Thermochimica Acta, 209 (1992) 7–24
Elsevier Science Publishers B.V., Amsterdam

Salt effects on the protonation of diethylenetriamine: a complex formation model

Alessandro De Robertis, Concetta De Stefano and Grazia Patanè

Istituto di Chimica Analitica dell'Università, Salita Sperone 31, I-98166 S. Agata di Messina (Italy)

(Received 5 February 1992)

Abstract

Protonation constants of diethylenetriamine (dien) have been determined potentiometrically, using (H^+)/glass electrode in different aqueous media (NaCl, KCl, $NaClO_4$, NaI, $NaNO_3$, $MgCl_2$, $CaCl_2$ and tetraethylammonium iodide) at 25°C and $0 < I \leqslant 1$ mol l^{-1}. Measurements at very low ionic strength and in KCl ($0 < I \leqslant 1$ mol l^{-1}) were also carried out at different temperatures ($10 \leqslant T \leqslant 40$°C). The differences in $\lg K_j^H$ values are explained using a complex formation model by taking into account the formation of $(dien)H_qX_p$ and $M(dien)H_q$ weak species ($X = Cl^-$, ClO_4^-, I^-, NO_3^-; $M = Ca^{2+}$, Mg^{2+}, tetraethylammonium cation). Formation thermodynamic parameters are given. The speciation of diethylenetriamine in mixed electrolytes is discussed in relation to the real composition of natural fluids.

INTRODUCTION

As an important part of our studies on the ionic strength dependence of formation constants and on the complexing ability of low molecular weight ligands towards alkali and alkaline earth metal ions, we have considered in several works the behaviour of mono- and diamines [1–9]. A literature data analysis allowed a simple model for the dependence on medium of amines protonation constants to be proposed [4]. The main features of this model are, (a) Na^+ and K^+ do not form any appreciable complex species with amines; (b) inorganic anions (Cl^-, ClO_4^-, I^-, NO_3^-, generically indicated with X^-) form $[(amine)H_qX_p]^{q-p}$ complex species; (c) the stability of these species is fairly independent of the nature of amine and X^-, but depends only on the stoichiometric coefficients p and q; (d) the dependence on ionic strength of protonation and formation constants can be described with a simple Debye–Hückel type equation, as previously found [10–12]. Moreover, some investigations showed that

---

Correspondence to: C. De Stefano, Istituto di Chimica Analitica dell'Università, Salita Sperone 31; I-98166 S. Agata di Messina, Italy.

alkaline earth and tetraalkylammonium cations form very weak, but significant, species [2, 3, 5–8].

In order to confirm the model also for the triamines, we decided to investigate the salt effects on the protonation of diethylenetriamine in several aqueous media ($NaCl$, $NaClO_4$, NaI, $NaNO_3$, KCl, $MgCl_2$, $CaCl_2$ and tetraethylammonium iodide).

EXPERIMENTAL

Materials

Diethylenetriamine (Fluka) was purified by transformation into the corresponding hydrochloride and its purity was checked by alkalimetric titrations (always greater than 99.7%). The solutions of alkali metal ions were prepared by weight, from the corresponding analytical grade salts (Fluka or C. Erba) previously dried in a stove at 110°C or under vacuum. Magnesium and calcium chlorides were prepared from analytical grade reagents (Fluka) and standardized with EDTA titrations [13]. Tetraethylammonium iodide (Et_4NI) was purified by recrystallization as described by Perrin et al. [14] HCl, NaOH and KOH stock solutions were prepared by diluting concentrates from ampoules (C. Erba) and were standardized against sodium carbonate (Fluka puriss.) and potassium biphthalate (Fluka puriss.), respectively. All solutions were prepared with double distilled water and grade A glassware was used.

Apparatus

The free hydrogen ion concentration was measured with two different equipments. (a) Potentiometer Metrohm E600 connected to a Ross combination pH electrode mod. 8102, supplied by Orion; the titrant was delivered manually by an Amel mod. 882 dispenser, readable to 1 μl. (b) Potentiometer Metrohm E605 coupled with a Metrohm grass electrode and an Ingold saturated calomel reference electrode; a Metrohm motorized burette was used to deliver the titrant automatically, by using an idoneous software. The measurement cell (50 ml) was thermostatted at $T \pm 0.2$°C and a magnetic stirrer was employed. All the titrations were carried out by bubbling purified nitrogen through the solution. The solution was preserved from CO_2 by means of soda lime traps.

Procedure

25–50 ml of aqueous solution containing protonated amine (3–6 mmol l^{-1}) were titrated with standard carbonate free KOH or NaOH 0.1 mol l^{-1} up to complete neutralization (40–60 experimental points). To the same solution was added the appropriate amount of the background salt in order to reach the prefixed ionic strength value; an excess of HCl (3–5 mmol l^{-1}) was also added in order to calculate the E^0 value in the same solution under study (E^0_{int}); by separate titration we calculate E^0_{ext} at the same ionic strength value; if $|E^0_{\text{int}} - E^0_{\text{ext}}| > 1.5$ mV, the titration was rejected. The liquid junction potential ($E_j = j_A c_H$) was always taken into consideration at pH < 2.

Calculations

Potentiometric data were first analyzed by the least square program ESAB2M [15] which refines some parameters as analytical reagent concentrations, conditional protonation constants E^0 and junction potentials. Formation constants of various complexes were calculated with the nonlinear least squares computer programs ES2WC [16] and STACO [17]. The distribution of the species was calculated by the computer program ES4EC [18]; this program can also calculate the errors in formation percentage arising from errors in formation constants.

THE MODEL

The dependence of protonation constants on ionic strength is defined by the Debye–Hückel type equation

$$\lg K_j^H = \lg {}^TK_j^H - z_j^* \mathscr{A}\sqrt{I}/(1 + B_j\sqrt{I}) + C_jI + D_jI^{3/2} \qquad (1)$$

where, for the general protonation reaction

$$H_{j-1}A^{j-1} + H^+ = H_jA^j \qquad (A^0 = \text{uncharged amine}) \qquad (2)$$

$z_j^* = 2(1-j)$, $\mathscr{A}$ is the Debye–Hückel coefficient and B_j, C_j, D_j are empirical coefficients.

When all the interactions among various components present in the solution are taken into account, it has been shown [10–12] that all the coefficients in eqn. (1), depend only on the charge and on the stoichiometry of the reaction, according to the equation

$$\lg K_j^H = \lg {}^TK_j^H - z_j^* \mathscr{A}\sqrt{I}/(1 + 1.5\sqrt{I}) + (c_0 + z_j^*c_1)I + (d_0 + z_j^*d_1)I^{3/2} \qquad (3)$$

where c_0, c_1, d_0 and d_1 are coefficients independent of the amine under consideration.

Amines in inorganic salt solutions (MX = generic inorganic salt) show the formation of both anion and cation complexes [4] according to the reaction

$$H_qA^{q+} + pX^- = AH_qX_p^{q-p} \qquad K_{pq}^X \qquad (4)$$

$$H_qA^{q+} + M^{z+} = MAH_q^{q+z} \qquad K_q^M \qquad (5)$$

Formation constants K_{pq}^{X} and K_q^{M} show an ionic strength dependence analogous to that of protonation constants, according to equations (1) or (3) with $z_j^* = p(1 - p + 2q)$ for K_{pq}^{X} and $z_j^* = -2qz$ for K_q^{M}.

Cumulative protonation and formation constants, relative to the equilibria

$$jH^+ + A^0 = H_jA^j \qquad \beta_j^H = \prod K_j^H \tag{6}$$

$$A^0 + qH^+ + pX^- = AH_qX_p^{q-p} \qquad \beta_{pq}^X = K_{pq}^X \times K_q^H \tag{7}$$

$$M^{z+} + A^0 + qH^+ = MAH_q^{q+z} \qquad \beta_q^M = K_q^M \times K_q^H \tag{8}$$

are dependent on ionic strength according to the general equation

$$\lg\beta = \lg{}^{T}\beta - z^*\mathscr{A}\sqrt{I}/(1 + 1.5\sqrt{I}) + (p^*c_0 + z^*c_1)I + (p^*d_0 + z^*d_1)I^{3/2} \tag{9}$$

with

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

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

In several preceding works [10–12, 19] we used the approximations $\mathscr{A} = 0.5$, $c_0 = -d_1 = 0.1$ and $d_0 = 0$, and therefore eqn. (9) becomes

$$\lg\beta = \lg{}^{T}\beta - z^*[\sqrt{I}/(2 + 3\sqrt{I}) + 0.1I^{3/2}] + (z^*c_1 + 0.1p^*)I \tag{10}$$

The value of c_1 reported elsewhere is also quite constant ($c_1 = 0.23 \pm 0.01$) and generally is treated in calculations as an adjustable parameter to check the reliability of the model.

In some preceding works we considered the association of the background salt in order to account for the effective ionic strength of solutions. Though formation constants for the weak species (e.g. $NaCl^0$, $CaCl^+$, $MgCl^+$ . . .) are in some cases quite doubtful (in particular for 1:1 electrolytes), the model which also considers these interactions allows us to explain the behaviour of protonation constants in different similar media. For example, protonation constants in $NaClO_4$ and NaCl always show small differences which disappear when considering the effective ionic strength I_e by taking into account the weak association of NaCl ($NaClO_4$ is completely dissociated) [6]. Also in this work we took into account the effective ionic strength I_e by considering the association of NaCl, $NaNO_3$, KCl, $MgCl_2$ and $CaCl_2$ (using formation constants from refs. 20 and 21) and considering as completely dissociated $NaClO_4$, NaI and Et_4NI.

In Table 1 we report some formation constants for weak amine complexes.

TABLE 1

Formation constants of weak amine complexes at 25°C and $I = 0$ mol l^{-1} [a]

Reaction	lg K	L	X	Ref.
$HL + X^- = LHX^0$	−0.3	am	Cl^-, ClO_4^-, NO_3^-	12
	−0.2	py	Cl^-	2
	−0.27	im	Cl^-	3
	−0.05	py	Cl^-, I^-	5
	−0.1	en	Cl^-, ClO_4^-, NO_3^-	6
$H_2L^{2+} + X^- = LH_2X^+$	0.59	am	Cl^-, ClO_4^-, NO_3^-	12
	0.66	en	Cl^-, ClO_4^-, NO_3^-	6
$H_3L^{3+} + X^- = LH_3X^{2+}$	1.34	am	Cl^-, ClO_4^-, NO_3^-	12
$Ca^{2+} + L^0 = CaL^{2+}$	−0.1	bipy		9(a)
	−0.35	py		2
	−0.2	im		3
	−0.48	py		5
	0.02	en		6
	−0.11	bipy		9(b)
$Mg^{2+} + L^0 = MgL^{2+}$	0.3	bipy		9(a)
	−0.30	py		2
	0.07	im		3
	−0.37	py		5
	0.42	bipy		9(b)
$Et_4N^+ + L^0 = (Et_4N)L^+$	0.07	py		5
	0.2	en		6
	−0.07	bipy		9(b)
	−0.07	im		3

[a] Key: am, generic amine; py, pyridine; im, imidazole; en, ethylenediamine; bipy, 2,2′-bipyridyl.

RESULTS AND DISCUSSION

Protonation constants

Experimental data were first analyzed without allowing for the weak interactions. In Table 2 the apparent protonation constants of diethylenetriamine in KCl aqueous solution are reported at different temperatures and ionic strengths together with related thermodynamic quantities. Extrapolation to zero ionic strength gave data reported in Table 3. In Table 4 the protonation constants of diethylenetriamine in different salt solutions are reported at five (smoothed) ionic strengths, at 25°C. As one can see, at $I \geqslant 0.5$ mol l^{-1} protonation contants determined in different ionic media differ more than expected experimental errors. Mean lg K_j^H values in NaCl, $NaClO_4$, NaI, $NaNO_3$ and KCl are acceptable only for $I \leqslant 0.25$ mol l^{-1}.

TABLE 2

Apparent protonation constants and protonation enthalpies and entropies of diethylenetriamine in aqueous solutions at different temperatures and ionic strengths[a]

j	I	T	$\lg K_j^{\mathrm{H},}$	$\Delta G_j^{\ominus}$	$\Delta H^{\ominus}$	$\Delta S^{\ominus}$
1	0.05	10	10.18[b]	−55.2	−38[c]	61
	0.05	20	9.94	−55.8	−40	53
	0.05	25	9.82	−56.0	−41	50
	0.05	30	9.70	−56.3	−42	46
	0.05	40	9.46	−56.7	−45	39
	0.10	10	10.16	−55.1	−34	76
	0.10	20	9.94	−55.8	−36	69
	0.10	25	9.83	−56.1	−36	66
	0.10	30	9.73	−56.4	−37	63
	0.10	40	9.52	−57.0	−39	56
	0.25	10	10.12	−54.8	−25	106
	0.25	20	9.95	−55.9	−26	101
	0.25	25	9.87	−56.4	−27	99
	0.25	30	9.80	−56.9	−27	97
	0.25	40	9.64	−57.8	−29	93
	0.50	10	10.12	−54.9	−20	123
	0.50	20	10.00	−56.1	−21	120
	0.50	25	9.93	−56.7	−21	118
	0.50	30	9.87	−57.3	−22	117
	0.50	40	9.75	−58.4	−23	114
	1.00	20	10.12	−56.8	−37	69
	1.00	25	10.01	−57.1	−38	66
	1.00	30	9.90	−57.5	−39	62
2	0.05	10	9.34	−50.6	−42	30
	0.05	20	9.07	−50.9	−44	22
	0.05	25	8.94	−51.0	−46	18
	0.05	30	8.80	−51.1	−47	14
	0.05	40	8.54	−51.2	−49	6
	0.10	10	9.38	−50.8	−38	45
	0.10	20	9.13	−51.2	−40	38
	0.10	25	9.01	−51.4	−41	34
	0.10	30	8.89	−51.6	−42	31
	0.10	40	8.65[b]	−51.9	−44	24
	0.25	10	9.44	−51.1	−30	73
	0.25	20	9.24	−51.9	−32	68
	0.25	25	9.14	−52.2	−33	65
	0.25	30	9.05	−52.5	−33	63
	0.25	40	8.86	−53.1	−35	58
	0.50	10	9.53	−51.6	−27	87
	0.50	20	9.35	−52.5	−28	83
	0.50	25	9.27	−52.9	−29	81
	0.50	30	9.18	−53.3	−29	78
	0.50	40	9.02	−54.0	−31	74
	1.00	20	9.50	−53.3	−47	23
	1.00	25	9.36	−53.4	−48	18
	1.00	30	9.22	−53.5	−49	14
3	0.05	10	4.40	−23.9	−41	−60
	0.05	20	4.16	−23.4	−35	−39
	0.05	25	4.07	−23.2	−31	−27
	0.05	30	3.98	−23.1	−28	−15

TABLE 2 (continued)

j	I	T	$\lg K_j^{H'}$	$\Delta G_j^\ominus$	$\Delta H^\ominus$	$\Delta S^\ominus$
	0.05	40	3.85	−23.1	−19	12
	0.10	10	4.55	−24.6	−41	−57
	0.10	20	4.31	−24.2	−35	−36
	0.10	25	4.21	−24.0	−31	−24
	0.10	30	4.13	−23.9	−28	−12
	0.10	40	4.00	−24.0	−19	15
	0.25	10	4.81	−26.1	−40	−51
	0.25	20	4.57	−25.6	−34	−30
	0.25	25	4.47	−25.5	−31	−18
	0.25	30	4.39	−25.5	−27	−6
	0.25	40	4.26	−25.5	−19	22
	0.50	10	5.02	−27.2	−40	−45
	0.50	20	4.79	−26.9	−34	−24
	0.50	25	4.70	−26.8	−30	−12
	0.50	30	4.61	−26.8	−27	1
	0.50	40	4.49	−26.9	−18	28
	1.00	20	4.89	−27.4	−33	−18
	1.00	25	4.80	−27.4	−29	−6
	1.00	30	4.72	−27.4	−25	6

[a] I (apparent, see text) in mol l^{-1}; T in °C; $\lg K_j^{H'}$ apparent protonation constant; $\Delta G^\ominus$ in kJ mol^{-1} ($\lg K^H$ and $\Delta G^\ominus$ in the molar scale); $\Delta H^\ominus$ in kJ mol^{-1}, $\Delta S^\ominus$ in J mol^{-1} deg^{-1}. [b] 3(std. dev.)($\lg K_j^{H'}$) ≈ 0.05, 0.02 and 0.02 for $j = 1$, 2, and 3, respectively. [c] 3(std. dev.)(ΔH_j^0) ≈ 1.5, 1 and 1 for $j = 1$, 2, and 3, respectively.

TABLE 3

Protonation constants of diethylenetriamine at $I = 0$ mol l^{-1} [a]

j	T	$\lg K_j^H$	$\Delta H_j^\ominus$	$\Delta C_p^\ominus$
1	10	10.220 ± 0.018 [b]		
	20	9.939 ± 0.010		
	25	9.799 ± 0.010	−48 ± 2 [b]	
	30	9.661 ± 0.009		
	40	9.385 ± 0.015		
2	10	9.195 ± 0.012		
	20	8.889 ± 0.006		
	25	8.738 ± 0.006	−52 ± 1	
	30	8.588 ± 0.005		
	40	8.290 ± 0.005		
3	10	4.004 ± 0.019		
	20	3.765 ± 0.012		
	25	3.666 ± 0.011	−31 ± 2	0.74 ± 0.32
	30	3.580 ± 0.010		
	40	3.449 ± 0.018		
		Literature data [c]		
1	25	9.80	−47	
2	25	8.74	−50	
3	25	3.64	−30	

[a] T in °C; $\Delta H^\ominus$ in kJ mol^{-1}; $\Delta C_p^\ominus$ in kJ K mol^{-1}. [b] ±3(std. dev.). [c] Ref. 23.

TABLE 4

Apparent protonation constants lg $K_j^{H'}$ of diethylenetriamine in different aqueous solutions at different ionic strengths at $T = 25°C$

Salt		I [a]				
	j	0.05	0.10	0.25	0.50	1.00
NaCl	1	9.81	9.83	9.87	9.93	10.05
	2	8.93	9.00	9.12	9.25	9.39
	3	4.08	4.22	4.47	4.68	4.81
$NaClO_4$	1	9.82	9.83	9.89	9.98	10.19
	2	8.93	9.01	9.15	9.29	9.46
	3	4.06	4.20	4.43	4.62	4.75
NaI	1	9.82	9.83	9.89	9.99	10.19
	2	8.92	8.98	9.09	9.20	9.36
	3	4.08	4.22	4.46	4.61	4.60
$NaNO_3$	1	9.81	9.83	9.87	9.95	10.11
	2	8.93	9.00	9.12	9.25	9.41
	3	4.08	4.23	4.49	4.70	4.85
KCl	1	9.82	9.83	9.87	9.93	10.01
	2	8.94	9.01	9.14	9.27	9.36
	3	4.07	4.21	4.47	4.70	4.80
Et_4NI	1	9.83	9.85	9.90	9.94	
	2	8.94	9.00	9.11	9.17	
	3	4.06	4.18	4.38	4.48	
$MgCl_2$	1	9.73	9.69	9.62	9.55	
	2	8.90	8.92	8.93	8.96	
	3	4.06	4.17	4.34	4.51	
$CaCl_2$	1	9.81	9.82	9.85	9.87	9.86
	2	8.93	8.99	9.10	9.19	9.27
	3	4.05	4.18	4.40	4.58	4.70
MX [b]	1	9.82(1) [c]	9.83(1)	9.88(1)	9.96(3)	10.11(10)
	2	8.93(1)	9.00(2)	9.12(3)	9.25(5)	9.40(6)
	3	4.07(1)	4.21(1)	4.46(3)	4.66(5)	4.76(16)

[a] Ionic strength (apparent, see text) in mol l^{-1}. [b] Mean lg $K_j'^{H}$ values in NaCl, NaI, $NaNO_3$ and KCl. [c] Maximum deviation from the mean on the last figure(s).

Complexes with X^-

As shown in Fig. 1, the dependence of formation constants on ionic strength is very different from that expected. As already proposed [4], this behaviour can be explained by assuming that the amine forms $(\text{dien})H_qX_p^{q-p}$ complexes. ES2WC calculations [16] are very consistent with the formation of $(\text{dien})HX^0$, $(\text{dien})H_2X^+$, $(\text{dien})H_3X^{2+}$ and $(\text{dien})H_3X_2^+$ species; in Table 5 we report some of these results. It is interesting to note

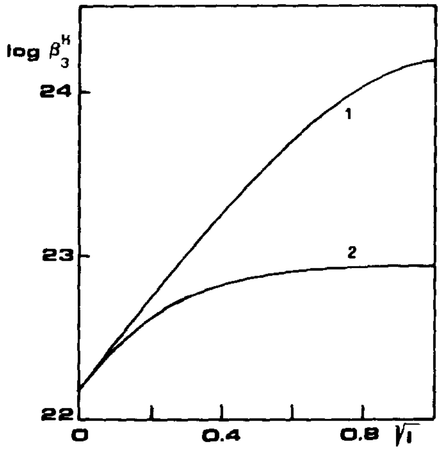

Fig. 1. Dependence on ionic strength of $\lg \beta_3^H$ of diethylenetriamine. Curve 1, apparent protonation constants in KCl; curve 2, expected protonation constants according to eqn. (3) with $c_0 = 0.1$, $c_1 = 0.23$, $d_0 = 0$ and $d_1 = -0.1$.

that the value of stability constants (β_{pq}^X or K_{pq}^X) is fairly independent of both the background salt and, in particular, of X^-. In Fig. 2, the distribution of the species in the (dien)–KCl system, is shown. As one can see, all (dien)$H_qCl_p^{q-p}$ species are formed in significant amounts, and, in particular, (dien)H_3Cl^{2+} and (dien)$H_3Cl_2^+$ account for more than 85% of the amine at pH < 3.

TABLE 5

Formation constants $\lg \beta_{pq}$ [a] ($I = 0$ mol l^{-1}) of (dien)$H_qX_p^{q-p}$ species, determined in different media at $T = 25$°C

Salt(s)	X^-	(dien)HX^0	(dien)H_2X^+	(dien)H_3X^{2+}	(dien)$H_3X_2^+$	c_1 [c]
KCl [f]	Cl^-	9.60 ± 0.2 [b]	19.31 ± 0.04 [b]	23.75 ± 0.07 [b]	24.07 ± 0.05 [b]	0.229
KCl + $CaCl_2$ [f]	Cl^-	9.64 ± 0.15	19.31 ± 0.04	23.77 ± 0.08	24.04 ± 0.15	0.230
$NaClO_4^+$ Et_4NI	I^-, ClO_4^-	9.81 ± 0.10	19.40 ± 0.04	23.76 ± 0.05	23.85 ± 0.10	0.229
MX	Cl^-, I^-, ClO_4^-, NO_3^-	9.71 ± 0.10	13.31 ± 0.04	23.63 ± 0.06	24.26 ± 0.12	0.223
Mean		9.7 ± 0.1 [d]	19.33 ± 0.07 [d]	23.75 ± 0.1 [d]	24.05 ± 0.20 [d]	0.228 ± 0.005 [d]
Reactions			$\lg K_{pq}^X$			
(dien)$H^+ + X^- =$ (dien)HX^0			−0.10 ± 0.1			
(dien)$H_2^{2+} + X^- =$ (dien)H_2X^+			0.79 ± 0.07 (0.72) [e]			
(dien)$H_3^{3+} + X^- =$ (dien)H_3X^{2+}			1.53 ± 0.1 (1.44) [e]			
(dien)$H_3X^{2+} + X^- =$ (dien)$H_3X_2^+$			0.3 ± 0.2			

[a] Overall formation constant, relative to the equilibrium (dien)$^0 + qH^+ + pX^- =$ (dien)$H_qX_p^{q-p}$. [b] ±3(std. dev.) [c] Empirical parameter of eqn. (3). [d] ±maximum deviation. [e] Values found for a general model for the effect of background on the protonation constants of amines [4]. [f] Corrected for the self association of medium.

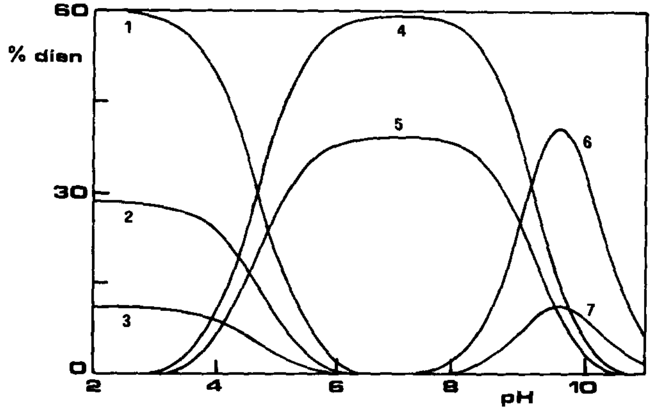

Fig. 2. Distribution of the species vs. pH in the system (dien)–KCl, at $T = 25°C$. $I_e = C_{Cl} = 0.5 \text{ mol } l^{-1}$; $C_{dien} = 1 \text{ mmol } l^{-1}$. Curve 1, $(dien)H_3Cl^{2+}$; curve 2, $(dien)H_3Cl_2^+$; curve 3, $H_3(dien)^{3+}$; curve 4, $(dien)H_2Cl^+$; curve 5, $H_2(dien)^{2+}$; curve 6, $H(dien)^+$; curve 7, $(dien)HCl^0$.

Complexes of tetraethylammonium cation

Protonation constants in tetraethylammonium iodide solutions are significantly lower than those determined in $NaClO_4$ (cf. Table 4). ES2WC calculations are consistent with the formation of $(Et_4N)H_q(dien)^{q+1}$ species ($q = 0, 1, 2$). The relative formation constants are reported in Table 6. In Fig. 3 the distribution diagram versus pH for the system $(dien)–H^+–Et_4NI$ is shown. In the reported conditions, $I = 1 \text{ mol } l^{-1}$, all the species of Et_4N^+ are significant over the pH range 3.5–11.5, in addition to the $(dien)H_qI_p^{q-p}$ species.

TABLE 6

Formation constants of diethylenetriamine complexes with Mg^{2+}, Ca^{2+} and Et_4N^+ at $T = 25°C$ and $I = 0 \text{ mol } l^{-1}$

Reaction	$\lg K_q^M$
$Et_4N^+ + (dien)^0 = (Et_4N)(dien)^+$	0.06 ± 0.12 [a]
$Et_4N^+ + H(dien)^+ = (Et_4N)H(dien)^{2+}$	-0.08 ± 0.15
$Et_4N^+ + H_2(dien)^{2+} = (Et_4N)H_2(dien)^{3+}$	-0.37 ± 0.16
$Mg^{2+} + (dien)^0 = Mg(dien)^{2+}$	1.22 ± 0.05
$Mg^{2+} + H(dien)^+ = MgH(dien)^{3+}$	0.21 ± 0.12
$Ca^{2+} + (dien)^0 = Ca(dien)^{2+}$	-0.01 ± 0.15
$Ca^{2+} + H(dien)^+ = CaH(dien)^{3+}$	$<-0.2, >-0.5$
$Ca^{2+} + H_2(dien)^{2+} = CaH_2(dien)^{4+}$	<-0.4

[a] ±3(std. dev.).

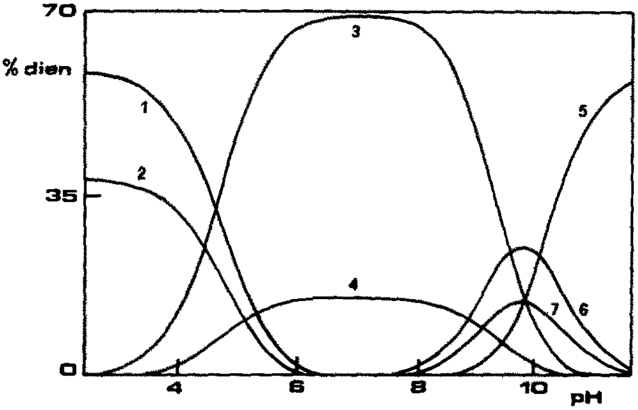

Fig. 3. Distribution of the species vs. pH in the system (dien)–Et_4NI, at $T = 25°C$. $I_e = C_{Et_4NI} = 1$ mol l^{-1}; $C_{dien} = 1$ mmol l^{-1}; curve 1, $(dien)H_3I^{2+}$; curve 2, $(dien)H_3I_2^+$; curve 3, $H_2(dien)I^+$; curve 4, $(Et_4N)H_2(dien)^{3+}$; curve 5, $(Et_4N)(dien)^+$; curve 6, $(Et_4N)H(dien)^{2+}$; curve 7, $(dien)HI^0$.

Complexes of alkaline-earth metal cations

Protonation constants in $CaCl_2$ and $MgCl_2$ are also lower than those determined in $NaClO_4$ (see Table 4). ES2WC calculations are consistent with the formation of $M(dien)H_q^{2+q}$ species. Mg^{2+} complexes are quite significant, whilst Ca^{2+} complexes are very weak (Table 6). In particular the species $CaH(dien)^{3+}$ shows a stability constant so small that its value cannot be calculated with sufficient accuracy (K_1^{Ca} and $K_2^{Ca} \ll 1$). In Fig. 4, we can note that $Ca(dien)^{2+}$ complex becomes significant (at the relatively high Ca^{2+} concentration of 200 mol l^{-1}) at pH > 9. Mg^{2+} complexes,

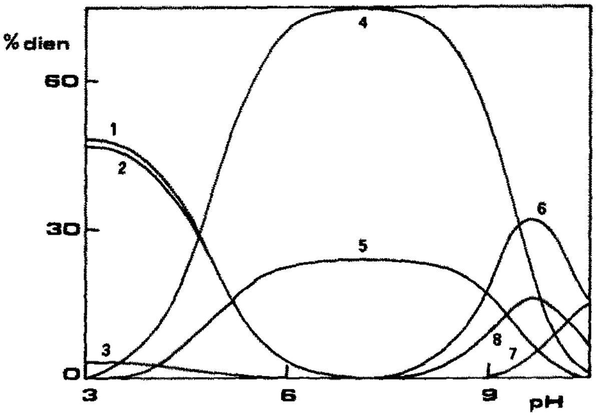

Fig. 4. Distribution of the species vs. pH in the systems Ca^{2+}–Cl^-–(dien)–H^+. $C_{Ca} = 0.2$, $C_{Cl} = 0.8$ mol l^{-1}; $C_{dien} = 1$ mmol l^{-1}; $I_e \approx 1$ mol l^{-1}. Curve 1, $(dien)H_3Cl^{2+}$; curve 2 $(dien)H_3Cl_2^+$; curve 3, $H_3(dien)^{3+}$; curve 4, $(dien)H_2Cl^+$; curve 5, $H_2(dien)^{2+}$; curve 6, $H(dien)^+$; curve 7, $Ca(dien)^{2+}$; curve 8, $(dien)HCl^0$.

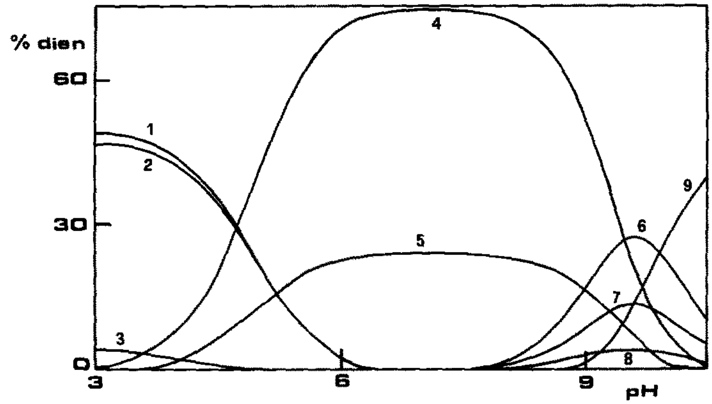

Fig. 5. Distribution of the species vs. pH in the systems Mg^{2+}–Cl^-–(dien)–H^+. $C_{Mg} = 0.05$, $C_{dien} = 0.01$; $C_{Cl} = 0.8\ mol\ l^{-1}$; $I_e \approx 0.8\ mol\ l^{-1}$. Curve 1, $(dien)H_3Cl^{2+}$; curve 2, $(dien)H_3Cl_2^+$; curve 3, $H_3(dien)^{3+}$; curve 4, $(dien)H_2Cl^+$; curve 5, $H_2(dien)^{2+}$; curve 6, $H(dien)^+$; curve 7, $(dien)HX^0$; curve 8, $MgH(dien)^{3+}$; curve 9, $Mg(dien)^{2+}$.

$MgH(dien)^{3+}$ and $Mg(dien)^{2+}$ are quite significant ($C_{Mg} = 0.05\ mol\ l^{-1}$, a concentration similar to that of oceanic sea water) at $pH > 8.5$, as shown in Fig. 5.

Dependence on temperature and on ionic strength of protonation and formation constants

The dependence of protonation constant on temperature is that expected for the amine (see Tables 2 and 3) with very exothermic $\Delta H^{\ominus}$

TABLE 7

Empirical parameters for the calculation of the formation constants of diethylenetriamine in the range $10 \leqslant T \leqslant 40°C$[a]

Reaction	$10^2 \times \alpha_T$	$10^4 \times \alpha'_T$	$10^3 \times \alpha_{T,I}$
$(dien)^0 + H^+ + X^- = (dien)HX^0$	2.1	0	−5
$(dien)^0 + 2H^+ + X^- = (dien)H_2X^+$	−1.5	0	−9
$(dien)^0 + 3H^+ + X^- = (dien)H_3X^{2+}$	−6.5	0	−15
$(dien)^0 + 3H^+ + 2X^- = (dien)H_3X_2^+$	0.1	0	−14
$Et_4N^+ + (dien)^0 = (Et_4N)(dien)^+$	0.7	0	−4
$Et_4N^+ + H^+ + (dien)^0 = (Et_4N)H(dien)^{2+}$	2.4	0	−10
$Et_4N^+ + 2H^+ + (dien)^0 = (Et_4N)H_2(dien)^{3+}$	5.5	0	−18
$Mg^{2+} + (dien)^0 = Mg(dien)^{2+}$	0	0	−4
$Mg^{2+} + H^+ + (dien)^0 = MgH(dien)^{3+}$	2.5	0	−12
$Ca^{2+} + (dien)^0 = Ca(dien)^{2+}$	0.2	0	−4
$H^+ + (dien)^0 = H(dien)^+$	−2.78	0.15	−4
$2H^+ + (dien)^0 = H_2(dien)^{2+}$	−5.79	0.25	−10
$3H^+ + (dien)^0 = H_3(dien)^{3+}$	−7.64	3.1	−18

[a] $\lg \beta_{T,I} = \lg \beta_{25,I} + \alpha_T(T-25) + \alpha'_T(T-25)^2 + \alpha_{T,I}I_e(T-25)$ (T in °C, I_e effective ionic strength in $mol\ l^{-1}$).

TABLE 8

Dependence on ionic strength of protonation and formation constants (L = diethylenetriamine; $X^- = Cl^-$, I^-, NO_3^-, ClO_4^-), at $T = 25$°C

I_c [a]	lg β [b]												
	HL^+	H_2L^{2+}	H_3L^{3+}	LHX^0	LH_2X^+	LH_3X^{2+}	$LH_3X_2^+$	$(Et_4N)L^+$	$(Et_4N)HL^{2+}$	$(Et_4N)H_2L^{3+}$	MgL^{2+}	$MgHL^{3+}$	CaL^{2+}
0	9.80	18.54	22.20	9.7	19.33	23.7	24.0	0.1	9.7	18.2	1.22	10.0	0.0
0.05	9.81	18.70	22.65	9.6	19.19	23.7	23.7	0.1	9.8	18.6	1.23	10.1	0.0
0.1	9.81	18.74	22.75	9.5	19.18	23.7	23.7	0.1	9.9	18.7	1.23	10.2	0.0
0.15	9.81	18.76	22.81	9.5	19.18	23.8	23.7	0.1	9.9	18.8	1.24	10.2	0.0
0.25	9.82	18.79	22.86	9.6	19.20	23.8	23.7	0.1	9.9	18.8	1.25	10.2	0.0
0.5	9.85	18.82	22.90	9.6	19.29	23.9	23.9	0.1	9.9	18.9	1.27	10.2	0.0
0.75	9.88	18.85	22.91	9.7	19.39	24.0	24.1	0.1	10.0	18.9	1.30	10.3	0.1
1	9.90	18.88	22.92	9.8	19.49	24.1	24.2	0.2	10.0	18.9	1.32	10.4	0.1

[a] Effective ionic strength (see text). [b] Cumulative formation constants (β_j^H, β_{pq}^X and β_q^M, eqns (6)–(8)).

values. As regards (dien)$H_qX_p^{q-p}$ complexes, large uncertainties in the formation constant values do not allow reliable $\Delta H^{\ominus}$ values to be calculated; nevertheless fairly correct $\partial \lg K/\partial T$ values can be obtained for a good speciation of the system under study in the range $10 \leqslant T \leqslant 40$°C. Calcium, magnesium and tetraethylammonium complexes should behave as other similar amine complexes; for these species we guessed the temperature coefficients. In Table 7 we report some empirical parameters for the calculation of formation constants in the range $10 \leqslant T \leqslant 40$°C. As reported in Table 5, in some calculations we checked the value of the empirical parameter c_1 of eqn. (3). The constancy of its value ($c_1 = 0.228 \pm 0.005$) ensures, in our opinion, the correctness of the model. In Table 8, all the formation constants are reported at different ionic strengths, at $T = 25$°C.

Reliability of the model and relevance of the species

The reliability of the model can be discussed by considering two factors: the self consistency and the accordance with similar systems. As regards the self consistency, we report in Tables 9–11 some details of ES2WC [16] calculations: the residuals ($\lg K_{j,\mathrm{exp}}^{\mathrm{H}} - \lg K_{j,\mathrm{calcd}}^{\mathrm{H}}$) are always very small and compatible with experimental errors. Independent calculations with the program STACO [17] gives the same results. As already mentioned, the ionic strength dependence of formation constant is also, in practice, independent of the formation reaction. The similarity with analogous systems (see Table 1) is also very good: Ca^{2+} and Mg^{2+} complexes with diethylenetriamine show a stability very similar to that of other amines,

TABLE 9

Details of ES2WC calculations for the determination of (dien)$H_qX_p^{q-p}$ formation constants from apparent protonation constants in $NaClO_4$ and Et_4NI aqueous solution, at $T = 25$°C

Salt	I_e [a]	$\lg K_1^{\mathrm{H,}}$ [b]	δ [c]	$\lg K_2^{\mathrm{H,}}$	δ	$\lg K_3^{\mathrm{H,}}$	δ
$NaClO_4$	0.05	9.82	0.00	8.93	−0.02	4.06	−0.05
	0.10	9.83	−0.01	9.01	−0.01	4.20	−0.03
	0.25	9.89	0.00	9.15	0.01	4.43	0.02
	0.50	9.98	−0.01	9.29	0.01	4.62	0.06
	1.00	10.19	0.01	9.46	0.00	4.75	−0.03
Et_4NI	0.05	9.83	0.01	8.94	0.00	4.06	−0.04
	0.10	9.85	0.01	9.00	0.00	4.18	−0.02
	0.25	9.90	0.01	9.11	0.02	4.38	0.04
	0.50	9.94	−0.01	9.17	−0.01	4.48	0.00
			<0.01 [d]		<0.01 [d]		0.036 [d]

[a] Effective ionic strength in mol l^{-1}. [b] Apparent protonation constants in the considered medium. [c] $\delta = \lg K_{\mathrm{exp}}^{\mathrm{H,}} - \lg K_{\mathrm{calcd}}^{\mathrm{H,}}$ (from ES2WC). [d] Mean deviations.

TABLE 10

Details of ES2WC calculations for the determination of (dien)$H_qX_p^{q-p}$ formation constants from average apparent protonation constants in alkali metal salts aqueous solution, at $T = 25°C$

I_e [a]	lg $K_1^{H,}$ [b]	δ [c]	lg $K_2^{H,}$	δ	lg $K_3^{H,}$	δ
0.05	9.82	0.00	8.93	−0.01	4.07	−0.02
0.10	9.83	0.00	9.00	−0.01	4.21	−0.01
0.25	9.88	0.00	9.12	0.00	4.46	0.03
0.50	9.96	0.0	9.25	0.00	4.66	−0.01
		<0.01 [d]		<0.01 [d]		<0.0018 [d]

[a] Effective ionic strength in mol l^{-1}. [b] Apparent protonation constants in the considered medium. [c] $\delta = \lg K_{exp}^{H,} - \lg K_{calcd}^{H,}$ (from ES2WC). [d] Mean deviations.

and the differences can be ascribed simply to the presence of one, two or three N-donor atoms. If we indicate with n the number of N atoms in the amine, the formation constants of Mg^{2+} and Ca^{2+} complexes can be expressed by the equations

$$\lg K^{Mg}(\pm 0.11) = -0.23 + 0.68(n-1)$$

$$\lg K^{Ca}(\pm 0.16) = -0.32 + 0.195(n-1)$$

(dien)$H_qX_p^{q-p}$ complex stability constants are quite close to those of the general model for amines [4] (see Table 5). Note that our model is based on the "nonspecificity" of activity effects and the mean deviations in

TABLE 11

Details of ES2WC calculations for the determination of (dien)$H_qX_p^{q-p}$ and Ca(dien)$^{2+}$ formation constants from apparent protonation constants in KCl and $CaCl_2$ aqueous solution, at $T = 25°C$

Salt	I_e [a]	lg $K_1^{H,}$ [b]	δ [c]	lg $K_2^{H,}$	δ	lg $K_3^{H,}$	δ
KCl	0.05	9.82	0.00	8.94	0.00	4.07	−0.07
	0.10	9.83	0.00	9.01	0.00	4.21	−0.06
	0.23	9.87	0.00	9.14	0.03	4.47	0.02
	0.44	9.93	0.00	9.27	0.04	4.70	0.07
	0.78	10.01	−0.03	9.36	−0.02	4.80	−0.04
$CaCl_2$	0.05	9.81	0.01	8.93	0.01	4.05	−0.03
	0.09	9.82	0.01	8.99	0.01	4.18	−0.02
	0.22	9.85	0.03	9.10	0.03	4.40	0.03
	0.40	9.87	0.03	9.19	0.03	4.58	0.05
	0.67	9.86	−0.03	9.27	−0.03	4.70	−0.02
			0.014 [d]		0.02 [d]		0.04 [d]

[a] Effective ionic strength in mol l^{-1}. [b] Apparent protonation constants in the considered medium. [c] $\delta = \lg K_{exp}^{H,} - \lg K_{calcd}^{H,}$ (from ES2WC). [d] Mean deviations.

TABLE 12

Some formation percentages[a] of diethylenetriamine weak complexes, together with uncertainties (±3(std. dev.)), at $T = 25°C$

pH	Complex formed (%)
Conditions of Fig. 2	
2.5	$H_3(dien)^{3+}$, 10.7 ± 1.6; $(dien)H_3Cl^{2+}$, 60 ± 8; $(dien)H_3Cl_2^+$, 29 ± 8
8	$H_2(dien)^{2+}$, 37.8 ± 1.6; $(dien)H_2Cl^+$, 57 ± 2
10	$H(dien)^+$, 34.2 ± 1.6; $(dien)HCl^0$, 10 ± 4
Conditions of Fig. 3	
7	$(Et_4N)H_2(dien)^{3+}$, 15 ± 5
9.5	$(Et_4N)H(dien)^{2+}$, 24 ± 6
10.5	$(Et_4N)(dien)^+$, 43 ± 6
Conditions of Fig. 4	
9	$Ca(dien)^{2+}$, 0.6 ± 0.2
10	$Ca(dien)^{2+}$, 9 ± 3
Conditions of Fig. 5	
8.5	$MgH(dien)^{3+}$, 1.1 ± 0.4
10	$Mg(dien)^{2+}$, 28 ± 3

[a] Calculated by the computer program ES4EC [18].

Tables 9–11 can be considered a measure of the validity of this assumption. The relevance of all this species can be seen in Figs. 2–5, where some distribution diagrams are reported. In particular, we must draw attention to the very high formation percentages of $(dien)H_qX_p^{q-p}$ species: in several conditions these species are predominant. Though errors in formation constants are in some cases quite high, the formation percentages are affected by an error, as reported in Table 12, compatible with a correct picture of the systems under investigation.

Speciation of diethylenetriamine in multielectrolyte solutions

All the data reported in this work can be correctly used for the speciation of multielectrolyte solutions in which are present the ions Na^+, K^+, Et_4N^+, Mg^{2+}, Ca^{2+}, Cl^-, ClO_4^-, NO_3^-, I^- in the ranges $0 \leq I \leq 1\ mol\ l^{-1}$ and $10 \leq T \leq 40°C$. Formation constants of Tables 7, 8 and 10 can be used for the whole speciation of a natural fluid or for the calculation of apparent formation parameters. In the first case using a computer program (ES4EC or similar) all the weak species are determined. In the second case one can simulate apparent conditions. As an example, we can calculate apparent protonation constants in synthetic sea water to take into account only strong interactions in the speciation of sea water. Simple calculations give [22]: $\lg K^{H}_{1,ssw} = 9.83$, $\lg K^{H}_{2,ssw} = 19.06$, $\lg K^{H}_{3,ssw} = 23.73$ (ssw = synthetic sea water; $I_e \approx 0.55\ mol\ dm^{-3}$). In Table 13,

TABLE 13

Smoothed (one decimal figure) overall formation constants[a] in the ranges $0 \leqslant I \leqslant 1$ mol l^{-1}, $10 \leqslant T \leqslant 40$°C

		Complex[b]												
I	*T*	a	b	c	d	e	f	g	h	i	l	m	n	o
0	10	10.2	19.4	23.4	9.4	19.6	24.7	24.0	0.0	10.1	19.0	1.2	10.4	0.0
	20	9.9	18.8	22.6	9.6	19.4	24.0	24.0	0.0	9.8	18.5	1.2	10.1	0.0
	30	9.7	18.3	21.8	9.8	19.3	23.4	24.0	0.1	9.6	17.9	1.2	9.9	0.0
	40	9.4	17.7	21.1	10.0	19.1	22.7	24.0	0.2	9.3	17.4	1.2	9.6	0.0
0.25	10	10.3	19.7	24.1	9.3	19.5	24.8	23.7	0.0	10.3	19.7	1.3	10.6	0.0
	20	10.0	19.1	23.3	9.5	19.3	24.1	23.7	0.1	10.0	19.1	1.3	10.3	0.0
	30	9.7	18.5	22.5	9.7	19.1	23.5	23.7	0.1	9.8	18.5	1.2	10.1	0.0
	40	9.4	17.9	21.7	9.9	18.9	22.8	23.7	0.2	9.5	17.9	1.2	9.8	0.0
0.50	10	10.3	19.8	24.3	9.3	19.6	25.0	24.0	0.0	10.3	19.9	1.3	10.7	0.0
	20	10.0	19.1	23.3	9.5	19.4	24.3	23.9	0.1	10.0	19.2	1.3	10.4	0.0
	30	9.7	18.5	22.5	9.7	19.2	23.5	23.9	0.1	9.8	18.6	1.3	10.0	0.0
	40	9.4	17.9	21.7	9.9	19.0	22.8	23.8	0.2	9.5	17.9	1.2	9.7	0.0
0.75	10	10.3	19.8	24.3	9.4	19.7	25.1	24.2	0.1	10.5	19.9	1.3	10.8	0.1
	20	10.0	19.2	23.4	9.6	19.5	24.4	24.1	0.1	10.2	19.2	1.3	10.5	0.1
	30	9.7	18.5	22.5	9.8	19.3	23.6	24.1	0.2	9.8	18.6	1.3	10.1	0.1
	40	9.4	17.9	21.6	10.0	19.1	22.9	24.0	0.2	9.5	17.9	1.3	9.8	0.1
1.0	10	10.4	19.9	24.4	9.6	19.9	25.3	24.4	0.1	10.5	20.0	1.4	11.0	0.1
	20	10.1	19.2	23.4	9.7	19.6	24.5	24.3	0.1	10.2	19.3	1.3	10.6	0.1
	30	9.7	18.5	22.5	9.9	19.4	23.7	24.1	0.2	9.8	18.5	1.3	10.2	0.1
	40	9.4	17.9	21.6	10.0	19.1	22.9	24.0	0.2	9.5	17.8	1.3	9.8	0.1

[a] Key: see footnotes to Table 8. [b]a, $H(dien)^+$; b, $H_2(dien)^{2+}$; c, $H_3(dien)^{3+}$; d, $(dien)HX^0$; e, $(dien)H_2X^+$; f, $(dien)H_3X^{2+}$; g, $(dien)H_3X_2^+$; h, $(Et_4N)(dien)^+$; i, $(Et_4N)H(dien)^{2+}$; l, $(Et_4N)H_2(dien)^{3+}$; m, $Mg(dien)^{2+}$; n, $MgH(dien)^{3+}$; o, $Ca(dien)^{2+}$.

smoothed lg β value for all the species found here at different temperatures and ionic strengths, are reported, in order to give a general picture of the system in the I–T ranges studied.

ACKNOWLEDGEMENTS

This work was supported by MURST and CNR. We thank Professor Silvio Sammartano for helpful discussions.

REFERENCES

1 P.G. Daniele, C. Rigano and S. Sammartano, Talanta, 32 (1985) 78.
2 S. Capone, A. Casale, A. Currò, A. De Robertis, C. De Stefano, S. Sammartano and R. Scarcella. Ann. Chim. (Rome), 76 (1986) 441.
3 P.G. Daniele, A. De Robertis, C. De Stefano, and S. Sammartano, J. Solut. Chem., 18 (1989) 23.
4 A. Casale, P.G. Daniele, C. De Stefano and S. Sammartano, Talanta, 36 (1989) 903.
5 A. Casale, A. De Robertis and F. Licastro. Thermochim. Acta, 143 (1989) 289.
6 A. Casale, A. De Robertis, F. Licastro and C. Rigano. J. Chem. Res., (1990) (S) 204, (M) 1601–1620.
7 L. Abate, R. Maggiore, C. Rigano and C. De Stefano, Talanta, 38 (1991) 449.
8 L. Abate, C. De Stefano and P. Mineo, J. Chem. Res., (1991) (S) 76.
9 (a) S. Capone, A. De Robertis, C. De Stefano and R. Scarcella, Talanta, 32 (1985) 675. (b) C. De Stefano, A. Gianguzza and S. Sammartano, Thermochim. Acta, in press.
10 P.G. Daniele, A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, J. Chem. Soc., Dalton Trans., (1985) 2353.
11 P.G. Daniele, C. Rigano and S. Sammartano, Anal. Chem., 57 (1985) 2956.
12 P.G. Daniele, A. De Robertis, C. De Stefano and S. Sammartano, in S. Alegret (Ed.), Miscellany of Scientific Papers Offered to Enric Casassas, Universitat Autonoma de Barcelona, Balleteza, Spain, 1991.
13 H.A. Flaschka, EDTA Titrations, Pergamon, London, 1959.
14 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, 1966.
15 C. Rigano, M. Grasso and S. Sammartano, Ann. Chim. (Rome), 74 (1984) 537; C. De Stefano, P. Princi, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 77 (1987) 643.
16 A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, Talanta, 34 (1987) 933.
17 A. De Robertis, C. De Stefano, C. Rigano and S. Sammartano, Abstr. Colloquium Chemiometricum Mediterraneum, Barcelona, Spain, 1987, p. 87.
18 (a) A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, Anal. Chim. Acta, 191 (1986) 385. (b) C. De Stefano, P. Princi and C. Rigano, Ann. Chim. (Rome), 78 (1988) 671.
19 A. Casale, P.G. Daniele, C. De Stefano and S. Sammartano, Talanta, 36 (1989) 903.
20 A. De Robertis, C. Rigano, S. Sammartano and O. Zerbinati, Thermochim. Acta, 115 (1987) 241.
21 B.E. Conway, Electrochemical Data, Elsevier, Amsterdam, 1952.
22 A. De Robertis, C. De Stefano and S. Sammartano, in preparation.
23 A.E. Martell and R. Smith, Critical Stability Constants, Vol. II, Amines, Pergamon, New York, 1975.