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Complexes of Azelaic and Diethylenetrioxydiacetic Acids with Na^+, Mg^{2+}, and Ca^{2+} in NaCl Aqueous Solutions, at 25 °C

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Formation constants of Na^+, Mg^{2+}, and Ca^{2+} complexes of azelaic and diethylenetrioxydiacetic acids have been determined by potentiometry (H^+−glass electrode) at different ionic strengths ($0 \le I \le 1$ mol dm^{-3}), at $t = 25$ °C. For all the systems the species ML and MHL have been found. The relative formation constants are reported together with the parameters for the dependence on ionic strength. Results are discussed in comparison with those for other carboxylic ligands. Speciation problems are considered also.

Introduction

At the present in our laboratories two main problems are under study, that is, the binding of polyanions by polyammonium cations (De Robertis et al., 1996; Daniele et al., 1998) and the speciation of polyanions in natural waters (De Robertis et al., 1997). In both cases we paid particular attention to the complexing ability of polycarboxylic anions. On the basis of results up to now obtained, it can be affirmed that alkali, alkaline earth, and polyammonium cation complexes of carboxylic ligands generally show a stability dependent on charges involved in the formation reaction (Daniele et al., 1998; De Robertis et al., 1997; De Stefano et al., 1998), while the effect of ligand structure is negligible. Nevertheless, two main factors must be considered: (a) the presence of other groups with potentially coordinating capacities and (b) the length of alkylic chains in the carboxylic ligand. In this connection, the investigations on dicarboxylic ligands, such as $(COOH)-(CH_2)_n-(COOH)$, with $n > 1$, and $(COOH)-O(CH_2CH_2O)_n-(COOH)$, with $n > 5$, might give useful information. Several reports on the complexation of carboxylic ligands can be found in the literature (Pettit and Powell, 1993; Martell and Smith, 1997, 1977; Sillén and Martell, 1964, 1971), but only a little information is available on dicarboxylic ligands with long alkylic chains or with more than one ethereal group. In this work we considered, as a preliminary investigation, the protonation and the formation of Na^+, Mg^{2+}, and Ca^{2+} complexes of azelaic (nonanedioic acid, aza) and diethylenetrioxydiacetic (3,6,9-trioxaundecanedioic acid, toda) acids at different ionic strengths, at $t = 25$ °C.

Experimental Section

Materials. Azelaic acid (Fluka, puriss. product) was used without further purification; diethylenetrioxydiacetic acid was available (Fluka, techn. product) as a 90% aqueous solution and was used after purification (Perrin et al., 1966). Their purity, checked by potentiometric titration, was >99.5%. Sodium chloride solutions were prepared by weighing pure salt (Fluka, p.a.). Calcium and magnesium chloride solutions were standardized with EDTA titrations. Et_4NI was recrystallized from an ethanol−acetone mixture and dried at 40 °C in order to eliminate the solvent. Sodium and tetramethylammonium hydroxide, and hydrochloric acid solutions were standardized against potassium biphthalate and sodium carbonate, respectively; Me_4NOH solutions were used as titrant when the background salt was tetraethylammonium iodide, to avoid any interference of the Na^+ cation. For all solutions grade A glassware and water of analytical grade ($R = 18$ MΩ cm^{-1}) were employed.

Procedure. Potentiometric measurements were performed by means an apparatus consisting of a Metrohm model 605 potentiometer, connected to a Metrohm model 665 automatic buret and to an Orion combination electrode Ross Type 8102. The potentiometric apparatus was connected to a PC, and a suitable computer program allowed acquiring the potentiometric data. The reproducibility of the potentiometric apparatus was as follows: titrant volume, $v \pm 0.002$ cm^3; emf, $E \pm 0.15$ mV. The measurement cells were thermostated at $t = (25.0 \pm 0.1)$ °C. Purified N_2 was bubbled into the measurement cell in order to preserve all solutions from CO_2 and O_2.

A volume of 20−25 mL of solution containing the carboxylic ligand under investigation [$C_L = 5$, 10, and 20 mmol dm^{-3} (L = aza or toda)] and the background salt (in turn, Et_4NI, NaCl, $CaCl_2$ + NaCl, and $MgCl_2$ + NaCl) at different values of ionic strength was titrated with NaOH or Me_4NOH standard solutions; independent titrations of HCl solutions under the same experimental conditions (ionic strength and temperature) as those for the systems to be analyzed were performed in order to calculate the electrode potential.

Calculations. The program ESAB2M (De Stefano et al., 1987) was used to determine all the parameters related to an acid−base titration (analytical concentration of the reagents; K_w; junction potential coefficient; $E°$). The following other computer programs were used: (a) BSTAC (De Stefano et al., 1993) and STACO (De Stefano et al., 1996) to calculate the protonation and formation constants at different ionic strengths, (b) ES4ECI (De Stefano et al., 1993) to draw the distribution diagrams of the species in

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Table 1. Protonation Constants of Azelaic and Diethylenetrioxydiacetic Acids in Et$_4$NI Aqueous Solution, at t = 25 °C

	aza[a]		toda[b]	
I/mol dm^{-3}	log β^H_1	log β^H_2	log β^H_1	log β^H_2
0.10	5.149	9.548	3.901	7.049
0.15	5.131	9.521	3.875	7.026
0.25	5.117	9.534	3.870	7.002
0.50	5.176	9.666	3.888	7.099
0.75	5.264	9.849	3.957	7.224
1.00	5.355	10.018	4.022	7.366

[a] log β^H_1 ± 0.007; log β^H_2 ± 0.007 (3 std dev). [b] log β^H_1 ± 0.005; log β^H_2 ± 0.007 (3 std dev). β^H_1 and β^H_2 refer to the reactions (L = aza or toda) $L^{2-} + H^+ = [HL]^-$ and $[HL]^- + H^+ = [H_2L]^0$.

Table 2. Protonation Constants of Azelaic and Diethylenetrioxydiacetic Acids in NaCl Aqueous Solution, at t = 25 °C

	aza[a]		toda[b]	
I/mol dm^{-3}	log β^H_1	log β^H_2	log β^H_1	log β^H_2
0.10	5.076	9.427	3.807	6.876
0.15	5.033	9.365	3.752	6.785
0.25	4.988	9.296	3.703	6.692
0.51	4.952	9.244	3.670	6.575
0.77	4.948	9.240	3.680	6.518
1.05	4.955	9.260	3.709	6.490

[a] log β^H_1 ± 0.006; log β^H_2 ± 0.008 (3 std dev). [b] log β^H_1 ± 0.004; log β^H_2 ± 0.007 (3 std dev).

Table 3. Parameters for the Dependence on Ionic Strength of the Protonation Constants in Et$_4$NI Aqueous Solutions (Eq 1)

ligand	j	log $^T\beta^H$	C	D[b]
aza	1	5.489 ± 0.007[a]	0.964	−0.30
	2	10.040 ± 0.008	1.632	−0.45
toda	1	4.254 ± 0.010	0.867	−0.30
	2	7.562 ± 0.012	1.451	−0.45

[a] 3 std dev. [b] $D = -0.075z^*$.

Table 4. Parameters for the Dependence on Ionic Strength of the Protonation Constants in NaCl Aqueous Solutions (Eq 2)

ligand	j	log $^T\beta^H_j$	a_1	a_2
aza	1	5.49 ± 0.01[a]	2.475	−1.013
	2	10.04 ± 0.02	3.752	−1.538
toda	1	4.25 ± 0.02	2.152	−0.698
	2	7.56 ± 0.03	3.065	−1.130

[a] 3 std dev.

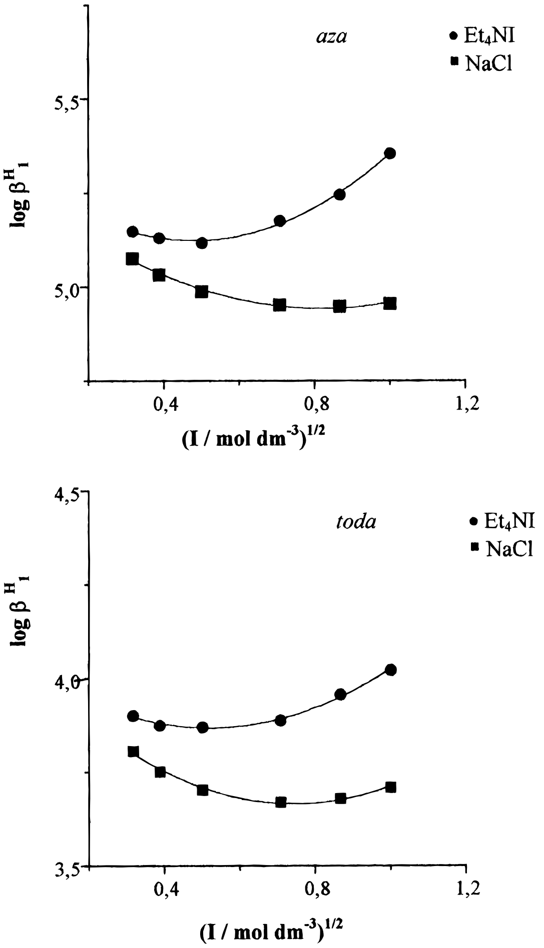

Figure 1. Dependence on ionic strength of log β^H_1 for the systems aza−H and toda−H in NaCl and Et$_4$NI ionic media.

solution and to compute the percentage formation of the species, and (c) LIANA (De Stefano et al., 1997) to calculate parameters for the dependence on ionic strength of protonation constants.

Results

Protonation Constants. Protonation constants of azelaic and trioxydiacetic acids were determined in two background salts, namely, NaCl and Et$_4$NI. This last salt was chosen in order to obtain baseline protonation constants, under the assumption that the Et$_4$N$^+$ cation does not form complexes with carboxylic anions (Daniele et al., 1985). Protonation constant values at different ionic strengths are reported in Tables 1 and 2.

The dependence on ionic strength of protonation constants determined in Et$_4$NI can be taken into account using the Debye−Hückel type equation (Casale et al., 1988; Daniele et al., 1991, 1997)

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

where $^T\beta^H_j$ is the overall constant at infinite dilution, C and D are empirical parameters, and $z^* = \sum(\text{charges})^2_{\text{reactants}} - \sum(\text{charges})^2_{\text{products}}$. Calculated values of C and log $^T\beta^H_j$ are reported in Table 3 [$D = -0.075z^*$ (Daniele et al., 1997)].

Protonation constants in NaCl can be fitted using the polynomial equation

$$\log \beta^H_j = \log {}^T\beta^H_j - 0.5z^* I^{1/2} + a_1 I + a_2 I^{3/2} \quad (2)$$

where a_1 and a_2 are empirical parameters (values in Table 4). The protonation constants in the two salt media are quite different, as can be seen in Figure 1.

Na$^+$ Complexes. If we assume that the Et$_4$N$^+$ cation does not significantly interact with the carboxylic anion, for $I \leq 1$ mol dm^{-3}, the differences in the log β^H_j values of NaCl and Et$_4$NI (see Figure 1) can be attributed to the formation of Na$^+$ complex species (Daniele et al., 1985). Least squares calculations are consistent with the formation of NaL$^-$ and NaHL^0 complexes, whose formation constants are reported in Table 5. On the basis of the results reported in Table 5, we can observe that dianion diethylenetrioxydiacetic and azelaic acids form weak complexes with the Na$^+$ cation. Though the formation constants are not very high, by considering the concentration levels of many natural and biologic fluids (blood [Na$^+$] = 140 mmol dm^{-3}, seawater (S = 35 ‰) [Na$^+$] = 485 mmol dm^{-3}), the formation percentages of these complexes may be

Table 5. Protonation and Formation Constants of Azelaic and Diethylenetrioxydiacetic Acids in the Systems H−Na−aza and H−Na−toda ($I = 0$ mol dm^{-3}, t = 25 °C), Together with Parameters for the Dependence on Ionic Strength (Eq 1)

reaction	log β	C	D
$H^+ + aza^{2-} = H(aza)^-$	5.490 ± 0.005[a]	0.958 ± 0.011[a]	−0.30
$2H^+ + aza^{2-} = H_2(aza)^0$	10.044 ± 0.008	1.625 ± 0.018	−0.45
$Na^+ + aza^{2-} = Na(aza)^-$	0.86 ± 0.02	0.91 ± 0.02	−0.30
$Na^+ + H^+ + aza^{2-} = NaH(aza)^0$	5.76 ± 0.03	1.35 ± 0.04	−0.45
$H^+ + toda^{2-} = H(toda)^-$	4.249 ± 0.003	0.875 ± 0.006	−0.30
$2H^+ + toda^{2-} = H_2(toda)^0$	7.557 ± 0.006	1.458 ± 0.011	−0.45
$Na^+ + toda^{2-} = Na(toda)^-$	1.02 ± 0.01	0.89 ± 0.02	−0.30
$Na^+ + H^+ + toda^{2-} = NaH(toda)^0$	4.67 ± 0.02	1.42 ± 0.04	−0.45

[a] ± 3 std dev.

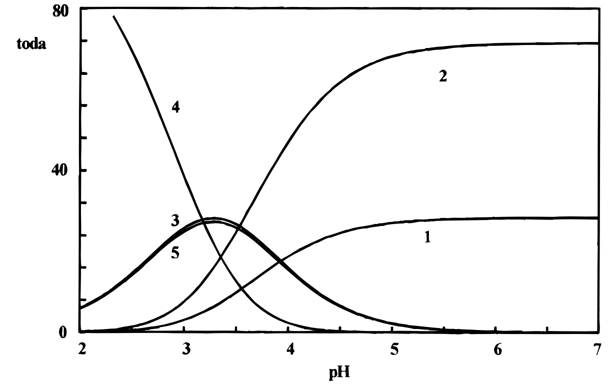

Figure 2. Speciation diagram for the system $H^+{-}Na^+{-}toda^{2-}$, at $I = 0.5$ mol dm^{-3} and t = 25 °C. C_{toda} = 1 mmol dm^{-3}; C_{NaCl} = 500 mmol dm^{-3}. Curves: (1) $[toda]^{2-}$; (2) $[Na(toda)]^-$; (3) $[toda(H)]^-$; (4) $[toda(H)_2]^0$; (5) $[NaH(toda)]^0$.

highly significant. In Figure 2 we report the speciation diagram of 500 mmol dm^{-3} diethylenetrioxydiacetic acid in NaCl. As can be seen in the distribution diagram in Figure 2, the only species present in the pH range of interest of natural fluids are $[toda]^{2-}$ and $[Na(toda)]^-$, this last reaching a considerable formation percentage (~70%); other protonated species, $[NaH(toda)]^0$, $[(toda)H_2]^0$, and $[(toda)H]^-$ are formed at pH < 4.5, with a maximum formation percentage (~30%) at pH = 3.3.

Mg^{2+} and Ca^{2+} Complexes. Potentiometric measurements carried out on the aza and toda systems, in the presence of Mg^{2+} and Ca^{2+}, give evidence for the formation of ML^0 and MHL^+ complexes for both ligands. In the case of the Ca^{2+}−toda system a weak binuclear species is formed too, under our experimental conditions. The formation constants are reported in Table 6. The stability of these complexes is fairly high with a sharp difference, for Ca^{2+} species, between aza and toda. The speciation diagrams for Ca^{2+}−aza and Mg^{2+}−aza and Ca^{2+}−toda and Mg^{2+}−toda systems are reported in Figures 3−6. Concentrations were chosen in order to simulate roughly seawater conditions. At pH ~ 8 (natural waters) a considerable yield of alkaline earth complexes is observed in the neutral form: protonated complexes are significant at pH < 6 (aza) and pH < 4 (toda).

Discussion

Stability of Metal Complexes. As we have pointed out in the previous section, highly significant differences can be observed between the stability of aza and toda complexes. On the basis of the literature data analysis (Daniele et al., 1985; De Robertis et al., 1984, 1987; Pettit and Powell, 1993; this work) in Table 7 we report, for comparison, the formation constants of some dicarboxylic acids. As concerns Na^+ complexes, differences are not very significant, also considering that for these species large confidence intervals arise from experimental uncertainties. For the species NaL^- we have a mean value log K = 0.94 ± 0.15 (I = 0 mol dm^{-3}, t = 25 °C), in excellent accordance with previous findings (Daniele et al., 1985) for several dicarboxylic acids, i.e. log K = 0.95 ± 0.2 (I = 0 mol dm^{-3}, t = 37 °C). The differences in the stability of Mg^{2+} or Ca^{2+} complexes for the various dicarboxylic ligands are likely due to two factors: (i) the length of the alkylic chains with the consequent change in chelate ring size for different complexes and (ii) the presence of ethereal oxygen(s) in the chain. Among others, we will discuss two interesting trends. For both Mg^{2+} and Ca^{2+}complexes we have for ML^0

Table 6. Formation Constants of Azelaic and Diethylenetrioxydiacetic Acids in the Systems H−Mg/Ca−Aza and H−Mg/Ca−toda at $I = 0$ mol dm^{-3} and t = 25 °C, Together with Parameters for the Dependence on Ionic Strength (Eq 1)

reaction	log β	C	D
$Mg^{2+} + aza^{2-} = Mg(aza)^0$	2.10 ± 0.03[a]	1.71	−0.60
$Mg^{2+} + H^+ + aza^{2-} = MgH(aza)^+$	6.80 ± 0.05	1.82	−0.60
$Ca^{2+} + aza^{2-} = Ca(aza)^0$	2.28 ± 0.04	1.55 ± 0.10[a]	−0.60
$Ca^{2+} + H^+ + aza^{2-} = CaH(aza)^+$	7.15 ± 0.10	1.75 ± 0.10	−0.60
$Mg^{2+} + toda^{2-} = Mg(toda)^0$	2.28 ± 0.02	1.97 ± 0.06	−0.60
$Mg^{2+} + H^+ + toda^{2-} = MgH(toda)^+$	5.53 ± 0.04	1.82	−0.60
$Ca^{2+} + toda^{2-} = Ca(toda)^0$	3.65 ± 0.02	2.10 ± 0.02	−0.60
$Ca^{2+} + H^+ + toda^{2-} = CaH(toda)^+$	6.38 ± 0.04	1.82	−0.60
$Ca(toda)^0 + Ca^{2+} = Ca_2(toda)^{2+}$	0.6 ± 0.2	0	0

[a] ±3 std dev.

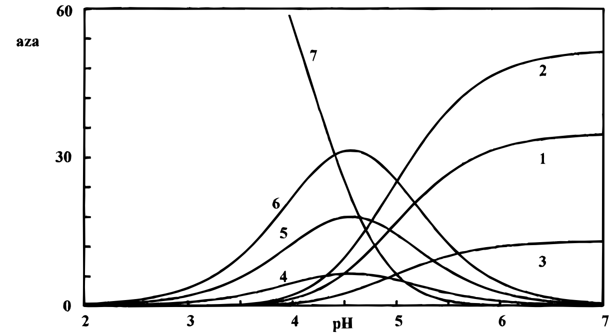

Figure 3. Speciation diagram for the system $H^+{-}Na^+{-}Ca^{2+}{-}aza^{2-}$, at $I = 0.5$ mol dm^{-3} (NaCl) and t = 25 °C. C_{aza} = 1 mmol dm^{-3}; $C_{Ca^{2+}}$ = 10 mmol dm^{-3}. Curves: (1) $[aza]^{2-}$; (2) $[Na(aza)]^-$; (3) $[Ca(aza)]^0$; (4) $[CaH(aza)]^+$; (5) $[NaH(aza)]^0$; (6) $[aza(H)]^-$; (7) $[aza(H)_2]^0$.

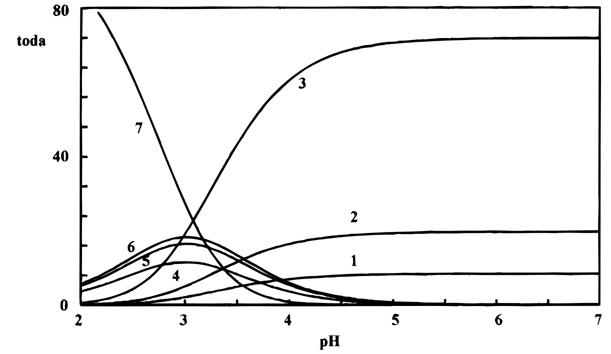

Figure 4. Speciation diagram for the system $H^+{-}Na^+{-}Ca^{2+}{-}toda^{2-}$, at $I = 0.5$ mol dm^{-3} (NaCl) and t = 25 °C. C_{toda} = 1 mmol dm^{-3}; $C_{Ca^{2+}}$ = 10 mmol dm^{-3}. Curves: (1) $[toda]^{2-}$; (2) $[Na(toda)]^-$; (3) $[Ca(toda)]^0$; (4) $[CaH(toda)]^+$; (5) $[NaH(toda)]^0$; (6) $[toda(H)]^-$; (7) $[toda(H)_2]^0$.

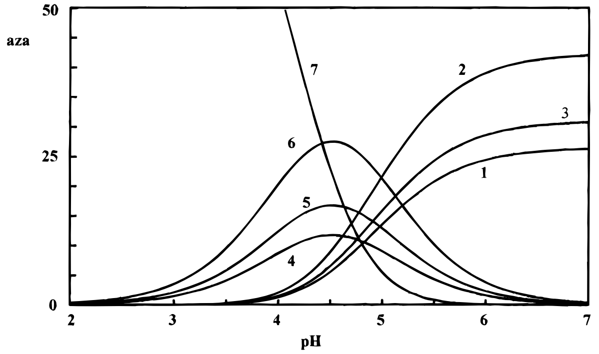

Figure 5. Speciation diagram for the system $H^+-Na^+-Mg^{2+}-aza^{2-}$, at t = 25 °C. C_{aza} = 1 mmol dm^{-3}; C_{Na^+} = 485 mmol dm^{-3}; $C_{Mg^{2+}}$ = 55 mmol dm^{-3}. Curves: (1) $[aza]^{2-}$; (2) $[Na(aza)]^-$; (3) $[Mg(aza)]^0$; (4) $[MgH(aza)]^+$; (5) $[NaH(aza)]^0$; (6) $[aza(H)]^-$; (7) $[aza(H)_2]^0$.

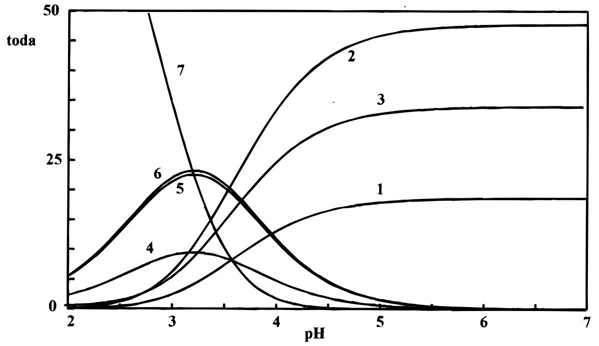

Figure 6. Speciation diagram for the system $H^+-Na^+-Mg^{2+}-toda^{2-}$, at t = 25 °C. C_{toda} = 1 mmol dm^{-3}; C_{Na^+} = 485 mmol dm^{-3}; $C_{Mg^{2+}}$ = 55 mmol dm^{-3}. Curves: (1) $[toda]^{2-}$; (2) $[Na(toda)]^-$; (3) $[Mg(toda)]^0$; (4) $[MgH(toda)]^+$; (5) $[NaH(toda)]^0$; (6) $[toda(H)]^-$; (7) $[toda(H)_2]^0$.

Table 7. Stability of Ca^{2+}, Mg^{2+}, and Na^+ Complexes of Some Carboxylic Ligands at I = 0 mol dm^{-3} and t = 25 °C

	log *K*				
	mal[a]	succ[a,b]	aza[d]	oda[a,c]	toda[d]
$Ca^{2+} + L^{2-} = CaL^0$	2.39	2.24	2.28	4.28	3.65
$Ca^{2+} + HL^- = CaHL^+$	0.84	1.04	1.66	2.76	2.13
$Mg^{2+} + L^{2-} = MgL^0$	2.85	2.18	2.10	2.51	2.28
$Mg^{2+} + HL^- = MgHL^+$	0.9[e]	1.01	1.31	0.76	1.28
$Na^+ + L^{2-} = NaL^-$	0.91	0.85	0.86	0.71	1.02

[a] Daniele et al., 1985. [b] De Robertis et al., 1984. [c] De Robertis et al., 1987. [d] This work. [e] Pettit and Powell, 1993 (I = 0.1 mol dm^{-3}).

mal > succ ≥ aza and the opposite trend for MHL^+. The first trend is simply due to the chelate ring size, while the second may be due to the hydrophobic effect. In the complexes of oxy and trioxy diacetic acids ethereal oxygen(s) are effective in the coordination, in particular for Ca^{2+} complexes, but it seems that for oda complexes two chelate rings are formed of favorable size, while for toda the steric configuration is less favorable. Finally we must consider the real incidence of the formation of complexes with the major cations of natural fluids. The low-molecular-weight ligand concentrations being very low with respect to Na^+, Mg^{2+}, and Ca^{2+} (in natural systems), we can write the crude relationship

$$B = \beta FC \tag{3}$$

where B is a *formation factor* (or *incidence factor*), depending on the considered fluid, C is the concentration of the cation in the fluid, and F is the correction for the ionic strength. For 35‰ seawater we have FC = 0.4, 0.0089, and 0.045 for Na^+, Ca^{2+}, and Mg^{2+}, respectively. Using these value, we calculated the incidence factors reported in Table 8. This parameter is proportional to the formation percentages of the various species: note that this gives rise to the higher $Na(aza)^-$ formation percentage with respect to $Ca(aza)^0$, although $\beta_{[Ca(aza)]} \gg \beta_{[Na(aza)]}$. The percentages plotted in Figures 2−6 are easily explained by considering the *incidence factor* for the experimental conditions used very close to that of seawater (35 ‰ of salinity) ($[Na^+]$ = 485 mmol dm^{-3}; $[Ca^{2+}]$ = 11 mmol dm^{-3}; $[Mg^{2+}]$ = 55 mmol dm^{-3}).

Table 8. Values of the *Incidence Factor* B (Eq 3) for Na^+, Mg^{2+}, and Ca^{2+} Unprotonated Complexes of aza and toda at t = 25 °C

	B	
M	aza	toda
Na^+	2.9 ± 0.3[a]	4.2 ± 0.5[a]
Mg^{2+}	5.6 ± 0.6	8.5 ± 1.0
Ca^{2+}	1.7 ± 0.2	40 ± 5

[a] ± 3 std dev.

Dependence on I of Protonation and Formation Constants. In Tables 5 and 6 we reported the parameters for the dependence on ionic strength of protonation and formation constants. In a previous investigation we and some colleagues from these laboratories showed that when considering weak interactions (such as Na^+ complexes) the parameters of eq 1 can be expressed as

$$C = c_0 p^* + c_1 z^* \tag{1a}$$

$$D = d_1 z^* \tag{1b}$$

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

where the empirical parameters c_0, c_1, and d_1 do not depend on the formation reaction in the ionic strength range $0 \le I \le 1$ mol dm^{-3}. From several systems examined in different works we obtained different but quite close values of c_0, c_1, and d_1. In a recent review we reported c_0 = 0.11, c_1 = 0.20, and d_1 = −0.075. The values of D reported in Tables 5 and 6 were $D = -0.075z^*$, and the C values were refined. By considering altogheter C values for all the species formed in this work, we obtained (± std dev)

$$C = 0.073\ (\pm\ 0.039)\ p^* + 0.211\ (\pm\ 0.011)\ z^*$$

which is in excellent accordance with previous findings. Moreover, this result confirms the validity of using eqs 1−1b for very different systems, at I < 1 mol dm^{-3}. Recently several protonation data have been reported (De Robertis et al., 1999) for simple polycarboxylic acids, and also in this case the dependence on ionic strength of protonation constants, in different ionic media, is comparable to that found in this work.

Literature Comparison. Protonation constants of azelaic acid have been reported at different ionic strengths in NaCl and KCl aqueous solutions (Martell and Smith, 1977, 1997). The values log K^H_1 = 5.41 and log β^H_2 = 9.95 (I = 0 mol dm^{-3}, t = 25 °C) and log K^H_1 = 4.98 and log β^H_2 = 9.30 (I = 1 mol dm^{-3}, NaCl, t = 18 °C) are in fairly good agreement with those reported in Table 2. No data have been found for the complexes of azelaic acid with Na^+, Mg^{2+}, and Ca^{2+}. For diethylenetrioxydiacetic acid some formation data are reported by Miyazaki et al. (1974): log

$K^{H}_{1} = 3.83$, log $\beta^{H}_{2} = 6.82$; for ML, log $K^{ML} = 1.9$ and 3.15 for Mg^{2+} and Ca^{2+}, respectively ($I = 0.1$ mol dm^{-3}, $t = 25$ °C). Our values at $I = 0.1$ mol dm^{-3} are log $K = 1.6$ and 3.0. In this case too there is fairly good agreement.

Final Remarks. In this work we reported stability data regarding the complexation with major cationic constituents of natural fluids of two interesting dicarboxylic acids. Differences are evidenced in the stability of different complexes species, in particular as far as calcium is concerned. A simple *incidence factor* is proposed to take into account the real incidence of these complexes in the speciation of natural fluids. The ionic strength dependence of protonation and formation constants follows the same trend shown by other low-molecular-weight ligand complexes.

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Literature Cited

Casale, A.; Daniele, P. G.; De Robertis, A.; Sammartano, S. Ionic Strength Dependence of Formation Constants. Part XI. An Analysis of Literature Data on Carboxylate Ligand Complexes. *Ann. Chim. (Rome)* **1988**, *78*, 249−260.

Daniele, P. G.; De Robertis, A.; De Stefano, C.; Rigano, C.; Sammartano, S. On the Possibility of Determining the Thermodynamic Parameters for the Formation of Weak Complexes Using a Simple Model for the Dependence on Ionic Strength of Activity Coefficients. Na^{+}, K^{+} and Ca^{2+} Complexes of Low Molecular Weight Ligands in Aqueous Solution. *J. Chem. Soc., Dalton Trans.* **1985**, 2353−2361.

Daniele, P. G.; De Robertis, A.; De Stefano, C.; Sammartano, S. Ionic Strength Dependence of Formation Constants. XIII. A Critical Examination of Preceding Results. In *Miscellany of scientific papers offered to Enric Casassas*, Alegret, S., Arias, J. J., Barcelò, D., Casal, J., Router, G., Eds.; Barcelona, Spain, 1991; pp 121−126.

Daniele, P. G.; De Stefano, C.; Foti, C.; Sammartano, S. The Effect of Ionic Strength and Ionic Medium on the Thermodynamic Parameters of Protonation and Complex Formation. *Curr. Top. Solution Chem.* **1997a**, *2*, 253−274.

Daniele, P. G.; Prenesti, E.; De Robertis, A.; De Stefano, C.; Foti, C.; Giuffrè, O.; Sammartano, S. Binding of Inorganic and Organic Polyanions by Protonated Open Chain Polyamines in Aqueous Solution. *Ann. Chim. (Rome)* **1997b**, *87*, 415−447. Errata corrige: **1998**, *88*, 447−448.

De Robertis, A.; De Stefano, C. Formation and Stability of Magnesium-Oxydiacetate Complexes at Different Temperatures and Ionic Strengths in Aqueous Solutions. *Thermochim. Acta* **1987**, *117*, 317−323.

De Robertis, A.; De Stefano, C.; Scarcella, R.; Rigano, C. Thermodynamics of Formation of Magnesium(II), Calcium(II), Strontium(II) and Barium(II)-Succinate Complexes in Aqueous Solution. *Thermochim. Acta* **1984**, *80*, 197.

De Robertis, A.; De Stefano, C.; Giuffrè, O.; Sammartano, S. Binding of Carboxylic Ligands by Protonated Amines. *J. Chem. Soc., Faraday Trans.* **1996**, *92* (21), 4219−4226.

De Robertis, A.; Foti, C.; Gianguzza, A.; Sammartano, S. Chemical Speciation of Some Classes of Low Molecular Weight Ligands in Seawater. In *Marine Chemistry*—*An Environmental Analytical Chemistry Approach*; Gianguzza, A., Pelizzetti, E., Sammartano, S., Eds.; Kluwer Academic Publishers: Amsterdam, 1997; pp 59−70.

De Robertis, A.; De Stefano, C.; Foti, C. Medium effects on the protonation of carboxylic acids at different temperatures. *J. Chem. Eng. Data* **1999**, *44*, 262−270.

De Stefano, C.; Princi, P.; Rigano, C.; Sammartano, S. Computer Analysis of Equilibrium Data in Solution. ESAB2M: An Improved Version of the ESAB Program. *Ann. Chim. (Rome)* **1987**, *77*, 643−675.

De Stefano, C.; Mineo, P.; Rigano, C.; Sammartano, S. Ionic Strength Dependence of Formation Constants. XVII. The Calculation of Equilibrium Concentrations and Formation Constants. *Ann. Chim. (Rome)* **1993**, *83*, 243−277.

De Stefano, C.; Foti, C.; Giuffré, O.; Mineo, P.; Sammartano, S. Binding of Tripolyphosphate by Aliphatic Amines: Formation, Stability and Calculation Problems. *Ann. Chim. (Rome)* **1996**, *86*, 257−280.

De Stefano, C.; Mineo, P.; Rigano, C.; Sammartano, S. Computer Tools for the Speciation of Natural Fluids. In *Marine Chemistry*—*An Environmental Analytical Chemistry Approach*; Gianguzza, A., Pelizzetti, E., Sammartano, S., Eds.; Kluwer Academic Publisher: Amsterdam, 1997; pp 71−83.

De Stefano, C.; Giuffrè, O.; Sammartano, S. $\Delta G°$ and $T\Delta S°$ charge relationships for the binding of carboxylic anions by open-chain polyammonium cations. *J. Chem. Soc., Faraday Trans.* **1998**, *94* (16), 2395−2398.

Martell, A. E.; Smith, R. M. *Critical Stability Constants*, 3rd ed.; Plenum Press: New York, 1977**a**.

Martell, A. E.; Smith, R. M. *Stability Constants of Metal Complexes*; NIST PC-based Database; National Institute of Standards and Technology: Gaithersburg, M D, 1997**b**.

Miyazaki, M.; Shimoishi, Y.; Miyata, H.; Tôei, K. The reaction of dicarboxylic acids containing ether linkages with alkaline earth metals. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2033−2038.

Perrin, D. D.; Armorego, W. L. F.; Perrin, D. R. *Purification of laboratory chemicals*; Pergamon: Oxford, 1966.

Pettit, L. D.; Powell, K. J. *IUPAC Stability Constants Database*; Academic Software: Outlay, U.K., 1993.

Sillén, L. G.; Martell A. E. *Stability constants of metal-ion complexes*; Spec. Pub. 17, The Chemical Society; Wiley: London, 1964.

Sillén, L. G.; Martell, A. E. *Stability constants of metal ion complexes*; Supplement. Special Pub. 25; The Chemical Society: London, 1971.

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