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# Medium effects on the protonation enthalpies of linear diamines in NaCl aqueous solutions at 25°C

Concetta De Stefano*, Claudia Foti, Ottavia Giuffrè

*Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina,*
*Salita Sperone, 31 I-98116 Messina, (Vill. S.Agata), Italy*

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## Abstract

Protonation enthalpies of ethylenediamine, 1,6-hexanediamine, 1,8-octanediamine and 1,10-decanediamine were determined at 25°C in NaCl aqueous solutions, $0 < I \leq 3$ mol dm$^{-3}$ ($0 < I \leq 5$ mol dm$^{-3}$, for 1,6-hexanediamine). The dependence on ionic strength of $\Delta H^0$ can be expressed by the equation $-\Delta H^0 = -\Delta H^0\ (I = 0) + a_1 I + a_2 I^2$. Values of enthalpy changes at different ionic strengths made it possible to determine the temperature gradients of the specific interaction parameters of Pitzer equations. The functions $\Delta G^0$ and $\Delta H^0$ versus ionic strength are very similar and the resulting $T\Delta S^0$ values are quite low and fairly constant. Other empirical relationships for the dependence of both $\Delta H^0$ and $\Delta G^0$ on alkyl chain length and ionic strength are reported. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Amines; Protonation enthalpies; Calorimetry; Ionic strength dependence; Aqueous solution

## 1. Introduction

The study of the dependence on ionic strength of thermodynamic parameters for protonation and complex formation is of primary importance in speciation studies [1]. The salt effect on the protonation constants of amines has been widely studied, in particular by the Finnish school [2–6], mainly using $NaClO_4$ as medium, and in this laboratory, mainly in NaCl aqueous solution [7–11]. On the contrary, the dependence on ionic strength of other thermodynamic parameters, such as $\Delta H^0$ and $T\Delta S^0$, has been scarcely investigated. A few thermodynamic data can be formed in some compilations [12–14]. The interest of studies on the dependence on ionic strength of $\Delta G^0$ and $\Delta H^0$ comes from the evidences for the strong variation of these parameters, for example, the second protonation step of a diamine shows an increment in $\Delta G^0$ of about 4.5 kJ mol$^{-1}$ from very diluted solutions to $I = 3$ mol dm$^{-3}$. The most interesting medium for these studies is NaCl, since this salt is present in almost all the natural and biological fluids. Recently we decided to investigate this matter, and this is the first contribution dealing with the protonation of diamines in NaCl aqueous solution $0 < I \leq 3$ mol dm$^{-3}$ (ethylenediamine, 1,8-octanediamine, 1,10-decanediamine) and $0 < I \leq 5$ mol dm$^{-3}$ (1,6-hexanediamine).

## 2. Experimental

### 2.1. Materials

Amines (ethylenediamine (en), 1,6-hexanediamine (1,6d), 1,8-octanediamine (1,8d) and 1,10-decanedi-

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* Corresponding author. Tel.: +39-90-393-756;
fax: +39-90-392-827.
*E-mail address*: destefano@chem.unime.it (C. De Stefano).

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amine (1,10d), Aldrich or Sigma products) were purified by transformation into the corresponding hydrochlorides and were used in this form. Sodium chloride (Fluka, puriss.) was prepared by weighting the pure salt after drying at 110°C. Standard solutions of NaOH and HCl were prepared by diluting concentrated Fluka ampoules and were standardised against potassium biphthalate or sodium carbonate, respectively. Grade A glassware and twice distilled water were used for all solutions.

### 2.2. Calorimetric measurements

Calorimetric measurements were performed by titrating 50 ml of the solution containing the amine hydrochloride under study (5–10 mmol $dm^{-3}$) at 25.000 ± 0.001°C, using a Tronac Isoperibolic Titration calorimeter model 450, coupled with a Keithley 196 system Dmm digital multimeter. The titrant NaOH was delivered by a 2.5 ml capacity Hamilton syringe, model 1002TLL. A computer program was used for the acquisition of the calorimetric data. The accuracy was checked by titrating a TRIS (tris-(hydroxymethyl)amino-methane) buffer with HCl. The heat of dilution was measured before each experiment. The accuracy of calorimetric apparatus was $Q \pm 0.008$ J and $v \pm 0.001$ $cm^3$.

### 2.3. Calculations

Calorimetric titration data were analysed by the computer program ES5CM [15]. The different functions for the dependence on ionic strength of thermodynamic parameters were analysed by the general linear and nonlinear least squares computer program LIANA [16]. Protonation equilibria are expressed as (A = amine)

$$i\mathrm{H}^+ + \mathrm{A}^0 = \mathrm{AH}_i^{i+} \qquad \text{(I)}$$

The values of protonation constants for $I \leq 1$ mol $dm^{-3}$ are taken from [10,11], value for $I > 1$ mol $dm^{-3}$ are unpublished results from this laboratory.

## 3. Results and discussion

### 3.1. $\Delta H^0$ values for the protonation at different ionic strength

Values of $\Delta H^0$ for the protonation of diamines are reported in Table 1, together with the other thermodynamic parameters (log $\beta^H$, $\Delta G^0$ and $T\Delta S^0$). Both $\Delta G^0$ and $\Delta H^0$ are strongly dependent on $I$ as shown in Fig. 1, where the parameters for the protonation of 1,6-hexanediamine are plotted versus ionic strength. On the contrary, $T\Delta S^0$ shows very little variation and the mean value for the whole ionic strength range is reported for each amine and protonation step (Table 1), with an error comparable with or slightly higher than the experimental one. This can be seen also in Fig. 1. $\Delta G^0$ values and $\Delta H^0$ plotted altogether, are fairly parallel, in particular for $I > 0.25$ mol $dm^{-3}$.

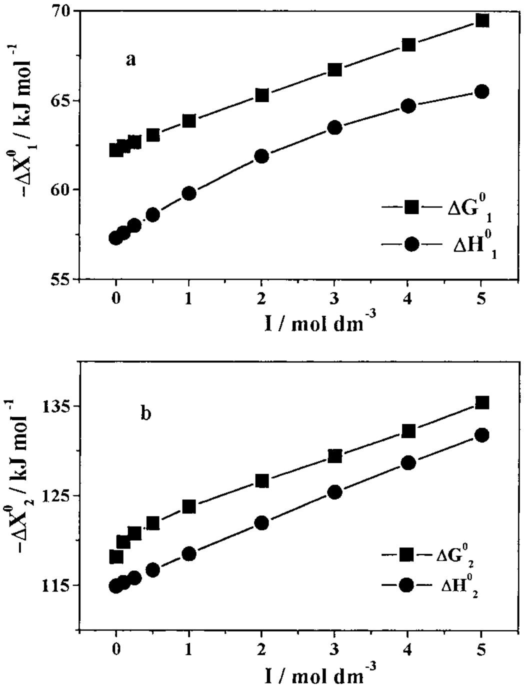

Fig. 1. Dependence on ionic strength of protonation $\Delta G^0$ and $\Delta H^0$ for 1,6-hexanediamine, at 25°C: (a) first step; (b) second step.

The dependence on ionic strength of $\Delta H^0$ can be expressed by the simple equation

$$-\Delta H^0 = -\Delta H^0(I = 0) + a_1 I + a_2 I^2 \qquad (1)$$

were $a_1$ and $a_2$ are empirical parameters, which are reported in Table 2. Values of $a_1$ and $a_2$ are fairly similar for all the diamines with a small systematic variation as a function of alkyl chain, and can be expressed by the equations

$$a_1 = 1.705 + 0.196n \qquad \text{(1a)}$$

Table 1
Thermodynamic parameters[a] for the protonation of diamines, at $T = 25°C$, at different ionic strengths, in NaCl aqueous solution

| Amine | $i$[b] | $I$[c] | $\log \beta_i^{H}$ | $-\Delta G_i^0 \pm 3\sigma$[d] | $-\Delta H_i^0 \pm 3\sigma$[d] | $T\Delta S_i^0 \pm 3\sigma$[d] |
|---|---|---|---|---|---|---|
| en | 1 | 0 | 9.90 | 56.51 ± 0.11 | 49.1 ± 0.3 | 7.4 ± 0.3 |
| | | 0.1 | 9.94 | 56.74 ± 0.11 | 49.3 ± 0.3 | 7.4 ± 0.3 |
| | | 0.25 | 9.99 | 57.02 ± 0.06 | 49.6 ± 0.2 | 7.4 ± 0.2 |
| | | 0.5 | 10.06 | 57.42 ± 0.06 | 50.2 ± 0.2 | 7.2 ± 0.2 |
| | | 1 | 10.20 | 58.22 ± 0.06 | 51.1 ± 0.1 | 7.1 ± 0.1 |
| | | 2 | 10.45 | 59.65 ± 0.06 | 52.8 ± 0.2 | 6.8 ± 0.2 |
| | | 3 | 10.71 | 61.13 ± 0.06 | 54.1 ± 0.4 | 7.0 ± 0.4 |
| | | | | | | 7.2 ± 0.3[e] |
| | 2 | 0 | 16.77 | 95.72 ± 0.06 | 93.8 ± 0.2 | 1.9 ± 0.2 |
| | | 0.1 | 17.04 | 97.26 ± 0.06 | 94.1 ± 0.2 | 3.2 ± 0.2 |
| | | 0.25 | 17.19 | 98.12 ± 0.06 | 94.5 ± 0.2 | 3.6 ± 0.2 |
| | | 0.5 | 17.36 | 99.09 ± 0.06 | 95.3 ± 0.1 | 3.8 ± 0.1 |
| | | 1 | 17.65 | 100.75 ± 0.06 | 96.7 ± 0.1 | 4.0 ± 0.1 |
| | | 2 | 18.17 | 103.71 ± 0.06 | 99.6 ± 0.1 | 4.1 ± 0.1 |
| | | 3 | 18.74 | 106.97 ± 0.06 | 102.3 ± 0.3 | 4.7 ± 0.3 |
| | | | | | | 3.6 ± 1.0[e] |
| 1,6d | 1 | 0 | 10.90 | 62.22 ± 0.11 | 57.3 ± 0.2 | 4.9 ± 0.2 |
| | | 0.1 | 10.94 | 62.45 ± 0.06 | 57.6 ± 0.1 | 4.8 ± 0.1 |
| | | 0.25 | 10.98 | 62.67 ± 0.06 | 58.0 ± 0.1 | 4.7 ± 0.1 |
| | | 0.5 | 11.05 | 63.07 ± 0.06 | 58.6 ± 0.1 | 4.5 ± 0.1 |
| | | 1 | 11.19 | 63.87 ± 0.06 | 59.8 ± 0.1 | 4.1 ± 0.1 |
| | | 2 | 11.44 | 65.30 ± 0.06 | 61.9 ± 0.1 | 3.4 ± 0.1 |
| | | 3 | 11.69 | 66.73 ± 0.06 | 63.5 ± 0.1 | 3.2 ± 0.1 |
| | | 4 | 11.93 | 68.10 ± 0.06 | 64.7 ± 0.1 | 3.4 ± 0.1 |
| | | 5 | 12.17 | 69.47 ± 0.06 | 65.5 ± 0.1 | 4.0 ± 0.1 |
| | | | | | | 4.1 ± 0.7[e] |
| | 2 | 0 | 20.70 | 118.16 ± 0.06 | 114.9 ± 0.3 | 3.3 ± 0.3 |
| | | 0.1 | 20.99 | 119.81 ± 0.06 | 115.3 ± 0.3 | 4.5 ± 0.3 |
| | | 0.25 | 21.16 | 120.78 ± 0.06 | 115.8 ± 0.2 | 5.0 ± 0.2 |
| | | 0.5 | 21.36 | 121.92 ± 0.06 | 116.7 ± 0.1 | 5.2 ± 0.1 |
| | | 1 | 21.68 | 123.75 ± 0.06 | 118.5 ± 0.1 | 5.2 ± 0.1 |
| | | 2 | 22.19 | 126.66 ± 0.06 | 122.0 ± 0.3 | 4.7 ± 0.3 |
| | | 3 | 22.67 | 129.40 ± 0.06 | 125.4 ± 0.3 | 4.0 ± 0.3 |
| | | 4 | 23.17 | 132.25 ± 0.06 | 128.7 ± 0.2 | 3.6 ± 0.2 |
| | | 5 | 23.73 | 135.45 ± 0.06 | 131.8 ± 0.1 | 3.7 ± 0.1 |
| | | | | | | 4.4 ± 0.7[e] |
| 1,8d | 1 | 0 | 10.94 | 62.45 ± 0.11 | 58.0 ± 0.2 | 4.4 ± 0.2 |
| | | 0.1 | 10.98 | 62.67 ± 0.11 | 58.3 ± 0.2 | 4.4 ± 0.2 |
| | | 0.25 | 11.03 | 62.96 ± 0.11 | 58.8 ± 0.1 | 4.2 ± 0.2 |
| | | 0.5 | 11.10 | 63.36 ± 0.11 | 59.5 ± 0.1 | 3.9 ± 0.2 |
| | | 1 | 11.23 | 64.10 ± 0.11 | 60.8 ± 0.3 | 3.3 ± 0.3 |
| | | 2 | 11.49 | 65.58 ± 0.06 | 62.8 ± 0.4 | 2.8 ± 0.4 |
| | | 3 | 11.74 | 67.01 ± 0.06 | 64.0 ± 0.1 | 3.0 ± 0.1 |
| | | | | | | 3.7 ± 0.8[e] |
| | 2 | 0 | 20.90 | 119.3 ± 0.06 | 117 ± 0.2 | 2.3 ± 0.2 |
| | | 0.1 | 21.18 | 120.89 ± 0.06 | 117.4 ± 0.1 | 3.5 ± 0.1 |
| | | 0.25 | 21.34 | 121.81 ± 0.06 | 117.9 ± 0.1 | 3.9 ± 0.1 |
| | | 0.5 | 21.53 | 122.89 ± 0.06 | 118.8 ± 0.2 | 4.1 ± 0.2 |
| | | 1 | 21.83 | 124.61 ± 0.06 | 120.5 ± 0.4 | 4.1 ± 0.4 |
| | | 2 | 22.34 | 127.52 ± 0.06 | 123.6 ± 0.4 | 3.9 ± 0.4 |
| | | 3 | 22.85 | 130.43 ± 0.06 | 126.2 ± 0.3 | 4.2 ± 0.3 |
| | | | | | | 3.7 ± 0.8[e] |
| 1,10d | 1 | 0 | 10.94 | 62.45 ± 0.06 | 58.1 ± 0.4 | 4.3 ± 0.4 |

Table 1 (*Continued*)

| Amine | $i^{b}$ | $I^{c}$ | $\log \beta_i^{H}$ | $-\Delta G_i^0 \pm 3\sigma^{d}$ | $-\Delta H_i^0 \pm 3\sigma^{d}$ | $T\Delta S_i^0 \pm 3\sigma^{d}$ |
|---|---|---|---|---|---|---|
| | | 0.1 | 10.98 | 62.67 ± 0.06 | 58.5 ± 0.3 | 4.2 ± 0.3 |
| | | 0.25 | 11.02 | 62.90 ± 0.06 | 59.0 ± 0.2 | 3.9 ± 0.2 |
| | | 0.5 | 11.09 | 63.30 ± 0.06 | 59.9 ± 0.1 | 3.4 ± 0.1 |
| | | 1 | 11.22 | 64.04 ± 0.06 | 61.4 ± 0.4 | 2.6 ± 0.4 |
| | | 2 | 11.46 | 65.41 ± 0.06 | 63.7 ± 0.6 | 1.7 ± 0.6 |
| | | 3 | 11.70 | 66.78 ± 0.06 | 65.0 ± 0.2 | 1.8 ± 0.2 |
| | | | | | | 3.1 ± 1.2$^{e}$ |
| | 2 | 0 | 20.99 | 119.81 ± 0.06 | 117 ± 0.3 | 2.8 ± 0.3 |
| | | 0.1 | 21.27 | 121.41 ± 0.06 | 117.4 ± 0.2 | 4.0 ± 0.2 |
| | | 0.25 | 21.42 | 122.27 ± 0.06 | 118 ± 0.1 | 4.3 ± 0.1 |
| | | 0.5 | 21.61 | 123.35 ± 0.06 | 119 ± 0.2 | 4.3 ± 0.2 |
| | | 1 | 21.89 | 124.95 ± 0.06 | 120.8 ± 0.4 | 4.1 ± 0.4 |
| | | 2 | 22.37 | 127.69 ± 0.06 | 124 ± 0.5 | 3.7 ± 0.5 |
| | | 3 | 22.85 | 130.43 ± 0.06 | 126.6 ± 0.1 | 3.8 ± 0.1 |
| | | | | | | 3.9 ± 0.6$^{e}$ |

[a] $\Delta G^0$, $\Delta H^0$ and $T\Delta S^0$ in kJ mol$^{-1}$.

[b] Parameters refer to the reaction (1).

[c] $I$ in mol dm$^{-3}$.

[d] $\sigma$ = standard deviation.

[e] Mean value of $T\Delta S^0$ at different ionic strengths $\pm 3\ s/\sqrt{N}$ ($N$ = number of $T\Delta S^0$ values).

$$a_2 = -0.054 - 0.042n \qquad \text{(1b)}$$

for $\Delta H^0{}_1$ and

$$a_1 = 2.74 + 0.135n \qquad \text{(1c)}$$

$$a_2 = 0.057 - 0.033n \qquad \text{(1d)}$$

for $\Delta H^0{}_2$. In Eqs. (1a)–(1d), $n$ represents the number of –CH$_2$– groups in the diamine. Values of $-\Delta H^0$ for the different amines increase sharply, for $n < 6$, and quite smoothly for $n \geq 6$. Recently we found that for protonation constants a polynomial equation in $1/n$ fits very well experimental data. The behavior of the enthalpy change is very similar, as can be seen in Fig. 2, where $\Delta H^0$ is plotted versus $n$. In the same function, the effect of ionic strength can be roughly

Table 2
Empirical parameters of Eq. (1) for the dependence of protonation $\Delta H^0$ on ionic strength

| Amine | $i^{a}$ | $a_1$ | $a_2$ |
|---|---|---|---|
| en | 1 | 2.20 | −0.177 |
| | 2 | 2.98 | −0.047 |
| 1,6d | 1 | 2.72 | −0.217 |
| | 2 | 3.67 | −0.057 |
| 1,8d | 1 | 3.20 | −0.402 |
| | 2 | 3.73 | −0.211 |
| 1,10d | 1 | 3.81 | −0.503 |
| | 2 | 4.11 | −0.303 |

[a] Refer to reaction (I).

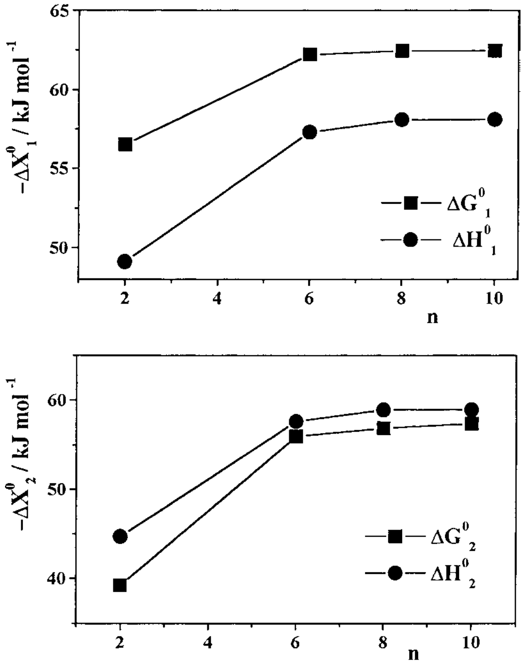

Fig. 2. Dependence of $\Delta G^0$ and $\Delta H^0$ for the protonation of diamines on the alkyl chain length, at 25°C and $I = 0$ mol dm$^{-3}$.

Table 3
Empirical parameters[a] of Eq. (2) for predicting protonation $\Delta G^0$ and $\Delta H^0$ of diamines as a function of ionic strength and alkyl chain length

| $\Delta X^0$ | $i$[b] | $b_0$ | $b_1$ | $b_2$ | $\sigma$[c] |
|---|---|---|---|---|---|
| $-\Delta G^0$ | 1 | 62.93 | −24.9 | 1.475 | 0.2 |
| | 2 | 122.42 | −100.8 | 3.258 | 0.6 |
| $-\Delta H^0$ | 1 | 59.01 | −39.6 | 1.849 | 0.6 |
| | 2 | 118.31 | −99.2 | 3.228 | 0.4 |

[a] $\Delta G^0$ and $\Delta H^0$ in kJ mol$^{-1}$.

[b] Refer to reaction (1).

[c] Standard deviation on the fit of Eq. (2).

taken into account by a single linear term. The resulting equation is

$$\Delta H^0 = b_0 + \frac{b_1}{n^2} + b_2 I \tag{2}$$

The empirical parameters $b_0$, $b_1$ and $b_2$ are reported in Table 3. The same equation can be used also for $\Delta G^0$. The standard deviation on the fit of Eq. (2) is not very low, but it is acceptable for predictive purposes.

### 3.2. Pitzer interaction parameters

Since Pitzer published its first paper on the treatment of thermodynamic parameters using a specific interaction model [17] (now generally called Pitzer model or Pitzer equations), many investigations have been performed in order to give interaction parameters for several equilibrium systems with the final aim to collect as many parameters as possible for constructing useful database for speciation studies. Using data from this work we can calculate both specific interaction parameters and their dependence on temperature. Protonation constants can be expressed as a function of activity coefficients ($\gamma$) ($I$, $K_1^{\mathrm{H}}$ and $\beta_2^{\mathrm{H}}$ expressed in the molal concentration scale)[1]

$$\ln K_1^{\mathrm{H}} = \ln {}^{\mathrm{T}}K_1^{\mathrm{H}} + \ln \gamma_{\mathrm{H}} + \ln \gamma_{\mathrm{A}} - \ln \gamma_{\mathrm{HA}}$$

$$\ln \beta_2^{\mathrm{H}} = \ln {}^{\mathrm{T}}\beta_2^{\mathrm{H}} + 2\ln \gamma_{\mathrm{H}} + \ln \gamma_{\mathrm{A}} - \ln \gamma_{\mathrm{H_2A}}$$

and using Pitzer equation we have

$$\begin{aligned}\ln K_1^{\mathrm{H}} = {} & \ln {}^{\mathrm{T}}K_1^{\mathrm{H}} + 2I(\beta^{(0)}_{\mathrm{H,Cl}} - \beta^{(0)}_{\mathrm{HA,Cl}} + \theta_{\mathrm{H,Na}} - \theta_{\mathrm{HA,Na}} \\ & + \lambda_{\mathrm{HA}}) + I^2(C^{(\phi)}_{\mathrm{H,Cl}} - C^{(\phi)}_{\mathrm{HA,Cl}} + \Psi_{\mathrm{H,Na,Cl}} \\ & - \Psi_{HA,N\mathrm{a,Cl}}) + (\beta^{(1)}_{\mathrm{H,Cl}} - \beta^{(1)}_{\mathrm{HA,Cl}})f_1\end{aligned} \tag{3}$$

$$\begin{aligned}\ln \beta_2^{\mathrm{H}} = {} & \ln {}^{\mathrm{T}}\beta_3^{\mathrm{H}} + 2f^{\gamma} + 2I(\beta^{(0)}_{\mathrm{H,Cl}} - \beta^{(0)}_{\mathrm{H_2A,Cl}} + \theta_{\mathrm{H,Na}} \\ & - \theta_{\mathrm{H_2A,Na}}) + I^2\left(C^{\phi}_{\mathrm{H,Cl}} - \frac{C^{(\phi)}_{\mathrm{H_2A,Cl}}}{1.41} + \Psi_{\mathrm{H,Na,Cl}}\right. \\ & \left. - \Psi_{\mathrm{H_2A,Na,Cl}}\right) + (\beta^{(1)}_{\mathrm{H,Cl}} - \beta^{(1)}_{\mathrm{H_2A,Cl}})f_1 - \beta^{(1)}_{\mathrm{Na,Cl}}f_2\end{aligned} \tag{3a}$$

where

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

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

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

$\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters between two ions of opposite signs, $\Theta$ interaction parameters between two ions of the same sign, $\Psi$ triple interaction parameters $(+-+, -+-)$, $\lambda$ the interaction parameter for neutral species.

By differentiation with respect to temperature of Eqs. (3) and (3a) we have similar equations for $\Delta H^0$ containing temperature gradients $\partial\beta^{(0)}/\partial T$, $\partial\beta^{(1)}/\partial T$ and $\partial C^{(\phi)}/\partial T$. Both parameters and temperature gradients are very similar for all the diamines, $\beta^{(1)}$ and $\partial\beta^{(1)}/\partial T$ are slight dependent on $n$. The calculated parameters are reported in Table 4.

Table 4
Parameters of Pitzer equation and their temperature gradients for the protonation of diamines

| | $\mathrm{HA^+,Cl^-}$ | $\mathrm{H_2A^{2+},Cl^-}$ |
|---|---|---|
| $\beta^{(0)}$ | −0.047 | 0.079 |
| $C^{(\phi)}$ | 0.0068 | −0.036 |
| $\beta^{(1)}$ | 0.0198 + 0.0097n | 0.749 + 0.0090n |
| $\sigma$[a] | 0.007 | 0.01 |
| $\partial\beta^{(0)}/\partial T$ | 0.0011 | 0.000965 |
| $\partial C^{(\phi)}/\partial T$ | −0.00013 | 0.00036 |
| $\partial\beta^{(1)}/\partial T$ | −0.00073 + 0.00033n | 0.0064 + 0.00021n |
| $\sigma$[b] | 0.1 | 0.2 |

[a] Standard deviations on the fit of Eqs. (3) and (3a).

[b] Standard deviations on the fit of the equation of $\Delta H^0$ expressed as a function of temperature gradients.

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[1] Protonation constants reported in Table 1 are expressed in the molar concentration scale using density values for NaCl solutions, conversion factors are 0.001, 0.002, 0.003, 0.005, 0.009, 0.018 and 0.028 for each protonation step, at $I = 0$, 0.1, 0.25, 0.5, 1, 2, 3 mol dm$^{-3}$, respectively. In most cases these corrections are negligible, since they are lower than experimental errors.

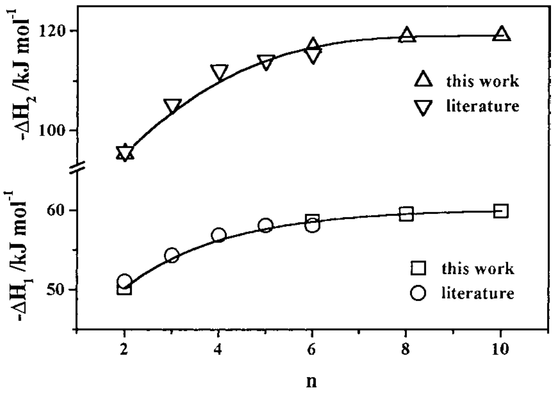

Fig. 3. Dependence on the length of alkyl chain for the enthalpy changes of diamines, at $I = 0.5$ mol dm$^{-3}$ and $T = 25°C$.

### 3.3. Literature comparison

The dependence of protonation $\Delta H^0$ values on the length of alkyl chain ($n$), can be expressed using the data of this work, by a function of $n$. Literature data [12–14] confirm this behavior, as can be seen in Fig. 3 where our values are reported together with data taken from some compilations. Enthalpy changes at different ionic strengths (for $I > 1$ mol dm$^{-3}$) in NaCl aqueous solution are reported for few amines, and we considered data for 1,3d (12–14 and references reported therein). $\Delta H^0$ versus $I$ are reported in Fig. 4 for 1,3d and 1,6d (this work), the behavior is quite similar, suggesting that the conclusions obtained for the amines studied in this work can be extended to other amines.

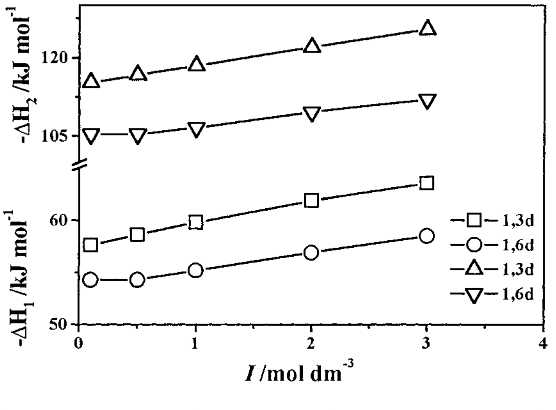

Fig. 4. Dependence on ionic strength of protonation enthalpies for 1,3d (literature data) and 1,6d (this work), at $T = 25°C$.

### 3.4. Concluding remarks

We have reported in this paper a number of thermodynamic data for the protonation of diamines at different temperatures, in NaCl aqueous solution. Main results can be summarised as follows

1. $\Delta H^0$ values are dependent on the number of –$CH_2$– groups ($n$) such as $\Delta G^0$, according to the simple Eq. (2).
2. Also the dependence on ionic strength of enthalpy changes is related to $n$, according to Eqs. (1a)–(1d). Moreover, interaction coefficients of Pitzer equation can be expressed as a function of $n$ (eqs. in Table 4).
3. $T\Delta S^0$ values are fairly independent of ionic strength (~4 kJ mol$^{-1}$).

All the above points are consistent with the possibility of considering diamines as a very homogeneous class of ligands where thermodynamic protonation data can be predicted using simple empirical equations. Parallel studies on the protonation of tri and tetramines, and on the complexes of polyamines with $Mg^{2+}$ and $Ca^{2+}$ [18], confirm this suggestion.

## Acknowledgements

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