Protonation Constants and Association of Polycarboxylic Ligands with the Major Components of Seawater

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Apparent protonation constants, log β_j^{H*}, of 11 carboxylic acids were determined potentiometrically ([H$^+$]-glass electrode) in artificial seawater containing six of the major components (Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, and SO$_4^{2-}$) at different salinities: S (‰) = 5, 15, 25, 35, 45. Values of log β_j^{H*} were fitted by the simple polynomial equation log β_j^{H*} = log $^T\beta_j^H + a_1S^{1/2} + a_2S + a_3S^{3/2}$ (log $^T\beta_j^H$ = protonation constants at infinite dilution; a_1, a_2, a_3 = empirical parameters), for mono-, di-, and tricarboxylates. For carboxylic anions with charge < −3, a better fit was obtained using the equation log β_j^{H*} = log $^T\beta_j^H + b_1I + b_0z^* \log(1 + b_2I)$ (b_0, b_1, b_2 = empirical parameters, z^* = square sum of reactants minus square sum of products). The potentiometric data were also interpreted in terms of complex formation between the cationic component of artificial seawater and the carboxylic anion (also partially protonated) using the single-salt approximation (the artificial seawater considered as a single salt with B$^{1.117+}$ cation and A$^{1.117-}$ anion). Calculations were also performed, for comparison, on potentiometric data for phenolic compounds (already published) to obtain the formation constants of seasalt complexes. Generally, both empirical parameters for dependence on ionic strength and complex formation constants are dependent on the charge of the (poly)carboxylic anions. Some useful stability−charge and stability−structure relationships are reported. The interaction of carboxylic ligands with the major components of seawater is discussed in relation to speciation problems.

Introduction

In speciation studies of natural waters, different classes of ligands have to be considered. Among these, carboxylates are the most common and ubiquitous naturally occurring organic complexants, present in all the fractions of natural organic matter (NOM), particularly in fulvic compounds (Buffle, 1988). It can be estimated that the main binding sites of aquagenic refractory organic matter (AROM) and fulvic acids (FA) are COO$^-$ (2−10 mmol/g), often of aliphatic nature, and phenolic OH (1−5 mmol/g). A number [about 25 μg (of C atoms) L^{-1}] of carboxylic groups in seawaters are also present as amino acids, both as free and combined hydrolyzable amino acids (Daumas, 1976; Lee and Wakeham, 1989; Stumm and Brauner, 1975; Williams, 1971) and as fatty acids (about 40 μg C L^{-1}, free and combined) (Stumm and Brauner, 1975). Some important di- and tricarboxylic acids, such as pyruvic, succinic, and citric acids, are always present in natural waters and derive from the biochemical processes of living organisms.

Therefore, the importance of carboxylic and polycarboxylic ligands in the general picture of organic complexation in natural waters is evident. A number of data are reported in the literature concerning the binding capacity of carboxylic ligands (Martell and Smith, 1977, 1997; Sillén et al., 1964, 1971; Pettit et al., 1997), but no data are reported for the complex formation of these ligands in seawater.

With the aim of giving a systematic study of the binding capacity of low molecular weight carboxylic ligands in seawater, this work reports apparent protonation constants and complex formation constants with the cationic macrocomponents of seawater for the following carboxylic ligands: acetate (ac$^-$), malonate (mal^{2-}), succinate (succ^{2-}), malate (mala^{2-}), tartrate (tar^{2-}), azelate (nonanedioc acid, aza^{2-}), oxydiacetate (diglycolic acid, oda^{2-}), trioxydiacetate (3,6,9-trioxaundecanedioc acid, toda^{2-}), tricarballylate (1,2,3-propanetricarboxylate, tca^{3-}), citrate (cit^{3-}), methyltricarballylate (mtca^{3-}), butanetetracarboxylate (1,2,3,4-butanetetracarboxylate, btc^{4-}), mellitate (benzenehexacarboxylate, mlt^{6-}). Measurements were performed at t = 25 °C and at five salinities: S (‰) = 5, 15, 25, 35, 45.

Previously reported protonation data for some phenolic compounds were reelaborated to obtain formation constants for marine salt complexes.

Experimental Section

Materials. Carboxylic ligands (Fluka or Aldrich products) were used without further purification and their purity, checked alkalimetrically, was found to be >99%. Sodium chloride, potassium chloride, and sodium sulfate were used as anhydrous salts (Fluka) and always dried before use. Magnesium and calcium chloride solutions were prepared using pure salts (Fluka) and standardized against EDTA standard solutions. Synthetic seawater solutions were prepared by mixing salts as reported in Table 1. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated ampules (Fluka). Solutions of acid and hydroxide were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All solutions were prepared with analytical grade water (R = 18 MΩ cm^{-1}), using grade A glassware.

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Table 1. Composition of Artificial Seawater (SSWE) at 35‰ Salinity[a] and at $t = 25$ °C

component	c (mol L^{-1})	m (mol kg^{-1})
NaCl	0.4221	0.427 40
Na_2SO_4	0.0288	0.029 19
KCl	0.0110	0.011 12
$CaCl_2$	0.0111	0.011 21
$MgCl_2$	0.0548	0.055 52
BA[b]	0.5751	0.582 40
I	0.717	0.726

[a] Concentrations at different salinities (S, ‰) are given by $m_S = m_{35}[27.56572S/(1000 - 1.005714S)]$. [b] Seawater salt.

Apparatus. Potentiometric measurements were made using apparatus consisting of a potentiometer Metrohm model 605, equipped with an Orion combination glass electrode (Ross type 8102) and a Metrohm motorized buret (model 654). The estimated accuracy was ±0.15 mV and ±0.003 mL for emf and titrant volume readings, respectively. The apparatus was connected to a personal computer, and automatic titrations were carried out using a suitable computer program (titrant delivery, data acquisition, check for the stability of emf). All titrations were carried out by stirring magnetically and by bubbling purified and presaturated N_2 through the solution, to preserve all solutions from O_2 and CO_2.

Procedure. A volume of 20−25 mL of synthetic seawater at different salinities ($5 \leq S$ (‰) ≤ 45), containing the carboxylic ligand under investigation (1−10 mmol L^{-1}), was titrated with standard NaOH solution up to 80−90% neutralization. For each experiment, independent titration of HCl solutions under the same experimental conditions as those for the systems under study (at the same ionic salinities) was carried out in order to determine the electrode potential ($E°_{\text{ext}}$) and the acidic junction potential ($E_j = j_a[H^+]$). The free hydrogen ion concentration scale was used (pH $= -\log [H^+]$).

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 following additional computer programs were also used: (a) BSTAC and STACO to calculate protonation and formation constants; (b) ES4ECI to draw distribution diagrams of the species in solution and to compute species formation; (c) LIANA to test the dependence of log K on ionic strength by using different equations. Details on these computer programs were already reported (De Stefano et al., 1997, and references reported therein).

Dependence on ionic strength was taken into account by using an extended Debye−Hückel (EDH) type equation (Daniele et al., 1997, and references reported therein):

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

where K is the protonation constant (concentration quotient); ^{T}K is the protonation constant at infinite dilution; I is the ionic strength; C and D are empirical parameters and can be expressed as

$$C = c_0 p^{*} + c_1 z^{*}$$

$$D = d_0 p^{*} + d_1 z^{*}$$

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

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

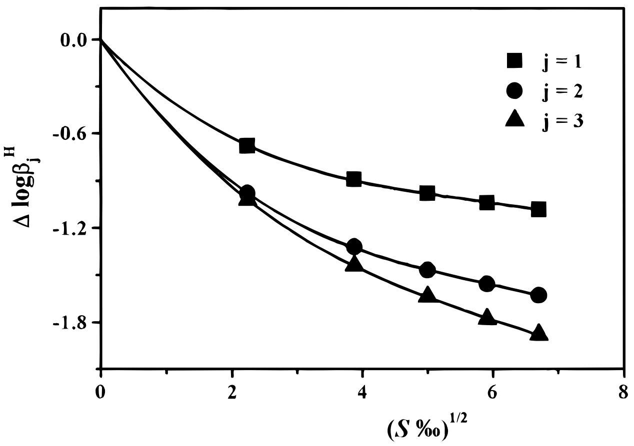

Figure 1. $\Delta \log \beta_j^{H} = \log \beta_j - \log {}^{T}\beta_j^{H}$ versus (S (‰))$^{1/2}$, for tca at $t = 25$ °C.

Table 2. Thermodynamic Parameters[a] for the Self-Association of BA, the Protonation of A^{z-}, and the Hydrolysis of B^{z+}, at 25 °C and $I = 0$ mol L^{-1}

reaction	log K	z^*	C[b]
$B^{z+} + A^{z-} = BA^0$	−0.03	2.494	0.105
$H^+ + A^{z-} = HA^{(1-z)}$	0.24	2.233	0.095
$B^{z+} = B(OH)^{(z-1)} + H^+$	−12.75	−0.234	−0.205

[a] De Stefano et al., 1998, 1999. [b] Empirical parameter of eq 1.

where the empirical parameters c_0, c_1, d_0, and d_1 are dependent only on the stoichiometry of the reaction. In the range $0 \leq I$ (mol L^{-1}) ≤ 1 (Daniele et al., 1997)

$$C = 0.1p^{*} + 0.20z^{*}$$

$$D = -0.075z^{*}$$

Artificial Seawater. An artificial seawater containing six components (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}, see Table 1) was used to study the interactions of carboxylic ligands with the major components of seawater. Some investigations (De Robertis et al., 1994; De Stefano et al., 1998) performed to evaluate the internal interactions between the components of the ionic medium (SSWE) showed that very weak [$NaCl^0$, KCl^0, $Na(OH)^0$, and $K(OH)^0$], weak [$MgCl^+$, $CaCl^+$, $Ca(OH)^+$, and $Na(SO_4)^-$], and fairly stable [$Mg(OH)^+$, $Mg(SO_4)^0$, and $Ca(SO_4)^0$] species are formed.

To simplify equilibrium calculations, we express the composition of SSWE in terms of a single salt BA, with an ionic charge ±1.117 (De Stefano et al., 1998). The concentration of BA (mean ionic concentration) is reported in Table 1. By using the single-salt approximation, only three species deriving from internal ionic medium interactions must be considered: two species formed by interactions of anion salt, BA^0 and $HA^{(1-z)}$, and the cation species $B(OH)^{(z-1)}$. Equilibrium constants for these species are reported in Table 2 and are included in the calculations in order to determine the formation constants of carboxylic ligands and the seawater salt.

Results and Discussion

Apparent Protonation Constants. Potentiometric data were first interpreted in terms of apparent protonation constants, log β_j^{H*}, obtained by extrapolation to zero ligand concentration of the conditional protonation constants (De Stefano et al., 1999). Values at different salinities of log β_j^{H*} are reported in Tables 3 and 4. Log β_j^{H*} versus S (‰) is a steadily decreasing function, as shown in Figure 1,

Table 3. Apparent Protonation Constants of Mono- and Dicarboxylic Ligands in Artificial Seawater, at $t = 25$ °C

S (‰)	$\log K_1^{H*}$ ± 0.01[a]	$\log \beta_2^{H*}$ ± 0.01[a]	S (‰)	$\log K_1^{H*}$ ± 0.01[a]	$\log \beta_2^{H*}$ ± 0.01[a]
	ac			tar	
5	4.54		5	3.92	6.75
15	4.47		15	3.74	6.50
25	4.43		25	3.66	6.38
35	4.40		35	3.62	6.32
45	4.37		45	3.60	6.27
	mal			aza	
5	5.00	7.66	5	5.11	9.43
15	4.75	7.32	15	5.04	9.26
25	4.64	7.17	25	5.04	9.19
35	4.59	7.08	35	5.05	9.15
45	4.56	7.02	45	5.06	9.12
	succ			toda	
5	5.16	9.15	5	3.70	6.80
15	5.00	8.91	15	3.50	6.52
25	4.94	8.80	25	3.43	6.39
35	4.91	8.73	35	3.39	6.32
45	4.90	8.68	45	3.37	6.26
	mala				
5	4.61	7.87			
15	4.43	7.63			
25	4.36	7.53			
35	4.33	7.46			
45	4.30	7.41			

[a] ±3 standard deviations.

Table 4. Apparent Protonation Constants of Tri-, Tetra-, and Hexacarboxylic Ligands in Artificial Seawater, at $t = 25$ °C

S (‰)	$\log K_1^{H*}$	$\log \beta_2^{H*}$	$\log \beta_3^{H*}$	$\log \beta_4^{H*}$	$\log \beta_5^{H*}$
			tca		
	±0.02[a]	±0.02[a]	±0.03[a]		
5	5.81	10.42	14.07		
15	5.60	10.08	13.65		
25	5.51	9.93	13.45		
35	5.45	9.84	13.31		
45	5.41	9.77	13.21		
			mtca		
	±0.02[a]	±0.03[a]	±0.03[a]		
5	6.86	11.64	15.01		
15	6.59	11.21	14.51		
25	6.46	11.00	14.24		
35	6.37	10.87	14.06		
45	6.30	10.78	13.93		
			btc		
	±0.02[a]	±0.03[a]	±0.03[a]	±0.03[a]	
5	5.74	10.74	14.81	18.03	
15	5.56	10.36	14.34	17.47	
25	5.55	10.31	14.23	17.35	
35	5.57	10.28	14.20	17.30	
45	5.56	10.31	14.18	17.28	
			mlt		
	±0.03[a]	±0.03[a]	±0.04[a]	±0.05[a]	±0.2[a]
5	5.03	9.50	13.10	15.79	16.6
15	4.89	9.17	12.70	15.35	15.8
25	4.89	9.10	12.66	15.33	15.6
35	4.92	9.08	12.68	15.39	15.5
45	4.96	9.07	12.72	15.46	15.5

[a] ±3 standard deviations.

Table 5. Empirical Parameters for the Dependence on Salinity (Eq 2) of the Apparent Protonation Constants of Di- and Tricarboxylic Ligands

ligand	j	$\log {}^{T}\beta_j^{H}$	a_1	a_2	a_3	σ^a
ac	1	4.75	−0.134	0.0213	−0.0015	0.003
mal	1	5.70	−0.423	0.0561	−0.0027	0.004
	2	8.57	−0.550	0.0732	−0.0038	0.004
succ	1	5.64	−0.297	0.0419	−0.0021	0.003
	2	9.85	−0.434	0.0631	−0.0036	0.004
mala	1	5.10	−0.301	0.0411	−0.0021	0.002
	2	8.57	−0.439	0.0652	−0.0038	0.003
tar	1	4.43	−0.308	0.0411	−0.0020	0.004
	2	7.46	−0.434	0.0603	−0.0033	0.005
aza	1	5.49	−0.268	0.0508	−0.0031	0.002
	2	10.04	−0.398	0.0657	−0.0040	0.005
toda	1	4.25	−0.337	0.0459	−0.0023	0.001
	2	7.56	−0.462	0.0629	−0.0034	0.003
tca	1	6.49	−0.434	0.0680	−0.0041	0.005
	2	11.40	−0.608	0.0880	−0.0050	0.004
	3	15.09	−0.602	0.0749	−0.0040	0.004
mtca	1	7.58	−0.439	0.0607	−0.0035	0.003
	2	12.71	−0.630	0.0773	−0.0039	0.005
	3	16.13	−0.634	0.0682	−0.0034	0.006

[a] Standard deviation.

Table 6. Empirical Parameters for the Dependence on Salinity (Eq 3) of the Apparent Protonation Constants of Tetra- and Hexacarboxylic Ligands

ligand	j	$\log {}^{T}\beta_i^{H}$	b_1	b_2	b_0	σ^a
btc	1	7.18	0.0096	74	0.0720	0.016
	2	13.01	0.0135	43	0.0720	0.014
	3	17.54	0.0154	29	0.0720	0.013
	4	20.92	0.0160	23	0.0720	0.016
mlt	1	7.85	0.0097	2.2×10^5	0.0396	0.004
	2	14.30	0.0103	7.5×10^4	0.0396	0.009
	3	19.39	0.0192	4.8×10^4	0.0396	0.013
	4	22.86	0.0262	2.3×10^4	0.0396	0.016

[a] Standard deviation on the fit.

where $\Delta \log \beta_j^{H} = \log \beta_j - \log {}^{T}\beta_j^{H}$ is plotted versus S (‰), for the protonation of 1,2,3-propanetricarboxylic acid. The sharply decreasing trend can be explaned by considering the high complexing ability of carboxylic ligands toward alkaline earth metal cations and to a lesser extent alkali metal cations (De Robertis et al., 1999, and references reported therein; De Stefano et al., 2000, and references reported therein). This is particularly evident for ligands containing more than two carboxylic groups. For mellitic acid, only the first four protonation constants can be calculated: in the presence of the artificial seawater salt, the last carboxylic groups behave like a strong acid.

The apparent protonation constants of mono-, di-, and tricarboxylic ligands can be expressed as a function of salinity by the equation

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

where a_1, a_2, and a_3 are empirical parameters, reported in Table 5. The fit is very good, with a standard deviation $\sigma < 0.01$. For tetra- and hexacarboxylic ligands, eq 2 is inadequate, and we found that it is possible to use the relationship

$$\log \beta_j^{H*} = \log {}^{T}\beta_j^{H} + b_1 I + b_0 z^* \log(1 + b_2 I) \qquad (3)$$

where b_0, b_1, and b_2, reported in Table 6, are empirical parameters. Good fits were obtained with a standard deviation $\sigma < 0.02$.

As concerns the empirical parameters of eq 2 for mono-, di-, and tricarboxylic ligands, we can observe a regular trend as a function of z^*. Trials demonstrated that the simplest equation is

$$a_i = c_i z^*$$

valid for all the ligands. For the three parameters, we have

$$a_1 = -(0.00648 \pm 0.0029) z^* \qquad (2a)$$

$$a_2 = -(0.00872 \pm 0.00054) z^* \qquad (2b)$$

$$a_3 = -(0.00047 \pm 0.00003) z^* \qquad (2c)$$

Table 7. Formation Constants for Mono- and Dicarboxylic Ligand Complexes with $B^{1.117+}$, at $I = 0$ mol L^{-1} and $t = 25$ °C

ligand	log β_{110}[a]	log β_{111}[b]	log K_{111}[c]
ac^{-}	0.30 ± 0.02[d]		
mal^{2-}	1.68 ± 0.06	6.05 ± 0.07[d]	0.35
succ^{2-}	1.26 ± 0.04	6.04 ± 0.06	0.39
mala^{2-}	1.25 ± 0.02	5.37 ± 0.04	0.27
tar^{2-}	1.29 ± 0.02	4.69 ± 0.04	0.26
oda^{2-} [e]	1.80	4.69	0.33
aza^{2-}	0.95 ± 0.05	6.00 ± 0.07	0.51
toda^{2-}	1.41 ± 0.03	4.63 ± 0.06	0.38

[a] β_{110}: $L^{z-} + B^{1.117+} = BL^{(1.117-z)}$. [b] β_{111}: $L^{z-} + H^+ + B^{1.117+} = BHL^{(2.117-z)}$. [c] K_{111}: $HL^{(z-1)-} + B^{1.117+} = BHL^{(2.117-z)}$; $K_{111} = \beta_{111}/K_1^H$. [d] ±3 standard deviations. [e] De Stefano et al., 1999.

Table 8. Formation Constants for Tricarboxylic Ligand Complexes with $B^{1.117+}$, at $I = 0$ mol L^{-1} and $t = 25$ °C

ligand	log β_{10}[a]	log β_{11}[a]	log β_{12}[a]	log β_{20}[a]
tca^{3-}	1.83 ± 0.03[d]	7.52 ± 0.05[d]	11.60 ± 0.07[d]	2.10 ± 0.10[d]
mtca^{3-}	1.90 ± 0.07	8.75 ± 0.05	12.94 ± 0.06	2.6 ± 0.2
cit^{3-} [e]	3.24	7.82	11.30	3.57

	log K_{11}[b]	log K_{12}[b]	log K_{20}[c]
tca^{3-}	1.03	0.19	0.3
mtca^{3-}	1.17	0.23	0.7
cit^{3-} [e]	1.40	0.13	0.3

[a] β_{pq}: $pB^{1.117+} + L^{z-} + qH^+ = B_pLH_q^{(1.117p+q-z)}$. [b] K_{pq}: $pB^{1.117+} + H_qL = B_pLH_q^{(1.117p+q-z)}$. [c] K_{M2L}: $pB^{1.117+} + BL^{(1.117-z)} = B_2L^{(2.234-z)}$. [d] ±3 standard deviations. [e] De Stefano et al., 1999.

Very probably, the empirical parameters of eq 3 can also be related to some specific parameters for carboxylic ligands; in particular, b_2 can be related to the mean stability of the alkali and alkaline metal complexes of fully deprotonated or partially protonated ligands. [Note the similarity of eq 3 with the equation for calculating formation constants in self-medium, $\log K^{H*} = \log K^H - \log(1 + K^M C_M)$, where M is the background salt cation, in excess with respect to the ligand (Daniele et al., 1997).] Nevertheless, we did not perform further calculations, owing to the scarceness of available data (only two ligands).

Complex Formation with Seawater Salt. The sharp decrease in apparent protonation constants with salinity can also be interpreted in terms of complex formation between the carboxylic anion and the cation $B^{1.117+}$ of artificial seawater. By performing appropriate calculations we found that, for all the systems studied, complex species are formed with both unprotonated and partially protonated ligands.

Dicarboxylic ligands form two species, $BL^{0.883-}$ and $BHL^{0.117+}$, with a mean stability of 25 and 2 mol^{-1} L, respectively. The acetate anion only forms a complex species, whose stability is very close to that of the monoprotonated dianion species. Formation constants are reported in Table 7. Tricarboxylic ligands form four species, $BL^{1.883-}$, $BHL^{0.883-}$, $BH_2L^{0.117+}$, and $B_2L^{0.766-}$, with mean stabilities of 80, 15, 1.5, and 2.5 mol^{-1} L, respectively. Formation constants are reported in Table 8. Butanetetracarboxylate and mellitate form several unprotonated and protonated species, five and seven, respectively, with quite high stability. Formation constants are reported in Table 9.

In a preceding work (Demianov et al., 1995) we reported potentiometric data for the protonation of some phenols in artificial seawater: using these data, we have now investigated the interaction between phenolates and $B^{1.117+}$. The formation constants are reported in Table 10. In these systems, as in monocarboxylate ones, the weak species $BL^{0.117+}$ is formed, with a mean stability of 1.3 mol^{-1} L. This stability is rather lower than that of monocarboxylic ligands but is comparable (same order of magnitude).

The formation constants reported in Tables 7−9 are strictly related to the number of carboxylic groups involved in the coordination, n. For example

$$\mathrm{btc}^{4-} + B^{1.117+} = B(\mathrm{btc})^{2.883+} \qquad n = 4$$

$$H_3(\mathrm{mlt})^{3-} + B^{1.117+} = BH_3(\mathrm{mlt})^{1.883+} \qquad n = 3$$

The most simple relationship between log K and n is

$$\log K = (0.37 \pm 0.01)n^{3/2} \quad (1 \le n \le 5) \tag{4}$$

with the standard deviation on the fit $\sigma = 0.22$. More careful inspection of stability data reveals some interesting trends. (i) Stability is inversely proportional to the length of the alkyl chain. If we consider malonate, succinate, and azelate (Table 7), we have $\beta_{110} = 48$, 18, and 9 mol^{-1} L, respectively: the decreasing function is not linear, owing to the higher flexibility of longer chains. (ii) The higher stability of oda and toda is due to the involvement of the ethereal group in the coordination. This is in accordance with previous findings on the stability of calcium complexes of oda and toda (De Stefano et al., 2000).

Figure 2 shows the percent formation versus pH speciation diagram for the system tca−BA at 35‰ salinity. In this system we observe that all the species show high yields (>20%) and that, at pH > 7, the sum of $B(\mathrm{tca})^{1.883-}$ plus $B_2(\mathrm{tca})^{0.766-}$ is >90%. The same holds for the btc system with higher yield (except for the triprotonated complex), and at pH > 7 we have ~100% of the ligand as $B(\mathrm{btc})^{2.883-}$ and $B_2(\mathrm{btc})^{1.766-}$. Formation percentages are strongly dependent on the number of carboxylic groups in the ligand: to show this trend quantitatively, in Figure 3 we plotted $\Sigma_{\mathrm{species}}$ % versus salinity, at pH 8.2 for mono-, di-, tri-, and

Table 9. Formation Constants for Tetra- and Hexacarboxylic Ligand Complexes with $B^{1.117+}$, at $I = 0$ mol L^{-1} and $t = 25$ °C

ligand	log β_{110}[a]	log β_{111}[a]	log β_{112}[a]	log β_{113}[a]	log β_{210}[a]
btc^{4-}	3.05 ± 0.05[e]	9.12 ± 0.05[e]	14.01 ± 0.06[e]	17.65 ± 0.08[e]	3.18 ± 0.15[e]
mlt^{6-}	7.05 ± 0.15	13.00 ± 0.10	18.22 ± 0.05	22.28 ± 0.10	8.81 ± 0.10

other species	log β_{114}[a]	log β_{121}[a]
	25.26 ± 0.15	14.25 ± 0.15

	log K_{111}[b]	log K_{112}[b]	log K_{113}[b]	log K_{114}[b]	log K_{210}[c]	log K_{211}[d]
btc^{4-}	1.94	1.00	0.11		0.13	
mlt^{6-}	5.15	3.92	2.89	2.4	1.76	1.25

[a−c] See footnotes in Table 8. [d] K_{M2HL}: $B^{1.117+} + BHL^{(2.117-z)} = B_2HL^{(3.234-z)}$. [e] ±3 standard deviations.

Table 10. Formation Constants for Phenol Complexes with $B^{1.117+}$, at $I = 0$ mol L^{-1} and $t = 25$ °C

ligand	log K^a
phenol	0.3 ± 0.1^b
o-cresol	0.1 ± 0.1
p-cresol	0.3 ± 0.2
o-nitrophenol	0.2 ± 0.2
p-nitrophenol	-0.1 ± 0.2
mean value	0.15 ± 0.2

[a] K: B + L = BL. [b] ±3 standard deviations.

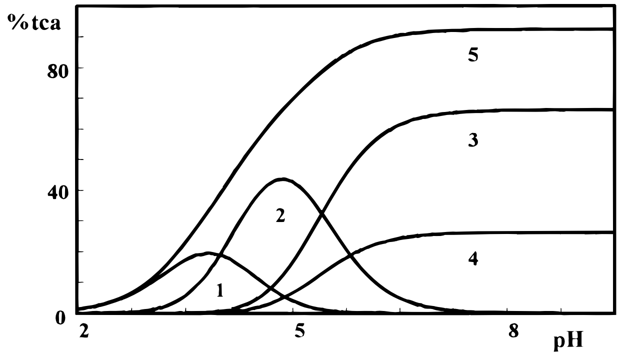

Figure 2. Speciation diagram of tca in artificial seawater S = 35‰ at t = 25 °C; $C_B = 0.5752$ mol L^{-1}; $C_{tca} = 10^{-4}$ mol L^{-1}. Curves: 1, $B(tca)H_2$; 2, B(tca)H; 3, B(tca); 4, $B_2(tca)$; 5, $\Sigma_{species}$ % (charges are omitted for simplicity).

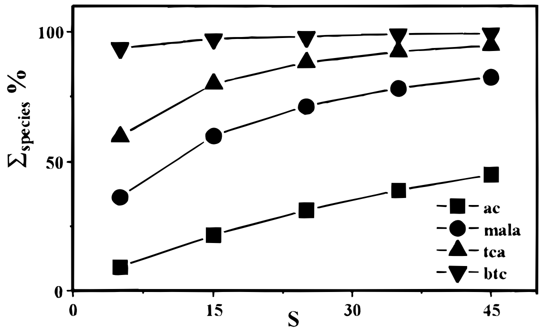

Figure 3. Sum of species percentages versus salinity (S (‰)), at pH = 8.2.

tetracarboxylic ligands. Percentages increase with n: for mellitate, at pH > 5, a 100% yield is always observed.

In the literature we found only one paper dealing with the determination of apparent protonation constants of carboxylic acids in artificial seawater: Johansson and Wedborg (1985) studied acetic acid in the range 5−40‰ salinity and $5 \le t \le 45$ °C.

Final Remarks. The protonation constants of polycarboxylic acids in artificial seawater are a decreasing function of salinity (S (‰)) according to their complexing ability toward alkali and alkaline earth cations. Apparent protonation constants can be expressed as a function of salinity by simple empirical equations (eqs 2 and 3). By using the single-salt approximation for artificial seawater, we calculated the formation constants of carboxylate−seawater cation complexes, whose stabilities are a function of the number of carboxylic groups involved in the coordination. It is possible to set down some relationships between the empirical parameters of eq 2 and the stoichiometry of the protonation reaction (eqs 2a−2c) and between formation constants and the number of carboxylic groups (eq 4). Others factors regarding the stability of these complexes must be considered, such as the length of the alkyl chain and the presence of ethereal atoms in the carboxylic ligands. Protonation percentages, reported in Figure 2, show that most carboxylic ligands are complexed in (S (‰) = 35, pH = 8.2) seawater conditions.

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