have different relevant applications in medicine, biochemistry, industry, and food conservation.[1−4] In medicine, biogenic or naturally occurring amines have been the subject of a great deal of research, particularly in neuroscience,[1] and in general an excess of these compounds in biological tissues and fluids may indicate disease.[2] In biological systems, amines are involved in a variety of fundamental cellular processes such as mRNA translation and tissue differentiation and they also aid the stabilization of the structures of tRNA and DNA.[3] In foodstuffs the concentrations of bioamines give information on freshness and good conservation.[4]

The study of basicity of amines in aqueous solution is important for speciation studies, and it has to be investigated before a complexation study. In the literature are present many data on protonation of polyamines, but in several cases the authors have studied the amines at a single ionic strength.[5−37] Instead the dependence of protonation constants of amines on ionic strengths has been largely studied by Finnish authors, using mainly $NaClO_4$ as background salt.[12,14−16,38−41] We carried out a systematic study on the protonation of amines in NaCl, because this salt is present in almost all the biological and natural fluids. We published some works on thermodynamic parameters of linear unsubstituted and substituted polyamines at different ionic strengths.[42−48]

In this work we report new data obtained by a potentiometric investigation (H^+-glass electrode) of the protonation of nine substituted diamines in aqueous NaCl solutions at different ionic strengths, $0.1 \le I \le 5$ mol·L^{-1} and $t = 25$ °C; the considered diamines are different for extent of substitution, structure (symmetrical or asymmetrical), and type of substitution (methyl or ethyl groups) in order to understand the influence of *N*-alkyl substitution on the protonation. We have considered some different models for the dependence on medium (Debye−Hückel and Pitzer type equations) both of new protonation data on substituted diamines and of previous data relative to another substituted one.[44] The trends in protonation constants and parameters for dependence on ionic strengths are examined for predictive applications. In the Supporting Information (Table s3) we have reported numerous comparisons between our data and literature protonation data on substituted diamines[5−37] (which refer to a maximum value of ionic strength equal to 1 or 2 mol·L^{-1}). Table 1 shows formulas and abbreviations of the diamines considered in this work.

Experimental Section

Chemicals. The diamines [*N*-ethylethylenediamine (**1**); *N*,*N*′-dimethylethylenediamine (**2**); *N*,*N*-dimethylethylenediamine (**3**); 1,2-diamino-2-methylpropane (**4**); *N*-methylethylenediamine (**5**); *N*,*N*,*N*′-trimethylethylenediamine (**6**); *N*,*N*′-dimethyl-1,3-diaminopropane (**7**); *N*,*N*′-diethyl-1,3-diaminopropane (**8**); *N*,*N*-dimethyl-1,3-diaminopropane (**9**)] were Aldrich or Sigma products and were purified by transformation into the corresponding hydrochlorides: their purity, checked alkalimetrically, was always >99.5%. HCl and NaOH solutions were prepared by diluting concentrated Fluka ampules and were standardized against sodium carbonate or potassium biphthalate, respectively. Sodium chloride (Fluka, puriss., p.a.) was prepared by mass from the solid product previously dried in stove at 140 °C. All the solutions were prepared using analytical grade water ($R = 18$ MΩ cm^{-1}) and grade A glassware.

Apparatus and Procedure. Potentiometric titrations were carried out at (25.0 ± 0.1 °C) using apparatus consisting of a model 713 Metrohm potentiometer, equipped with a combined glass electrode (Ross type 8102, from Orion) and a model 765 Metrohm motorized burette. The estimated accuracy was ±0.2 mV and ±0.003 mL for emf and titrant volume readings, respectively. The apparatus was connected to a PC, and automatic titrations were performed using a suitable computer program to control titrant delivery and data acquisition and to check for emf stability. All titrations were carried out under magnetic

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Table 1. Polyamines Considered in This Work

symbol	amine	name
1	$H_2N-(CH_2)_2-NH-C_2H_5$	*N*-ethylethylenediamine
2	$CH_3-NH-(CH_2)_2-NH-CH_3$	*N*,*N*′-dimethylethylenediamine
3	$H_2N-(CH_2)_2-N(CH_3)_2$	*N*,*N*-dimethylethylenediamine
4	$H_2N-CH_2-C(CH_3)_2-NH_2$	1,2-diamino-2-methylpropane
5	$H_2N-(CH_2)_2-NH-CH_3$	*N*-methylethylenediamine
6	$CH_3-NH-(CH_2)_2-N(CH_3)_2$	*N*,*N*,*N*′-trimethylethylenediamine
7	$CH_3-NH-(CH_2)_3-NH-CH_3$	*N*,*N*′-dimethyl-1,3-diaminopropane
8	$H_5C_2-NH-(CH_2)_3-NH-C_2H_5$	*N*,*N*′-diethyl-1,3-diaminopropane
9	$H_2N-(CH_2)_3-N(CH_3)_2$	*N*,*N*-dimethyl-1,3-diaminopropane
10[a]	$(CH_3)_2N-(CH_2)_2-N(CH_3)_2$	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine

[a] Reference 44.

stirring, and presaturated N_2 was bubbled through the purified solution in order to exclude O_2 and CO_2 inside. A volume of 25 mL of the solution containing the amine hydrochloride under study was titrated with standard NaOH up to 80−90% neutralization. The concentrations used in the experiments were $C_{\mathrm{amine \cdot HCl}} = 4-6\ \mathrm{mmol \cdot L^{-1}}$ and $C_{\mathrm{NaCl}} = 0.1-5\ \mathrm{mol \cdot L^{-1}}$. Separate titrations of HCl at the same ionic strength as that of the sample under study were carried out to determine the standard electrode potential $E°$ and to obtain $\mathrm{pH} = -\log [H^+]$ readings. The reliability of the calibration in the alkaline range was checked by calculating $\mathrm{p}K_{\mathrm{w}}$ values.

Calculations. All the parameters relative to the electrode system (formal potential $E°$ and coefficient of junction potential j_{a}, $E_j = j_{\mathrm{a}}[H^+]$) and to alkalimetric purity determination were refined using the nonlinear least squares computer program ESAB2M.[49] This program also refines the conditional protonation constants of diamines at the specific ionic strength value of the titration. The nonlinear fitting program LIANA[50] calculates the protonation constant values of the diamines at $I = 0\ \mathrm{mol \cdot L^{-1}}$, from the conditional values at different ionic strengths, using different equations and the relative parameters for the ionic strength dependence. Other details of calculation methods and programs have already been reported.[50] The conversion of concentrations and protonation constants from the molar to the molal scale was obtained using densities of NaCl aqueous solutions as previously reported.[51]

Results and Discussion

Amine protonation constants are expressed according to the following equilibria:

1. stepwise protonation reaction

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

2. overall protonation reaction

$$A^0 + iH^+ = H_iA^{i+} \qquad \beta_i^{\mathrm{H}} = \Pi K_i^{\mathrm{H}}$$

The apparent molar protonation constants were calculated at each ionic strength from each experimental measure, and these values are reported in Table 2. In this table we report all the experimental protonation values. The effective ionic strength was calculated, for each solution, at each protonation step: differences in $\log K_i^{\mathrm{H}}$, at the same I value, and standard deviations are compatible with the precision of the experimental apparatus. For all the amines and for both protonation steps K_i^{H} increases sharply with ionic strength. As an example we report in Figure 1 $\log \beta_2^{\mathrm{H}}$ versus $I^{1/2}$ for **1**: as can be seen, we have a regular increasing function. The thermodynamic molar and molal values of protonation constants ${}^{\mathrm{T}}K_{i\ \mathrm{c}}^{\mathrm{H}}$ and ${}^{\mathrm{T}}K_{i\ \mathrm{m}}^{\mathrm{H}}$, respectively, are calculated by extrapolation to zero ionic strength (Table 3 and Table s1 in the Supporting Information). The dependence on ionic strength was taken into account using the Debye−Hückel type equation:[52]

$$\log K_i^{\mathrm{H}} = \log {}^{\mathrm{T}}K_i^{\mathrm{H}} - z_i^{*}0.51\sqrt{I}/(1 + 1.5\sqrt{I}) + C_iI + E_iI^2 \qquad (1)$$

where $z_i^* = 2(i - 1)$, ${}^{\mathrm{T}}K_i^{\mathrm{H}}$ is the protonation constant at infinite dilution, and C_i and E_i are empirical parameters. This equation has been widely used in our laboratory (sometimes with an additional term, $D_iI^{3/2}$), and in several cases it was not necessary to consider the quadratic term EI^2, in particular for $I < 2\ \mathrm{mol \cdot L^{-1}}$. Recently we revised our extensive database on the protonation of carboxylates and amines and found that in eq 1 we may use only the first-order linear term CI, but with C depending on ionic strength:

$$C = C_\infty + (C_0 - C_\infty)F(I) \qquad (1a)$$

$$F(I) = (I + 1)^{-1} \qquad (1b)$$

where C_∞ and C_0 are the values of C at $I \to \infty$ and $I = 0$, respectively. This approach is quite similar to that already proposed by Pitzer, who suggested for the function $F(I)$ the form[53]

$$F(I) = [1 - (1 + 2\sqrt{I} - 2I) \exp(-2\sqrt{I})]$$

In Table 3 we report (a) the protonation constants at $I = 0\ \mathrm{mol \cdot L^{-1}}$, that is, ${}^{\mathrm{T}}\log K^{\mathrm{H}}$; (b) the parameter C_i considered as constant in the whole ionic strength range; and (c) the parameters C_∞ and C_0 of eq 1a. For each protonation step of each amine we report also the standard deviation on the fit, and we can see that there is a significant improvement by using eq 1a instead of a C value independent of I. Analogous calculations were performed for molal protonation constant, and the relative table is given as Supporting Information (Table s1). Using eq 1 is equivalent to the SIT (specific ion interaction theory) approach for the dependence of molal equilibrium constants on medium,[54] where $C = \Delta\epsilon$ (ϵ = specific interaction parameter).

In the last three decades there has been an always increasing interest in the use of Pitzer equations[53] to take into account the dependence on medium of equilibrium thermodynamic parameters. Using data from this work, we have calculated specific interaction parameters. Protonation data can be expressed as a function of activity coefficient (γ) (I, $K_{1\mathrm{m}}^{\mathrm{H}}$, and $K_{2\mathrm{m}}^{\mathrm{H}}$ are expressed in the molal concentration scale)

Table 2. Protonation Constants (Molar Concentration Scale) of Substituted Diamines at Different Ionic Strengths, at t = 25 °C

amine[a]	I/mol·L^{-1}	log $K_1^{\mathrm{H}} \pm \sigma^b$	I/mol·L^{-1}	log $K_2^{\mathrm{H}} \pm \sigma^b$	amine[a]	I/mol·L^{-1}	log $K_1^{\mathrm{H}} \pm \sigma^b$	I/mol·L^{-1}	log $K_2^{\mathrm{H}} \pm \sigma^b$
1	0.108	10.131 ± 0.003	0.112	7.114 ± 0.003	**1**	0.958	10.424 ± 0.002	0.985	7.517 ± 0.002
	0.108	10.130 ± 0.002	0.112	7.107 ± 0.002		0.958	10.445 ± 0.003	0.985	7.527 ± 0.003
	0.112	10.165 ± 0.003	0.117	7.118 ± 0.003		2.883	11.076 ± 0.004	2.944	8.049 ± 0.005
	0.112	10.166 ± 0.001	0.117	7.121 ± 0.001		2.881	11.098 ± 0.006	2.944	8.058 ± 0.007
	0.491	10.288 ± 0.002	0.501	7.346 ± 0.002		2.834	11.042 ± 0.003	2.917	8.050 ± 0.003
	0.491	10.310 ± 0.002	0.501	7.338 ± 0.002		2.835	11.036 ± 0.005	2.917	8.052 ± 0.006
	0.488	10.293 ± 0.002	0.502	7.343 ± 0.002		4.819	11.553 ± 0.006	4.930	8.548 ± 0.007
	0.488	10.300 ± 0.002	0.502	7.357 ± 0.002		4.818	11.546 ± 0.007	4.930	8.56 ± 0.01
	0.970	10.422 ± 0.002	0.989	7.513 ± 0.002		4.730	11.531 ± 0.007	4.874	8.559 ± 0.008
	0.971	10.443 ± 0.001	0.990	7.523 ± 0.002		4.730	11.53 ± 0.01	4.874	8.546 ± 0.008
2	0.102	9.978 ± 0.002	0.108	7.076 ± 0.003	**2**	0.888	10.241 ± 0.005	0.942	7.513 ± 0.005
	0.102	9.999 ± 0.002	0.108	7.081 ± 0.002		0.880	10.297 ± 0.004	0.935	7.528 ± 0.004
	0.103	9.975 ± 0.002	0.111	7.072 ± 0.002		2.695	10.933 ± 0.007	2.827	8.136 ± 0.008
	0.103	9.939 ± 0.007	0.111	7.061 ± 0.007		2.695	10.924 ± 0.007	2.827	8.133 ± 0.008
	0.464	10.117 ± 0.003	0.484	7.330 ± 0.003		2.497	10.819 ± 0.008	2.655	8.08 ± 0.01
	0.464	10.140 ± 0.003	0.484	7.346 ± 0.004		2.502	10.729 ± 0.007	2.655	8.043 ± 0.008
	0.449	10.082 ± 0.004	0.477	7.319 ± 0.004		4.444	11.684 ± 0.009	4.844	8.76 ± 0.01
	0.449	10.114 ± 0.004	0.478	7.335 ± 0.005		4.444	11.69 ± 0.01	4.736	8.77 ± 0.01
	0.922	10.262 ± 0.004	0.963	7.523 ± 0.005		4.293	11.55 ± 0.01	4.657	8.73 ± 0.01
	0.923	10.248 ± 0.004	0.962	7.515 ± 0.005		4.302	11.55 ± 0.01	4.662	8.73 ± 0.02
3	0.102	9.513 ± 0.002	0.108	6.443 ± 0.002	**3**	0.895	9.829 ± 0.003	0.950	6.931 ± 0.003
	0.102	9.528 ± 0.003	0.108	6.456 ± 0.003		0.895	9.820 ± 0.002	0.950	6.930 ± 0.002
	0.103	9.564 ± 0.003	0.112	6.471 ± 0.002		2.745	10.390 ± 0.003	2.860	7.538 ± 0.003
	0.103	9.537 ± 0.002	0.112	6.457 ± 0.002		2.729	10.472 ± 0.004	2.844	7.554 ± 0.004
	0.467	9.696 ± 0.003	0.487	6.733 ± 0.003		2.617	10.469 ± 0.005	2.773	7.554 ± 0.005
	0.467	9.720 ± 0.002	0.487	6.751 ± 0.002		2.602	10.439 ± 0.003	2.754	7.548 ± 0.004
	0.453	9.695 ± 0.002	0.481	6.738 ± 0.002		4.165	11.005 ± 0.008	4.505	8.095 ± 0.009
	0.453	9.698 ± 0.002	0.481	6.741 ± 0.002		4.166	11.025 ± 0.009	4.506	8.10 ± 0.01
	0.929	9.836 ± 0.002	0.968	6.937 ± 0.003		4.450	11.115 ± 0.009	4.684	8.14 ± 0.01
	0.929	9.839 ± 0.002	0.968	6.933 ± 0.002		4.447	11.096 ± 0.008	4.682	8.13 ± 0.01
4	0.108	9.814 ± 0.003	0.112	6.502 ± 0.003	**4**	0.961	10.095 ± 0.002	0.988	6.891 ± 0.002
	0.108	9.830 ± 0.003	0.112	6.509 ± 0.003		0.961	10.067 ± 0.002	0.988	6.886 ± 0.002
	0.112	9.808 ± 0.002	0.117	6.504 ± 0.003		2.895	10.575 ± 0.002	2.948	7.372 ± 0.002
	0.112	9.787 ± 0.002	0.117	6.497 ± 0.002		2.896	10.535 ± 0.002	2.948	7.368 ± 0.002
	0.495	9.930 ± 0.002	0.505	6.727 ± 0.003		2.844	10.508 ± 0.003	2.920	7.357 ± 0.004
	0.491	9.947 ± 0.001	0.501	6.732 ± 0.001		2.846	10.510 ± 0.006	2.919	7.367 ± 0.006
	0.487	9.935 ± 0.002	0.502	6.728 ± 0.003		4.794	11.120 ± 0.005	4.902	7.876 ± 0.006
	0.487	9.917 ± 0.002	0.502	6.715 ± 0.002		4.795	11.166 ± 0.008	4.902	7.896 ± 0.009
	0.974	10.079 ± 0.002	0.992	6.880 ± 0.002		4.686	11.211 ± 0.007	4.827	7.897 ± 0.008
	0.974	10.103 ± 0.002	0.992	6.889 ± 0.002		4.688	11.147 ± 0.006	4.826	7.881 ± 0.006
5	0.108	10.006 ± 0.005	0.115	7.037 ± 0.002	**5**	0.888	10.292 ± 0.003	0.942	7.443 ± 0.003
	0.108	10.026 ± 0.002	0.115	7.037 ± 0.002		0.888	10.295 ± 0.003	0.942	7.442 ± 0.003
	0.106	10.024 ± 0.002	0.110	7.039 ± 0.002		2.645	10.821 ± 0.004	2.763	7.936 ± 0.005
	0.106	10.008 ± 0.002	0.110	7.032 ± 0.003		2.720	10.869 ± 0.003	2.937	7.952 ± 0.004
	0.472	10.153 ± 0.002	0.491	7.259 ± 0.002		2.607	10.886 ± 0.004	2.775	7.963 ± 0.005
	0.472	10.120 ± 0.004	0.491	7.260 ± 0.004		2.612	10.844 ± 0.006	2.778	7.960 ± 0.007
	0.496	10.134 ± 0.002	0.494	7.262 ± 0.002		4.445	11.538 ± 0.006	4.707	8.488 ± 0.006
	0.496	10.136 ± 0.002	0.493	7.260 ± 0.003		4.454	11.478 ± 0.003	4.707	8.469 ± 0.004
	0.923	10.290 ± 0.002	0.962	7.433 ± 0.002		4.349	11.48 ± 0.01	4.666	8.49 ± 0.01
	0.923	10.307 ± 0.002	0.962	7.440 ± 0.002		4.353	11.442 ± 0.009	4.670	8.47 ± 0.01
6	0.102	9.607 ± 0.003	0.108	6.323 ± 0.004	**6**	0.965	10.028 ± 0.002	0.991	6.862 ± 0.002
	0.102	9.603 ± 0.003	0.108	6.319 ± 0.003		0.965	10.025 ± 0.002	0.991	6.871 ± 0.002
	0.103	9.613 ± 0.003	0.111	6.326 ± 0.003		2.896	10.650 ± 0.002	2.949	7.564 ± 0.002
	0.103	9.622 ± 0.002	0.112	6.329 ± 0.002		2.895	10.690 ± 0.003	2.948	7.580 ± 0.003
	0.464	9.785 ± 0.003	0.484	6.634 ± 0.003		2.844	10.652 ± 0.004	2.919	7.563 ± 0.004
	0.464	9.796 ± 0.002	0.484	6.641 ± 0.002		2.844	10.629 ± 0.003	2.919	7.558 ± 0.003
	0.481	9.828 ± 0.002	0.497	6.639 ± 0.002		4.804	11.344 ± 0.005	4.904	8.250 ± 0.006
	0.481	9.823 ± 0.002	0.497	6.633 ± 0.002		4.806	11.315 ± 0.003	4.905	8.241 ± 0.004
	0.978	10.006 ± 0.003	0.995	6.860 ± 0.003		4.698	11.257 ± 0.005	4.838	8.214 ± 0.006
	0.978	10.013 ± 0.002	0.996	6.866 ± 0.002		4.700	11.215 ± 0.005	4.839	8.199 ± 0.006
7	0.109	10.588 ± 0.004	0.112	8.800 ± 0.004	**7**	0.957	10.911 ± 0.002	0.986	9.260 ± 0.003
	0.109	10.633 ± 0.003	0.112	8.818 ± 0.003		0.957	10.914 ± 0.003	0.986	9.260 ± 0.004
	0.112	10.619 ± 0.003	0.117	8.810 ± 0.003		2.865	11.48 ± 0.01	2.948	9.851 ± 0.009
	0.112	10.606 ± 0.003	0.117	8.807 ± 0.004		2.872	11.39 ± 0.01	2.948	9.84 ± 0.01
	0.492	10.763 ± 0.002	0.502	9.069 ± 0.003		2.819	11.316 ± 0.006	2.911	9.828 ± 0.007
	0.492	10.781 ± 0.002	0.502	9.074 ± 0.002		2.818	11.324 ± 0.007	2.911	9.821 ± 0.008
	0.488	10.771 ± 0.003	0.503	9.064 ± 0.003		4.617	12.19 ± 0.02	4.803	10.37 ± 0.01
	0.488	10.767 ± 0.002	0.503	9.064 ± 0.003		4.629	12.16 ± 0.02	4.802	10.36 ± 0.01
	0.970	10.941 ± 0.002	0.992	9.271 ± 0.003		4.630	12.267 ± 0.009	4.866	10.477 ± 0.004
	0.969	10.985 ± 0.001	0.992	9.283 ± 0.002		4.630	12.280 ± 0.009	4.866	10.480 ± 0.004
8	0.108	10.677 ± 0.004	0.113	8.961 ± 0.004	**8**	0.952	10.916 ± 0.006	0.981	9.413 ± 0.007
	0.108	10.670 ± 0.004	0.113	8.954 ± 0.005		0.951	11.045 ± 0.003	0.981	9.433 ± 0.003
	0.104	10.677 ± 0.004	0.108	8.965 ± 0.005		2.840	11.67 ± 0.01	2.943	10.04 ± 0.01
	0.104	10.676 ± 0.004	0.108	8.963 ± 0.005		2.845	11.72 ± 0.01	2.943	10.057 ± 0.008
	0.491	10.921 ± 0.002	0.502	9.245 ± 0.003		2.802	11.57 ± 0.01	2.915	10.03 ± 0.01

Table 2 (Continued)

amine[a]	I/mol·L^{-1}	log $K_1^{\mathrm{H}} \pm \sigma^b$	I/mol·L^{-1}	log $K_2^{\mathrm{H}} \pm \sigma^b$	amine[a]	I/mol·L^{-1}	log $K_1^{\mathrm{H}} \pm \sigma^b$	I/mol·L^{-1}	log $K_2^{\mathrm{H}} \pm \sigma^b$
8	0.491	10.853 ± 0.005	0.502	9.234 ± 0.005	**8**	2.802	11.59 ± 0.01	2.916	10.035 ± 0.009
	0.487	10.869 ± 0.003	0.503	9.234 ± 0.004		4.690	12.56 ± 0.02	4.871	10.659 ± 0.003
	0.487	10.863 ± 0.004	0.503	9.239 ± 0.005		4.700	12.53 ± 0.02	4.870	10.669 ± 0.002
	0.964	10.948 ± 0.008	0.986	9.437 ± 0.009		4.650	12.37 ± 0.02	4.840	10.663 ± 0.004
	0.968	10.88 ± 0.01	0.989	9.42 ± 0.01		4.650	12.38 ± 0.02	4.840	10.652 ± 0.005
9	0.108	10.191 ± 0.003	0.112	8.223 ± 0.003	**9**	0.957	10.490 ± 0.001	0.984	8.699 ± 0.001
	0.108	10.229 ± 0.004	0.112	8.243 ± 0.004		0.957	10.500 ± 0.002	0.984	8.708 ± 0.002
	0.112	10.193 ± 0.002	0.117	8.218 ± 0.003		2.875	11.037 ± 0.002	2.936	9.320 ± 0.002
	0.112	10.185 ± 0.002	0.117	8.226 ± 0.002		2.879	11.035 ± 0.002	2.939	9.324 ± 0.003
	0.491	10.331 ± 0.002	0.501	8.498 ± 0.002		2.832	11.026 ± 0.004	2.912	9.320 ± 0.005
	0.491	10.350 ± 0.002	0.501	8.503 ± 0.002		2.832	10.994 ± 0.002	2.912	9.322 ± 0.003
	0.487	10.338 ± 0.002	0.502	8.493 ± 0.002		4.784	11.63 ± 0.01	4.902	9.91 ± 0.01
	0.487	10.350 ± 0.002	0.502	8.496 ± 0.002		4.784	11.633 ± 0.008	4.901	9.922 ± 0.008
	0.971	10.476 ± 0.002	0.989	8.702 ± 0.003		4.720	11.655 ± 0.009	4.867	9.928 ± 0.009
	0.970	10.491 ± 0.002	0.989	8.709 ± 0.002		4.724	11.614 ± 0.007	4.867	9.915 ± 0.008

[a] Abbreviations are reported in Table 1. [b] σ = standard deviation.

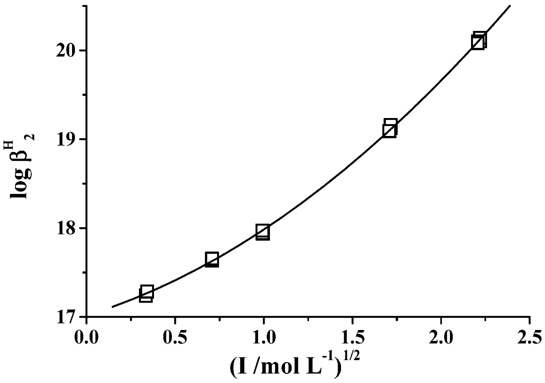

Figure 1. Dependence on ionic strength of the overall protonation constant of **1**, at t = 25 °C, in $\mathrm{NaCl_{aq}}$.

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

$$\ln K_{1\mathrm{m}}^{\mathrm{H}} = \ln {}^{\mathrm{T}}K_{1\mathrm{m}}^{\mathrm{H}} + \ln \gamma_{\mathrm{H^+}} + \ln \gamma_{\mathrm{A^0}} - \ln \gamma_{\mathrm{HA^+}}$$

$$\mathrm{H^+ + HA^+ = H_2A^{2+}}$$

$$\ln K_{2\mathrm{m}}^{\mathrm{H}} = \ln {}^{\mathrm{T}}K_{2\mathrm{m}}^{\mathrm{H}} + \ln \gamma_{\mathrm{H^+}} + \ln \gamma_{\mathrm{HA^+}} - \ln \gamma_{\mathrm{H_2A^{2+}}}$$

and, using Pitzer equations, we have

$$\ln K_{1\mathrm{m}}^{\mathrm{H}} = \ln {}^{\mathrm{T}}K_{1\mathrm{m}}^{\mathrm{H}} + P_1 I + P_2 f + P_3 I^2 \qquad (2)$$

$$\ln K_{2\mathrm{m}}^{\mathrm{H}} = \ln {}^{\mathrm{T}}K_{2\mathrm{m}}^{\mathrm{H}} + P_4 I + P_5 f + P_6 I^2 - 2f'' - 0.2664 f_1 \qquad (2a)$$

where

$$P_1 = 2(\beta^{(0)}{}_{\mathrm{H,Cl}} - \beta^{(0)}{}_{\mathrm{HA,Cl}} + \theta_{\mathrm{H,Na}} - \theta_{\mathrm{HA,Na}} + \lambda_{\mathrm{A}})$$

$$P_2 = (\beta^{(1)}{}_{\mathrm{H,Cl}} - \beta^{(1)}{}_{\mathrm{HA,Cl}})$$

$$P_3 = (C^{\phi}{}_{\mathrm{H,Cl}}/|z_{\mathrm{H}}z_{\mathrm{Cl}}|^{1/2} - C^{\phi}{}_{\mathrm{HA,Cl}}/|z_{\mathrm{HA}}z_{\mathrm{Cl}}|^{1/2} + \psi_{\mathrm{H,Na,Cl}} - \psi_{\mathrm{HA,Na,Cl}})$$

$$P_4 = 2(\beta^{(0)}{}_{\mathrm{H,Cl}} + \beta^{(0)}{}_{\mathrm{HA,Cl}} - \beta^{(0)}{}_{\mathrm{H_2A,Cl}} + \theta_{\mathrm{H,Na}} + \theta_{\mathrm{HA,Na}} - \theta_{\mathrm{H_2A,Na}})$$

$$P_5 = (\beta^{(1)}{}_{\mathrm{H,Cl}} + \beta^{(1)}{}_{\mathrm{HA,Cl}} - \beta^{(1)}{}_{\mathrm{H_2A,Cl}})$$

$$P_6 = (C^{\phi}{}_{\mathrm{H,Cl}}/|z_{\mathrm{H}}z_{\mathrm{Cl}}|^{1/2} + C^{\phi}{}_{\mathrm{HA,Cl}}/|z_{\mathrm{HA}}z_{\mathrm{Cl}}|^{1/2} - C^{\phi}{}_{\mathrm{H_2A,Cl}}/|z_{\mathrm{H_2A}}z_{\mathrm{Cl}}|^{1/2} + \psi_{\mathrm{H,Na,Cl}} + \psi_{\mathrm{HA,Na,Cl}} - \psi_{\mathrm{H_2A,Na,Cl}})$$

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

$$f'' = -0.3912 + 0.0006636\Delta T + 0.000003562\Delta T^2[I^{1/2}/(1 + 1.2I^{1/2}) + 1.667 \ln (1 + 1.2I^{1/2})]$$

$$f_1 = [-1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2})]$$

$\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters between two ions of opposite signs, θ is an interaction parameter between two ions of the same sign, ψ is a triple interaction parameter (+ − +, − + −), and λ is the interaction parameter for neutral species. The parameters P_1−P_6 are reported in Table 4. Note that, in fitting molal protonation constants to eqs 2 and 2a, the parameters P_2 and P_5 (and the relative terms) are not necessary (statistical parameters of the fit are not improved using the relative terms) and were not considered. Moreover, also other Pitzer models were analyzed which neglect the quadratic term but consider the term containing f, P_5 (an example is reported as Supporting Information in Table s2); the best one is that represented by the parameters reported in Table 4. From the numerical values of empirical P parameters it is possible, using reported values of Pitzer interaction parameters, such as $\beta^{(0)}{}_{\mathrm{H,Cl}}$, $\theta_{\mathrm{H,Na}}$, $\beta^{(1)}{}_{\mathrm{H,Cl}}$, and so forth, to calculate specific interaction parameters relative to the amines studied in this work.

Now we can compare the results obtained by using eqs 1 or 2. The standard deviations in the fit for the two models are (molal scale) σ = 0.034 and 0.012 (log K_1^{H}, log K_2^{H}) and σ = 0.033 and 0.012, respectively. By this criterion the two models are equivalent.

Influence of Substitution. In the gas phase and in some solvents which cannot form hydrogen bonds, the order of basicity for ammonia and mono-, di-, and trisubstituted amines is $\mathrm{(CH_3)_3N > (CH_3)_2NH > (CH_3)NH_2 > NH_3}$. Instead, in aqueous solution is present the solvation effect, and for example, at t = 25 °C, the order is $\mathrm{(CH_3)_2NH \approx (CH_3)NH_2 > (CH_3)_3N > NH_3}$. In this case the basic-increasing effect of methyl substitution is opposed by the basic-weakening effect caused by a reduction in hydrogen bonding, since the methyl group exercises a “solvent exclusion” effect.[55] Also in the case of diamines, such as those studied in this work, the basicity depends both on inductive effects and on hydrogen bonding. Both methyl and ethyl substitution affect the basicity of the diamines, and the effect of N-ethyl substitution is significantly higher. These effects have been studied by Näsänen et al., and a linear combination of effects has been proposed.[16] The

Table 3. Molar Values of Protonation Constants of Substituted Amines at Infinite Dilution, Together with the Parameters for the Dependence on Ionic Strength, at $t = 25$ °C

amine	$\log^{T} K^{H}_{1c} \pm \sigma$[a]	σ_1 [b]	$\log^{T} K^{H}_{2c} \pm \sigma$[a]	σ_2 [b]	$C_1 \pm \sigma$, $C_{1\infty} \pm \sigma$, $C_{10} \pm \sigma$[a]	$C_2 \pm \sigma$, $C_{2\infty} \pm \sigma$, $C_{20} \pm \sigma$[a]
1	10.141 ± 0.002	0.0351	6.871 ± 0.001	0.0103	0.305 ± 0.002, 0.273 ± 0.004, 0.49 ± 0.02	0.2346 ± 0.0007, 0.227 ± 0.002, 0.28 ± 0.01
	10.087 ± 0.007	0.0276	6.857 ± 0.003	0.0089		
2	9.919 ± 0.005	0.0525	6.826 ± 0.002	0.0190	0.384 ± 0.004, 0.418 ± 0.005, 0.19 ± 0.02	0.292 ± 0.002, 0.291 ± 0.002, 0.30 ± 0.01
	9.97 ± 0.02	0.0460	6.823 ± 0.005	0.0190		
3	9.511 ± 0.003	0.0306	6.234 ± 0.004	0.0205	0.357 ± 0.001, 0.359 ± 0.003, 0.34 ± 0.02	0.295 ± 0.001, 0.278 ± 0.002, 0.40 ± 0.01
	9.515 ± 0.007	0.0305	6.199 ± 0.004	0.0163		
4	9.788 ± 0.004	0.0433	6.252 ± 0.002	0.0213	0.283 ± 0.002, 0.293 ± 0.005, 0.22 ± 0.02	0.225 ± 0.001, 0.229 ± 0.003, 0.19 ± 0.02
	9.805 ± 0.003	0.0424	6.260 ± 0.007	0.0202		
5	9.977 ± 0.002	0.0238	6.787 ± 0.001	0.0168	0.340 ± 0.001, 0.347 ± 0.004, 0.30 ± 0.02	0.2466 ± 0.0006, 0.246 ± 0.002, 0.25 ± 0.01
	9.987 ± 0.004	0.0230	6.786 ± 0.002	0.0168		
6	9.633 ± 0.005	0.0395	6.112 ± 0.005	0.0244	0.351 ± 0.002, 0.307 ± 0.002, 0.62 ± 0.01	0.327 ± 0.001, 0.301 ± 0.002, 0.50 ± 0.01
	9.556 ± 0.003	0.0220	6.055 ± 0.001	0.0136		
7	10.586 ± 0.005	0.0906	8.573 ± 0.006	0.0250	0.326 ± 0.006, 0.34 ± 0.01, 0.26 ± 0.06	0.271 ± 0.003, 0.252 ± 0.007, 0.37 ± 0.03
	10.61 ± 0.02	0.0872	8.547 ± 0.007	0.0238		
8	10.632 ± 0.003	0.0749	8.723 ± 0.004	0.0184	0.373 ± 0.003, 0.41 ± 0.01, 0.18 ± 0.05	0.290 ± 0.001, 0.277 ± 0.005, 0.37 ± 0.02
	10.67 ± 0.02	0.0678	8.699 ± 0.007	0.0163		
9	10.181 ± 0.001	0.0219	7.993 ± 0.003	0.0174	0.304 ± 0.001, 0.302 ± 0.003, 0.32 ± 0.02	0.286 ± 0.001, 0.269 ± 0.002, 0.40 ± 0.02
	10.178 ± 0.006	0.0219	7.962 ± 0.005	0.0120		
10	9.22 ± 0.01	0.0249	5.672 ± 0.007	0.0178	0.343 ± 0.005, 0.274 ± 0.004, 0.60 ± 0.01	0.333 ± 0.005, 0.288 ± 0.004, 0.51 ± 0.01
	9.151 ± 0.004	0.0031	5.624 ± 0.004	0.0058		
		0.044[c]		0.019[c]		
		0.037[c]		0.015[c]		

[a] σ = standard deviation. [b] σ_1 and σ_2 are the standard deviations on the fit of log K_1^H and log K_2^H, respectively. [c] Mean values of the standard deviation on the fit; first row values are obtained by considering C (eq 1) independent of I, and second row values are obtained using eq 1a.

Table 4. Pitzer Parameters (Molal Concentration Scale) Calculated with Eqs 2 and 2a

amine	$\log^{T} K^{H}_{1m} \pm \sigma$[a]	σ_1 [b]	$\log^{T} K^{H}_{2m} \pm \sigma$[a]	σ_2 [b]	$P_1 \pm \sigma$[a]	$P_3 \pm \sigma$[a]	$P_4 \pm \sigma$[a]	$P_6 \pm \sigma$[a]
1	10.111 ± 0.004	0.0217	6.815 ± 0.003	0.0123	0.81 ± 0.01	−0.037 ± 0.002	0.132 ± 0.007	0.023 ± 0.001
2	9.957 ± 0.003	0.0381	6.783 ± 0.002	0.0136	0.68 ± 0.01	0.022 ± 0.002	0.211 ± 0.007	0.031 ± 0.001
3	9.520 ± 0.004	0.0279	6.172 ± 0.002	0.0128	0.77 ± 0.01	−0.009 ± 0.002	0.277 ± 0.009	0.021 ± 0.002
4	9.809 ± 0.002	0.0360	6.214 ± 0.002	0.0118	0.53 ± 0.01	0.007 ± 0.002	0.030 ± 0.007	0.039 ± 0.001
5	9.986 ± 0.003	0.0214	6.742 ± 0.003	0.0143	0.71 ± 0.01	−0.005 ± 0.003	0.107 ± 0.009	0.033 ± 0.002
6	9.600 ± 0.004	0.0319	6.037 ± 0.001	0.0089	0.915 ± 0.008	−0.039 ± 0.001	0.399 ± 0.004	0.0102 ± 0.0008
7	10.65 ± 0.01	0.0659	8.518 ± 0.003	0.0175	0.44 ± 0.03	0.044 ± 0.006	0.20 ± 0.01	0.027 ± 0.03
8	10.67 ± 0.01	0.0581	8.669 ± 0.01	0.0110	0.62 ± 0.03	0.029 ± 0.007	0.250 ± 0.007	0.023 ± 0.001
9	10.188 ± 0.002	0.0207	7.930 ± 0.001	0.0086	0.644 ± 0.008	−0.007 ± 0.002	0.276 ± 0.004	0.0168 ± 0.0007
10	9.174 ± 0.006	0.0081	5.608 ± 0.002	0.0058	1.00 ± 0.02	−0.073 ± 0.008	0.38 ± 0.01	0.030 ± 0.005
		0.0330[c]		0.0117[c]				

[a] σ = standard deviation. [b] Standard deviations on the fit. [c] Mean values.

parameters that define the dependence on ionic strength using both models are quite similar for all the diamines here studied (Tables 3 and 4), and this is in accordance with our previous findings. Nevertheless, some small differences can be evidenced as a function of alkyl substitution.

By considering the C_∞ and C_0 parameters of eq 1a versus the substitution of each aminic group present on the 10 diamines of this work, we have obtained some general equations for the dependence of these parameters on substitution:

$$C_{1\infty} = 0.33\ (\pm 0.01)$$

$$C_{10} = 0.15\ (\pm 0.03) + 0.023\ (\pm 0.003)(x_1^{\ 2} + x_2^{\ 2}) \quad (3)$$

$$C_{2\infty} = 0.268\ (\pm 0.008)$$

$$C_{20} = 0.16\ (\pm 0.02) + 0.017\ (\pm 0.005)[x_1^{\ 2} + 1.5\ (\pm 0.5)x_2^{\ 2}]$$

where x = 1, 2, or 3 for primary, secondary, or tertiary aminic group, respectively (x_1 refers to the first protonable amino groups and x_2 to the second) with a mean deviation $\epsilon = 0.046$. These results are in very good agreement with those obtained in ref 44.

Comparisons with Literature Data. Some diamines whose protonation constants are reported in this work were already studied in different laboratories. In particular, for **1**, **2**, **3**, **4**, **5**, **6**, and **7** we found several data that can be compared with present findings. By using both literature data and our data, we made interpolations and found some recommended values, reported in Table 5, at $I \leq 1$ mol·L^{-1}. The analysis of literature data (in the Supporting Information we report the comparison with literature, in Table s3), together with our data and the results of the interpolation (Table 5), shows that (a) there is no appreciable difference, at the same ionic strength, for constants determined in different ionic media ($I < 1$ mol·L^{-1}), and in many cases it seems that experimental error is higher than these differences; (b) confidence intervals are fairly low and quite constant for all the amines; (c) many of the constants reported in Table 5 can be considered as "recommended" by assuming that for a recommended value an equilibrium value is sufficient at a confidence interval (95% c.i.) ≤ 5%, that is, ±0.02 in log K^H; the other values can be reasonably defined as "tentative". The protonation constant values at $I \geq 2$ mol·L^{-1} cannot be compared with literature, since this (together with our previous reports) is the first systematic investigation on the medium effect at high ionic strengths.

Table 5. Some Recommended or Tentative Values (Molar Concentration Scale), in the Range $0 \le I \le 1$ mol·L^{-1}, Calculated by Considering Both Literature and Present Protonation Constants, at $t = 25$ °C

		log K_i^{H} at the following values of I/mol·L^{-1}			
amine	i	0	0.1	0.5	1.0
1	1	10.13 ± 0.03[a]	10.18 ± 0.02[a]	10.29 ± 0.03[a]	10.44 ± 0.04[a]
	2	6.87 ± 0.03	7.11 ± 0.02	7.34 ± 0.03	7.52 ± 0.04
2	1	10.03 ± 0.02	10.05 ± 0.01	10.13 ± 0.02	10.26 ± 0.02
	2	6.96 ± 0.04	7.17 ± 0.03	7.31 ± 0.04	7.43 ± 0.06
3	1	9.68 ± 0.04	9.69 ± 0.03	9.73 ± 0.02	9.84 ± 0.02
	2	6.42 ± 0.06	6.61 ± 0.04	6.70 ± 0.03	6.79 ± 0.05
4	1	9.75 ± 0.02	9.77 ± 0.02	9.89 ± 0.01	10.05 ± 0.01
	2	6.25 ± 0.01	6.48 ± 0.01	6.67 ± 0.02	6.83 ± 0.03
5	1	10.01 ± 0.01	10.04 ± 0.01	10.17 ± 0.01	10.33 ± 0.02
	2	6.79 ± 0.01	7.03 ± 0.01	7.26 ± 0.01	7.44 ± 0.01
6	1	9.68 ± 0.02	9.71 ± 0.01	9.83 ± 0.01	9.98 ± 0.01
	2	6.13 ± 0.01	6.38 ± 0.01	6.63 ± 0.01	6.83 ± 0.01
7	1	10.62 ± 0.03	10.65 ± 0.03	10.79 ± 0.01	10.96 ± 0.02
	2	8.58 ± 0.03	8.84 ± 0.02	9.10 ± 0.01	9.31 ± 0.02

[a] Errors are expressed as ≥95% confidence intervals.

Final Remarks

The protonation constants of several diamines, partially *N*-alkyl substituted, were reported in a wide ionic strength range in $\mathrm{NaCl_{aq}}$. For all these amines these are the first data at high ionic strength. The dependence on medium was taken into account by using a simple Debye−Hückel type equation (eq 1) and the Pitzer model (eqs 2 and 2a). Both models give reliable results, and when using in the fitting the same number of parameters, the standard deviation in the fit is the same. Small differences can be observed, in the ionic strength dependence, for differently substituted amines (eq 3). In general, it can be affirmed that the low molecular weight aliphatic amine class clearly shows several similarities as concerns both the values of protonation constants and their dependence on ionic strength.

Supporting Information Available:

Tables of protonation data on substituted diamines. This material is available free of charge via the Internet at http://pubs.acs.org.

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