J. Chem. Eng. Data **1999,** *44,* 735−738

Protonation of Diamines $H_2N-(CH_2)_n-NH_2$ ($n = 2-10$) in NaCl Aqueous Solution at Different Ionic Strengths

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Protonation constants of diamines $H_2N-(CH_2)_n-NH_2$ ($n = 3, 4, 5, 6, 8, 10$) were determined potentiometrically (H^+-glass electrode) in different NaCl aqueous solutions, at $I \leq 1$ mol dm^{-3}. Dependence on ionic strength was considered by using Debye−Hückel and Pitzer type equations. General relationships for both protonation constants and parameters for the dependence on ionic strength are reported.

Introduction

Despite the great importance of amines both as model molecules and in several biological processes, few studies have been carried out on their speciation in natural waters and in biological fluids. To do this, the dependence of protonation constants on ionic strength must be investigated in different ionic media, first of all in NaCl, which is the most abundant salt in natural fluids. The dependence on medium of the protonation of several amines has been reported by Scandinavian authors, but in general $NaClO_4$ has been used as background salt. Since we are involved in speciation studies of some classes of ligands (amines, carboxylates, phenols, etc.), we carried out systematic investigations into the protonation of amines in NaCl. This paper reports an investigation on the protonation of the linear diamines 1,3-diaminopropane (1,3d), 1,4-diaminobutane (putrescine, 1,4d), 1,5-diaminopentane (cadaverine, 1,5d), 1,6-diaminohexane (1,6d), 1,8-diaminooctane, (1,8d) and 1,10-diaminodecane (1,10d) at $t = 25$ °C and in aqueous NaCl media at $I \leq 1$ mol dm^{-3} [previously published data on ethylenediamine (en) were considered too]. Different models were considered for dependence on medium (Debye−Hückel and Pitzer type equations), and regularities in both protonation constants and parameters for dependence on ionic strength were analyzed for predictive purposes.

Experimental Section

Chemicals. Some amine (A = 1,3d; 1,4d; 1,5d; 1,6d) hydrochlorides (Aldrich-Sigma) were used without further purification, since alkalimetric titration showed their purity to be 98−99%. 1,8d and 1,10d (Fluka) were purified by transformation into the corresponding hydrochlorides and were used in this form. Standard solutions of NaCl (Fluka puriss. p.a.) were prepared by weight after drying in a stove at 110 °C. Working solutions of NaOH and HCl were prepared by diluting concentrated Fluka ampules and were standardized against potassium biphthalate (Fluka puriss. p.a.) and sodium carbonate (Fluka puriss. p.a.), respectively. All solutions were prepared by using twice-distilled water and grade A glassware.

Apparatus. Potentiometric measurements were carried out with a Metrohm 654 potentiometer (resolution ±0.1 mV) coupled with an Orion combination pH electrode, model 8102 (Ross type); the titrant was delivered with a Metrohm Dosimat 665 dispenser. The estimated accuracy of the system was ±0.15 mV and ±0.003 cm^3 for emf and titrant volume readings, respectively. The apparatus was coupled with a PC, so automatic titrations were carried out using a suitable computer program for the acquisition of data (volume of titrant, check for the stability of emf, and relative value). The measurement cell (25 cm^3) was thermostated at $t = 25 \pm 0.2$ °C, and a magnetic stirrer was employed. Purified N_2 was bubbled through the solutions during the titrations.

Procedure. 25 cm^3 of the solution containing the amine hydrochloride (5−10 mmol dm^{-3}), NaCl (to achieve the prefixed ionic strength, ≤1 mol dm^{-3}), and an excess of HCl (10 mmol dm^{-3}) was titrated with standard NaOH (0.2 mol dm^{-3}) up to 90% neutralization (70−90 experimental points, pH ∼ 11.5). HCl was added in order to calculate $E°_{int}$. In this way pH $= -\log [H^+]$, and therefore concentration constants were measured. By separate titrations (as a check) of HCl at the same temperature and ionic strength, we calculated $E°_{ext}$. If $|E°_{int} - E°_{ext}| \geq 1.0$ mV, the titration was rejected and repeated.

Calculations. Potentiometric data were first analyzed by the least squares computer program ESAB2M (De Stefano et al., 1987), which refines the parameters of the acid−base titration ($E°$, Kw) and calculates the purity of the reagents and the conditional protonation constants of diamines at the ionic strength values of specific titration. With the computer program LIANA (De Stefano et al., 1997), using a nonlinear fitting program, we were able to calculate the protonation constant values of the diamines at $I = 0$ mol dm^{-3}, starting from the relative conditional protonation constants using different equations. The computer programs BSTAC (De Stefano et al., 1993) and STACO (De Stefano et al., 1996) were used to calculate the formation constants of diamine chloride complexes. The ES4ECI (De Stefano et al., 1993) program was used to draw the distribution diagrams of the species. Equilibrium constants were expressed as

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10.1021/je980311d CCC: $18.00

$$i\mathrm{H}^+ + \mathrm{A}^0 = \mathrm{H}_i\mathrm{A}^{i+} \qquad \beta_i^{\mathrm{H}} \qquad (1)$$

$$\mathrm{H}_{i-1}\mathrm{A}^{(i-1)+} + \mathrm{H}^+ = \mathrm{H}_i\mathrm{A}^{i+} \qquad K_i^{\mathrm{H}} \qquad (1a)$$

$$i\mathrm{H}^+ + \mathrm{A}^0 + \mathrm{Cl}^- = \mathrm{AH}_i\mathrm{Cl}^{(i-1)+} \qquad \beta_i^{\mathrm{Cl}} \qquad (1b)$$

$$\mathrm{H}_i\mathrm{A}^{i+} + \mathrm{Cl}^- = \mathrm{AH}_i\mathrm{Cl}^{(i-1)+} \qquad K_i^{\mathrm{Cl}} \qquad (1c)$$

Results

Protonation constants of different diamines, at different ionic strengths, are reported in Table 1. Figure 1, as an example, shows the protonation constants of 1,3d and 1,8d versus I or $I^{1/2}$. Both log K_1^{H} and log β_2^{H} are increasing functions of ionic strength. These values were extrapolated to zero ionic strength using the equation

$$\log K_i^{\mathrm{H}} = \log {}^{\mathrm{T}}K_i^{\mathrm{H}} - z^*[I^{1/2}/(2 + 3I^{1/2}) + dI^{3/2}] + C_iI \quad (2)$$

(${}^{\mathrm{T}}K_i^{\mathrm{H}}$ = protonation constant at infinite dilution, $z^* = 0$ for $i = 1$, and $z^* = -2$ for $i = 2$; d and C_i are empirical parameters). Table 2 shows both log ${}^{\mathrm{T}}K_i^{\mathrm{H}}$ (and log ${}^{\mathrm{T}}\beta_2^{\mathrm{H}}$) and C_i values for each diamine. The value of d was kept as a common parameter for all the diamines. Values of C_i for both protonation steps are fairly constant, and average values are $C_1 = 0.32 \pm 0.05$ and $C_2 = 0.87 \pm 0.09$ (considering values for ethylenediamine too). Protonation constants show a very regular trend versus n (number of CH_2 groups), as does the $\Delta\log K^{\mathrm{H}} = \log K_2^{\mathrm{H}} - \log K_1^{\mathrm{H}}$ difference, as can be seen in Figure 2, and tend asymptotically to a constant value.

In previous works (Foti et al., 1997, 1998) we found that the log $K = f(I)$ function can also be usefully expressed by a Pitzer type equation (Pitzer, 1991):

$$\ln K_i = \ln {}^{\mathrm{T}}K_i + 2z_{\mathrm{A}}f^{\gamma} + P_1I + P_2f_1 + P_3I^2 \qquad (3)$$

where P_1, P_2, and P_3 are empirical parameters and f^{γ} and f_1 are defined by the equations

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

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

At $I \leq 1$ mol dm^{-3} the I^2 term can be neglected. Table 3 shows the values of the empirical parameters of eq 3. The standard deviation of the fit is the same when using eqs 2 and 3, that is 0.01 for log K_1^{H} and 0.015 for log β_2^{H}. From the parameters of eq 3, the interaction Pitzer parameters $\beta^{(0)}$ and $\beta^{(1)}$ (Pitzer, 1991) can be calculated.

Table 1. Protonation Constants[a] of Diamines, at t = 25 °C and at Different Ionic Strengths in NaCl Aqueous Solution

	log K_1^{H}					
I/mol dm^{-3}	1,3-d	1,4-d	1,5-d	1,6-d	1,8-d	1,10-d
0.10	10.52	10.57	10.82	10.93	10.99	10.97
0.25	10.56	10.61	10.88	10.98	11.04	11.03
0.50	10.64	10.66	10.96	11.06	11.12	11.12
0.75	10.74	10.74	11.04	11.15	11.20	11.23
1.00	10.81	10.79	11.12	11.22	11.28	11.32

	log β_2H					
I/mol dm^{-3}	1,3-d	1,4-d	1,5-d	1,6-d	1,8-d	1,10-d
0.10	19.20	19.88	20.63	20.98	21.16	21.22
0.25	19.38	20.05	20.81	21.14	21.35	21.43
0.50	19.63	20.30	21.02	21.37	21.54	21.61
0.75	19.83	20.43	21.23	21.55	21.69	21.76
1.00	20.00	20.57	21.39	21.70	21.83	21.90

[a] Average values from three determinations: ±0.01.

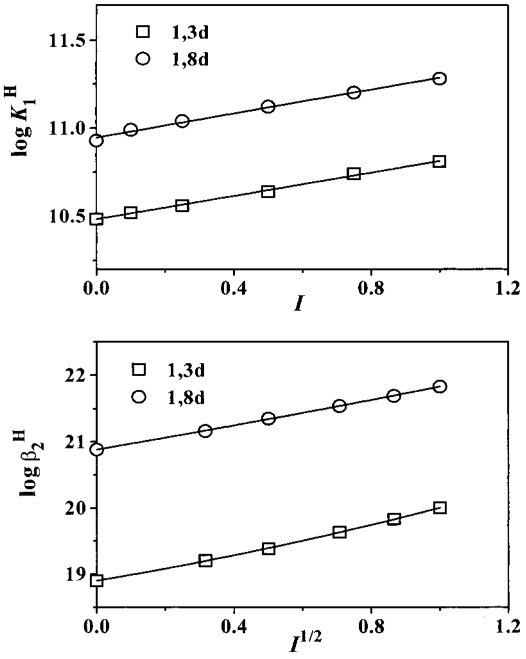

Figure 1. Dependence of protonation constants on ionic strength, for 1,3d and 1,8d, at 25 °C (I/mol dm^{-3}).

Table 2. Protonation Constants of Diamines at I = 0 mol dm^{-3} and Relative Parameters for Dependence on Ionic Strength According to Eq 2 at 25 °C

A	log K_1^{H}	C_1	log β_2^{H}	C_2[a]	log K_2^{H}
en[b]	9.91	0.29	16.77	0.75	6.86
1,3d	10.485(5)[c]	0.34	18.899(6)[c]	1.00	8.41
1,4d	10.545(8)	0.24	19.59(3)	0.86	9.05
1,5d	10.80(1)	0.32	20.33(1)	0.95	9.53
1,6d	10.896(7)	0.32	20.681(7)	0.91	9.78
1,8d	10.93(1)	0.37	20.88(1)	0.84	9.95
1,10d	10.935(6)	0.39	20.98(2)	0.80	10.05

[a] With $d = -0.15$ (eq 2). [b] Casale et al., 1990. [c] Standard deviation in the last significant figure in parentheses.

The dependence on medium of protonation constants of amines can be also interpreted in terms of chloride complex formation. In previous studies (Daniele et al., 1997) it has been demonstrated that, in the absence of significant interaction, dependence on ionic strength can be expressed by eq 2 with

$$C = c_0p^* + c_1z^* = 0.11p^* + 0.20z^* \qquad (4)$$

$$d = 0.075 \qquad (4a)$$

$$p^* = \sum(\mathrm{moles})_{\mathrm{reactants}} - \sum(\mathrm{moles})_{\mathrm{products}}$$

in the range $0 \leq I$ (mol dm^{-3}) ≤ 1. The model on which this assumption is based has been discussed in several preceding papers (Daniele et al., 1991, 1994, 1997; De Robertis et al., 1994, 1997). Under this assumption, differences in log K_1^{H} for $I > 0$ are attributed to the formation of chloride complexes, according to equilibrium 1b or 1c. Calculations using eq 2 gave the formation constants for chloride complexes shown in Table 4. Both log K_1^{Cl} and log K_2^{Cl} show very good constancy with average values: −0.13 ± 0.15 and 0.77 ± 0.08, respectively. Figure 3 shows the

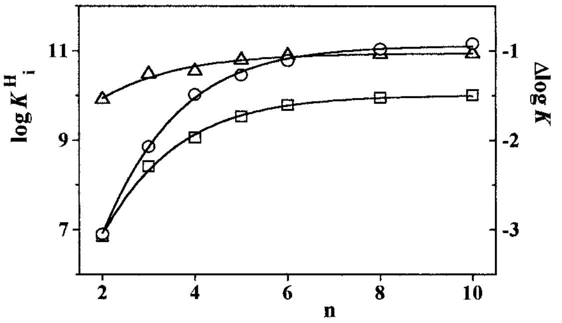

Figure 2. log K_1^H (□), log K_2^H (△), and Δlog K (○) (log K_2^H − log K_1^H) of diamines versus n (number of CH_2 groups).

Table 3. Parameters for the Pitzer Type Equation (eq 3) for log β_2^H

A	P_1	P_2
1,3d	1.15[a]	0.013[b]
1,4d	0.74	0.113
1,5d	1.02	0.022
1,6d	0.96	−0.007
1,8d	0.84	−0.031
1,10d	0.69	0.015

[a] Mean standard deviation: ±0.05. [b] Mean standard deviation: ±0.02.

Table 4. Formation Constants of Chloride Complexes at I = 0 mol dm^{-3} and t = 25 °C

amines	log β_1^{Cl} [a]	log β_2^{Cl} [a]	log K_1^{Cl} [b]	log K_2^{Cl} [b]
en[c]	9.80	17.43	−0.11	0.66
1,3d	10.42(1)[d]	19.76(1)[d]	−0.07	0.86
1,4d	10.12(2)	20.31(1)	−0.43	0.72
1,5d	10.64(2)	21.21(1)	−0.16	0.88
1,6d	10.74(1)	21.47(1)	−0.16	0.79
1,8d	10.89(1)	21.66(1)	−0.04	0.77
1,10d	10.99(3)	21.70(1)	0.05	0.72

[a] Equilibrium 1b. [b] Equilibrium 1c. [c] Casale et al., 1990. [d] Standard deviation in the last significant figure in parentheses.

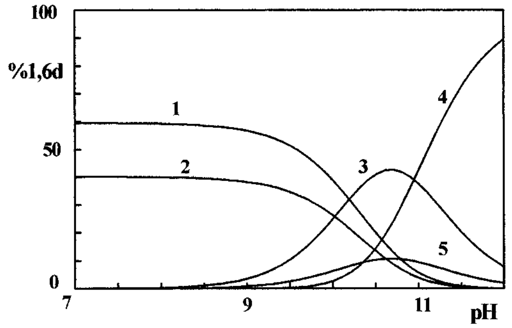

Figure 3. Speciation diagram of the H^+−1,6d−Cl^- system at I = 0.5 mol dm^{-3} (NaCl) and 25 °C. Curves: (1) AH_2Cl^+; (2) AH_2^{2+}; (3) AH^+; (4) A^0; (5) $AHCl^0$.

speciation diagram for the system H^+−1,6d−Cl^-: at I = 0.5 mol dm^{-3} (NaCl), AH_2Cl^+ yields (60%) are very high at pH < 9, while $AHCl^0$ forms in fairly low percentages (~10%) at pH 10−11. Formation constants for amine chloride complexes are in agreement with those found for similar systems (Casale et al., 1990, 1998; Daniele et al., 1995; De Robertis et al. 1998).

Discussion

As already seen, protonation constants versus n show an increasing trend (Figure 2) tending asymptotically to a constant value. Their values can be expressed as a polynomial function of 1/n:

$$\log K_1^H = 11.070 - 0.785/n - 3.070/n^2 \qquad (5)$$

$$\log K_2^H = 10.616 - 4.558/n - 5.923/n^2 \qquad (6)$$

with a mean deviation from experimental findings of 0.04. [Recently, Lloris et al. (1998) proposed a semiempirical relationship for predicting protonation constants in polyamines in terms of a polynomial function or 1/r (r = distance between the protonated atoms), which is in accordance with the results of this investigation.] This allows us to estimate values of log K_i^H for n = 7, 9, 11, 12 (n = 7: log K_1^H = 10.90; log K_2^H = 9.84. n = 9: log K_1^H = 10.94; log K_2^H = 10.04. n = 11: log K_1^H = 10.97; log K_2^H = 10.15. n = 12: log K_1^H = 10.98; log K_2^H = 10.20). The protonation constants shown here are compared in Table 5 with those reported in the literature. In general, agreement is fairly good, but the comparison has been limited to very low ionic strength values.

Table 5. Comparison with Literature Data (t = 25 °C)

amine	log K_1^H	log K_2^H	I/mol dm^{-3}	ref
1,3d	10.48	8.42	0	this work
	10.45	8.43	0	De Robertis et al., 1998
	10.49	8.48	0	Martell et al., 1997
	10.49	8.74	0.1 (KNO_3)	Daniele et al., 1978
	10.53	8.83	0.1 (KNO_3)	Jameson et al., 1980
1,4d	10.54	9.05	0	this work
	10.49	9.10	0	De Robertis et al., 1998
	10.69	9.22	0	Martell et al., 1997
1,5d	10.80	9.53	0	this work
	10.79	9.59	0	De Robertis et al., 1998
	10.78	9.85	0.1	Martell et al., 1997
1,6d	10.90	9.78	0	this work
	10.93	9.83	0	Martell et al., 1997
	10.93	9.86	0	Daniele et al., 1995
1,8d	10.93	9.95	0	this work
	10.88	10.06	0	Daniele et al., 1995
1,10d	10.93	10.04	0	this work

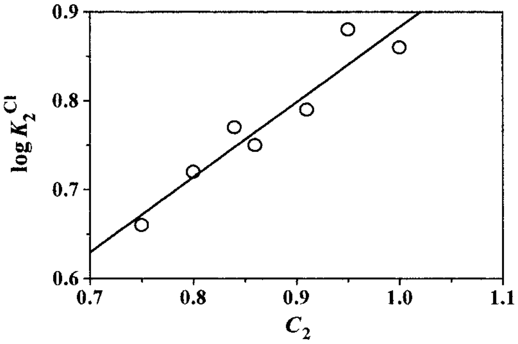

Figure 4. Dependence of log K_2^{Cl} of diamines on C_2.

Amine chloride complexes show fairly constant stability. Average values are log K_1^{Cl} = −0.13 ± 0.15 and log K_2^{Cl} = 0.77 ± 0.08. Note that log K_2^{Cl} versus C_2 is in a straight line, as shown in Figure 4:

$$\log K_2^{Cl} = 0.0393 + 0.844C_2 \qquad (7)$$

As shown above, the regular trend of both protonation constants and their dependence on ionic strength allows us to predict protonation parameters for other amines too. We have seen that protonation constants can also be evaluated for n = 7, 9, 11, and 12 with a good degree of precision. As regards the parameters for dependence on ionic strength, we have the following results: C_1 and C_2

are in practice constant; also considering the Pitzer type equation, we found that parameters can be reduced to

$$P_1 = 1.25\ (\pm 0.03) - [0.058\ (\pm 0.004)]n \qquad (8)$$

$$P_2 = 0.05 \pm 0.02 \qquad (9)$$

Our concluding remarks are as follows. Protonation parameters in NaCl, $I \le 1$ mol dm^{-3}, are defined for $n \le 10$ (for $10 \le n \le 12$ reliable estimates are found). The regular trend of these parameters has been highlighted (eqs 7−9). Debye−Hückel and Pitzer type equations show the same ability to describe dependence on ionic strength in the range studied.

Acknowledgment

We thank professor Silvio Sammartano for helpful discussions.

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Received for review December 17, 1998. Accepted March 23, 1999. We thank CNR and MURST for financial support.

JE980311D