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Interaction of Polyamines with Mg^{2+} and Ca^{2+}

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The interaction of some polyamines (ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and spermine) with Ca^{2+} and Mg^{2+} has been studied potentiometrically at different ionic strengths ($0.03 \le I$ /mol dm$^{-3} \le 0.96$; $0.01 \le C_{CaCl_2}$/mol dm$^{-3} \le 0.32$; $0.01 \le C_{MgCl_2}$/mol dm$^{-3} \le 0.32$), at $t = 25$ °C. Experimental data have been interpreted in terms of both M^{2+}−polyamine complexation and specific interaction (using Pitzer equations). For all the M^{2+}−polyamine systems, $MAH_i^{(i+2)+}$ species ($i = 0, 1, ..., n - 1$; n = maximum degree of protonation of polyamine A) are formed, generally in the order $Mg^{2+} > Ca^{2+}$. For spermine and tetraethylenepentamine a binuclear species is also formed. By using the Pitzer specific interaction approach, we determined $\beta^{(0)}$, $\beta^{(1)}$, $C^{(\phi)}$, and Θ coefficients. The two approaches have been compared, and general equations for stability constants and interaction coefficients, which are valid for all the polyamines studied, are reported.

Introduction

Amines are present in all natural and biological fluids as trace components. In particular, polyamines are found in all living organisms, and their concentration becomes quite high in tissues and biological fluids in some pathologies (Bachrach, 1973; Bachrack and Heimer, 1989; Morris and Marton, 1981). The mean concentration of amino groups in some biological fluids is 1−2, 0.1−0.05, 15−30, and 0.2−0.3 mmol dm^{-3} in urine, blood, sperm, and sweat, respectively (Lentner, 1981). Amines are rarely present as free ligands: in general they are protonated or complexed (metal, mixed proton−metal, or mixed proton−anion complexes). $C_{2(n-1)}N_nH^+_{(6n-2)}$ (n = 2, ..., 6) polyamines are partially protonated in the pH range of interest for natural waters and biological fluids ($5 \le pH \le 9$), while biogenic amines, such as putrescine or spermine, are generally fully protonated. The protonated polyamines may interact with (poly)anions to give $ALH_i^{(i-z)}$ (L^{z-} inorganic or organic anion) (Daniele et al., 1997b; De Robertis et al., 1997), and the free or partially protonated amines form metal complexes (Martell and Smith, 1975, 1982, 1989, 1997; Pettit and Powell, 1993; Sillén and Martell, 1964, 1971). Transition metal complexes of polyamines are quite stable and have been widely studied. Alkaline earth metal complexes are not very stable (in some cases they are quite weak), and few investigations can be found in the literature regarding their stability (Abate et al., 1991a,b; Casale et al., 1989a,b, 1990; De Robertis et al., 1996; De Stefano et al., 1993b).

Speciation studies require a knowledge of all the interactions between trace and major components of natural and biological fluids. Among the major components, the most important are Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}. Alkali metal cations virtually do not interact with polyamines in either protonated or free form. Chloride and sulfate anions form weak complexes with partially or fully protonated polyamines, whose stability is strictly dependent on the charge of the polyammonium cation. A few studies have been carried out on Cl^- and SO_4^{2-} complexes (Daniele et al., 1994, 1995, 1997b; De Robertis et al., 1998) and are still in progress in this laboratory. Mg^{2+} and Ca^{2+} form complexes of low stability with polyamines, and very few studies have been reported. Bearing in mind the importance of both alkaline earth cations and polyamines in natural systems, we carried out a potentiometric (H^+−glass electrode) investigation, at $t = 25$ °C and $0.03 \le I$/mol dm^{-3} ≤ 0.96, into the interaction of Mg^{2+} and Ca^{2+} with ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien), tetraethylenepentamine (tetren), and spermine (sper) in order to obtain information on their speciation, using different models, and to draw some general relationships.

Experimental Section

Chemicals. Amines (ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and spermine, Fluka products) were purified by transformation into the corresponding hydrochlorides (Perrin et al., 1966), and were used in this form. Magnesium chloride and calcium chloride (Fluka, purum) solutions were standardized against EDTA. Solutions of NaOH and HCl were prepared by diluting concentrated ampules (Fluka) and were standardized against potassium biphthalate and sodium carbonate, respectively. Grade A glassware and twice-distilled water were used for all the solutions.

Apparatus. The free hydrogen ion concentration was measured with a potentiometric titrator (with appropriate software) for fully computerized titrations. The equipment consists of a Metrohm E654 potentiometer coupled with a combination Ross type electrode 8102. The titrant was delivered by a Metrohm Dosimat 665 dispenser. The titration program allows the evaluation of equilibrium potential values and determines the amount of titrant required based on the actual buffering properties of the titrated solution, so that there is a difference in pH values of 0.05−0.08 between two successive readings; the emf was considered to be stable when the variation was less than 0.1 mV within 5 min.

Procedure. A sample of 25 mL of the solution containing the amine hydrochloride under study and calcium or

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Table 1. Protonation Constants and Proton−Cl^- Complex Formation Constants of Amines at $t = 25$ °C and $I = 0$ mol dm^{-3}

		log β_{pq}[a]				
p	q	en[b]	dien[c]	trien[d]	tetren[d]	sper[e]
0	1	9.91	9.80	9.67	9.83	10.70
0	2	16.77	18.54	18.54	18.84	20.40
0	3		22.20	24.66	26.57	28.72
0	4			27.04	30.47	35.94
0	5				32.35	
1	1	9.80	9.70	9.36	9.31	10.58
1	2	17.43	19.33	19.32	19.36	21.09
1	3		23.73	26.08	27.73	29.87
1	4			28.78	32.15	37.47
1	5				34.53	
2	3		24.05	26.43	27.99	30.29
2	4			30.39	33.37	38.69
2	5				36.00	
3	5				37.05	

[a] Formation constants. β_{pq} refers to the reaction $A^0 + pCl^- + qH^+ = ACl_pH_q^{(q-p)}$. [b] Casale et al., 1990. [c] De Robertis et al., 1992. [d] De Robertis et al., 1993. [e] Unpublished results from this laboratory.

magnesium chloride was titrated with standard NaOH up to pH ~ 12 (for the solution containing Mg^{2+}, up to precipitation; in the calculations points for pH ≤ log K_1^H + 0.3 were considered). Concentrations used in the experiments were $C_{\text{amine}} = 5-10$ mmol dm^{-3}, $C_{Ca} = 0.01-0.32$ mol dm^{-3}, and $C_{Mg} = 0.01-0.32$ mol dm^{-3}. Separate titration of HCl at about the same ionic strength (adjusted with $CaCl_2$ or $MgCl_2$) as the sample under study was carried out to determine the standard electrode potential $E°$. A stream of purified and presaturated N_2 was bubbled through all solutions in order to exclude the presence of CO_2 and O_2. Experiments in NaCl have already been reported (Casale et al., 1998), and in this work we performed new calculations.

Calculations. The computer program ESAB2M (De Stefano et al., 1987) was used to calculate the purity of the reagents and to refine all the parameters related to the calibration of the electrode system. The computer programs BSTAC (De Stefano et al., 1993a) and STACO (De Stefano et al., 1996) were used to calculate the formation constants. The dependence on ionic strength of formation constants was taken into account by using the Debye−Hückel type equation (Daniele et al., 1997a):

$$\log \beta = \log {}^{T}\beta - z^* I^{1/2} (2 + 3\, I^{1/2})^{-1} + CI + DI^{3/2} \qquad (1)$$

$$C = c_0 p^* + c_1 z^*; \quad D = d_1 z^*$$

$$p^* = \sum p_{\text{reactants}} - \sum p_{\text{products}}$$

$$z^* = \sum z_{\text{reactants}}{}^2 - \sum z_{\text{products}}{}^2$$

(β is formation constant; ${}^{T}\beta$ is formation constant at zero ionic strength; c_0, c_1, and d_1 are empirical parameters; p and z are the stoichiometric coefficients and the charges, respectively). For the calculations performed in this work we used the values $c_0 = 0.10$, $c_1 = 0.23$, and $d_1 = -0.1$ (Casale et al., 1988). Distribution diagrams and simulated titration curves were obtained using the computer program ES4ECI (De Stefano et al., 1993a). The protonation constants of amines and the formation constants of proton−amine−chloride complexes at $I = 0$ mol dm^{-3} have already been studied and are shown in Table 1. Ion product of water values were taken from De Robertis et al. (1984).

Table 2. Empirical Parameters for the Eq 1a

		a_2[a]					
amine	i	NaCl	ϵ[b]	$MgCl_2$	ϵ[b]	$CaCl_2$	ϵ[b]
en	1	0.31	0.009	0.22	0.009	0.35	0.009
	2	−0.69	0.011	−1.07	0.009	−0.91	0.011
dien	1	0.33	0.037	−0.36	0.037	0.095	0.037
	2	−0.58	0.038	−1.19	0.038	−0.78	0.038
	3	−2.43	0.038	−3.36	0.040	−2.77	0.040
trien	1	0.25	0.030	−0.49	0.025	−0.56	0.030
	2	−0.59	0.025	−1.44	0.025	−1.40	0.027
	3	−2.57	0.045	−3.83	0.045	−3.64	0.045
	4	−5.57	0.050	−7.12	0.050	−6.66	0.050
sper	1	0.33	0.050	−1.70	0.045	−0.63	0.045
	2	−0.67	0.050	−2.49	0.045	−1.25	0.045
	3	−2.87	0.065	−5.06	0.060	−3.57	0.060
	4	−6.32	0.070	−8.72	0.060	−6.93	0.070
tetren	1	0.19	0.055	−1.60	0.054	−1.18	0.055
	2	−0.80	0.060	−1.98	0.040	−1.91	0.055
	3	−2.94	0.055	−4.64	0.055	−4.58	0.060
	4	−6.11	0.050	−8.21	0.050	−7.93	0.050
	5	−10.59	0.055	−12.91	0.050	−12.33	0.055

[a] Values obtained by keeping a_1 and a_2 as reported in the text. [b] Mean deviation of eq 1a fits.

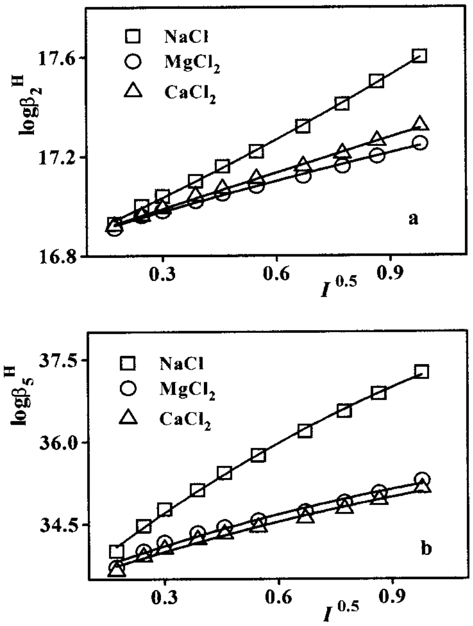

Figure 1. Apparent protonation constants of ethylenediamine (a) and tetraethylenepentamine (b), in NaCl, $MgCl_2$, and $CaCl_2$ at different ionic strengths (I/mol dm^{-3}) and at $t = 25$ °C.

Results

Apparent protonation constants of different amines in $MgCl_2$, $CaCl_2$, or NaCl media show the trend NaCl > $CaCl_2$ ≥ $MgCl_2$, as reported for some cases in Figure 1. They can be expressed by the simple equation

$$\log K^{H*} = \log {}^{T}K^{H} + a_1 I^{1/2} + a_2 I + a_3 I^{3/2} \qquad (1a)$$

where log ${}^{T}K^{H}$ is the constant at $I = 0$ (Table 1) and a_1, a_2, and a_3 are empirical parameters. A very regular trend has been observed for these parameters as a function of z^* and n (n = number of amino groups), and their values can be simply expressed. For $|z^*| > 0$: $a_1 = a_1^{(0)} z^*$ and $a_3 = a_3^{(0)} z^*$, with $a_1^{(0)} = -0.527 \pm 0.005$ (NaCl), -0.447 ± 0.009 ($MgCl_2$), -0.446 ± 0.009 ($CaCl_2$), and $a_3^{(0)} = -0.524 \pm$

Table 3. Formation Constants of Mg^{2+}− and Ca^{2+}−Polyamine (A) Complexes at $I = 0$ mol dm^{-3} and $t = 25$ °C

		$\log K_i^M \pm 3\sigma$				
reaction	M^{2+}	en	dien	trien	tetren	sper
$M^{2+} + A^0$	Mg^{2+}	0.38 ± 0.05	0.95 ± 0.07	1.39 ± 0.12	1.67 ± 0.13	1.69 ± 0.13
	Ca^{2+}	0.15 ± 0.10	0.42 ± 0.12	1.4 ± 0.2	1.85 ± 0.08	1.07 ± 0.08
$M^{2+} + HA^+$	Mg^{2+}	−0.15 ± 0.10	0.25 ± 0.10	1.05 ± 0.10	1.05 ± 0.12	0.79 ± 0.10
	Ca^{2+}	−0.28 ± 0.10	0.10 ± 0.09	0.8 ± 0.2	1.30 ± 0.15	0.23 ± 0.12
$M^{2+} + H_2A^{2+}$	Mg^{2+}		−0.21 ± 0.15	0.25 ± 0.12	0.55 ± 0.2	0.11 ± 0.10
	Ca^{2+}		−0.32 ± 0.15	0.2 ± 0.2	0.7 ± 0.2	−0.15 ± 0.15
$M^{2+} + H_3A^{3+}$	Mg^{2+}			−0.33 ± 0.25	0.0 ± 0.3	−0.6 ± 0.3
	Ca^{2+}			−0.5 ± 0.3	0.0 ± 0.3	≤−0.8
$M^{2+} + H_4A^{4+}$	Mg^{2+}				−0.5 ± 0.3	
	Ca^{2+}				−0.6 ± 0.3	
$M^{2+} + MA^{2+}$	Mg^{2+}				−0.1 ± 0.2	0.1 ± 0.3
	Ca^{2+}				−0.2 ± 0.2	

Table 4. Values of $\beta_{H_iA^{i+},Cl^-}{}^{(1)}$ Pitzer Parameter (Eqs 3−7)

	$\beta_{H_iA^{i+},Cl^-}{}^{(1)\,a}$									
A	HA^+	ϵ^b	H_2A^{2+}	ϵ^b	H_3A^{3+}	ϵ^b	H_4A^{4+}	ϵ^b	H_5A^{5+}	ϵ^b
en	−0.05 ± 0.02^c	0.052	0.55 ± 0.12^c	0.077						
dien	0.36 ± 0.03	0.026	1.65 ± 0.03	0.028	1.94 ± 0.04^c	0.057				
trien	1.50 ± 0.15	0.094	4.00 ± 0.08	0.056	6.02 ± 0.03	0.070	6.32 ± 0.10^c	0.10		
sper	2.05 ± 0.19	0.12	4.42 ± 0.29	0.17	7.06 ± 0.30	0.20	9.29 ± 0.25	0.23		
tetren	2.61 ± 0.03	0.041	6.66 ± 0.06	0.064	10.92 ± 0.12	0.095	13.27 ± 0.12	0.10	14.56 ± 0.13^c	0.13

[a] $\beta_{H_iA^{i+},Cl^-}{}^{(1)}$ (eqs 5 and 6) values calculated by keeping the values of other parameters from eqs 10−10c constant. [b] Mean deviation of Pitzer equation fits. [c] $\pm\sigma$.

0.009 (NaCl), −0.359 ± 0.013 ($MgCl_2$), −0.312 ± 0.006 ($CaCl_2$). For $z^* = 0$: $a_1 = 0$, $a_3 = -0.05$ (NaCl); $a_3 = a_3(0)n - 1$, with $a_3(0) = 0.44 \pm 0.03$ ($MgCl_2$), 0.37 ± 0.02 ($CaCl_2$). Results for a_2 (obtained by keeping the above values of a_1 and a_3) are shown in Table 2.

The $\log K^{H*} = f(I)$ function can be interpreted in two ways: (a) by considering the formation of some complex species or (b) by considering the apparent activity coefficients of the various species which take part in the protonation reaction using appropriate models. In the first case, we must take into account the formation of the following species: (i) chloride complexes, $H_iA^{i+}-Cl^-$; (ii) alkaline earth complexes, A^0 or $H_iA^{i+}-Mg^{2+}$, $-Ca^{2+}$; (iii) self-association of medium and hydroysis of Mg^{2+} and Ca^{2+}.

Chloride complexes have been widely investigated in this laboratory (Casale et al., 1998), and the relative formation constants are reported in Table 1. The self-association of NaCl (very weak), $MgCl_2$, and $CaCl_2$ (weak) and the hydrolysis constants of Mg^{2+} and Ca^{2+} have been already reported (De Robertis et al., 1984, 1987, 1994). Formation constants of Mg^{2+} and Ca^{2+} amine complexes have been calculated using a model which considers both chloride complexes and self-association of medium (fixed parameters) and the formation of several species between unprotonated amines and alkaline earth cations. Least-squares calculations are consistent with the formation of $MAH_i^{(i+2)+}$ species, with $i = 0, 1, ..., (n - 1)$ (n = number of amino groups). Formation constants for the reaction

$$M^{2+} + H_iA^{i+} = M(H_iA)^{(i+2)+} \qquad K_i^M \tag{2}$$

are reported in Table 3. For tetren and sper, a weak binuclear species is also formed, whose formation constant is reported in Table 3.

In the second case, a specific interaction model can be used. The Pitzer equation (Pitzer, 1991) has been widely applied to apparent protonation constants (Millero et al., 1987, 1997; Hershey et al., 1988, 1989). According to the Pitzer equations (Pitzer, 1991), for electrolytes 1−1, 1−2, and 2−1, the activity coefficients of cation M or anion X can be expressed by

$$\ln \gamma_M = z_M^2 f^\gamma + 2\sum_a m_a(B_{Ma} + EC_{Ma}) + \sum_a\sum_c m_c m_a(z_M^2 B'_{ca} + z_M C_{ca}) + \sum_c m_c(2\Theta_{Mc} + \sum_a m_a \Psi_{Mca}) + \sum_a\sum_{a'} m_a m_{a'} \Psi_{Maa'} \tag{3}$$

$$\ln \gamma_X = z_X^2 f^\gamma + 2\sum_c m_c(B_{Xc} + EC_{Xc}) + \sum_a\sum_c m_c m_a(z_X^2 B'_{ca} + z_X C_{ca}) + \sum_a m_a(2\Theta_{Xa} + \sum_c m_c \Psi_{Xca}) + \sum_c\sum_{c'} m_c m_{c'} \Psi_{Xaa'} \tag{3a}$$

and for neutral species

$$\ln \gamma_{MX^0} = 2\lambda I \tag{4}$$

where m_i is the molality of the cation (c) and anion (a) in the solution, z the charge, E the equivalent molality ($E = (1/2)\sum_i m_i|z_i|$), I the ionic strength in molal scale, and

$$B_{MX} = \beta_{MX}{}^{(0)} + \beta_{MX}{}^{(1)}\,(2I)^{-1} f_1 \tag{5}$$

$$B'_{MX} = \beta_{MX}{}^{(1)}\,(2I^2)^{-1} f_2 \tag{6}$$

$$C_{MX} = C_{MX}{}^{(\phi)}\,(2|z_M z_X|^{1/2})^{-1} \tag{7}$$

$$f^\gamma = -0.392[I^{1/2}(1 + 1.2I^{1/2})^{-1} + 1.667 \ln(1 + 1.2I^{1/2})] \tag{8}$$

$$f_1 = 1 - (1 + 2I^{1/2}) \exp(-2I^{1/2}) \tag{8a}$$

$$f_2 = -1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2}) \tag{8b}$$

$\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters (Pitzer, 1991) between two ions of opposite signs, Θ represents interaction parameters between two ions of the same sign, Ψ represents triple interaction parameters (+ − +, − + −), and λ is the interaction parameter for neutral species. At $I < 3$ mol kg^{-1}, Θ and Ψ parameters can generally be neglected. Owing to the complexity of the

Table 5. Values of P_3 for Simplified Pitzer Type Equation (eq 9)

		P_3[a]					
amine	i	NaCl	ϵ[b]	$MgCl_2$	ϵ[b]	$CaCl_2$	ϵ[b]
en	1	0.57	0.005	−0.48	0.005	−0.64	0.006
	2	0.39	0.004	−0.70	0.004	−1.06	0.005
dien	1	0.46	0.037	−1.70	0.040	−0.91	0.037
	2	3.15	0.035	−2.01	0.040	−1.39	0.040
	3	5.02	0.035	−4.27	0.040	−3.96	0.040
trien	1	0.13	0.015	−1.34	0.015	−2.53	0.015
	2	1.48	0.015	−2.13	0.015	−2.37	0.016
	3	2.05	0.016	−4.73	0.016	−5.26	0.016
	4	2.91	0.016	−7.69	0.018	−8.47	0.018
sper	1	0.30	0.028	−5.33	0.024	−1.91	0.025
	2	1.23	0.024	−5.55	0.025	−1.91	0.025
	3	1.04	0.037	−8.74	0.037	−5.06	0.037
	4	0.41	0.037	−12.90	0.040	−9.41	0.040
tetren	1	−0.14	0.028	−4.21	0.025	−4.02	0.025
	2	0.78	0.028	−3.84	0.025	−4.02	0.028
	3	0.84	0.030	−7.34	0.030	−8.28	0.030
	4	1.09	0.045	−11.19	0.050	−12.64	0.045
	5	−2.58	0.050	−14.86	0.050	−18.18	0.045

[a] Values obtained by keeping P_1 and P_2 as reported in the text.
[b] Mean deviation of eq 9 fits.

Pitzer equation, we tested a simplified version depending on three empirical parameters only:

$$\ln K_i = \ln {}^{\mathrm{T}}K_i + 2z_{\mathrm{A}}f^{\gamma} + P_1 I + P_2 I^2 + P_3 f_1 \tag{9}$$

(P_1, P_2, and P_3 are empirical parameters; f^{γ} and f_1 are defined by eqs 8 and 8a, respectively).

As concerns the full Pitzer equation, by using some literature interaction parameters [$\beta_{H,Cl}^{(0)} = 0.1775$, $C_{H,Cl}^{(\phi)} = 0.00080$, $C_{Na,Cl}^{(\phi)} = 0.00127$, $C_{Mg,Cl}^{(\phi)} = 0.00519$, $C_{Ca,Cl}^{(\phi)} = -0.00034$, $\beta_{H,Cl}^{(1)} = 0.2945$, $\beta_{Na,Cl}^{(1)} = 0.2664$, $\beta_{Mg,Cl}^{(1)} = 1.6815$, $\beta_{Ca,Cl}^{(1)} = 1.614$, $\Theta_{H,Na} = 0.036$, $\Theta_{H,Mg} = -0.024$, $\Theta_{H,Ca} = -0.033$, $\Psi_{H,Na,Cl} = -0.004$, $\Psi_{H,Mg,Cl} = 0.0122$, $\Psi_{H,Ca,Cl} = 0.016$ (Pitzer, 1991)], we are able to calculate $\beta^{(0)}$, $\beta^{(1)}$, $C^{(\phi)}$, and Θ coefficients of H_iA^{i+}. All these parameters show a regular trend vs i and n, and the following relationships were found (in parentheses, $\pm\sigma$):

$$\beta_{H_iA^{i+},Cl^-}^{(0)} = 0.47(\pm 0.08)i^2 + 0.27(\pm 0.06)n - 0.43(\pm 0.07)ni \tag{10}$$

$$C_{H_iA^{i+},Cl^-}^{(\phi)} = -0.94(\pm 0.09)i^2 - 0.55(\pm 0.09)n + 0.87(\pm 0.09)ni \tag{10a}$$

$$\theta_{Mg^{2+},H_iA^{i+}} = -0.13(\pm 0.01)i^2 - 0.31(\pm 0.04)n \tag{10b}$$

$$\theta_{Ca^{2+},H_iA^{i+}} = 0.11(\pm 0.03)i^2 + 0.22(\pm 0.07)n \tag{10c}$$

Results [$\beta_{H_iA^{i+},Cl^-}^{(1)}$ obtained by keeping other parameters from eqs 10−10c constant] are reported in Table 4. As expected, also by using the simplified Pitzer type equation (eq 9), a regular trend is observed when calculating P_1, P_2, and P_3. The first two parameters can be expressed as: $P_1 = P_1^{(0)}z^*$ and $P_2 = P_2^{(0)}z^*$ with the following. For $|z^*| > 0$: $P_1^{(0)} = 0.307 \pm 0.008$ (NaCl), -0.13 ± 0.02 ($MgCl_2$), -0.190 ± 0.004 ($CaCl_2$); $P_2^{(0)} = -0.17 \pm 0.02$ (NaCl), -0.006 ± 0.020 ($MgCl_2$), 0.02 ± 0.002 ($CaCl_2$). For $z^* = 0$: $P_1^{(0)} = 0.09 \pm 0.02$ (NaCl), 0.46 ± 0.02 ($MgCl_2$), 0.53 ± 0.02 ($CaCl_2$); $P_2^{(0)} = 0.01 \pm 0.02$ (NaCl), -0.17 ± 0.02 ($MgCl_2$), -0.22 ± 0.04 ($CaCl_2$). Results for P_3 (obtained by keeping the above values of P_1 and P_2) are reported in Table 5.

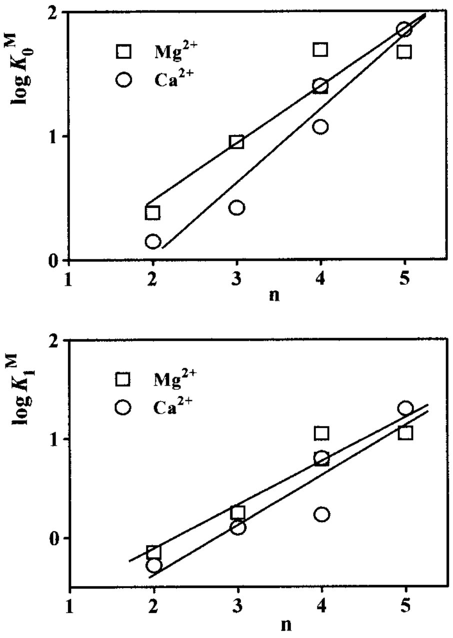

Figure 2. Log K_i^M (refer to the reaction $M^{2+} + H_iA^{i+} = M(H_iA)^{(i+2)+}$; $i = 0, 1$) values for magnesium and calcium complexes of polyamines vs n (number of amino groups).

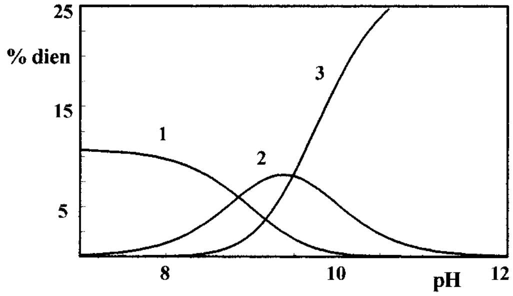

Figure 3. Distribution of the species in the system dien−Mg^{2+}−H^+ vs pH ($C_{dien} = 0.001$ mol dm^{-3}, $C_{Mg} = 0.05$ mol dm^{-3}, $C_{Cl} = 0.1$ mol dm^{-3}). Species: **1**, $MgH_2(dien)^{4+}$; **2**, $MgH(dien)^{3+}$; **3**, $Mg(dien)^{2+}$.

Discussion

Magnesium and Calcium Complexes. The stability of magnesium and calcium complexes of polyamines shows a regular increasing trend as a function of the number of amino groups (n), as can be seen in Figure 2, for both unprotonated and protonated species. Moreover, it is possible to express the stability of all these complexes [log $K_i^M(I)$, eq 2] using the general equation

$$\log K_i^{M} = b_0 + b_1 n + b_2 n_H \tag{11}$$

($n_H = i$ = number of protons in the complex species). For the Mg^{2+} complexes we have $b_0 = 0.39$, $b_1 = 0.44$, and $b_2 = -0.16$, with a mean deviation, with respect to experimental values, of $\epsilon = 0.11$; for Ca^{2+}, $b_0 = -0.95$, $b_1 = 0.55$, $b_2 = -0.05$, and $\epsilon = 0.13$.

The stability of these complexes is not very high, in particular for Ca^{2+} species, for $n < 3$ and $n_H > n - 1$. Nevertheless, since the concentration of alkaline metal cation is generally quite high in natural fluids, M^{2+}−polyamine species can be very significant. As an example, Figures 3 and 4 show speciation diagrams for the systems Mg^{2+}−diethylenetriamine and −spermine, respectively. As one can see, for $C_{Mg} = 50$ mmol dm^{-3} (approximately the concentration in seawater, 35‰ salinity), quite significant

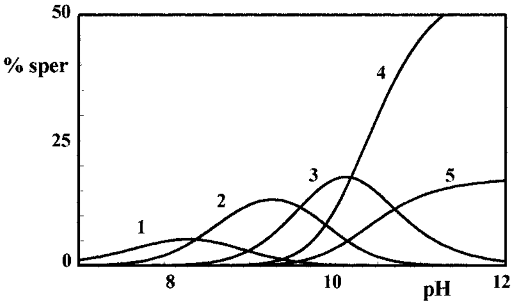

Figure 4. Distribution of the species in the system sper−Mg^{2+}−H^+ vs pH (C_{sper} = 0.001 mol dm^{-3}, C_{Mg} = 0.05 mol dm^{-3}, C_{Cl} = 0.1 mol dm^{-3}). Species: **1**, $MgH_3(sper)^{5+}$; **2**, $MgH_2(sper)^{4+}$; **3**, $MgH(sper)^{3+}$; **4**, $Mg(sper)^{2+}$; **5**, $Mg_2(sper)^{4+}$.

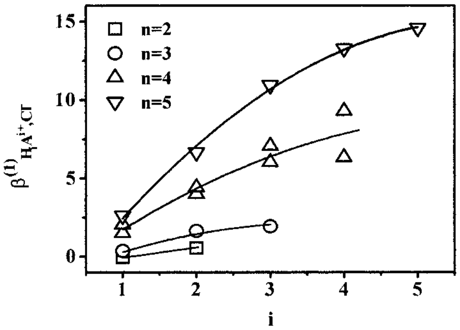

Figure 5. Values of $\beta_{H_iA^{i+},Cl^-}{}^{(1)}$ parameter of Table 4 vs i (n = 2 en; n = 3 dien; n = 4 trien and sper; n = 5 tetren).

percentages (in terms of ligand species) are formed. Note that, despite the higher stability of spermine complexes, formation percentages, in the pH range where protonated species are present, are similar for both dien and sper: this is due to the interference of chloride complexes, whose stability is higher for spermine. As regards the unprotonated complexes, higher formation percentages are observed for spermine complexes, since $K_0{}^{Mg}(sper) > K_0{}^{Mg}(dien)$ and no interference with Cl^- occurs.

Interaction Parameters. The use of Pitzer interaction coefficients allows us to predict activity coefficients in NaCl−$MgCl_2$−$CaCl_2$ mixtures at $I < 1$ mol dm^{-3}. If we combine these results with the data on the interaction of polyamines with $SO_4{}^{2-}$ (Daniele et al., 1995; De Robertis et al., 1998), the speciation of natural waters can be obtained. Note that, owing to the marked regularity of these parameters, as a function of the number of amino groups and the degree of protonation, prediction values can also be found for other amines not studied here. In fact, $\beta^{(0)}$, $C^{(\phi)}$, and Θ parameters are given by eqs 10−10c, and for $\beta^{(1)}$ we calculated

$$\beta_{H_iA^{i+},Cl^-}{}^{(1)} = -0.83i^2 - 1.22n + 1.63in \qquad (10d)$$

In Figure 5 the regular trend of $\beta_{H_iA^{i+},Cl^-}{}^{(1)}$ is shown.

Comparison between Different Models. The efficiency of the two models (i.e., the complex formation model and the Pitzer specific interaction model) can be tested in two ways: (a) by calculating the standard deviation on the fit for the two approaches and (b) by performing the same calculations using the general equation for the formation constants (eq 11) and for the interaction coefficients (eqs 10−10d). For the first type of comparison (a) we got almost exactly the same results for both models (standard deviation on the fit $\sigma \sim 0.01-0.02$ for calculated log protonation constants). For the second type of comparison, we generally have (different systems and different protonation constants behave differently) small differences in favor of the Pitzer approach.

Final Remarks. The interaction data reported in this work (in terms of both complex formation constants and specific interaction coefficients) allow us to study the speciation of amines in multielectrolyte natural waters, such as seawater. General relationships (eqs 10−11) may predict the interaction of Mg^{2+} and Ca^{2+} (and Cl^-) for other amines. The speciation picture of amines is also fully described considering parallel investigations on the interaction of polyamines with polyanions (Daniele et al., 1994, 1995, 1997b; De Robertis et al., 1998).

Supporting Information Available:

Tables containing smoothed protonation constants in NaCl, $CaCl_2$, and $MgCl_2$ aqueous solutions, at different ionic strengths (molar concentration scale) and at t = 25 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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