J. Chem. Eng. Data **2007,** *52,* 2195−2203

SIT Parameters for the Dependence of (Poly)carboxylate Activity Coefficients on Ionic Strength in $(C_2H_4)_4NI_{aq}$ ($0 \le I \le 1.2$ mol·kg^{-1}) and $(CH_3)_4NCl_{aq}$ ($0 \le I \le 3.9$ mol·kg^{-1}) in the Temperature Range 278 K $\le T \le$ 328 K and Correlation with Pitzer Parameters[†]

Francesco Crea, Concetta De Stefano,* Claudia Foti, and Silvio Sammartano

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università degli Studi di Messina,
Salita Sperone 31, 98166 Messina (Vill. S. Agata), Italy

Parameters for the dependence on ionic strength of activity coefficients for several protonated and unprotonated mono-hexacarboxylates in $(C_2H_5)_4NI$ and $(CH_3)_4NCl$ aqueous solution were calculated from protonation data [31 polycarboxylates, 613 protonation constants at $T = 298$ K, 1244 at $T \neq 298$ K, in $(C_2H_5)_4NI$; 16 polycarboxylates, 433 protonation constants at $T = 298$ K, 308 at $T \neq 298$ K ($T = 278$ K to 328 K), in $(CH_3)_4NCl$], at different ionic strengths [0 mol·kg^{-1} $\le I \le$ 1.2 mol·kg^{-1}, for $(C_2H_5)_4NI$ and 0 mol·kg^{-1} $\le I \le$ 3.9 mol·kg^{-1}, for $(CH_3)_4NCl$)] using a modified SIT model. In this model, the interaction coefficients are considered as dependent on ionic strength according to the equation $\epsilon = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(I + 1)$. The analysis of protonation data showed that the parameters for the dependence on both ionic strength and temperature are a simple function of the charge of carboxylate species. Mean values of interaction coefficients are given by the relationships $\epsilon = \bar{\epsilon}z^2$; $\bar{\epsilon}_\infty = -0.0188$ and -0.0063; $\bar{\epsilon}_0 = 0.2420$ and 0.1642 for $(C_2H_5)_4NI$ and $(CH_3)_4NCl$, respectively. For the activity coefficients of neutral species, a simple relationship as a function of the number n of carboxylic groups was found: $\log \gamma_N = k_m I$ (k_m = Setschenow coefficient); $k_m = \bar{k}_m \cdot n$, $\bar{k}_m = -0.0198$ and 0.0055, for $(C_2H_5)_4NI$ and $(CH_3)_4NCl$, respectively. Mean values of interaction coefficients were also reported for some synthetic and natural polyelectrolytes in $(C_2H_5)_4NI$ ($\bar{\epsilon}_\infty = -0.007$; $\bar{\epsilon}_0 = 0.199$). Furthermore, calculations were made to find the parameters of Pitzer equations. Also in this case, we found a simple relationship between $\beta^{(0)}$ and $\beta^{(1)}$ parameters and species charges. A comparison is given between the SIT and Pitzer models. An almost perfect correlation was found between the SIT and Pitzer coefficients.

Introduction

Acid−base properties of (poly)carboxylates in aqueous solution are strongly dependent on the ionic medium, and a large amount of thermodynamic data on the protonation of these ligands have been reported in the literature.[4−12] Most of these data were obtained in aqueous solutions containing, as supporting electrolytes, alkali metal chlorides, nitrates, and perchlorates. Protonation of carboxylates in aqueous tetraethylammonium iodide and tetramethylammonium chloride has been widely studied in this laboratory.[13−29] Protonation constants in different supporting electrolytes follow almost always the trend $Li^+ < Na^+ < K^+ \ll (CH_3)_4N^+ < (C_2H_5)_4N^+$, independent of the anion (Cl^-, NO_3^-, ClO_4^-, Br^-, I^-), and often, tetraalkylammonium salts have been used as a baseline in the quantitative determination of the interaction between carboxylates and alkali metal cations. In fact, from the study of the dependence on ionic strength of weak acid protonation constants in different ionic media, it is possible to determine the weak complex formation constants of one of the medium cations if it can be assumed that the cation of the other salt does not form complexes (often this procedure is called "Δ*pK* method"). It can also be assumed that activity coefficients are approximately the same in both ionic media if their ionic strengths are also the same. From a comparison of weak complex formation constants obtained using this method (protonation constants in $(C_2H_5)_4NI$ and in a sodium salt at $I \le 1$ mol·dm^{-3}) with those obtained with other methods (conductimetry, ion selective electrodes, etc.), it has been possible to observe consistent results (this frequently does not happen using other tetraalkylammonium salts).[13,16−18,21−24] The use of other tetraalkylammonium salts as supporting electrolytes in these studies can also be of interest because it has been shown that small formation constants obtained in $(C_2H_5)_4NI$ and $(CH_3)_4NCl$ converge to the same value at infinite dilution.[30] Specific effects on the properties of solutions containing tetraalkylammonium salts, such as protonation constants, metal complex formation constants, and solubility (salting effects are often opposite with respect to those shown by alkali metal salts[26,27]), are due mainly to the different water structure breaking/ordering of these salts in comparison with inorganic salts. To understand these effects, it is important to study the solution properties in tetraalkylammonium salts at different concentrations (and in different temperature conditions).

The dependence on ionic strength of protonation constants can be used to calculate the activity coefficients of the different protonated and unprotonated species of different types of ligands, using different approaches such as SIT[31−38] and Pitzer[39,40] models described in the following sections. Pitzer equations, used in a large number of papers on equilibrium studies,[41−47] are quite complete and allow activity coefficients to be modeled in a wide range of ionic strengths. Nevertheless, Pitzer equations are quite complicated and in some cases difficult

---

* Corresponding author. E-mail: cdestefano@unime.it.

[†] Calculation of SIT parameters: Part IV; Part I−III, refs 1−3.

10.1021/je700223r CCC: $37.00

Table 1. Carboxylates Taken into Account in This Work

carboxylate	abbr.	ionic medium	T/K	ref
formiate	Form	Et_4NI	278,283,288,298,308,310,318,328	14,15,19
acetate	Ac	Et_4NI	278,288,298,308,310,318,328	14,17,19
		Me_4NCl	298	28
propionate	Prop	Et_4NI	278,283,288,298,308,318,328	15,19
salicilate	Sal	Et_4NI	278,288,298,308,318,328	19
phenoxyacetate	Phen	Et_4NI	283,298,310,318	16,19
benzoate	Benz	Et_4NI	310	14,19
oxalate	Ox	Et_4NI	283,298,318	13,14,19,20,25
malonate	Mal	Et_4NI	283,288,298,308,310,318	14,15,19,25
		Me_4NCl	298	28
succinate	Succ	Et_4NI	288,298,308,310,318	14,15,19,25
		Me_4NCl	298	28
tartrate	Tar	Et_4NI	283,293,298,303,310,313	14,19
		Me_4NCl	288,298,308,318	29
itaconate	Ita	Et_4NI	283,288,298,308,318	15,19
oxidiacetate	Oda	Et_4NI	283,293,298,303,313,323	15,19
thiodiacetate	Tda	Et_4NI	283,288,298,308,318	15,19
thiodipropionate	Tdp	Et_4NI	283,288,298,308,318	15,19
phthalate	Pht	Et_4NI	278,283,288,298,308,310,318,328	14,15,19,262
		Me_4NCl	298	6
malate	Mala	Et_4NI	278,288,298,308,310,318,328	14,15,19
		Me_4NCl	288,298,308,318	29
maleate	Male	Et_4NI	283,293,298,303,313	14,19
glutarate	Glu	Et_4NI	298	25
adipate	Adip	Et_4NI	298	25[a]
		Me_4NCl	298	a
pimelate	Pim	Et_4NI	298	25[a]
		Me_4NCl	298	a
suberate	Sub	Et_4NI	298	25,27
		Me_4NCl	298	27
azelate	Aze	Et_4NI	298	24,25,27
		Me_4NCl	298	27
sebacate	Seb	Et_4NI	298	27
		Me_4NCl	298	27
diethylenetrioxydiacetate	Toda	Et_4NI	298	24
1,2,3-propanetricarboxylate, tricarballylate	Tca	Et_4NI	278,288,298,308,318278,288,298,308,318	22
		Me_4NCl	278,288,298,308,318	28,29
2-methyl-1,2,3-propanetricarboxylate	Mtca	Me_4NCl	298	28
citrate	Cit	Et_4NI	283,293,298,303,310,313,323	14,19
		Me_4NCl	298	28
1,2,3-benzenetricarboxylate	123btca	Et_4NI	283,293,298,303,313,323	19
1,2,4-benzenetricarboxylate	124btca	Et_4NI	298	19
butanetetracarboxylate	Btc	Et_4NI	278,288,298,308,318	21
		Me_4NCl	278288,298,308,318	28,29
1,2,4,5-benzenetetracarboxylate	Pymel	Et_4NI	283,293,298,303,313,323	18,19
benzenehexacarboxylate, mellitate	Mlt	Et_4NI	298	23
		Me_4NCl	298	28

[a] Unpublished data from this laboratory.

to handle. The SIT approach has the advantage of being quite simple but, in its original version, is not very accurate in fitting γ values at $I < 0.5\ \text{mol}\cdot\text{kg}^{-1}$ and at $I > 3\ \text{mol}\cdot\text{kg}^{-1}$. Another interesting one-parameter equation for the dependence on ionic strength of activity coefficients has been proposed by Bromley[48] and has been widely used by Madariaga and co-workers[49−51] for the dependence of protonation and metal complex formation constants on ionic strength.

In this paper, we used a modified version of the SIT model, previously proposed,[1−3] and we report parameters for the dependence on ionic strength of activity coefficients of carboxylates in aqueous $(C_2H_5)_4NI$ and $(CH_3)_4NCl$ solutions, at different temperatures ($278\ \text{K} \le T \le 328\ \text{K}$) and ionic strengths [$0\ \text{mol}\cdot\text{kg}^{-1} \le I \le 1.2\ \text{mol}\cdot\text{kg}^{-1}$ for $(C_2H_5)_4NI$ and $0\ \text{mol}\cdot\text{kg}^{-1} \le I \le 3.9\ \text{mol}\cdot\text{kg}^{-1}$ for $(CH_3)_4NCl$]. In Table 1, the (poly)-carboxylic acids taken into consideration in this work, together with the relative abbreviations, are reported.

Protonation data of several synthetic and natural polyelectrolytes were also taken into account, and the relative mean interaction coefficients are reported.

SIT Model

Protonation constants of carboxylates in a salt solution can be expressed by (L^{z-} = anion carboxylate)

$$\log K_i^{\mathrm{H}} = \log {}^{\mathrm{T}}K_i^{\mathrm{H}} + \log \gamma(\mathrm{H}^+) + \log \gamma(\mathrm{H}_{i-1}\mathrm{L}^{(i-1-z)}) - \log \gamma(\mathrm{H}_i\mathrm{L}^{(i-z)}) \qquad (1)$$

where

$$K_i^{\mathrm{H}} = \frac{[\mathrm{H}_i\mathrm{L}^{(i-z)}]}{[\mathrm{H}_{i-1}\mathrm{L}^{(i-1-z)}][\mathrm{H}^+]} \qquad (2)$$

${}^{\mathrm{T}}K_i^{\mathrm{H}}$ is the protonation constant at infinite dilution, and γ is the activity coefficient of a single species. According to the SIT model, the molal activity coefficient γ_j of an ion j of charge z_j is given by

$$\log \gamma_j = z_j^2 \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k \epsilon_{j,k} m_k \qquad (3)$$

where ϵ is the specific interaction coefficient of the jth ion and the sum is extended over all ions k present in solution at the molality m_k. Activity coefficients for the neutral species are given by the linear relationship

$$\log \gamma_{\mathrm{N}} = k_{\mathrm{m}} I \tag{3a}$$

where k_{m} is the Setschenow coefficient.[52] By combining eqs 1 to 3, we can write

$$\log K_i^{\mathrm{H}} = \log {}^{\mathrm{T}}K_i^{\mathrm{H}} - z^* \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} + I\Delta\epsilon \tag{4}$$

where I is the ionic strength in the molal concentration scale and

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

$$A = 0.510 + 76.286\left(\frac{1}{\theta} - \frac{1}{T}\right) + 1.4189\left(\frac{\theta}{T} - 1 + \ln\frac{T}{\theta}\right)$$

($\theta = 298.15$ K). In a generic salt MX we have

$$\Delta\epsilon = [\epsilon(\mathrm{H}^+, \mathrm{X}^-) + \epsilon(\mathrm{M}^{z+}, \mathrm{H}_{i-1}\mathrm{L}^{i-1-z}) - \epsilon(\mathrm{M}^{z+}, \mathrm{H}_i\mathrm{L}^{i-z})] \tag{5}$$

In the classic SIT approach, ϵ parameters are true constants, but recently, a modified version of the SIT equation was used,[1−3] in which interaction coefficients ϵ are not constant but depend on ionic strength according to the simple relationship

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{I + 1} \tag{5a}$$

Another expression was previously proposed for taking into account the dependence on ionic strength of ϵ[34−37]

$$\epsilon = \epsilon^{(0)} + \epsilon^{(1)} \ln(1 + I) \tag{5b}$$

Very often, fitting experimental data (activity coefficients or related parameters, such as protonation constants at different ionic strengths) to eqs 5a or 5b gives very similar results, but we observed in general a small statistical improvement when using eq 5a.

Literature values of HI ($\epsilon_\infty = 0.173$, $\epsilon_0 = 0.204$)[2] and of HCl [$\epsilon_\infty = 0.136 + 0.07165\ (1/298 - 1/T) + 0.1159\ (298/T - 1 + \ln(T/298))$; $\epsilon_0 = 0.0848 - 0.1024\ (1/298 - 1/T) + 0.1970\ (298/T - 1 + \ln(T/298))$][1,2] were used in the calculations. Temperature gradients of HI, calculated in this work, are $\partial\epsilon_\infty/\partial T = -0.0024 \pm 0.0005$ and $\partial\epsilon_0/\partial T = 0.0094 \pm 0.0015$.

Pitzer Model

According to the Pitzer equations,[39,40] in the presence of a 1:1 salt MX, the activity coefficients of a cation or an anion are given by

$$\ln \gamma_{\mathrm{H^+}} = f^{\gamma} + 2I(B_{\mathrm{HX}} + IC_{\mathrm{HX}}) + I^2(B'_{\mathrm{MX}} + C_{\mathrm{MX}}) + I(2\theta_{\mathrm{HM}} + I\psi_{\mathrm{HMX}}) \tag{6}$$

$$\ln \gamma_{\mathrm{L}} = z_{\mathrm{L}}^2 f^{\gamma} + 2I(B_{\mathrm{ML}} + IC_{\mathrm{ML}}) + I^2(z_{\mathrm{L}}^2 B'_{\mathrm{MX}} + z_{\mathrm{L}} C_{\mathrm{MX}}) + I(2\theta_{\mathrm{LX}} + I\psi_{\mathrm{LMX}}) \tag{6a}$$

[$\mathrm{L} = \mathrm{H}_{i-1}\mathrm{L}^{i-1-z}$ or $\mathrm{H}_i\mathrm{L}^{i-z}$], and for neutral species

$$\ln \gamma_{\mathrm{N}} = 2\lambda I \tag{6b}$$

where

$$B_{\mathrm{c,a}} = \beta_{\mathrm{c,a}}{}^{(0)} + \frac{\beta_{\mathrm{c,a}}{}^{(1)}}{2I} f_1 \tag{6c}$$

$$B'_{\mathrm{c,a}} = \frac{\beta_{\mathrm{c,a}}{}^{(1)}}{2I^2} f_2 \tag{6d}$$

$$C_{\mathrm{c,a}} = \frac{C^{(\phi)}_{\mathrm{c,a}}}{2|z_{\mathrm{c}} z_{\mathrm{a}}|^{1/2}} \tag{6e}$$

$$f^{\gamma} = -A_{\phi}[I^{1/2}(1 + 1.2I^{1/2})^{-1} + 1.667 \ln(1 + 1.2I^{1/2})] \tag{6f}$$

$$f_1 = 1 - (1 + 2I^{1/2}) \exp(-2I^{1/2}) \tag{6g}$$

$$f_2 = -1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2}) \tag{6h}$$

with

$$A_{\phi} = 0.3912 + 6.636 \cdot 10^{-4}(T - 298) + 3.562 \cdot 10^{-6}(T - 298);\ T/\mathrm{K}$$

(c,a = generic cation and anion, respectively). $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters between two ions of opposite sign; θ represents an interaction parameter between two ions of the same sign (+ +, − − interactions); ψ is a triplet interaction parameter (+ − +, − + −); and λ is an interaction parameter of neutral species. At $I < 2$ mol·kg^{-1}, the $C^{(\phi)}$ term can be neglected. Literature values were used for the interaction parameters of HI, HCl, $(\mathrm{C_2H_5})_4\mathrm{NI}$, and $(\mathrm{CH_3})_4\mathrm{NCl}$. In particular, we used the following. For HI: $\beta^{(0)} = 0.2211$, $10^4 \cdot \partial\beta^{(0)}/\partial T = -0.23$, $\beta^{(1)} = 0.4907$, $10^4 \cdot \partial\beta^{(1)}/\partial T = 8.86$. For HCl: $\beta^{(0)} = 0.1775$, $10^4 \cdot \partial\beta^{(0)}/\partial T = -3.08$, $\beta^{(1)} = 0.2945$, $10^4 \cdot \partial\beta^{(1)}/\partial T = 1.42$. For $(\mathrm{C_2H_5})_4\mathrm{NI}$: $\beta^{(1)} = -0.571$, $10^4 \cdot \partial\beta^{(1)}/\partial T = 92.0$. For $(\mathrm{CH_3})_4\mathrm{NCl}$: $\beta^{(1)} = -0.029$, $10^4 \cdot \partial\beta^{(1)}/\partial T = 49.0$.[40] Concerning the θ and ψ parameters, they are not reported in the literature for $(\mathrm{C_2H_5})_4\mathrm{NI}$ and $(\mathrm{CH_3})_4\mathrm{NCl}$ media and so were considered equal to zero in our calculations.

Owing to the complexity of the Pitzer equations, we also tested a simplified version depending on three empirical parameters only

$$\ln K_i^{\mathrm{H}} = \ln {}^{\mathrm{T}}K_i^{\mathrm{H}} + 2zf^{\gamma} + 2P_1 I + P_2 f_1 + P_3 I^2 + z\beta_{\mathrm{MX}}{}^{(1)} f_2 \tag{7}$$

where P_1, P_2, and P_3 are empirical parameters; f_1 is defined by eq 6g, and

$$f_2 = I \exp(-2I^{1/2}) \tag{7a}$$

Analogous to Pitzer equations, at $I < 2$ mol·kg^{-1}, the P_3 term can be neglected.

Results

$(C_2H_5)_4NI$ Ionic Medium. Protonation constants of carboxylic acids in $(\mathrm{C_2H_5})_4\mathrm{NI}$ reported in Table 1 were used to calculate parameters of the SIT equations. Calculations were performed by considering the different eqs 4 to 5b.

In Tables 2 to 4, we report the $\Delta\epsilon_\infty$ and $\Delta\epsilon_0$ values (eq 4) together with the relative temperature gradients. Analysis of data reported in these tables allows the following general observations:

(a) Values of $\Delta\epsilon_0$ are significantly higher than those of $\Delta\epsilon_\infty$, the ratio $\Delta\epsilon_0/\Delta\epsilon_\infty$ generally being > 6.

Table 2. SIT Parameters (Equation 4) at T = 298 K, Together with Temperature Gradients, for Monocarboxylates in Et$_4$NI

carboxylate	$\Delta\epsilon_\infty$[a]	$\Delta\epsilon_0$	$10^4\cdot\partial\Delta\epsilon_0/\partial T$	σ[b]
Form	0.037 ± 0.007[c]	0.376 ± 0.005[c]	41 ± 1[c]	0.015
Ac	0.061 ± 0.005	0.483 ± 0.004	47 ± 1	0.006
Prop	0.131 ± 0.003	0.522 ± 0.003	39 ± 1	0.012
Sal	0.023 ± 0.015	0.332 ± 0.013	17 ± 4	0.015
Phen	0.297 ± 0.018	0.403 ± 0.015	15 ± 4	0.016
Benz	0.072 ± 0.009	0.506 ± 0.011	−	0.002

[a] The temperature gradient for $\Delta\epsilon_\infty$ was kept constant, $10^4\cdot\partial\Delta\epsilon_\infty/\partial T = -11$. [b] Standard deviation on the fit. [c] ± std. dev.

Table 3. SIT Parameters (Equation 4) at T = 298 K, Together with Temperature Gradients, for Dicarboxylates in Et$_4$NI

carboxylate	i[a]	$\Delta\epsilon_\infty$[b]	$\Delta\epsilon_0$	$10^4\cdot\partial\Delta\epsilon_0/\partial T$	σ[c]
Ox	1	0.022 ± 0.023[d]	1.054 ± 0.018[d]	51 ± 6[d]	0.042
	2	0.116 ± 0.039	0.453 ± 0.029	21 ± 9	
Mal	1	0.131 ± 0.010	1.051 ± 0.011	111 ± 3	0.020
	2	0.077 ± 0.013	0.528 ± 0.011	19 ± 5	
Succ	1	0.081 ± 0.007	0.900 ± 0.008	34 ± 3	0.015
	2	0.093 ± 0.008	0.554 ± 0.008	18 ± 5	
Tar	1	0.073 ± 0.004	0.851 ± 0.004	49 ± 1	0.012
	2	0.091 ± 0.003	0.513 ± 0.002	17 ± 1	
Ita	1	0.132 ± 0.005	0.932 ± 0.003	61 ± 1	0.009
	2	0.078 ± 0.009	0.528 ± 0.007	0.4 ± 3	
Oda	1	0.071 ± 0.004	0.847 ± 0.004	56 ± 1	0.005
	2	0.045 ± 0.003	0.441 ± 0.003	17 ± 1	
Tda	1	0.097 ± 0.017	0.745 ± 0.014	64 ± 4	0.022
	2	0.022 ± 0.018	0.581 ± 0.016	−2 ± 5	
Tdp	1	0.116 ± 0.012	0.887 ± 0.010	66 ± 3	0.016
	2	0.119 ± 0.010	0.592 ± 0.006	16 ± 3	
Pht	1	0.281 ± 0.011	1.155 ± 0.011	117 ± 3	0.026
	2	0.215 ± 0.010	0.464 ± 0.010	14 ± 2	
Mala	1	0.075 ± 0.005	0.868 ± 0.005	66 ± 2	0.009
	2	0.072 ± 0.005	0.491 ± 0.004	27 ± 1	
Male	1	0.259 ± 0.014	1.157 ± 0.013	31 ± 9	0.022
	2	0.096 ± 0.006	0.569 ± 0.007	14 ± 3	
Glu	1	0.103 ± 0.019	0.822 ± 0.017	−	0.006
	2	0.173 ± 0.019	0.500 ± 0.015	−	
Adip	1	0.059 ± 0.011	0.974 ± 0.009	−	0.015
	2	0.275 ± 0.023	0.365 ± 0.026	−	
Pim	1	0.095 ± 0.024	0.917 ± 0.021	−	0.012
	2	0.334 ± 0.038	0.355 ± 0.032	−	
Sub	1	0.311 ± 0.009	0.699 ± 0.005	−	0.005
	2	0.184 ± 0.016	0.574 ± 0.012	−	
Aze	1	0.185 ± 0.006	0.909 ± 0.006	−	0.007
	2	0.145 ± 0.008	0.648 ± 0.003	−	
Seb	1	0.177 ± 0.016	0.998 ± 0.017	−	0.016
	2	0.212 ± 0.025	0.336 ± 0.021	−	
Toda	1	0.102 ± 0.011	0.834 ± 0.013	−	0.009
	2	0.119 ± 0.017	0.529 ± 0.021	−	

[a] Index i referes to eq 1. [b] The temperature gradient for $\Delta\epsilon_\infty$ was kept constant, $10^4\cdot\partial\Delta\epsilon_\infty/\partial T = -23$ and -11 for i = 1 and 2, respectively. [c] Standard deviation on the fit. [d] ± std. dev.

(b) Both $\Delta\epsilon_\infty$ and $\Delta\epsilon_0$ increase regularly with increasing z^*; for example, for $\Delta\epsilon_0$ we have, by considering all the protonation data with $2 \leq z^* \leq 8$, $\Delta\epsilon_0 = 0.23\ (\pm\ 0.02)z^*$.

(c) Temperature gradients are quite small, generally < 1 %, with respect to the values of the relative parameter.

Observation (a) clearly indicates that the classic SIT approach (one parameter) cannot be applied to the system under investigation because for ϵ = true constant we must have $\Delta\epsilon_\infty = \Delta\epsilon_0$ [where $\Delta\epsilon$ is defined in eq 5]. This is confirmed also by higher values of the standard deviation in the fit obtained by using the classic SIT approach with respect to those reported in Tables 2 to 4: for example, we obtain σ = 0.047, 0.028, and 0.036 for malonate, tricarballylate, and butanetetracarboxylate, respectively, when considering ϵ as a true constant. Figure 1 shows the comparison between experimental and calculated values of the first protonation constant of malonic acid, by using a one-parameter or two-parameter SIT equation. As a consequence of observation (b), we must have constant $\Delta\epsilon$ values for each z^*: mean values are reported in Table 5. Standard deviations of $\Delta\epsilon$ parameters reported in Table 5 are < 20 % for $\Delta\epsilon_\infty$ and < 0.5 % for $\Delta\epsilon_0$. A further step to obtain general

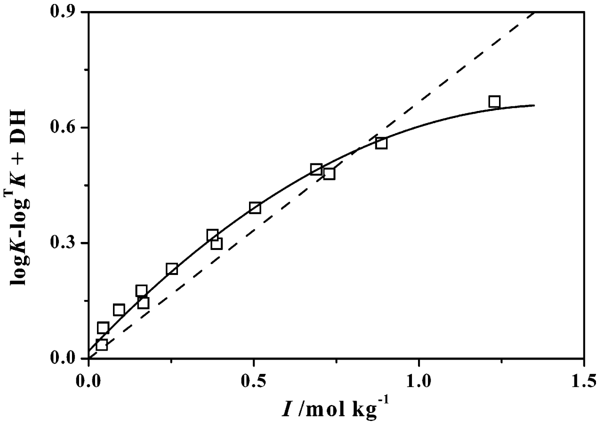

Figure 1. Comparison between experimental (□) and calculated values of the first protonation constant of malonic acid in Et$_4$NI, by using the one-parameter (dash line, eq 4) or two-parameter (dot line, eqs 4 and 5a) SIT equation {DH = Debye−Hückel term = $-4[0.51\sqrt{I}/(1 + 1.5\sqrt{I})]$}.

Table 4. SIT Parameters (Equation 4) at T = 298 K, Together with Temperature Gradients, for Tri-, Tetra-, and Hexa-carboxylates, in Et$_4$NI

carboxylate	i[a]	$\Delta\epsilon_\infty$[b]	$\Delta\epsilon_0$	$10^4\cdot\partial\Delta\epsilon_0/\partial T$	σ[c]
Tca	1	0.421 ± 0.007[d]	1.179 ± 0.005[d]	81 ± 1[d]	0.005
	2	0.305 ± 0.004	0.791 ± 0.004	55 ± 1	
	3	0.178 ± 0.006	0.395 ± 0.004	54 ± 1	
Cit	1	0.166 ± 0.004	1.382 ± 0.003	33 ± 1	0.006
	2	0.070 ± 0.002	0.859 ± 0.002	12 ± 1	
	3	0.062 ± 0.006	0.492 ± 0.004	−11 ± 2	
123btca	1	0.130 ± 0.006	1.307 ± 0.0055	63 ± 2	0.006
	2	0.1109 ± 0.006	0.928 ± 0.0055	37 ± 1	
	3	0.151 ± 0.005	0.653 ± 0.0046	20 ± 1	
124btca	1	0.175 ± 0.007	1.381 ± 0.0074	−	0.002
	2	0.008 ± 0.005	0.745 ± 0.0053	−	
	3	0.118 ± 0.005	0.576 ± 0.0049	−	
Btc	1	0.614 ± 0.019	1.593 ± 0.015	27 ± 6	0.001
	2	0.429 ± 0.013	1.157 ± 0.010	38 ± 5	
	3	0.333 ± 0.011	0.842 ± 0.009	23 ± 3	
	4	0.239 ± 0.010	0.419 ± 0.007	51 ± 3	
Pymel	1	0.272 ± 0.041	1.537 ± 0.041	164 ± 11	0.004
	2	0.178 ± 0.029	1.117 ± 0.031	108 ± 8	
	3	0.077 ± 0.015	0.777 ± 0.015	41 ± 3	
	4	0.140 ± 0.020	0.656 ± 0.020	24 ± 6	
Mlt	1	1.001 ± 0.028	1.969 ± 0.021	−	0.009
	2	1.069 ± 0.033	2.002 ± 0.027	−	
	3	0.949 ± 0.018	1.836 ± 0.008	−	
	4	0.926 ± 0.016	1.624 ± 0.012	−	
	5	0.864 ± 0.036	1.581 ± 0.028	−	
	6	0.977 ± 0.047	1.032 ± 0.035	−	

[a] Index i referes to eq 1. [b] The temperature gradient for $\Delta\epsilon_\infty$ was kept constant, $10^4\cdot\partial\Delta\epsilon_\infty/\partial T = -40, -36, -23$, and -11 for i = 1, 2, 3, and 4, respectively. [c] Standard deviation on the fit. [d] ± std. dev.

Table 5. Mean Values of $\Delta\epsilon_\infty$ and $\Delta\epsilon_0$, in Et$_4$NI and at T = 298 K

z^*	$\Delta\epsilon_\infty$	$\Delta\epsilon_0$	σ[a]
2	0.105 ± 0.013[b]	0.508 ± 0.012[b]	0.04
4	0.107 ± 0.022	0.952 ± 0.020	0.06
6	0.181 ± 0.031	1.282 ± 0.029	0.04
8	0.206 ± 0.035	1.712 ± 0.050	0.05

[a] Standard deviation on the fit. [b] ± std. dev.

Table 6. Mean Values of Interaction Coefficients for the Dependence on Ionic Strength, Together with Temperature Gradients, for Carboxylate Ligands in Et_4NI and in Me_4NCl, Both in Molal and Molar Concentration Scales

		Et_4NI	Me_4NCl		Et_4NI	Me_4NCl
eqs 4,5a	$\bar{\epsilon}_\infty$	-0.019 ± 0.003^a	-0.006 ± 0.001^a	$10^4 \cdot \partial\bar{\epsilon}_\infty/\partial T$	1.2 ± 0.4^a	-5.6 ± 0.5^a
	$\bar{\epsilon}_0$	0.242 ± 0.002	0.164 ± 0.002	$10^4 \cdot \partial\bar{\epsilon}_0/\partial T$	1.2 ± 0.2	7.0 ± 0.6
	$\bar{k}_m{}^{(0)}$	-0.020 ± 0.001	0.006 ± 0.001	$10^4 \cdot \partial\bar{k}_m{}^{(0)}/\partial T$	5.0 ± 0.5	1.6 ± 0.2
	σ^b	0.069	0.067	σ	0.055	0.028
eqs 4,5a	$\bar{\epsilon}^{(0)}$	0.221 ± 0.001	0.113 ± 0.001	$10^4 \cdot \partial\bar{\epsilon}^{(0)}/\partial T$	0	2.7 ± 0.7
	$\bar{\epsilon}^{(1)}$	-0.158 ± 0.002	-0.055 ± 0.001	$10^4 \cdot \partial\bar{\epsilon}^{(1)}/\partial T$	2.6 ± 0.3	-3.6 ± 0.4
	$\bar{k}_m{}^{(0)}$	-0.020 ± 0.001	0.005 ± 0.001	$10^4 \cdot \partial\bar{k}_m{}^{(0)}/\partial T$	4.9 ± 0.2	1.7 ± 0.3
	σ^b	0.068	0.072	σ	0.054	0.034
eqs 6 to 6h	$\bar{\beta}^{(0)}$	-0.034 ± 0.003	0.015 ± 0.001	$10^4 \cdot \partial\bar{\beta}^{(0)}/\partial T$	3.7 ± 0.7	-1.9 ± 0.2
	$\bar{\beta}^{(1)}$	1.047 ± 0.008	0.616 ± 0.004	$10^4 \cdot \partial\bar{\beta}^{(1)}/\partial T$	-18.3 ± 1.7	2.3 ± 1.3
	$\bar{\lambda}$	-0.025 ± 0.001	0.010 ± 0.001	$10^4 \cdot \partial\bar{\lambda}/\partial T$	3.9 ± 0.2	1.1 ± 0.2
	σ^b	0.069	0.071	σ	0.055	0.030
eqs 7 to 7a	$\bar{P}_1$	0.029 ± 0.003	0.052 ± 0.001	$10^4 \cdot \partial\bar{P}_1/\partial T$	2.1 ± 0.2	1.9 ± 0.3
	$\bar{P}_2$	0.917 ± 0.007	0.527 ± 0.002	$10^4 \cdot \partial\bar{P}_2/\partial T$	-11.1 ± 2.8	-9.0 ± 1.4
	σ^b	0.075	0.082	σ	0.057	0.039
eqs 9 to 9a	$\bar{b}_\infty$	-0.025 ± 0.004	-0.007 ± 0.001	$10^4 \cdot \partial\bar{b}_\infty/\partial T$	-1.3 ± 1.4	-7.5 ± 0.8
	$\bar{b}_0$	0.198 ± 0.002	0.143 ± 0.002	$10^4 \cdot \partial\bar{b}_0/\partial T$	-3.3 ± 1.1	7.4 ± 0.8
	$\bar{k}_c{}^{(0)}$	0.013 ± 0.001	0.014 ± 0.001	$10^4 \cdot \partial\bar{k}_c{}^{(0)}/\partial T$	29.6 ± 0.8	3.4 ± 0.7
	σ^b	0.074			0.059	
eqs 9,9b	$\bar{b}^{(0)}$	0.184 ± 0.002	0.106 ± 0.002	$10^4 \cdot \partial\bar{b}^{(0)}/\partial T$	3.3 ± 0.9	5.2 ± 0.7
	$\bar{b}^{(1)}$	-0.145 ± 0.004	-0.057 ± 0.001	$10^4 \cdot \partial\bar{b}^{(1)}/\partial T$	-2.7 ± 1.7	-6.2 ± 0.8
	$\bar{k}_c{}^{(0)}$	0.014 ± 0.001	0.014 ± 0.001	$10^4 \partial\bar{k}_c{}^{(0)}/\partial T$	5.5 ± 0.5	2.3 ± 1.0
	σ^b	0.073			0.059	

[a] ± std. dev. [b] Standard deviation on the fit.

predictive equations is to consider the protonation data altogether at different z^* values; namely

$$\Delta\epsilon = az^* \qquad (8)$$

Preliminary trials showed that values for $z^* = 2$ deviate significantly from the overall fit, and therefore, we calculated separately a of eq 8. Results of this are

$$z^* = 2;\ \Delta\epsilon_\infty,\ a = 0.021 \pm 0.002;\ \Delta\epsilon_0,\ a = 0.233 \pm 0.001;\ \sigma = 0.08$$

$$z^* = 4, 6, 8, 12;\ \Delta\epsilon_\infty,\ a = 0.050 \pm 0.004;\ \Delta\epsilon_0,\ a = 0.273 \pm 0.003;\ \sigma = 0.026$$

How can this difference be explained? Let us consider the expression for $\Delta\epsilon$ ($\Delta\epsilon_\infty$ or $\Delta\epsilon_0$) for $z^* = 2$ and $z^* > 2$. For $z^* = 2$, we have

$$\Delta\epsilon = [\epsilon(H^+, X^-) + \epsilon(M^{z+}, H_{n-1}L^-) - k_m]$$

For $z^* > 2$, we may write

$$\Delta\epsilon = [\epsilon(H^+, X^-) + \epsilon(M^{z+}, H_{i-1}L^{i-1-z}) - \epsilon(M^{z+}, H_iL^{i-z})]$$

On the basis of previous observations, according to which $\Delta\epsilon = az^*$, we may write for the single specific interaction coefficient

$$\epsilon(M^+, H_iL^{(i-z)}) = \bar{\epsilon}z^2$$

$$\epsilon(M^+, H_{i-1}L^{(i-1-z)}) = \bar{\epsilon}(z-1)^2$$

By performing suitable calculations, we found that $\bar{\epsilon}$ is fairly constant for all the (poly)carboxylates considered here, and in addition, we observed a better fit when k_m is expressed as a function of n (number of carboxylic groups), namely

$$k_m = \bar{k}_m \cdot n$$

Moreover, calculations showed that ϵ parameters can be expressed by using eq 5a or 5b.

The same behavior was found for the Pitzer and simplified Pitzer parameters, for which we can write

$$P(M^+, H_iL^{(i-z)}) = \bar{P}z^2$$

$$P(M^+, H_{i-1}L^{(i-1-z)}) = \bar{P}(z-1)^2$$

$$\lambda = \bar{\lambda} \cdot n$$

with $P = \beta^{(0)}$ or $\beta^{(1)}$ (eqs 6 to 6h) or P_1 or P_2 (eqs 7 to 7a). Mean values of parameters obtained by using different models are reported in Table 6.

In the same table, we report the mean temperature gradients for the different models, calculated from protonation constants at different temperatures (278 K ≤ T ≤ 328 K).

$(CH_3)_4NCl$ Ionic Medium. Table 1 shows carboxylic acids in $(CH_3)_4NCl$ considered in this paper. Protonation constants are relative to different ionic strengths (0 $mol \cdot kg^{-1} \le I \le 3.9$ $mol \cdot kg^{-1}$) and temperatures (278 K ≤ T ≤ 328 K). For these data, we followed the same procedure used for $(C_2H_5)_4NI$. Previously, we calculated $\Delta\epsilon_\infty$ and $\Delta\epsilon_0$ values (eq 4) for each carboxylic acid. Results are reported in Table 7. Subsequent calculations considering the protonation data altogether showed that, for this ionic medium too, the values of ϵ_∞, ϵ_0, $\epsilon^{(0)}$, $\epsilon^{(1)}$, $\beta^{(0)}$, $\beta^{(1)}$, P_1, and P_2 parameters were fairly constant for all the polycarboxylates. Their mean values are reported in Table 6. Temperature gradients from data at $T \neq 298$ K are reported in the same table.

Parameters for the Dependence on Ionic Strength Using the Molar Concentration Scale. Interaction coefficients in the molar scale were calculated analogously to the molal scale. In this case, eq 3 can be written as

$$\log y_j = z_j^2 \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k b_{j,k}c_k \qquad (9)$$

Table 7. SIT Parameters (Equation 4) at $T = 298$ K, Together with Temperature Gradients, for Mono-hexacarboxylates in Me_4NCl

carboxylate	i	$\Delta\epsilon_\infty$	$10^4 \cdot \partial\Delta\epsilon_\infty/\partial T$	$\Delta\epsilon_0$	$10^4 \cdot \partial\Delta\epsilon_0/\partial T$	σ^a
Ac	1	0.124 ± 0.001^b	-	0.189 ± 0.002^b	−	0.003
Mal	1	0.102 ± 0.010	−	0.598 ± 0.020	−	0.020
	2	0.072 ± 0.008	−	0.325 ± 0.018	−	
Succ	1	0.115 ± 0.003	−	0.503 ± 0.005	−	0.008
	2	0.127 ± 0.001	−	0.207 ± 0.003	−	
Tar	1	0.118 ± 0.002	2.3 ± 1.4	0.468 ± 0.004	-8 ± 3	0.020
	2	0.098 ± 0.002	2.5 ± 2.0	0.274 ± 0.006	-24 ± 5	
Mala	1	0.109 ± 0.002	-0.5 ± 1.7	0.535 ± 0.005	1.1 ± 3.8	0.015
	2	0.113 ± 0.002	-4.4 ± 1.6	0.263 ± 0.005	-7 ± 4	
Pht	1	0.150 ± 0.002	−	0.470 ± 0.005	−	0.043
	2	0.111 ± 0.004	−	0.222 ± 0.008	−	
Adip	1	0.062 ± 0.002	−	0.658 ± 0.006	−	0.008
	2	0.106 ± 0.003	−	0.281 ± 0.007	−	
Pim	1	0.085 ± 0.006	−	0.583 ± 0.014	−	0.057
	2	0.059 ± 0.015	−	1.120 ± 0.004	−	
Sub	1	0.113 ± 0.003	−	0.436 ± 0.004	−	0.017
	2	0.126 ± 0.003	−	0.241 ± 0.008	−	
Aze	1	0.121 ± 0.002	−	0.477 ± 0.004	−	0.008
	2	0.129 ± 0.001	−	0.231 ± 0.002	−	
Seb	1	0.026 ± 0.016	−	0.736 ± 0.043	−	0.043
	2	0.165 ± 0.007	−	-0.095 ± 0.015	−	
Tca	1	0.113 ± 0.002	-61 ± 20	0.845 ± 0.006	65 ± 16	0.014
	2	0.105 ± 0.002	-50 ± 17	0.587 ± 0.004	35 ± 13	
	3	0.108 ± 0.002	-30 ± 15	0.252 ± 0.005	14 ± 15	
Mtca	1	0.193 ± 0.002	−	0.822 ± 0.007	−	0.020
	2	0.123 ± 0.006	−	0.487 ± 0.012	−	
	3	0.109 ± 0.006	−	0.159 ± 0.013	−	
Cit	1	0.091 ± 0.011	−	0.904 ± 0.025	−	0.018
	2	0.078 ± 0.011	−	0.523 ± 0.024	−	
	3	0.106 ± 0.010	−	0.226 ± 0.024	−	
Btc	1	0.087 ± 0.007	-72 ± 29	1.216 ± 0.014	93 ± 25	0.017
	2	0.101 ± 0.005	-57 ± 23	0.811 ± 0.010	76 ± 21	
	3	0.102 ± 0.004	-50 ± 20	0.592 ± 0.009	44 ± 18	
	4	0.123 ± 0.004	-28 ± 19	0.261 ± 0.008	15 ± 17	
Mlt	1	0.020 ± 0.037	−	2.046 ± 0.079	−	0.080
	2	-0.030 ± 0.032	−	1.976 ± 0.076	−	
	3	0.087 ± 0.040	−	1.472 ± 0.086	−	
	4	0.082 ± 0.021	−	1.225 ± 0.040	−	
	5	0.050 ± 0.025	−	0.963 ± 0.049	−	
	6	-0.041 ± 0.040	−	0.871 ± 0.098	−	

[a] Standard deviation on the fit. [b] ± std. dev.

where the molar interaction coefficient b can be expressed as

$$b = b_\infty + \frac{b_0 - b_\infty}{I + 1} \qquad (9a)$$

or as

$$b = b^{(0)} + b^{(1)} \ln(1 + I) \qquad (9b)$$

Before calculating b for carboxylate ligands, it was necessary to determine the interaction coefficient of HI and HCl in the same concentration scale. By using literature activity coefficients, converted in the molar scale by considering the solution density, we calculated the following values for HI

$$b_\infty = (0.223 \pm 0.002) - (15 \pm 2) \cdot 10^{-4}(T - 298)$$

$$b_0 = (0.260 \pm 0.001) + (59 \pm 4) \cdot 10^{-4}(T - 298)$$

($\sigma = 0.002$) by using eq 9a or

$$b^{(0)} = (0.256 \pm 0.001) + (26 \pm 1) \cdot 10^{-4}(T - 298)$$

$$b^{(1)} = (-0.022 \pm 0.002) - (26 \pm 2) \cdot 1^{-4}(T - 298)$$

($\sigma = 0.002$) by using eq 9b. For HCl we obtained

$$b_\infty = (0.139 \pm 0.001) - (2.9 \pm 0.2) \cdot 10^{-4}(T - 298)$$

$$b_0 = (0.100 \pm 0.001) - (4.2 \pm 0.6) \cdot 10^{-4}(T - 298)$$

($\sigma = 0.002$) by using eq 9a or

$$b^{(0)} = (0.107 \pm 0.001) - (8.5 \pm 0.3) \cdot 10^{-4}(T - 298)$$

$$b^{(1)} = (0.018 \pm 0.001) + (2.9 \pm 0.3) \cdot 10^{-4}(T - 298)$$

($\sigma = 0.002$) by using eq 9b. Therefore, mean values of interaction parameters for carboxylates were calculated by using molar protonation constants. Results, both in $(C_2H_5)_4NI$ and in $(CH_3)_4NCl$ medium salts, are reported in Table 6.

Polyelectrolytes. To give a complete picture on ionic strength dependence of carboxylate ligands, we tried to determine mean values of ϵ parameters ($\bar{\epsilon}$) for some synthetic[53−56] and natural polyelectrolytes (ref 57 and unpublished data from this laboratory), in $(C_2H_5)_4NI$: the list is reported in Table 8, together with their effective charge. Protonation constants for these systems were calculated as for diprotic acids (by considering the effective charge): it was demonstrated that this procedure allows the experimental data (unpublished data from this laboratory) to be fitted quite well. Calculations were performed

Table 8. Polyelectrolytes Considered in This Paper Together with Effective Charge

polyelectrolytes	*z*	ref
polyacrylate 2 kDa	3.0	53
polyacrylate 5.1 kDa	4.5	55
polyacrylate 20 kDa	4.6	55
polymethacrylate 5.4 kDa	4.4	54
polymethacrylate 4 kDa	3.7	54
polyacrylyc co-maleic 3 kDa	2.5	56
polyacrylyc co-maleic 70 kDa	2.5	56
alginate	3.5	57
humic acid (Fluka)	2.0	[a]
humic acid (synthetic) (a)	3.0	[a]
humic acid (synthetic) (b)	3.0	[a]
humic acid (peat)	2.0	[a]
fumic acid (standard, soil)	2.5	[a]
humic acid (Ficuzza)	2.0	[a]
humic acid (aquatic)	2.1	[a]
humic acid (S. Cataldo)	2.1	[a]
fulvic acid (Ficuzza)	2.9	[a]
humic acid (Piano Zucchi)	2.0	[a]
humic acid (Cefalù)	2.0	[a]
fumic acid (Swannee River)	2.6	[a]

[a] Unpublished data from this laboratory.

by considering the $\bar{k}_m$ values obtained for carboxylic acids ($\bar{k}_m = -0.0198$). Following the same procedure used for carboxylic acid, we obtain

$$\bar{\epsilon}_\infty = -0.007 \pm 0.012 \quad (-0.019 \pm 0.003)$$

$$\bar{\epsilon}_0 = 0.199 \pm 0.011 \quad (0.242 \pm 0.002)$$

by using eq 5a or

$$\bar{\epsilon}^{(0)} = 0.187 \pm 0.008 \quad (0.221 \pm 0.001)$$

$$\bar{\epsilon}^{(1)} = -0.132 \pm 0.013 \quad (-0.157 \pm 0.002)$$

by using eq 5b. The differences in $\bar{\epsilon}$ values with respect to low molecular ligands (reported in parentheses) are quite low, also taking into account the higher uncertainties for high molecular weight polyelectrolytes.

Correlations between Different Parameters. In previous papers concerning the determination of SIT parameters,[2,3] we have provided evidence of the possibility to determine correlations between interaction coefficients from different models and, in particular, between SIT and Pitzer parameters. Correlations have been determined for 1:1 and 1:2 salts with the same anion (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-), 1:2 salts with the same cation (Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}), 1:2 electrolytes, and 1:1 and 1:2 salts together. In this paper, we have verified the possibility of extending this kind of correlation to another class of ligands such as polycarboxylates. Also in this case, some very interesting correlations were found between both ϵ parameters of eq 5a and 5b and SIT and Pitzer parameters. In the $(C_2H_5)_4NI$ ionic medium, these correlations are

$$\epsilon_\infty = -0.085 \cdot \epsilon^{(0)}$$

$$\epsilon_0 = -1.537 \cdot \epsilon^{(1)}$$

$$\epsilon_\infty = 0.555 \cdot \beta^{(0)}$$

$$\epsilon_0 = 0.231 \cdot \beta^{(1)}$$

$$\partial\epsilon_\infty/\partial T = 0.319 \cdot \partial\beta^{(0)}/\partial T$$

$$\partial\epsilon_0/\partial T = -0.066 \cdot \partial\beta^{(1)}/\partial T$$

In $(CH_3)_4NCl$ we have

$$\epsilon_\infty = -0.056 \cdot \epsilon^{(0)}$$

$$\epsilon_0 = -2.996 \cdot \epsilon^{(1)}$$

$$\epsilon_\infty = -0.412 \cdot \beta^{(0)}$$

$$\epsilon_0 = 0.267 \cdot \beta^{(1)}$$

$$\partial\epsilon_\infty/\partial T = -2.04 \cdot \partial\epsilon^{(0)}/\partial T$$

$$\partial\epsilon_0/\partial T = -1.95 \cdot \partial\epsilon^{(1)}/\partial T$$

$$\partial\epsilon_\infty/\partial T = 2.99 \cdot \partial\beta^{(0)}/\partial T$$

$$\partial\epsilon_0/\partial T = 2.97 \cdot \partial\beta^{(1)}/\partial T$$

Fits of correlation equations were always very good (standard deviations in the fit range from $\sigma < 0.0001$ to $\sigma = 0.0002$).

Final Remarks

The main results of the analysis of protonation data in tetraalkylammonium aqueous solution at different ionic strengths can be summarized as follows.

1. Specific interaction coefficients of polycarboxylate anions in $(C_2H_5)_4NI_{aq}$ and $(CH_3)_4NCl_{aq}$ can be calculated using protonation constants at different ionic strengths with very good fitting results, if considering for these coefficients the dependence on ionic strength given by eqs 5a or 5b. The use of the original one-parameter equation gives significantly worse results.
2. The values of ϵ strictly depend on polyanion charge, and a mean value $\bar{\epsilon}$ was calculated which shows excellent predictive power.
3. Pitzer parameters were also calculated with comparable fitting results (with respect to the SIT method). Also, these parameters depend on charge, and mean values were obtained. A comparison of SIT and Pitzer models was recently reported.[44]
4. There is a strong correlation between SIT and Pitzer parameters which allows the two models to be used with the same results.

Literature Cited

(1) Bretti, C.; Foti, C.; Sammartano, S. Calculation of SIT parameters. Part I. A new approach in the use of SIT in determining the dependence on ionic strength of activity coefficients. Application to some chloride salts of interest in the speciation of natural fluids. *Chem. Spec. Bioavail.* **2004**, *16* (3), 105−110.

(2) Bretti, C.; Foti, C.; Porcino, N.; Sammartano, S. SIT parameters for 1:1 electrolytes and correlation with Pitzer coefficients (Part II). *J. Solution Chem.* **2006**, *35* (10), 1401−1415.

(3) Crea, F.; Foti, C.; De Stefano, C.; Sammartano, S. SIT parameters for 1:2 electrolytes and correlation with Pitzer coefficients (Part III). *Ann. Chim. (Rome)* **2007**, *97*, 85−95.

(4) Sillén, L. G.; Martell, A. E. *Stability constants of metal−ion complexes*, Special Publication No. 17; The Chemical Society: London, 1964.

(5) Sillén, L. G.; Martell, A. E. *Stability Constants*, Supplement 1, Special Publication No. 25; The Chemical Society: London, 1975.

(6) Smith, R. M.; Martel, A. E. *Critical Stability Constants*, second supplement; Plenum Press: New York, 1989; Vol. 6.

(7) Christensen, J. J.; Hansen, L. D.; Izatt, R. M. *Handbook of proton ionization heats*; Wiley: New York, 1976.

(8) Serjeant, E. P.; Dempsey, B. *Ionisation Constants of Organic Acids in Aqueous Solution*; Pergamon: Oxford 1979.

(9) Pettit, L.; Powell, K. J. *The IUPAC Stability Constants Database*; Academic Software, 2001.

(10) Martell, A. E.; Smith, R. M.; Motekaitis R. J. *NIST. Critically Selected Stability Constants of Metal Complexes*. PC-based Database, National Institute of Standard and Technology: Gaithersburg, MD 20899, 2004.

(11) May, P. M.; Murray, K. Database of Chemical Reactions Designed To Achieve Thermodynamic Consistency Automatically. *J. Chem. Eng. Data* **2001**, *46*, 1035−1040.

(12) Perrin, D. D. *Stability Constants of Metal Ions Complexes*, *Part B: Organic Ligands*, Chemical Data Series No. 22; IUPAC, 1979.

(13) Daniele, P. G.; Rigano, C.; Sammartano, S. The Formation of Proton and Alkali-Metal Complexes with Ligands of Biological Interest in Aqueous Solution. Thermodynamics of H^+, Na^+ and K^+ -Oxalate Complexes. *Thermochim. Acta* **1981**, *46*, 103−116.

(14) Daniele, P. G.; Rigano, C.; Sammartano, S. Ionic Strength Dependence of Formation Constants-I Protonation Constants of Organic and Inorganic Acids. *Talanta* **1983**, *30*, 81−87.

(15) Capone, S.; De Robertis, A.; De Stefano, C.; Sammartano, S.; Scarcella, R.; Rigano, C. Ionic Strength Dependence of Formation Constants. Part 7. Protonation Constants of Low Molecular Weight Carboxylic Acids at 10, 25 and 45 °C. *Thermochim. Acta* **1985**, *86*, 273−280.

(16) Casale, A.; De Robertis, A.; Sammartano, S. Complexing Ability of Pesticides and Related Compounds. Formation and Stability in Aqueous Solution of H^+, Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} Phenoxyacetate Complexes at Different Temperatures and Ionic Strengths. *Thermochim. Acta* **1985**, *95*, 15−25.

(17) De Robertis, A.; De Stefano, C.; Rigano, C.; Sammartano, S.; Scarcella, R. Studies on Acetate Complexes. Part 1. Formation of Proton, Alkali-metal, and Alkaline-earth-metal Ion Complexes at Several Temperatures and Ionic Strengths. *J. Chem. Res.* **1985**, (S) *42*, (M) 629−650.

(18) Daniele, P. G.; De Robertis, A.; De Stefano, C.; Sammartano, S. Studies on Polyfunctional O-Ligands. Formation and Stability of Alkali Metal-1,2,4,5-Benzenetetracarboxylate Complexes at Different Ionic Strengths in Aqueous Solution. *Ann. Chim. (Rome*) **1990**, *80*, 177−186.

(19) De Robertis, A.; De Stefano, C.; Rigano, C.; Sammartano, S. Thermodynamic Parameters for the Protonation of Carboxylic Acids in Aqueous Tetraethylammonium Iodide Solutions. *J. Solution Chem.* **1990**, *19*, 569−587.

(20) De Robertis, A.; De Stefano, C.; Rigano, C.; Sammartano, S. Salt Effects on the Protonation of Oxalate in Aqueous NaCl, KCl and Tetraethylammonium Iodide Solution at $5 \leq T \leq 50$ °C e $0 \leq I \leq 1$ mol dm^{-3}. *Thermochim. Acta* **1992**, *202*, 133−149.

(21) De Robertis, A.; Foti, C.; Gianguzza, A. Studies on Polyfunctional O-ligands. Alkali and Alkaline Earth Metal Complexes of Butanetetracarboxylate in Aqueous Solution. *Ann. Chim. (Rome*) **1993**, *83*, 485−497.

(22) De Stefano, C.; Foti, C.; Gianguzza, A. Salt Effects on the Protonation and on Alkali and Alkaline Earth Metal Complex Formation of 1,2,3-Propanetricarboxylate in Aqueous Solution. *Talanta* **1994**, *41* (10), 1715−1722.

(23) De Robertis, A.; De Stefano, C.; Foti, C. Studies on Polyfunctional O-Ligands. Protonation in Different Ionic Media and Alkali and Alkaline Earth Metal Complex Formation of Benzenehexacarboxylate. *Ann. Chim. (Rome)* **1996**, *86*, 155−166.

(24) De Stefano, C.; Gianguzza, A.; Piazzese, D. Complexes of Azelaic and Diethylenetrioxydiacetic Acids with Na^+, Mg^{2+} and Ca^{2+} in NaCl Aqueous Solutions, at 25°C. *J. Chem. Eng. Data* **2000**, *45* (1), 15−19.

(25) Crea, F.; De Robertis, A.; Sammartano, S. Medium and alkyl chain effects on the protonation of dicarboxylates in $NaCl_{(aq)}$ and $Et_4NI_{(aq)}$ at 25 °C. *J. Solution Chem.* **2004**, *33*, 497−526.

(26) Bretti, C.; Crea, F.; Foti, C.; Sammartano, S. Solubility and activity coefficients of o-phthalic acid and cystine in $NaCl_{aq}$, $(CH_3)_4NCl_{aq}$ and $(C_2H_5)_4NI_{aq}$ at different ionic strengths, at $t = 25$ °C. *J. Chem. Eng. Data* **2005**, *50*, 1761−1767.

(27) Bretti, C.; Crea, F.; Foti, C.; Sammartano, S. Solubility and Activity Coefficients of Acidic and Basic Nonelectrolytes in Aqueous Salt Solutions. 2. Solubility and Activity Coefficients of Suberic, Azelaic and Sebacic Acids in $NaCl_{(aq)}$, $(CH_3)_4NCl_{(aq)}$ and $(C_2H_5)_4NI_{(aq)}$ at different ionic strengths and at $t = 25$ °C. *J. Chem. Eng. Data* **2006**, *51* (5), 1660−1667.

(28) Foti, C.; Gianguzza, A.; Sammartano, S. A Comparison of Equations for Fitting Protonation Constants of Carboxylic Acids in Aqueous Tetramethylammonium Chloride at Various Ionic Strengths. *J. Solution Chem.* **1997**, *26* (6), 631−648.

(29) 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.

(30) Crea, F.; De Stefano, C.; Gianguzza, A.; Piazzese, D.; Sammartano, S. Protonation of Carbonate in Aqueous Tetraalkylammonium Salts at 25 °C. *Talanta* **2006**, *68* (4), 1102−1112.

(31) Brönsted, J. N. Studies on solubility. IV. Principle of the specific interaction of ions. *J. Am. Chem. Soc.* **1922**, *44*, 877−898.

(32) Scatchard, G. Concentrated solutions of strong electrolytes. *Chem. Rev.* **1936**, *19*, 309−327.

(33) Guggenheim, E. A.; Turgeon, J. C. Specific interaction of ions. *Trans. Faraday Soc.* **1955**, *51*, 747−761.

(34) Ciavatta, L. The specific interaction theory in the evaluating ionic equilibria. *Ann. Chim. (Rome*) **1980**, *70*, 551−562.

(35) Ciavatta, L. The specific interaction theory in equilibrium analysis. Some empirical rules for estimate interaction coefficients of metal ion complexes. *Ann. Chim. (Rome*) **1990**, *80*, 255−263.

(36) Östhols, E.; Wanner, H. *The NEA thermochemical data base project*; AEN-NEA: Issy-les-Moulineaux, France, 2000.

(37) Grenthe, I.; Puigdomenech, I. *Modelling in aquatic chemistry*; OECD-NEA: Paris, France, 1997.

(38) Foti, C.; Sammartano, S.; Signorino, G. The Dependence on Ionic Strength of Protonation Constants of Carboxylic Acids in Aqueous Tetraethylammonium Iodide Solution, at Different Temperatures. *Fluid Phase Equilib.* **1998**, *149*, 91−101.

(39) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations *J. Phys. Chem.* **1973**, *77* (2), 268−277.

(40) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, Florida, 1991.

(41) Millero, F. J. The estimation of the pK_{HA} of acids in seawater using the Pitzer equations. *Geochim. Cosmochim. Acta* **1983**, *47*, 2121−2129.

(42) Millero, F. J.; Hawke, D. J. Ionic interactions of divalent metals in natural waters. *Mar. Chem.* **1992**, *40*, 19−48.

(43) Pierrot, D.; Millero, F. J.; Roy, L. N.; Roy, R. N.; Doneski, A.; Niederschmidt, J. The activity coefficients of HCl in HCl-Na_2SO_4 solutions from 0 to 50 °C and ionic strengths up to 6 molal. *J. Solution Chem.* **1997**, *26*, 31−45.

(44) Grenthe, I. Equilibrium analysis, the ionic medium method and activity factors. In *Chemistry of Marine Water and Sediments*; Gianguzza, A., Pelizzetti, E., Sammartano, S., Eds.; Springer-Verlag: Berlin, Heidelberg, 2002; pp 263−282.

(45) Barriada, J. L.; Brandariz, I.; Sastre de Vicente, M. E. Acid−base equilibria of monocarboxylic acids in various saline media: analysis of data using Pitzer equations. *J. Chem. Eng. Data* **2000**, *45*, 1173−1178.

(46) Sharma, V. K.; Moulin, A.; Millero, F. J.; De Stefano, C. Dissociation constants of protonated cysteine species in seawater media. *Mar. Chem.* **2006**, *99*, 52−61.

(47) Rey-Castro, C.; Castro-Varela, R.; Herrero, R.; Sastre de Vicente, M. E. Acid−base equilibria of phthalic acid in saline media: ion association from Pitzer equations. *Talanta* **2003**, *60* (1), 93−101.

(48) Bromley, L. A. Thermodynamic Properties of Strong Electrolytes in aqueous Solutions. *AlChE J.* **1973**, *19*, 313−320.

(49) Gil, R.; Corbillón, M. S.; Olazabal, M. A.; Madariaga, J. M Potentiometric study of the protonation equilibrium of Tris(Hydroxymethyl) aminomethane in aqueous sodium perchlorate solutions at 25 °C: construction of a thermodynamic model. *Talanta* **1997**, *44* (5), 891−896.

(50) Raposo, J. C.; Zuloaga, O.; Olazabal, M. A.; Madariaga, J. M. Development of a Modified Bromley Methodology for the estimation of ionic media effects on solution equilibria: Part 5. The chemical model of boric acid in aqueous solution at 25 °C and comparison with arsenious acid. *Fluid Phase Equilib.* **2003**, *207* (1−2), 81−95.

(51) Raposo, J. C.; Zuloaga, O.; Olazabal, M. A.; Madariaga, J. M. Development of a modified Bromley methodology for the estimation of ionic media effects on solution equilibria: Part 6. The chemical model of phosphoric acid in aqueous solution at 25 °C and comparison with arsenic acid. *Fluid Phase Equilib.* **2003**, *207* (1−2), 69−80.

(52) Setschenow, J. Z. Uber die konstitution der salzlosungenauf grund ihres verhaltens zu kohlensaure. *Z. Physik. Chem.* **1889**, *4*, 117−125.

(53) De Stefano, C.; Gianguzza, A.; Piazzese, D.; Sammartano, S. Polyacrylate protonation in various aqueous media at different temperatures and ionic strengths. *J. Chem. Eng. Data* **2000**, *45* (5), 876−881.

(54) De Stefano, C.; Sammartano, S.; Gianguzza, A.; Piazzese, D. Speciation of polyelectrolytes in natural fluids. Protonation and interaction of polymethacrylates with major components of seawater. *Talanta* **2002**, *58* (2), 405−417.

(55) De Stefano, C.; Gianguzza, A.; Piazzese, D.; Sammartano, S. Polyacrylates in aqueous solution. The Dependence of Protonation on Molecular Weight, Ionic Medium and Ionic Strength. *React. Funct. Polym.* **2003**, *55*, 9−20.

(56) Bretti, C.; Crea, F.; Rey-Castro, C.; Sammartano, S. Interaction of acrylic-maleic copolymers with H^+, Na^+, Mg^{2+} and Ca^{2+}: thermodynamic parameters and their dependence on medium. *React. Funct. Polym.* **2005**, *65* (3), 329−342.

(57) Crea, F.; Giacalone, A.; Gianguzza, A.; Piazzese, D.; Sammartano, S. Modelling of natural synthetic polyelectrolyte interactions in natural waters by using SIT, Pitzer and Ion Pairing approaches. *Mar. Chem.* **2006**, *99*, 93−105.

Received for review April 27, 2007. Accepted July 29, 2007. We thank the University of Messina for financial support (PRA).

JE700223R