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Protonation Constants of Ethylenediamine, Diethylenetriamine, and Spermine in NaCl(aq), NaI(aq), $(CH_3)_4NCl(aq)$, and $(C_2H_5)_4NI(aq)$ at Different Ionic Strengths and t = 25 °C

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The protonation constants of three linear unsubstituted polyamines were studied potentiometrically at 25 °C in different ionic media and at different ionic strengths (NaCl, NaI, and $(CH_3)_4NCl$: $I \leq 2.5$ mol·L^{-1}; $(C_2H_5)_4NI$: $I \leq 1$ mol·L^{-1}). The general trend for $\log K_i^H$ values is NaCl ≥ NaI ≫ $(CH_3)_4NCl > (C_2H_5)_4NI$. The dependence of the protonation constants on ionic strength was taken into account using a simple Debye−Hückel type equation (molar concentration scale) and the SIT (Specific ion Interaction Theory) approach (molal concentration scale). Differences in protonation constants in the different supporting electrolytes were also interpreted in terms of complex formation by considering the weak species (A = amine; $X^- = Cl^-, I^-$; $M^+ = (CH_3)_4N^+, (C_2H_5)_4N^+$) $H_iAX^{(i-1)}$ and $MH_jA^{(j+1)}$ with $i = 1 \ldots m$ and $j = 0 \ldots (m - 1)$, where m is the maximum protonation degree of the polyamine. The formation constants of these species are linearly dependent on the number of amino groups and on the protonation degree of the polyamine. Some empirical relationships are reported.

Introduction

Amines are of importance in several fields: in medicine, in biochemistry, in food conservation, and in industry.[1−4] In medicine, high quantities of amines in biological fluids and tissues can be indicators of disease. In biochemistry, amines aid the stabilization of the structure of tRNA and DNA and occur in several cellular processes. The freshness and state of conservation of foodstuffs are measured by their amine concentrations. In industry, ethylene amines have numerous uses: in the manufacture of lubricant and fuel additives, because they reduce the deposits caused by the low speed operation of motor vehicles; as asphalt additives; as chelating agents, consisting of polyaminocarboxylic acids and their salts, made from ethylene amines; as corrosion inhibitors in petroleum production operations in the form of amidoamines; in the manufacture of artificial fibers and fabrics; as plastic lubricants.

In nature, natural waters and all biological fluids (blood, urine, saliva) contain amines as trace components (in natural waters they have very variable and low concentrations; in biological fluids, in terms of amino groups, they range from 0.1 to 15 mmol·L^{-1}), which frequently makes them the focus of speciation studies. The protonation of amines in aqueous solution has been studied extensively, mainly using NaCl, $NaClO_4$, $NaNO_3$, KNO_3, and KCl as background salts (see, for example, refs 5−10, from the Finnish school and some databases, refs 11−16). We have published several papers on thermodynamic parameters for the protonation of linear (both N-alkyl-substituted and unsubstituted) polyamines at different ionic strengths in NaCl.[17−24] In some of these the effect of N-alkyl substitution and the interactions of protonated species with Cl^- anion were also considered,[22−24] but there are no studies of polyamine protonation constants in aqueous solutions containing tetralkyammonium salts as supporting electrolytes. These salts have, however, often been employed in studies of the protonation constants of carboxylic acids because they are not thought to interact with the latter compounds. We opted to examine the protonation constants of three linear amines: ethylenediamine, diethylenetriamine, and spermine in NaCl, NaI, $(CH_3)_4NCl$, and $(C_2H_5)_4NI$ aqueous solution at t = 25 °C and at different ionic strengths. Although protonation constants for these amines have been studied extensively in this laboratory in NaCl aqueous solutions,[19−22] new measurements were made in this work for two reasons: (i) to check previous data and (ii) to improve homogeneity within the total set of data since it is generally recognized that internal consistency is greater than external. In this work, the effect of salt on the protonation of three linear polyamines in aqueous solution was studied using four background salts. These contained the Cl^- and I^- anions with which the protonated H_iA^{i+} amines form ion pairs and cations of differing size, polarizability, charge density, and particularly, affinity toward water molecules. In fact, alkaline cations (such as Na^+ and K^+) are strongly hydrated, while tetralkylammonium cations (such as Me_4N^+ and Et_4N^+) are apolar in character and tend to join together to reduce the surface area accessible to water molecules. The addition of lipophilic salts (such as tetralkylammonium salts) to aqueous solutions containing polyamines leads to a decrease in protonation constants, which is a consequence of the hydrophobic driving force (i.e., an effect of solvation−desolvation processes).

Experimental Section

Chemicals. Amines [ethylenediamine (1,2-diaminoethane, en); diethylenetriamine (2,2′-diaminodiethylamine, dien); and spermine [*N*,*N*′-bis(3-aminopropyl)-1−4-diaminobutane), sper] were Fluka, Aldrich, or Sigma products. En and sper were in hydrochloride form, and their solutions were prepared by weighing. Dien was transformed into the corresponding hydrochloride and was used in this form.

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Table 1. Protonation Constants of Ethylenediamine in NaCl, NaI, Me_4NCl, and Et_4NI Aqueous Solution at t = 25 °C[a]

ionic medium	I/mol·L^{-1}	log K_1^H	log K_2^H
NaCl		±(0.01 to 0.03)[b]	±(0.005 to 0.02)[b]
	0.1	9.93	7.11
	0.1[c]	9.99	7.20
	0.25	9.97	7.21
	0.5	10.05	7.32
	0.75[c]	10.13	7.38
	1	10.19	7.48
	1.5	10.33	7.60
	2	10.46	7.71
	2[c]	10.45	7.72
	2.5	10.58	7.81
	3[c]	10.71	8.03
NaI		±(0.01 to 0.03)[b]	±(0.01 to 0.03)[b]
	0.1	9.93	7.10
	0.25	9.97	7.20
	0.5	10.03	7.30
	1	10.15	7.45
	1.5	10.28	7.58
	2	10.40	7.69
	2.5	10.51	7.80
Me_4NCl		±(0.01 to 0.03)[b]	±(0.01 to 0.03)[b]
	0.1	9.86	7.09
	0.25	9.83	7.15
	0.5	9.79	7.21
	1	9.78	7.29
	1.5	9.80	7.35
	2	9.84	7.39
	2.5	9.90	7.41
Et_4NI		±(0.01 to 0.04)[b]	±(0.01 to 0.03)[b]
	0.1	9.84	7.06
	0.25	9.78	7.10
	0.5	9.73	7.12
	0.75	9.71	7.15
	1	9.71	7.17

[a] Molar concentration scale. [b] ≥95 % confidence interval. [c] Data from ref 22.

Table 2. Protonation Constants of Diethylenetriamine in NaCl, NaI, Me_4NCl, and Et_4NI Aqueous Solution at t = 25 °C[a]

ionic medium	I/mol·L^{-1}	log K_1^H	log K_2^H	log K_3^H
NaCl		±(0.02 to 0.04)[b]	±(0.02 to 0.03)[b]	±(0.01 to 0.03)[b]
	0.1	9.83	8.97	4.25
	0.1[c]	9.84	9.00	4.20
	0.25	9.88	9.08	4.42
	0.5	9.96	9.19	4.59
	0.75[c]	9.99	9.32	4.74
	1	10.11	9.36	4.81
	2	10.39	9.64	5.12
	2[c]	10.04	9.37	4.78
	2.5	10.53	9.78	5.26
NaI		±(0.02 to 0.04)[b]	±(0.02 to 0.04)[b]	±(0.01 to 0.05)[b]
	0.1	9.83	9.02	4.14
	0.25	9.86	9.15	4.32
	0.5	9.92	9.27	4.47
	1	10.04	9.42	4.62
	2	10.36	9.63	4.91
	2.5	10.58	9.73	5.13
Me_4NCl		±(0.02 to 0.03)[b]	±(0.01 to 0.02)[b]	±(0.01 to 0.02)[b]
	0.1	9.79	8.96	4.25
	0.25	9.79	9.05	4.42
	0.5	9.80	9.14	4.57
	1	9.83	9.24	4.73
	2	9.95	9.39	4.88
	2.5	10.03	9.46	4.91
Et_4NI		±(0.01 to 0.04)[b]	±(0.02 to 0.04)[b]	±(0.01 to 0.04)[b]
	0.1	9.76	8.99	4.15
	0.25	9.74	9.05	4.31
	0.5	9.74	9.09	4.41
	1	9.79	9.11	4.45

[a] Molar concentration scale. [b] ≥95 % confidence interval. [c] Data from ref 22.

When necessary, the hydrochlorides of all three amines were recrystallized. Their purities, checked alkalimetrically, were always > 99.5 %. Tetramethylammonium chloride (Me_4NCl), tetraethylammonium iodide (Et_4NI), tetramethylammonium hydroxide (Me_4NOH), and tetraethylammonium hydroxide (Et_4NOH) were purified as recommended by Perrin et al.[25] HCl and NaOH solutions were prepared by diluting concentrated Fluka ampules. The acid (HCl) and the hydroxides (NaOH, Me_4NOH, and Et_4NOH) were standardized against dried sodium carbonate or potassium biphthalate, respectively. Sodium chloride and sodium iodide solutions were prepared by weighing pure salt (Fluka, p.a.), with only the former being predried in an oven at 110 °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 Metrohm model 713 potentiometer equipped with a combined glass electrode (Ross type 8102, from Orion) and a Metrohm model 765 motorized burette. Estimated accuracy was ± 0.2 mV and ± 0.003 mL for electromotive force (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 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 (4 to 6) mmol·L^{-1} and the background salt (NaCl, NaI, Me_4NCl: 0.1 ≤ I ≤ 2.5 mol·L^{-1}; Et_4NI: 0.1 ≤ I ≤ 1·mol·L^{-1}) was titrated with standard NaOH or Me_4NOH or Et_4NOH up to 80−90 % neutralization. Separate titrations of HCl at the same ionic strength as the sample under study were carried out to determine standard electrode potential ($E°$) and to obtain pH = −log [H$^+$] readings. The reliability of the calibration in the alkaline range was checked by calculating pK_w values.

Calculations. All the parameters relative to the electrode system (formal potential $E°$, coefficient of junction potential j_a, $E_j = j_a$ [H$^+$]) and to the determination of alkalimetric purity were refined using the nonlinear least squares computer program ESAB2M.[26] This program also refines the conditional protonation constants of amines at the specific ionic strength value of the titration. The non linear fitting program LIANA[27] calculates the protonation constant values of the amines at I = 0 mol·L^{-1} from the conditional values at different ionic strengths using different equations. The nonlinear least squares computer program ES2WC[28] was used to compute the formation constants of weak complexes. Details of calculation methods and programs have already been reported.[27]

Results and Discussion

Protonation Constants. Amine protonation constants refer to the reaction:

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

Protonation constants for en, dien, and sper (in the molar concentration scale) are reported in Tables 1−3 (values in the molal concentration scale are reported as Supporting Information). It is clear from cursory examination of the

Table 3. Protonation Constants of Spermine in NaCl, NaI, Me_4NCl, and Et_4NI Aqueous Solution at $t = 25$ °C[a]

ionic medium	I/mol·L^{-1}	log K_1^H	log K_2^H	log K_3^H	log K_4^H
NaCl		±(0.01 to 0.03)[b]	±(0.01 to 0.03)[b]	±(0.01 to 0.04)[b]	±(0.01 to 0.04)[b]
	0.1	10.82	9.95	8.81	7.88
	0.1[c]	10.73	9.94	8.77	7.84
	0.25	10.87	10.09	8.99	8.08
	0.5	10.96	10.23	9.14	8.24
	0.5[c]	10.86	10.16	9.09	8.33
	0.75[c]	10.94	10.26	9.18	8.43
	1	11.13	10.43	9.33	8.45
	2	11.42	10.68	9.61	8.81
	2.5	11.55	10.78	9.75	8.99
NaI		±(0.01 to 0.04)[b]	±(0.01 to 0.03)[b]	±(0.01 to 0.05)[b]	±(0.01 to 0.06)[b]
	0.1	10.83	9.98	8.84	7.97
	0.25	10.90	10.14	9.02	8.17
	0.5	11.00	10.30	9.16	8.32
	1	11.20	10.50	9.33	8.50
	2	11.53	10.73	9.58	8.82
	2.5	11.66	10.82	9.70	9.00
Me_4NCl		±(0.01 to 0.04)[b]	±(0.01 to 0.05)[b]	±(0.01 to 0.05)[b]	±(0.02 to 0.05)[b]
	0.1	10.79	9.87	8.76	7.88
	0.25	10.82	9.90	8.87	8.06
	0.5	10.87	9.94	8.95	8.21
	1	10.97	10.03	9.05	8.37
	2	11.19	10.26	9.21	8.53
	2.5	11.32	10.43	9.34	8.50
Et_4NI		±(0.02 to 0.05)[b]	±(0.02 to 0.05)[b]	±(0.01 to 0.05)[b]	±(0.01 to 0.07)[b]
	0.1	10.69	9.89	8.74	7.94
	0.25	10.68	9.97	8.82	8.10
	0.5	10.70	10.04	8.87	8.20
	1	10.80	10.14	8.93	8.24

[a] Molar concentration scale. [b] ≥95 % confidence interval. [c] Data from ref 22.

results in Tables 1−3 that protonation constants generally show the trend:

$$\mathrm{NaCl} \geq \mathrm{NaI} \gg \mathrm{Me_4NCl} > \mathrm{Et_4NI}$$

This trend is the opposite of that shown by low and high molecular weight carboxylic and inorganic acids.[29−31] In both cases, the trend reflects the interacting capabilities of different cations and anions, which is opposite for different classes of ligands. In the next section, we try to explain the effect of tetralkylammonium cations on the protonation of amines by the formation of weak complexes.

Dependence on Ionic Strength. The dependence on ionic strength of protonation constants can be expressed by a Debye−Hückel type equation:

$$\log K_i^{\mathrm{H}} = \log {}^{\mathrm{T}}K_i^{\mathrm{H}} - z_i^{*}0.51\sqrt{I}/(1 + 1.5\sqrt{I}) + C_iI + D_iI^{3/2} + E_iI^2 \quad (1)$$

where $z_i^* = 2(i - 1)$, ${}^{\mathrm{T}}K_i^{\mathrm{H}}$ is the protonation constant at infinite dilution, and C_i, D_i, and E_i are empirical parameters. This equation has been extensively used in this laboratory;[22] often, it was not necessary to consider the quadratic term EI^2, in particular for $I < 2$ mol·L^{-1}. As proposed in a previous work on N-alkyl-substituted diamines,[24] we used only the first CI linear term, with C depending on ionic strength:

$$C = c_\infty + \frac{c_0 - c_\infty}{I + 1} \quad (2)$$

where c_∞ and c_0 are the values of C at $I \to \infty$ and $I \to 0$, respectively. Protonation constants at infinite dilution and parameters for dependence on ionic strength according to eqs 1 and 2, expressed in the molar concentration scale, are reported in Tables 4−6 for en, dien, and sper, respectively. If ionic strengths and protonation constants are expressed in the molal concentration scale, we can calculate $\Delta\epsilon$ values, where ϵ represents the ion interaction coefficient according to SIT,[32,33] using equations very similar to eqs 1 and 2:

Table 4. Protonation Constants of Ethylenediamine at Infinite Dilution and parameters for dependence on ionic strength at $t = 25$ °C

	NaCl	NaI	Me_4NCl	Et_4NI	σ[c]
log K_1^H [a]	9.897 ± 0.015[d]				
c_∞	0.250	0.230	0.159	0.254	0.006
c_0	0.338	0.287	−0.397	−0.627	
log K_2^H [a]	6.866 ± 0.015[d]				
c_∞	0.165	0.191	0.049	0.114	0.006
c_0	0.241	0.160	−0.018	−0.323	
log K_1^H [b]	9.895 ± 0.015[d]				
$\Delta\epsilon_\infty$	0.223	0.186	0.065	0.141	0.005
$\Delta\epsilon_0$	0.336	0.276	−0.396	−0.672	
log K_2^H [b]	6.868 ± 0.015[d]				
$\Delta\epsilon_\infty$	0.145	0.152	−0.013	0.027	0.005
$\Delta\epsilon_0$	0.225	0.138	−0.071	−0.419	

[a] On the molar concentration scale, according to eqs 1 and 2. [b] On the molal concentration scale, according to eqs 3 and 4. [c] σ, standard deviation on the fit. [d] ≥95 % confidence interval.

$$\log K_i^{\mathrm{H}} = \log {}^{\mathrm{T}}K_i^{\mathrm{H}} - z_i^{*}0.51\sqrt{I}/(1 + 1.5\sqrt{I}) + \Delta\epsilon I \quad (3)$$

with

$$\Delta\epsilon = \Delta\epsilon_\infty + \frac{\Delta\epsilon_0 - \Delta\epsilon_\infty}{I + 1} \quad (4)$$

The $\Delta\epsilon$ differences are given by ($X^- = Cl^-, I^-$):

$$\Delta\epsilon_1 = \epsilon(\mathrm{H}^+, \mathrm{X}^-) + \lambda_{\mathrm{en}} - \epsilon(\mathrm{enH}^+, \mathrm{X}^-) \quad (5)$$

$$\Delta\epsilon_2 = \epsilon(\mathrm{H}^+, \mathrm{X}^-) + \epsilon(\mathrm{enH}^+, \mathrm{X}^-) - \epsilon(\mathrm{enH_2}^{2+}, \mathrm{X}^-) \quad (6)$$

where λ_{en} is the interaction coefficient of neutral species (i.e., the Setschenow coefficient)[34] for the first and the

Table 5. Protonation Constants of Diethylenetriamine at Infinite Dilution and Parameters for Dependence on Ionic Strength at t = 25 °C

	NaCl	NaI	Me_4NCl	Et_4NI	σ^c
$\log K_1^{\mathrm{H}\ a}$	9.80 ± 0.02^d				
c_∞	0.275	0.373	0.173	0.382	0.01
c_0	0.329	0.125	−0.118	−0.410	
$\log K_2^{\mathrm{H}\ \mathrm{a}}$	8.75 ± 0.02^d				
c_∞	0.251	0.094	0.108	−0.179	0.02
c_0	0.145	0.454	0.054	0.081	
$\log K_3^{\mathrm{H}\ a}$	3.77 ± 0.03^d				
c_∞	0.192	0.312	−0.030	−0.087	0.02
c_0	0.266	−0.241	0.336	−0.180	
$\log K_1^{\mathrm{H}\ b}$	9.81 ± 0.02^d				
$\Delta\epsilon_\infty$	0.256	0.318	0.078	0.230	0.01
$\Delta\epsilon_0$	0.289	0.087	−0.158	−0.490	
$\log K_2^{\mathrm{H}\ b}$	8.73 ± 0.02^d				
$\Delta\epsilon_\infty$	0.203	0.047	0.013	−0.280	0.01
$\Delta\epsilon_0$	0.220	0.508	0.078	0.110	
$\log K_3^{\mathrm{H}\ b}$	3.71 ± 0.03^d				
$\Delta\epsilon_\infty$	0.128	0.210	−0.105	−0.302	0.02
$\Delta\epsilon_0$	0.433	−0.057	0.429	0.011	

[a] On the molar concentration scale, according to eqs 1 and 2. [b] On the molal concentration scale, according to eqs 3 and 4. [c] σ, standard deviation on the fit. [d] ≥95 % confidence interval.

second protonation steps, respectively. Interaction coefficients $\epsilon(H^+, X^-)$ have already been reported,[35] while the other coefficients must be obtained from the fitting of log K^H versus I. Since it is impossible to calculate three parameters from two equations, we calculated these differences in $\Delta\epsilon$ (reported in Tables 4−6) as normal. If one of these parameters can be derived from independent measurements (e.g., λ can be obtained from solubility in different ionic media),[36] other interaction parameters can easily be calculated from eqs 5 and 6 (it is often assumed that $\lambda = 0$ and other parameters are calculated accordingly).

For each supporting electrolyte, both c (c_0, c_∞) and $\Delta\epsilon$ ($\Delta\epsilon_0$, $\Delta\epsilon_\infty$) values are fairly independent of the amine. After some trials, we found that the sum $S = \Delta\epsilon_0 + \Delta\epsilon_\infty$ is approximately constant for Me_4NCl and Et_4NCl (-0.04 ± 0.15 and -0.26 ± 0.13, respectively) and depends on z^* for NaCl and NaI. For these sodium salts, dependence on ionic strength is very similar, and a single equation can be written:

$$S = 0.62(\pm\ 0.06) + 0.095(\pm\ 0.019)z^* \qquad (7)$$

with a linear correlation coefficient $r = 0.895$. The trend for S

$$\mathrm{NaCl} \cong \mathrm{NaI} \gg \mathrm{Me_4NCl} > \mathrm{Et_4NI}$$

indicates that Na^+ does not interact, while Me_4N^+ and Et_4N^+ show a sort of interaction with amines (or, at least, the level of interaction of Na^+ is significantly lower than that of tetralkylammonium cations). The parallel effect on the protonation of polyamines of the presence in aqueous solution of alkylammonium cations and N-alkyl substitution is interesting:[21,24] in both cases K_i^H values decrease significantly, very likely due to variations in the capacity of amines to interact with water molecules and to the different structure of water in different ionic media. Moreover, in some investigations of the protonation of pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline,[37−39] it was found that protonation constants follow the trend LiCl ≥ NaCl ≥ KCl > Me_4NCl > Et_4NI, in agreement with the present findings.

Table 6. Protonation Constants of Spermine at Infinite Dilution and Parameters for Dependence on Ionic Strength at t = 25 °C

	NaCl	NaI	Me_4NCl	Et_4NI	σ^c
$\log K_1^{\mathrm{H}\ a}$	10.766 ± 0.015^d				
c_∞	0.251	0.261	0.231	0.651	0.01
c_0	0.475	0.607	0.188	−0.579	
$\log K_2^{\mathrm{H}\ a}$	9.687 ± 0.018^d				
c_∞	0.136	0.061	0.329	0.177	0.02
c_0	0.521	0.757	−0.463	−0.087	
$\log K_3^{\mathrm{H}\ a}$	8.38 ± 0.04^d				
c_∞	0.202	0.131	0.198	0.231	0.02
c_0	0.070	0.171	−0.498	−0.759	
$\log K_4^{\mathrm{H}\ a}$	7.28 ± 0.04^d				
c_∞	0.335	0.211	0.042	−0.324	0.02
c_0	−0.459	−0.164	−0.363	−0.215	
$\log K_1^{\mathrm{H}\ b}$	10.77 ± 0.02^d				
$\Delta\epsilon_\infty$	0.231	0.216	0.111	0.414	0.01
$\Delta\epsilon_0$	0.438	0.565	0.145	−0.620	
$\log K_2^{\mathrm{H}\ b}$	9.668 ± 0.018^d				
$\Delta\epsilon_\infty$	0.100	0.021	0.160	−0.008	0.01
$\Delta\epsilon_0$	0.574	0.788	−0.394	−0.067	
$\log K_3^{\mathrm{H}\ b}$	8.37 ± 0.04^d				
$\Delta\epsilon_\infty$	0.175	0.093	0.083	0.082	0.02
$\Delta\epsilon_0$	0.074	0.161	−0.511	0.792	
$\log K_4^{\mathrm{H}\ b}$	7.29 ± 0.04^d				
$\Delta\epsilon_\infty$	0.305	0.169	−0.027	−0.314	0.02
$\Delta\epsilon_0$	−0.476	−0.194	−0.420	−0.358	

[a] On the molar concentration scale, according to eqs 1 and 2. [b] On the molal concentration scale, according to eqs 3 and 4. [c] σ, standard deviation on the fit. [d] ≥95 % confidence interval.

Formation of Weak Complexes. Differences in log K_i^H for different supporting electrolytes can easily be described, as reported above, by using the SIT approach and calculating ϵ, or $\Delta\epsilon$, values. Alternatively, we can resort to a model that takes into account the formation of weak species. In this case, we must consider the interactions of both X^- (Cl^-, I^-) with protonated amines and M^+ (Me_4N^+, Et_4N^+) with unprotonated or partially protonated amines. A suitable calculation model, based on the comparison of different protonation constants and assuming no interaction to occur between Na^+ and amines in either protonated or unprotonated forms, can be used[28] to obtain quantitative data on these interactions. By computer analysis,[28] we found that for all the $M^+{-}X^-{-}A{-}H^+$ (A = en, dien, sper) systems the following species are formed:

$$H_iAX^{(i-1)} \quad (i = 1 \ldots m)$$

$$MH_jA^{(j+1)} \quad (j = 0 \ldots m-1)$$

relative to the reactions:

$$H_iA^{i+} + X^- = H_iAX^{(i-1)} \quad K_i^X \qquad (8)$$

$$M^+ + H_jA^{j+} = MH_jA^{(j+1)} \quad K_j^M \qquad (9)$$

(m = maximum protonation degree of amine). In these calculations it is assumed that (a) the complex formation model is valid at moderate ionic strength values ($0 \le I \le 1$ mol·L^{-1}); (b) the *effective* (by "effective", we mean constants that are independent of medium and dependent only on ionic strength) protonation constants are the same for all supporting electrolytes at the same ionic strengths; (c) the molar concentration scale is to be used. Relative formation constants are reported in Tables 7−9. The different speciation behaviors in different electrolyte solutions are clearly visible in Figure 1 where distribution diagrams for ethylenediamine in NaCl, Me_4NCl, and

Table 7. Molar Effective Protonation and Stability Constants of Species of Ethylenediamine with Cl^-, I^-, Me_4N^+, and Et_4N^+ at t = 25 °C

I/mol·L^{-1}	log K_1^H	log K_2^H	log K_1^{Cl}	log K_2^{Cl}	log K_1^I	log K_2^I	log $K_0^{Me_4N}$	log $K_1^{Me_4N}$	log $K_0^{Et_4N}$	log $K_1^{Et_4N}$
0.1	9.91	7.05	−0.44	0.16	−0.38	0.20	0.07	−0.90	0.42	−0.38
0.25	9.93	7.10	−0.46	0.11	−0.40	0.14	0.09	−0.84	0.44	−0.33
0.5	9.96	7.15	−0.45	0.10	−0.39	0.14	0.12	−0.80	0.46	−0.29
0.75	9.98	7.18	−0.43	0.11	−0.37	0.15	0.15	−0.76	0.49	−0.25
1	10.01	7.23	−0.42	0.11	−0.36	0.15	0.17	−0.72	0.52	−0.20

Table 8. Molar Effective Protonation and Stability Constants of Species of Diethylenetriamine with Cl^-, I^-, Me_4N^+, and Et_4N^+ at t = 25 °C

I/mol·L^{-1}	log K_1^H	log K_2^H	log K_3^H	log K_1^{Cl}	log K_2^{Cl}	log K_3^{Cl}	log K_1^I	log K_2^I	log K_3^I	log $K_0^{Me_4N}$	log $K_1^{Me_4N}$	log $K_2^{Me_4N}$	log $K_0^{Et_4N}$	log $K_1^{Et_4N}$	log $K_2^{Et_4N}$
0.1	9.84	8.97	4.13	−0.87	−0.08	0.43	−0.81	−0.11	0.63	0.03	−0.66	−1.45	0.40	−0.16	−0.80
0.25	9.87	9.02	4.21	−0.87	−0.10	0.39	−0.80	−0.13	0.58	0.06	−0.61	−1.37	0.43	−0.11	−0.72
0.5	9.91	9.06	4.24	−0.82	−0.04	0.46	−0.75	−0.07	0.65	0.10	−0.57	−1.34	0.47	−0.07	−0.69
0.75	9.96	9.08	4.24	−0.75	0.05	0.57	−0.68	0.02	0.77	0.15	−0.55	−1.34	0.52	−0.05	−0.69
1	10.01	9.11	4.24	−0.68	0.14	0.69	−0.61	0.12	0.89	0.20	−0.52	−1.34	0.57	−0.02	−0.69

Table 9. Molar Effective Protonation and Stability Constants of Species of Spermine with Cl^-, I^-, Me_4N^+, and Et_4N^+at t = 25 °C

I/mol·L^{-1}	log K_1^H	log K_2^H	log K_3^H	log K_4^H	log K_1^{Cl}	log K_2^{Cl}	log K_3^{Cl}	log K_4^{Cl}	log K_1^I	log K_2^I	log K_3^I	log K_4^I
0.1	10.83	9.95	8.64	7.44	−0.11	0.59	0.94	1.66	−0.36	0.01	0.52	0.93
0.25	10.85	10.04	8.80	7.52	−0.16	0.48	0.76	1.55	−0.41	−0.10	0.34	0.83
0.5	10.89	10.13	8.96	7.62	−0.18	0.40	0.62	1.47	−0.43	−0.18	0.20	0.74
0.75	10.93	10.21	9.09	7.70	−0.19	0.34	0.52	1.41	−0.45	−0.24	0.09	0.69
1	10.96	10.30	9.21	7.78	−0.19	0.29	0.42	1.36	−0.45	−0.29	0.00	0.64

I/mol·L^{-1}	log $K_0^{Me_4N}$	log $K_1^{Me_4N}$	log $K_2^{Me_4N}$	log $K_3^{Me_4N}$	log $K_0^{Et_4N}$	log $K_1^{Et_4N}$	log $K_2^{Et_4N}$	log $K_3^{Et_4N}$
0.1	0.46	0.11	−0.62	−1.60	1.19	0.61	0.09	−0.95
0.25	0.48	0.21	−0.46	−1.52	1.21	0.70	0.25	−0.87
0.5	0.52	0.30	−0.30	−1.42	1.25	0.79	0.41	−0.77
0.75	0.56	0.38	−0.17	−1.34	1.29	0.87	0.54	−0.69
1	0.59	0.47	−0.05	−1.26	1.32	0.96	0.66	−0.61

Et_4NI are shown. Yields of H_iAX species are fairly similar in the three systems while the formation of MH_jA species is quite different where tetralkylammonium cations are present, percentages of Et_4NH_jA being significantly higher than those of Me_4NH_jA. The dependence on ionic strength of these effective constants can be modeled as done for apparent protonation constants (i.e., using eqs 1 and 2). Formation constants at infinite dilution and parameters for dependence on ionic strength are reported in Tables 10−12. Below are some observations about the figures in Tables 7−12.

(i) The stability of $H_iAX^{(i-1)}$ species is very similar for Cl^- and I^-; the differences between chloride and iodide complexes are generally within experimental errors, except for spermine, whose iodide species are rather less stable than the corresponding chloride ones. By considering the formation constants of chloride and iodide species collectively, we can write the simple empirical relationship (K_i^X refers to reaction 8):

$$\log K_i^x = 0.71(\pm\, 0.03)i - 1$$

This result is consistent with previous findings on ion pair formation between polyammonium cations and inorganic anions.[17−19,21] Data from ref 19 on the interaction of chloride with polyamines of general formula $C_{2n-2}N_nH_{5n-2}$ gave

$$\log K_i^x = 0.80(\pm\, 0.06)i - 1$$

Analogously, for several other polyamines[24] we found

$$\log K_i^x = 0.754(\pm\, 0.025)i + B$$

with $B = -0.91 \pm 0.06$ and -0.56 ± 0.08 for unsubstituted and *N*-alkyl-substituted amines.

(ii) Tetralkylammonium species show two quite marked trends in stability:

$$Et_4N^+ > Me_4N^+$$

$$\text{en} < \text{dien} < \text{sper}$$

The formation constants also show linear trends as a function of the number of amino groups (n_N) and of protonation degree (n_H) that can be quantified by the empirical relationships (K_j^M refers to reaction 9):

$$\log K_j^{Me_4N} = -0.63 + 0.27n_N - 0.79n_H \quad (\sigma = 0.16)$$

$$\log K_j^{Et_4N} = -0.33 + 0.35n_N - 0.79n_H \quad (\sigma = 0.17)$$

(iii) For the same type of species (in terms of charges involved in the formation equilibrium), dependence on ionic strength is fairly similar. As reported in some previous works,[31,40] when all weak interactions are taken into account, as in the present paper, dependence on ionic strength can be expressed by a simple equation where the linear term of eq 1 is a function of z^* for all the species formed in the different systems. Owing to the strong correlation of c_0 and c_∞ it is better to consider the sum $c_0 + c_\infty$ (as done in the above section for $\Delta\epsilon$). By performing suitable calculations (data from Tables 10−12), we obtain

$$c_0 + c_\infty = 0.270(\pm\, 0.036) + 0.146(\pm\, 0.012)z^*$$

with a linear correlation coefficient r = 0.9816.

Final Remarks

Until now the protonation of polyamines in aqueous salt solutions has been studied using alkali metal halides,

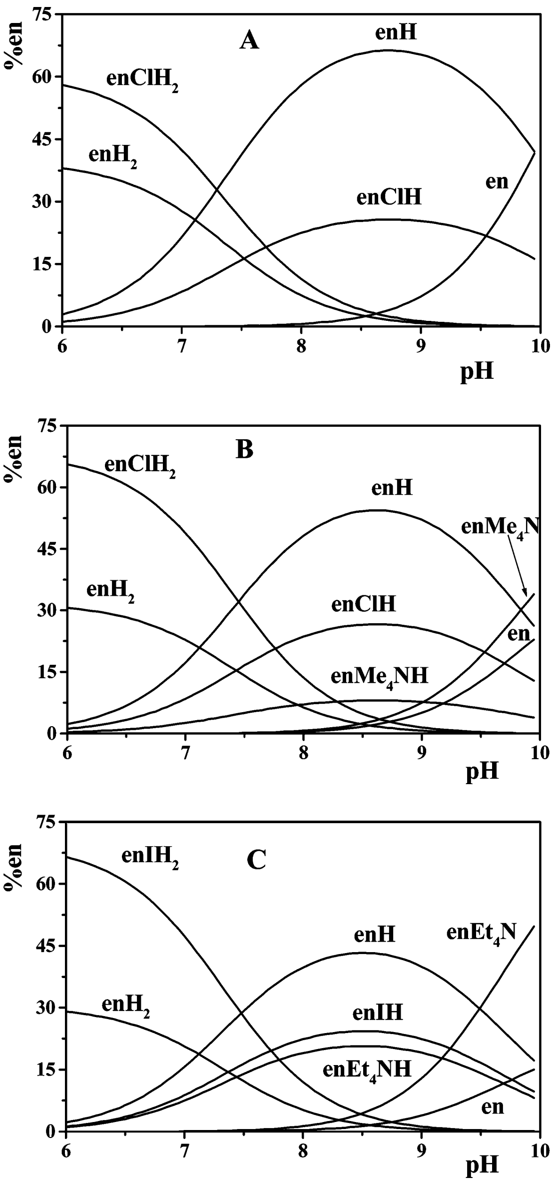

Figure 1. Speciation diagrams of en in different electrolyte solutions: C_{en} = 1 mmol·L^{-1}; C_{salt} = 1 mol·L^{-1}. A, NaCl; B, Me$_4$NCl; C, Et$_4$NI.

Table 10. Molar Effective Protonation and Stability Constants of Species of Ethylenediamine with Cl$^-$, I$^-$, Me$_4$N$^+$, and Et$_4$N$^+$ at I = 0 mol·L^{-1} and at t = 25 °C

equilibrium	log K	c_∞	c_0
$A^0 + H^+ = HA^+$	9.90 ± 0.02[a]	0.109	
$HA^+ + H^+ = H_2A^{2+}$	6.86 ± 0.02	0.238	−0.314
$HA^+ + Cl^- = HACl^0$	−0.27 ± 0.15	0.008	0.508
$H_2A^{2+} + Cl^- = H_2ACl^+$	0.52 ± 0.10	−0.065	0.879
$HA^+ + I^- = HAI^0$	−0.21 ± 0.15	0.008	0.507
$H_2A^{2+} + I^- = H_2AI^+$	0.55 ± 0.10	−0.072	0.905
$A^0 + Me_4N^+ = AMe_4N^+$	0.06 ± 0.10	0.115	
$HA^+ + Me_4N^+ = HAMe_4N^{2+}$	−1.09 ± 0.25	0.202	−0.277
$A^0 + Et_4N^+ = AEt_4N^+$	0.41 ± 0.10	0.108	
$HA^+ + Et_4N^+ = HAEt_4N^{2+}$	−0.58 ± 0.25	0.235	−0.302

[a] ≥95 % confidence interval.

Table 11. Molar Effective Protonation and Stability Constants of Species of Diethylenetriamine with Cl$^-$, I$^-$, Me$_4$N$^+$, and Et$_4$N$^+$ at I = 0 mol·L^{-1} and at t = 25 °C

equilibrium	log K	c_∞	c_0
$A^0 + H^+ = HA^+$	9.82 ± 0.03[a]	0.188	
$HA^+ + H^+ = H_2A^{2+}$	8.77 ± 0.03	0.094	−0.233
$H_2A^{2+} + H^+ = H_3A^{3+}$	3.75 ± 0.03	−0.043	−0.610
$HA^+ + Cl^- = HACl^0$	−0.709 ± 0.15	0.298	0.576
$H_2A^{2+} + Cl^- = H_2ACl^+$	0.260 ± 0.10	0.372	1.019
$H_3A^{3+} + Cl^- = H_3ACl^{2+}$	0.951 ± 0.10	0.489	1.436
$HA^+ + I^- = HAI^0$	−0.650 ± 0.15	0.277	0.618
$H_2A^{2+} + I^- = H_2AI^+$	0.232 ± 0.10	0.416	0.990
$H_3A^{3+} + I^- = H_3AI^{2+}$	1.151 ± 0.10	0.544	1.383
$A^0 + Me_4N^+ = AMe_4N^+$	0.010 ± 0.15	0.188	
$HA^+ + Me_4N^+ = HAMe_4N^{2+}$	−0.859 ± 0.15	0.094	−0.233
$H_2A^{2+} + Me_4N^+ = H_2AMe_4N^{3+}$	−1.830 ± 0.20	−0.043	−0.610
$A^0 + Et_4N^+ = AEt_4N^+$	0.380 ± 0.15	0.188	
$HA^+ + Et_4N^+ = HAEt_4N^{2+}$	−0.359 ± 0.15	0.094	−0.233
$H_2A^{2+} + Et_4N^+ = H_2AEt_4N^{3+}$	−1.180 ± 0.20	−0.043	−0.610

[a] ≥95 % confidence interval.

Table 12. Molar Effective Protonation and Stability Constants of Species of Spermine with Cl$^-$, I$^-$, Me$_4$N$^+$, and Et$_4$N$^+$ at I = 0 mol·L^{-1} and at t = 25 °C

equilibrium	log K	c_∞	c_0
$A^0 + H^+ = HA^+$	10.81 ± 0.02[a]	0.151	
$HA^+ + H^+ = H_2A^{2+}$	9.73 ± 0.03	0.340	−0.021
$H_2A^{2+} + H^+ = H_3A^{3+}$	8.21 ± 0.05	0.466	−0.104
$H_3A^{3+} + H^+ = H_4A^{4+}$	7.12 ± 0.07	1.481	−2.534
$HA^+ + Cl^- = HACl^0$	0.08 ± 0.15	0.018	0.255
$H_2A^{2+} + Cl^- = H_2ACl^+$	0.990 ± 0.10	−0.187	0.418
$H_3A^{3+} + Cl^- = H_3ACl^{2+}$	1.54 ± 0.10	−0.365	0.572
$H_4A^{4+} + Cl^- = H_4ACl^{3+}$	2.2 ± 0.20	−1.374	2.976
$HA^+ + I^- = HAI^0$	−0.17 ± 0.15	−0.011	0.262
$H_2A^{2+} + I^- = H_2AI^+$	0.410 ± 0.10	−0.187	0.418
$H_3A^{3+} + I^- = H_3AI^{2+}$	1.12 ± 0.10	−0.357	0.559
$H_4A^{4+} + I^- = H_4AI^{3+}$	1.4 ± 0.20	−1.338	2.947
$A^0 + Me_4N^+ = AMe_4N^+$	0.44 ± 0.10	0.151	
$HA^+ + Me_4N^+ = HAMe_4N^{2+}$	−0.10 ± 0.15	0.343	−0.019
$H_2A^{2+} + Me_4N^+ = H_2AMe_4N^{3+}$	−1.05 ± 0.20	0.466	−0.104
$H_3A^{3+} + Me_4N^+ = H_3AMe_4N^{4+}$	−1.9 ± 0.20	1.481	−2.534
$A^0 + Et_4N^+ = AEt_4N^+$	1.17 ± 0.10	0.151	
$HA^+ + Et_4N^+ = HAEt_4N^{2+}$	0.39 ± 0.15	0.340	−0.021
$H_2A^{2+} + Et_4N^+ = H_2AEt_4N^{3+}$	−0.34 ± 0.15	0.466	−0.104
$H_3A^{3+} + Et_4N^+ = H_3AEt_4N^{4+}$	−1.3 ± 0.20	1.481	−2.534

[a] ≥95 % confidence interval.

nitrate, and perchlorate as supporting electrolytes, while this paper presents data for protonation in tetralkylammonium salts. In these salts protonation behavior is very different, and some quantitative parameters have been given both in terms of ionic strength dependence and of cation/anion interaction. In conclusion, two remarks must be made about the interpretation of the very different salt effects of sodium and tetralkylammonium halides and about the validity of stability data for weak complexes.

(i) The protonation trend NaCl ≥ NaI ≫ Me$_4$NCl > Et$_4$NI is consistent with the promoting/breaking structure of supporting electrolytes.[41]

(ii) The method used here to derive quantitative information about the stability of weak species from differences in K^{H} (often called Δlog K^{H} method) has sometimes been criticized since it assumes the *effective* activity coefficients of different species to be the same in different supporting electrolytes. While this criticism is clearly sound, at moderate ionic strengths ($I \leq 1$ mol·L^{-1}), trace effective activity coefficients generally depend mainly on the charge of the species under examination. An indirect demonstration of this can be obtained from the measurement of weak complex stability constants using ISE-M$^+$ and ISE-X$^-$ electrodes. In two comparative investigations,[42,43] it was found that ISE-Na$^+$, ISE-K$^+$, and ISE-Ca^{2+} give the same results as Δlog K^{H} measurements for alkali and alkaline earth metal complexes of some inorganic and organic ligands.[42] Similar consistency was found for polyammonium cation−chloride complexes studied using ISE-Cl$^-$.[43]

Other investigations aimed at confirming the present findings and better explaining salt effect trends, including further amines and calorimetric measurements, are in progress in this laboratory. In particular, the determination of protonation ΔH and ΔS values as a function of different cation concentrations should give information on the type of interactions which determine different trends.

Supporting Information Available:

Three tables showing protonation constants of ethylenediamine, diethylenetriamine, and spermine. This material is available free of charge via the Internet at http://pubs.acs.org.

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