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Ionic Strength Dependence of Protonation Constants of Carboxylate Ions in $NaCl_{aq}$ ($0 \leq I \leq 5.6$ mol·kg^{-1}) and KCl_{aq} ($0 \leq I \leq 4.5$ mol·kg^{-1}): Specific Ion Interaction Theory and Pitzer Parameters and the Correlation between Them

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Parameters to correct protonation constants of carboxylate ions, defined as concentration quotients, for ionic strength dependence have been calculated from measured values of the constants obtained at 298 K with NaCl solutions at ionic strengths between (0 and 5.6) mol·kg^{-1} and with KCl solutions at ionic strengths between (0 and 4.5) mol·kg^{-1}. Mean values of specific ion interaction theory (SIT) and Pitzer interaction parameters for carboxylate anions and for some synthetic and natural polycarboxylates have been derived. They show a strong correlation with the charge on the carboxylate ion, similar to that previously found for protonation constants of carboxylate ions in solutions with $(C_2H_5)_4NI$ and $(CH_3)_4NCl$ as a background electrolyte. Any individual interaction parameter, x, can be calculated from the simple relationship: $x = \bar{x}z^2$, where z is the charge on the carboxylate anion and $\bar{x}$ is a global average scaled to unit charge. Both SIT and Pitzer interaction parameters give good fits to experimental data. The strong correlation between the SIT and the Pitzer parameters, proposed in previous papers, is confirmed. The temperature dependence of SIT interaction parameters was obtained from protonation enthalpy values with NaCl solutions, and empirical relationships are proposed for the temperature dependence.

Introduction

Since natural and biological fluids have a wide range of ionic strength and composition, a different equilibrium constant for a complex would have to be used for each individual system. The constant is used to calculate the speciation of the complex and its dissociation products in the fluid, which determine the mobility and toxicological effects of the complex. The experimental measurement of a large number of stability constants of different reactions under varying chemical and/or physical conditions is not an attractive option. Therefore accurate and reliable methods for predicting stability constants are desirable. Large databases of stability constant values are available, but data for ionic strength dependence is available in only a few cases.

There are two main methods used to specify ionic strength dependence of stability constants, the Brønsted−Guggenheim−Scatchard (specific ion interaction theory, SIT[5−9]) and the Pitzer models.[10,11] SIT models have the advantage of requiring fewer parameters. The Pitzer model offers a more precise description of activity coefficient data and equilibrium constants but requires more parameters and is difficult to handle in some cases. We have recently analyzed protonation constant data for carboxylate ions at various ionic strengths of $(C_2H_5)_4NI$ and $(CH_3)_4NCl$ and at various temperatures. Both a modified SIT equation and a Pitzer model were used.[4] It was found that each model parameter could be expressed as the product of a mean value and the square of the ionic charge.

In this paper we have determined the model parameters obtained from stepwise protonation constant data for carboxylate ions in aqueous NaCl and KCl solutions at ionic strengths in the range of $0 \leq I \leq 5.6$ mol·kg^{-1} for NaCl and $0 \leq I \leq 4.5$ mol·kg^{-1} for KCl. The models used are an extended Debye−Hückel equation,[12] a modified version of the SIT model,[1−4] and the Pitzer model.[10,11] For NaCl ionic medium, temperature gradients of SIT parameters were also determined from protonation enthalpy values at 298 K (ref 13 and unpublished data from this laboratory).

The carboxylates examined in this paper are listed in Table 1.

Models for Ionic Strength Dependence of Equilibrium Constants. A *stepwise* stoichiometric protonation constants K_i^H for the equilibrium 1

$$H^+ + H_{i-1}L^{i-1-z} = H_iL^{i-z} \tag{1}$$

in a medium of given ionic strength can be expressed by eq 2,

$$\log K_i^H = \log {}^TK_i^H + \log \gamma(H^+) + \log \gamma(H_{i-1}L^{(i-1-z)}) - \log \gamma(H_iL^{(i-z)}) \tag{2}$$

where the γ terms are activity coefficients. ${}^TK^H$ is the protonation constant, expressed as a *concentration quotient*, at infinite dilution in a particular medium and the determination of its value requires that the activity coefficient values are known. These can be calculated by fitting the parameters of various equations to experimental data. These equations relate to 298 K only.

Extended Debye−Hückel Equation.[12]

$$\log K_i^H = \log {}^TK_i^H - z^* \frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}} + CI + EI^2 \tag{3}$$

C and E are the empirical parameters that can be expressed as a function of the formation stoichiometry, by eqs 3a and 3b,

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$$C = c_0 p^* + c_1 z^* \tag{3a}$$

$$E = e_0 p^* + e_1 z^* \tag{3b}$$

and

$$z^* = \Sigma(\text{charge})^2_{\text{reactants}} - \Sigma(\text{charge})^2_{\text{products}} \tag{3c}$$

$$p^* = \Sigma(\text{moles})_{\text{reactants}} - \Sigma(\text{moles})_{\text{products}} \tag{3d}$$

In reaction 1, p^* is always equal to 1.

The extended Debye−Hückel eq 3 has been used in the study of the ionic strength dependence of protonation constants of many ligands.[12,14,15] c_0, c_1, e_0, and e_1 are empirical parameters which relate to a specific anion and supporting electrolyte. A good fit was obtained with this equation over the ionic strength range of $0 \leq I \leq 3\ \text{mol}\cdot\text{L}^{-1}$. With an ionic strength less than $1\ \text{mol}\cdot\text{L}^{-1}$ fitting can be simplified by removing the EI^2 term.

SIT Equation. According to the SIT model,[5−9] the molal activity coefficient γ_j of an ion j of charge z_j is given by eq 4

$$\log \gamma_j = z_j^2 \frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k \varepsilon_{j,k} m_k \tag{4}$$

where I is the molal ionic strength and $\varepsilon_{j,k}$ is the SIT coefficient for interaction between the j-th and the k-th ions. m_k is the molal concentration of the k-th ion. Activity coefficients for a neutral species are given by the linear relationship:

$$\log \gamma_N = k_m I \tag{4a}$$

where k_m is the Setschenow coefficient. Equation 5 is a combination of eqs 2 and 4, for 1:1 electrolytes NX

$$\log K_i^H = \log {}^T K_i^H - z^* \frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}} + I\Delta\varepsilon \tag{5}$$

where $\Delta\varepsilon$ can be expressed as:

$$\Delta\varepsilon = [\varepsilon(H^+, X^-) + \varepsilon(N^+, H_{i-1}L^{i-1-z}) - \varepsilon(N^+, H_iL^{i-z})] \tag{5a}$$

or for i = n (n = maximum protonation degree of carboxylate):

$$\Delta\varepsilon = [\varepsilon(H^+, X^-) + \varepsilon(N^+, H_{n-1}L^{n-1-z}) - k_m] \tag{5b}$$

Table 1. Carboxylates Examined

carboxylate	abbr.	ionic medium	ref(s)
acetate	ac	NaCl, KCl	20−22
phenoxyacetate	phen	NaCl	23
malate	mala	NaCl	21, 22, 24
tartrate	tar	NaCl	13, 21, 22, 24
diethylenetrioxydiacetate	toda	NaCl	25
phthalate	pht	NaCl	12
oxalate	ox	NaCl	14, 26, 27
malonate	mal	NaCl, KCl	13, 14, 21, 22
succinate	suc	NaCl	14, 21
glutarate	glu	NaCl	14
adipate	adip	NaCl	14, [a]
pimelate	pim	NaCl	14, [a]
suberate	sub	NaCl	14, [a]
azelate	aze	NaCl	25, [a]
sebacate	seb	NaCl	14, [a]
1,2,3-propanetricarboxylate, tricarballylate	tca	NaCl, KCl	13, 22, 28
citrate	cit	NaCl, KCl	13, 22, 24, 29
butanetetracarboxylate	btc	NaCl, KCl	13, 22, 30
1,2,4,5-benzenetetracarboxylate, pyromellitate	pymel	NaCl	31
1,2,3,4,5-benzenepentacarboxylate	bpca	NaCl	32
benzenehexacarboxylate, mellitate	mlt	NaCl, KCl	33

[a] Unpublished data from this laboratory.

In the classic SIT approach ε values are independent of ionic strength, but a modified version can be used[1−4] in which an interaction coefficient depends on ionic strength according to the simple relationship (eq 5c).

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{I + 1} \tag{5c}$$

A mean value for the Setschenow coefficient, k_m, was taken from ref 14 as 0.144. Interaction parameters for HCl were taken as $\varepsilon_\infty = 0.136$ and $\varepsilon_0 = 0.0848$.[1]

Equation 5d, which has been proposed previously, was also used.[8]

$$\varepsilon = \varepsilon^{(0)} + \varepsilon^{(1)} \ln(1 + I) \tag{5d}$$

Pitzer Equations. According to the Pitzer equations,[10,11] in the presence of a 1:1 salt NX, the activity coefficients of a cation or an anion are given by eq 6.

$$\ln \gamma_{H^+} = f^\gamma + 2I(B_{H,X} + IC_{H,X}) + I^2(B'_{N,X} + C_{N,X}) + I(2\theta_{H,N} + I\psi_{H,N,X}) \tag{6}$$

$$\ln \gamma_L = z_L^2 f^\gamma + 2I(B_{N,L} + IC_{N,L}) + I^2(z_L^2 B'_{N,X} + z_L C_{N,X}) + I(2\theta_{L,X} + I\psi_{L,N,X}) \tag{6a}$$

where L = $H_{i-1}L^{(i-1-z)}$ or $H_iL^{(i-z)}$ and:

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

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

$$C_{c,a} = \frac{C^{(\varphi)}_{c,a}}{2|z_c z_a|^{1/2}} \tag{6d}$$

$$f^\gamma = -0.3912\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + 1.667 \ln(1 + 1.2\sqrt{I})\right] \tag{6e}$$

$$f_1 = 1 - (1 + 2\sqrt{I}) \exp(-2\sqrt{I}) \tag{6f}$$

$$f_2 = -1 + (1 + 2\sqrt{I} + 2I) \exp(-2\sqrt{I}) \tag{6g}$$

where c represents a cation and a, an anion. $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters between two ions of opposite sign, and θ represents the interaction parameter between two ions of the same sign (+ +, − − interactions) and ψ the triplet interaction parameter (+ − +, − + −). At $I < 2\ \text{mol}\cdot\text{kg}^{-1}$, the $C^{(\phi)}$ term can be neglected.

The activity coefficient of a neutral species can be write as eq 6h,

$$\ln \gamma_N = 2(m_M \lambda_{M,HnL} + m_X \lambda_{X,HnL}) \tag{6h}$$

where λ is the interaction parameter of the neutral species. The value of $\lambda_{X,HnL}$ can be set equal to zero.

The following literature values were used in the calculations:[11] $\beta_{H,Cl}{}^{(0)} = 0.1775$, $\beta_{H,Cl}{}^{(1)} = 0.2945$, $C_{H,Cl}{}^{(\phi)} = 0.00080$, $\beta_{Na,Cl}{}^{(1)} = 0.2664$, $\beta_{K,Cl}{}^{(1)} = 0.2122$, $\theta_{H,Na} = 0.036$, $\psi_{H,Na,Cl} = -0.004$,

Table 2. Mean Parameter Values for Extended Debye−Hückel Equations 3 to 3b[a]

I	NaCl		KCl	
mol·dm^{-3}	0 to 5	0 to 1	0 to 3.9	0 to 1
c_0	0.152(4)	0.0164(4)	0.0164(4)	0.170(8)
c_1	0.002(1)	0.014(2)	−0.0068(7)	−0.003(1)
e_0	0		0	
e_1	−0.0016(3)		0.0031(3)	
Mean deviation on fit	0.06	0.06	0.06	0.04

[a] Least-squares errors on the last significant figure are shown in parentheses.

$\theta_{H,K} = 0.005$, and $\psi_{H,K,Cl} = -0.007$. Interaction parameters of neutral species were calculated from the Setschenow coefficient by combining eqs 4a and 6h:

$$\lambda = \frac{\ln 10 k_m}{2} \tag{6i}$$

Owing to the complexity of the Pitzer equations, we also tested a simplified version with only three empirical parameters, eq 7,[12]

$$\ln K_i^H = \ln {}^T K_i^H + 2zf^\gamma + 2IP_1 + P_2 f_1 + P_3 I^2 + z\beta_{MX}^{(1)} f_2 \tag{7}$$

where P_1, P_2, and P_3 are empirical parameters, f^γ and f_1 are defined by eqs 6e and 6f, and

$$f_2 = I \exp(-2\sqrt{I}) \tag{7a}$$

At $I < 2$ mol·kg^{-1}, the P_3 term can be neglected.

Results

Ionic Strength Dependence of Protonation Constants. The parameters obtained with the extended Debye−Hückel eq 3 are shown in Table 2.

SIT parameters from eqs 5 to 5b are given in Tables 3 and 4. The mean values of both ε_∞ and ε_0 are, to a first approximation, linearly dependent on the charge function z^*, defined in eq 3c, as illustrated in Figures 1 and 2. The following empirical relationships were found:

$$\varepsilon_\infty(\mathrm{Na}^+, \mathrm{L}) = 0.27(4) - 0.031(5)z^* \tag{8}$$

$$\varepsilon_0(\mathrm{Na}^+, \mathrm{L}) = 0.072(3)z^* \tag{8a}$$

$$\varepsilon_\infty(\mathrm{K}^+, \mathrm{L}) = 0.24(4) - 0.020(5)z^* \tag{9}$$

$$\varepsilon_0(\mathrm{K}^+, \mathrm{L}) = 0.081(4)z^* \tag{9a}$$

Pitzer interaction parameter values (eqs 6 to 6h) are shown in Tables 5 and 6. Pitzer parameters are also linearly dependent on z^*, as illustrated in Figure 3, for KCl as an example. Linear least-squares fitting gave the following quantitative expressions.

$$\beta^{(0)}_{\mathrm{Na}^+,\mathrm{L}} = 0.070(4)z^* \tag{10}$$

$$\beta^{(1)}_{\mathrm{Na}^+,\mathrm{L}} = -3.5(0.9) + 1.4(1)z^* \tag{10a}$$

$$C^{(\phi)}_{\mathrm{Na}^+,\mathrm{L}} = -0.005(4)z^* \tag{10b}$$

$$\beta^{(0)}_{\mathrm{K}^+,\mathrm{L}} = -0.14(2) + 0.107(2)z^* \tag{11}$$

$$\beta^{(1)}_{\mathrm{K}^+,\mathrm{L}} = -3.5(1.2) + 1.3(2)z^* \tag{11a}$$

$$C^{(\phi)}_{\mathrm{K}^+,\mathrm{L}} = 0.08(3) - 0.024(3)z^* \tag{11b}$$

Interaction parameters of both pymel and bpca were not considered in the calculation of eqs 8, 8a, and 10 to 10b owing to the too short-range of ionic strengths available for these ligands.

The SIT parameters for interaction between the metal of the medium and the carboxylate show a strong correlation with the square of the charge, z, on the carboxylate ($z = 0$ for H_nL, -1 for $H_{n-1}L$, etc.). To quantify this relationship, eqs 5 and 5a can be combined to give eq 12

Table 3. Interaction Parameters of Modified SIT Equations (Equations 5 to 5c) for Carboxylates in NaCl, at 298 K

L	z^*	ε_∞(Na$^+$,L)	σ^a	ε_0(Na$^+$,L)	σ^a	σ^b
ac	2	0.199	0.001	0.178	0.014	0.012
phen	2	0.298	0.014	0.240	0.012	0.007
mala	4	0.147	0.006	0.170	0.020	0.008
	2	0.128	0.003	0.115	0.014	0.008
tar	4	0.093	0.007	0.127	0.020	0.009
	2	0.102	0.004	0.096	0.014	0.008
toda	4	−0.185	0.034	−0.090	0.045	0.015
	2	−0.325	0.030	−0.060	0.023	0.005
pht	4	0.043	0.002	−0.079	0.006	0.017
	2	0.130	0.001	0.108	0.006	0.014
ox	4	−0.003	0.015	−0.082	0.025	0.013
	2	0.057	0.009	0.020	0.016	0.010
mal	4	0.152	0.016	0.299	0.022	0.021
	2	0.180	0.012	0.353	0.012	0.015
suc	4	0.221	0.004	0.331	0.015	0.014
	2	0.174	0.003	0.217	0.011	0.009
glu	4	0.257	0.004	0.432	0.013	0.009
	2	0.194	0.004	0.222	0.006	0.007
adip	4	0.261	0.006	0.442	0.023	0.016
	2	0.192	0.004	0.203	0.022	0.017
pim	4	0.288	0.005	0.434	0.007	0.006
	2	0.200	0.001	0.160	0.006	0.007
sub	4	0.270	0.004	0.422	0.010	0.012
	2	0.185	0.003	0.180	0.008	0.012
aze	4	0.282	0.006	0.452	0.009	0.009
	2	0.195	0.004	0.107	0.006	0.011
seb	4	0.200	0.034	−0.085	0.027	0.026
	2	0.070	0.031	−0.577	0.020	0.017
tca	6	0.183	0.009	0.356	0.032	0.033
	4	0.168	0.007	0.260	0.018	0.020
	2	0.123	0.006	0.067	0.014	0.019
cit	6	−0.017	0.012	0.102	0.024	0.009
	4	0.067	0.009	0.106	0.020	0.008
	2	0.096	0.005	0.090	0.014	0.008
btc	8	0.218	0.010	0.613	0.044	0.040
	6	0.164	0.009	0.361	0.040	0.033
	4	0.134	0.008	0.215	0.031	0.023
	2	0.111	0.007	0.057	0.024	0.02
pymel[c]	8	5.213	0.188	2.092	0.185	0.041
	6	3.131	0.126	1.243	0.136	0.026
	4	1.725	0.077	0.655	0.102	0.019
	2	0.891	0.041	0.279	0.099	0.034
bpca[c]	10	0.784	0.190	1.052	0.091	0.023
	8	0.188	0.162	0.512	0.069	0.018
	6	0.135	0.146	0.217	0.061	0.010
	4	−0.914	0.113	−0.326	0.047	0.020
	2	−0.916	0.098	−0.307	0.025	0.008
mlt	12	−0.141	0.005	0.846	0.014	0.008
	10	−0.026	0.004	0.760	0.014	0.006
	8	0.078	0.004	0.687	0.013	0.005
	6	0.176	0.003	0.613	0.013	0.005
	4	0.192	0.002	0.464	0.012	0.005
	2	0.225	0.002	0.362	0.010	0.021

[a] Standard deviation on the value. [b] Standard deviation on the global fit. [c] Not included in the calculation of the global mean values.

$$\log K_{\mathrm{i}}^{\mathrm{H}} - \log {}^{\mathrm{T}}\mathrm{K}_{\mathrm{i}}^{\mathrm{H}} + z^{*}\frac{0.5\sqrt{I}}{1 + 1.5\sqrt{I}} - I\varepsilon_{\mathrm{H^{+},X^{-}}} = [\varepsilon_{\mathrm{N^{+},H_{j-1}L^{j-1-z}}} - \varepsilon_{\mathrm{N^{+},H_{j}L^{j-z}}}]I \quad (12)$$

Each of the SIT parameters on the right-hand side of eq 12 can be expressed as

$$\varepsilon = \bar{\varepsilon} z^{2} \quad (12a)$$

where ε is a particular SIT interaction parameter and $\bar{\varepsilon}$ is a mean value for that parameter, calculated as follows. Substitution of eq 12a into 12 gives eq 12b.

$$\bar{\varepsilon} = \frac{\log K_{\mathrm{i}}^{\mathrm{H}} - \log {}^{\mathrm{T}}K_{\mathrm{i}}^{\mathrm{H}} + z^{*}\frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}} - I\varepsilon_{\mathrm{H^{+},X^{-}}}}{I[(\mathrm{i} - 1 - \mathrm{z})^{2} - (\mathrm{i} - \mathrm{z})^{2}]} \quad (12b)$$

Thus, the mean value, $\bar{\varepsilon}$, is obtained by averaging the data for all carboxylates (including pymel and bpca) using eq 12b. $\Delta\varepsilon$ values in eq 5a, obtained using this equation, are in good agreement with values calculated from eqs 8 to 11b. For example, $\Delta\varepsilon$ values for the first protonation step of a tetracarboxylate ligand in NaCl at $I = 3$ mol·kg^{-1} were found to be 0.113 by using eqs 8 and 8a and 0.101 from eq 12b.

The same procedure can be followed for the Pitzer and simplified Pitzer models, expressing the single interaction parameters by the general relationship:

$$x = \bar{x}z^{2} \quad (13)$$

where x is an interaction parameter and $\bar{x}$ is its "mean value". $\bar{x}$ values of the SIT (eqs 5 to 5d), the Pitzer (eqs 6 to 6h) and the simplified Pitzer (eq 7) interaction parameters in both NaCl and in KCl solutions are shown in Table 7. Previous results for $(C_2H_5)_4NI$ and $(CH_3)_4NCl$ solutions are given for comparison.[4]

The quality of the fit to experimental data with different models is good in all cases. For example, in NaCl the standard deviation in the fit is 0.14 to 0.15 for all models except for the simplified Pitzer model. Both SIT and Pitzer equations can be considered to provide equally good approximations to reality except when mixed electrolytes are involved, in which mixing effects may additionally need to be taken into account.

The good predictive power of $\bar{x}$ values in the calculation of carboxylate protonation constants is shown in Figures 4 and 5, where calculated versus experimental $\log K_{\mathrm{i}}^{\mathrm{H}}$ values for the two tricarboxylate ligands (tca and cit) are reported

Table 4. Interaction Parameters of Modified SIT Equations (Equations 5 to 5c) for Carboxylate Ions in KCl, at 298 K

L	z^*	$\varepsilon_\infty(\mathrm{K^+,L})$	σ^a	$\varepsilon_0(\mathrm{K^+,L})$	σ^a	σ^b
ac	2	0.205	0.001	0.207	0.022	0.038
mal	4	0.118	0.008	0.131	0.014	0.033
	2	0.145	0.004	0.211	0.011	0.012
tca	6	0.187	0.003	0.477	0.013	0.009
	4	0.157	0.003	0.305	0.011	0.014
	2	0.130	0.001	0.123	0.006	0.017
cit	6	0.031	0.008	0.111	0.037	0.017
	4	0.071	0.008	0.106	0.035	0.025
	2	0.089	0.007	0.029	0.028	0.034
btc	8	0.143	0.006	0.423	0.045	0.034
	6	0.109	0.006	0.280	0.033	0.021
	4	0.096	0.005	0.181	0.025	0.022
	2	0.111	0.002	0.114	0.018	0.018
mlt	12	−0.042	0.012	1.020	0.014	0.006
	10	0.035	0.012	0.871	0.013	0.009
	8	0.125	0.011	0.761	0.010	0.003
	6	0.237	0.009	0.674	0.010	0.004
	4	0.306	0.008	0.579	0.010	0.003
	2	0.366	0.006	0.479	0.008	0.015

[a] Standard deviation in the value. [b] Standard deviation on the global fit.

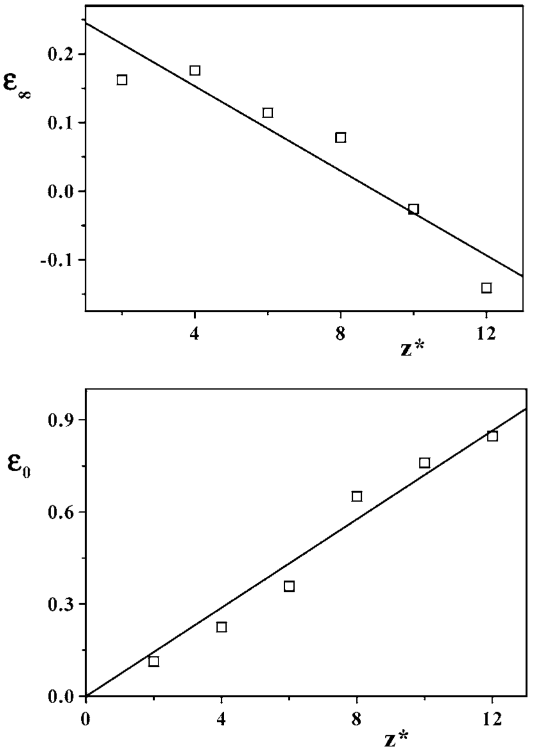

Figure 1. Mean values of SIT interaction parameters vs z^* for carboxylates in NaCl, at 298 K.

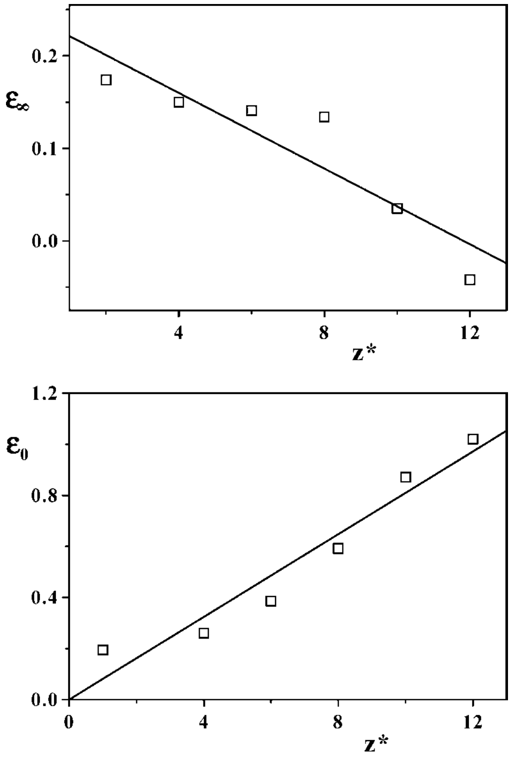

Figure 2. Mean values of SIT interaction parameters vs z^* for carboxylates in KCl, at 298 K.

Table 5. Interaction Parameters of Pitzer Equations (Equations 6 to 6h) for Carboxylate Ions in NaCl, at 298 K

L	z^*	$\beta_{\mathrm{Na+,L}}^{(0)}$	σ^a	$\beta_{\mathrm{Na+,L}}^{(1)}$	σ^a	$C_{\mathrm{Na+,L}}^{(\phi)}$	σ^a	σ^b
ac	2	0.240	0.004	0.874	0.063	0.005	0.002	0.005
phen	2	0.214	0.020	0.492	0.013	0.261	0.211	0.008
mala	4	0.313	0.004	1.499	0.026	−0.001	0.001	0.002
	2	0.177	0.003	0.439	0.025	0.005	0.0005	0.001
tar	4	0.264	0.004	1.180	0.020	−0.001	0.001	0.002
	2	0.153	0.003	0.301	0.017	0.004	0.0005	0.001
toda	4	0.378	0.040	0.940	0.063	−1.254	0.187	0.003
	2	−0.084	0.024	−0.357	0.025	−0.223	0.092	0.003
pht	4	0.251	0.003	0.707	0.017	−0.043	0.005	0.016
	2	0.181	0.002	0.522	0.016	−0.007	0.002	0.014
ox	4	0.217	0.005	0.527	0.039	0.018	0.001	0.001
	2	0.123	0.004	0.004	0.015	0.008	0.001	0.001
mal	4	0.286	0.010	1.634	0.045	−0.105	0.016	0.015
	2	0.171	0.007	0.893	0.021	−0.036	0.008	0.009
suc	4	0.352	0.005	1.989	0.041	−0.016	0.009	0.013
	2	0.201	0.004	0.745	0.038	0.003	0.002	0.005
glu	4	0.367	0.003	2.290	0.027	−0.033	0.006	0.004
	2	0.223	0.002	0.899	0.026	−0.014	0.004	0.006
adip	4	0.368	0.007	2.364	0.072	−0.045	0.015	0.016
	2	0.230	0.005	0.929	0.066	−0.015	0.009	0.017
pim	4	0.403	0.005	2.456	0.069	−0.037	0.005	0.006
	2	0.247	0.002	0.874	0.061	−0.006	0.001	0.006
sub	4	0.379	0.005	2.331	0.043	−0.051	0.007	0.012
	2	0.224	0.004	0.822	0.036	−0.017	0.004	0.012
aze	4	0.395	0.004	2.377	0.047	−0.025	0.006	0.009
	2	0.257	0.003	0.782	0.047	0.001	0.004	0.008
seb	4	0.443	0.012	1.709	0.078	0.031	0.023	0.026
	2	0.303	0.009	−0.212	0.067	0.023	0.007	0.010
tca	6	0.460	0.012	3.761	0.038	0.051	0.027	0.028
	4	0.312	0.009	1.661	0.029	0.019	0.016	0.018
	2	0.186	0.008	0.383	0.022	0.026	0.007	0.012
cit	6	0.304	0.004	2.541	0.047	−0.010	0.003	0.005
	4	0.240	0.003	1.021	0.026	−0.002	0.002	0.002
	2	0.148	0.003	0.269	0.021	0.004	0.001	0.001
btc	8	0.634	0.013	7.092	0.062	0.112	0.043	0.036
	6	0.441	0.012	3.661	0.055	0.080	0.027	0.028
	4	0.290	0.010	1.454	0.042	0.044	0.015	0.018
	2	0.175	0.009	0.316	0.033	0.025	0.004	0.012
pymel[c]	8	3.449	0.261	11.87	0.18	0		0.041
	6	2.246	0.194	6.79	0.16	0		0.026
	4	1.355	0.159	3.288	0.121	0		0.019
	2	0.710	0.148	1.241	0.066	0		0.035
bpca[c]	10	1.064	0.129	10.69	0.117	0		0.021
	8	0.737	0.111	6.263	0.097	0		0.017
	6	0.702	0.094	3.356	0.088	0		0.011
	4	0.020	0.079	0.140	0.068	0		0.021
	2	−0.327	0.046	−0.932	0.044	0		0.009
mlt	12	0.654	0.011	14.56	0.08	−0.330	0.020	0.011
	10	0.539	0.010	9.991	0.077	−0.245	0.016	0.009
	8	0.449	0.009	6.452	0.075	−0.173	0.013	0.007
	6	0.387	0.007	3.904	0.063	−0.111	0.010	0.005
	4	0.285	0.006	1.946	0.061	−0.062	0.008	0.005
	2	0.222	0.005	1.144	0.048	−0.021	0.005	0.020

[a] Standard deviation on the value. [b] Standard deviation on the global fit. [c] Not included in the calculation of global mean values.

as an example. In Figure 4 log K_i^H were calculated using the SIT equation with mean $\bar{\varepsilon}_\infty$ and $\bar{\varepsilon}_\infty$ values of Table 7, while in Figure 5 Pitzer equations and mean $\bar{\beta}^{(0)}$ and $\bar{\beta}^{(1)}$ values (Table 7) were used. Moreover, small errors in the calculated values do not affect severely the distribution of species: as an example, Figure 6 shows the distribution diagram of cit in NaCl at $I = 3\ \mathrm{mol \cdot kg^{-1}}$, by using experimental and calculated values (by SIT equation with $\bar{\varepsilon}_\infty$ and $\bar{\varepsilon}_\infty$ values). As can be observed, distribution is very similar with differences in the formation percentages of (3 to 4) % at the maximum of the formation curves. The same behavior was observed by using Pitzer equations.

Table 6. Interaction Parameters of Pitzer Equations (Equations 6 to 6h) for Carboxylate Ions in KCl, at 298 K

L	z^*	$\beta_{\mathrm{K+,L}}^{(0)}$	σ^a	$\beta_{\mathrm{K+,L}}^{(1)}$	σ^a	$C_{\mathrm{K+,L}}^{(\phi)}$	σ^a	σ^b
ac	2	0.107	0.005	0.918	0.029	0.180	0.055	0.040
mal	4	0.291	0.009	1.241	0.019	−0.116	0.015	0.022
	2	0.029	0.008	0.576	0.017	−0.027	0.004	0.008
tca	6	0.525	0.007	3.460	0.047	−0.023	0.025	0.009
	4	0.284	0.005	1.533	0.043	0.009	0.017	0.011
	2	0.039	0.003	0.469	0.032	0.002	0.009	0.017
cit	6	0.487	0.015	2.560	0.029	−0.022	0.042	0.012
	4	0.269	0.014	1.074	0.027	0.051	0.033	0.022
	2	0.039	0.008	0.300	0.021	0.031	0.017	0.031
btc	8	0.776	0.016	5.867	0.059	−0.189	0.036	0.032
	6	0.497	0.014	2.961	0.052	−0.151	0.026	0.019
	4	0.252	0.013	1.173	0.045	−0.063	0.018	0.018
	2	0.019	0.010	0.378	0.044	−0.046	0.006	0.008
mlt	12	1.166	0.008	13.50	0.05	−0.234	0.042	0.007
	10	0.897	0.007	9.228	0.051	−0.115	0.033	0.008
	8	0.675	0.006	5.962	0.050	−0.064	0.028	0.002
	6	0.514	0.006	3.703	0.045	−0.005	0.024	0.005
	4	0.349	0.005	2.202	0.039	0.027	0.016	0.004
	2	0.187	0.004	1.515	0.030	0.034	0.011	0.011

[a] Standard deviation on the value. [b] Standard deviation on the global fit.

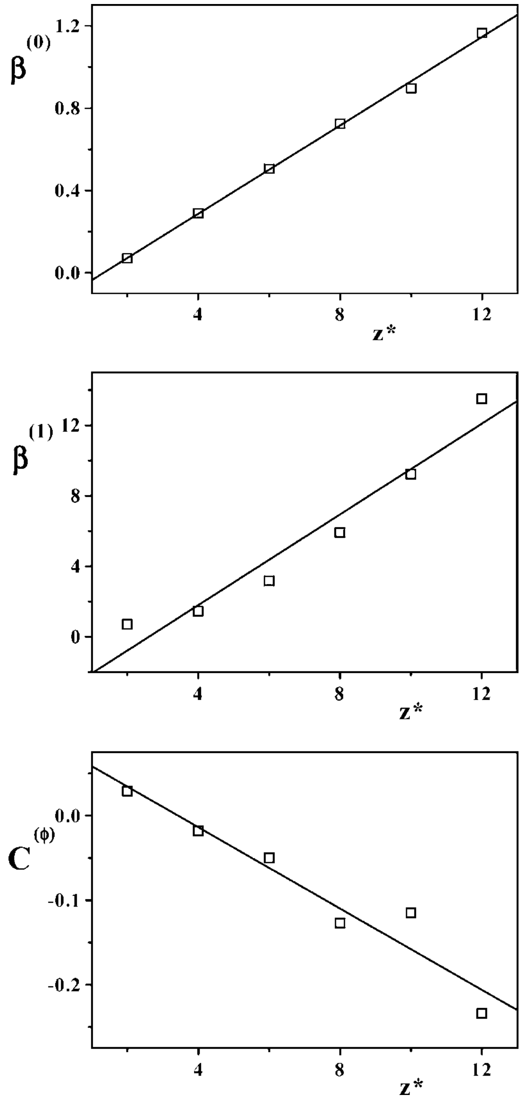

Figure 3. Mean values of Pitzer interaction parameters vs z^* for carboxylates in KCl, at 298 K.

Temperature Dependence of SIT Parameters. The ionic strength dependence of protonation enthalpy, ΔH_i^H, on temperature can be expressed by eq 14,

$$\Delta H_i^{H} = \Delta H_i^{H0} - 1.5z^* \frac{\sqrt{I}}{1 + 1.5\sqrt{I}} + \Delta\varepsilon_i' I \qquad (14)$$

where ΔH_i^{H0} is a protonation enthalpy at infinite dilution and $\Delta\varepsilon_i'$ is proportional to the temperature gradient of a SIT coefficient, eq 14a.

$$\Delta\varepsilon_i' = RT^2 \ln 10(\partial\Delta\varepsilon_i/\partial T) \qquad (14a)$$

$\Delta\varepsilon_i'$ values calculated from protonation enthalpies of carboxylates obtained from NaCl solutions are shown in Table 8, together with the temperature gradients $\partial\Delta\varepsilon/\partial T$ calculated with eq 14a. A general relationship for the dependence of $\Delta\varepsilon_i'$ on both the anion charge and the protonation degree i of the carboxylate was found as per eq 14b.

$$\Delta\varepsilon_i'(\pm 0.21) = -2.97 + 0.58\mathrm{i} + 0.27z^* \qquad (14b)$$

The standard deviation on the fit was 0.3. $\Delta\varepsilon_i'$ values are comparable to those found previously.[4]

Polyelectrolytes. To complete the picture of the ionic strength dependence of carboxylate anion SIT parameters, protonation data of the natural and synthetic polyelectrolytes given in Table 9 were also processed. The experimental data have been published previously.[16,17] Since the protonation data refer mostly to $I < 1.0$ mol·kg^{-1}, the ε parameters were taken to be independent of ionic strength as per eq 5. The same overall dependence on the square of ionic charge as with simple carboxylate ions was found. Application of eq 12b gave the following results.

$$\bar{\varepsilon} = 0.013(2)\ (\mathrm{NaCl})$$
$$\bar{\varepsilon} = 0.020(1)\ (\mathrm{KCl})$$

The value of $\bar{k}_m = 0$ was used; see Table 7.

Correlations between SIT and Pitzer Parameters. Correlations between SIT and Pitzer parameters have previously been determined for 1:1 and 1:2 electrolytes with the same anion (Cl^-, Br^-, I^-, NO_3^-, or ClO_4^-);[2,3] 1:2 electrolytes with the same cation (Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+});[3] carboxylates in tetralkylammonium salt solutions.[4] In a similar way canonical correlation analysis[18,19] of the data in Tables 3 and 5 gave the following correlations for interaction parameters between Na^+ and L,

$$\varepsilon_\infty = 0.02612 + 0.88880\beta^{(0)} - 0.06590\beta^{(1)} + 0.88209C^{(\varphi)}$$

$$\varepsilon_0 = -0.05660 + 0.53701\beta^{(0)} + 0.07238\beta^{(1)} + 0.53176C^{(\varphi)}$$

with an explained variance of 91.7 %. Moreover, a good fit is obtained when data for both NaCl and KCl solutions are included together in the calculation.

$$\varepsilon_\infty = 0.02308 + 0.88680\beta^{(0)} - 0.06652\beta^{(1)} + 0.92881C^{(\varphi)}$$

$$\varepsilon_0 = -0.03483 + 0.53709\beta^{(0)} + 0.06521\beta^{(1)} + 0.61087C^{(\varphi)}$$

The explained variance is 89.7 % in this case.

Conclusions

The ionic strength dependence of protonation constants of carboxylate anions in aqueous solution with $(C_2H_5)_4NI$ or $(CH_3)_4NCl$ as a background electrolyte has been investigated previously.[4] The carboxylate protonation study has now been

Table 7. Mean Values of Interaction Coefficients for the Dependence on Ionic Strength, for Carboxylate Ions in $(C_2H_5)_4NI$, $(CH_3)_4NCl$, NaCl, and KCl, at 298 K

		$(C_2H_5)_4NI$[a]	$(CH_3)_4NCl$[a]	NaCl	KCl
eqs 5 to 5c	$\bar{\varepsilon}_\infty$	−0.019	−0.006	−0.010(1)[b]	0.0067(8)[b]
	$\bar{\varepsilon}_0$	0.242	0.164	0.042(2)	0.002(2)
	$\bar{k}_m$	−0.020	0.006	0	0
	σ^c	0.069	0.067	0.14	0.09
eqs 5 to 5b, 5d	$\bar{\varepsilon}^{(0)}$	0.221	0.113	0.023(1)	0.001(1)
	$\bar{\varepsilon}^{(1)}$	−0.158	−0.055	−0.014(1)	0.0029(9)
	$\bar{k}_m$	−0.020	0.005	0	0
	σ^c	0.068	0.072	0.15	0.09
eqs 6 to 6h	$\bar{\beta}^{(1)}$	−0.034	0.015	0.015(1)	0.016(3)
	$\bar{\beta}^{(1)}$	1.047	0.616	0.294(6)	0.26(1)
	$\bar{C}^{\phi}$	0	0	0	0.005(1)
	$\bar{\lambda}$	−0.025	0.010	0	0
	σ^c	0.069	0.071	0.14	0.09
eqs 7 to 7a	$\bar{P}_1$	0.029	0.052	0.048(1)	0.031(5)
	$\bar{P}_2$	0.917	0.527	0.284(6)	0.29(1)
	$\bar{P}_3$	0	0	0	0.011(2)
	σ^c	0.075	0.082	0.23	0.18

[a] Ref 4. [b] Standard deviation on the value. [c] Standard deviation on the global fit.

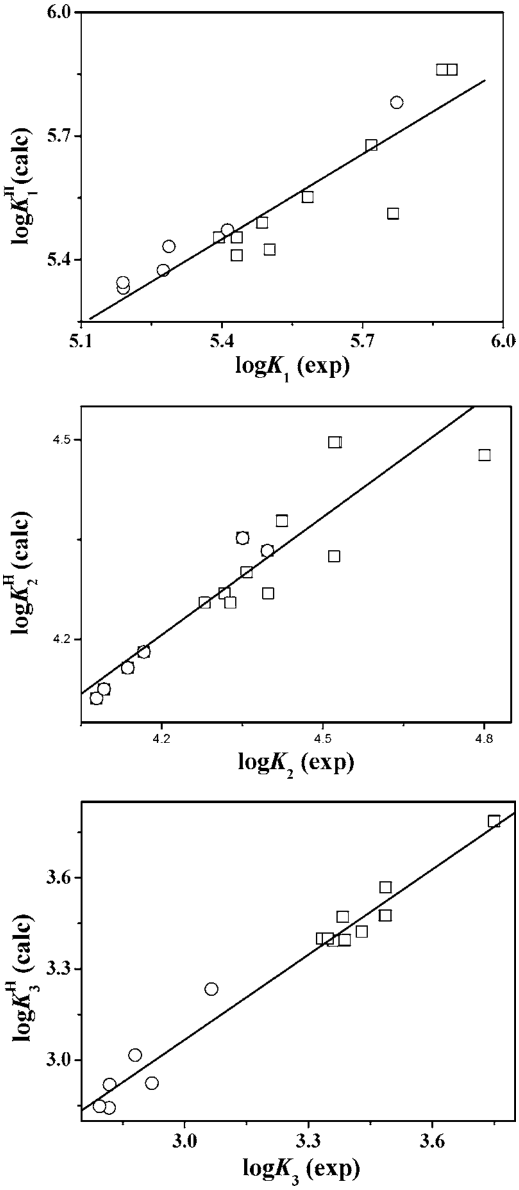

Figure 4. Calculated vs experimental values of log K_i^H for tca (□) and cit (○) in NaCl, using eqs 5 to 5c and mean $\bar{\varepsilon}_\infty$ and $\bar{\varepsilon}_0$ values of Table 7.

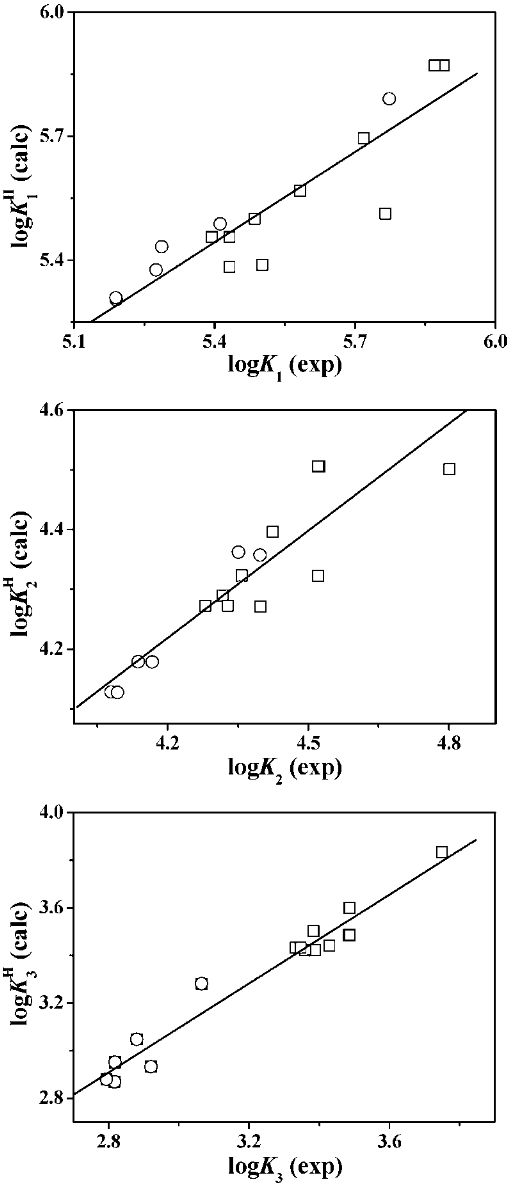

Figure 5. Calculated vs experimental values of log K_i^H for tca (□) and cit (○) in NaCl, using Pitzer equations (eqs 6 to 6h) and mean $\bar{\beta}^{(0)}$ and $\bar{\beta}^{(1)}$ values of Table 7.

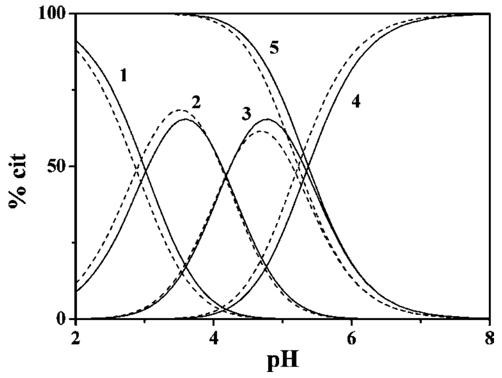

Figure 6. Distribution diagram of cit vs pH at $I = 3$ mol·kg^{-1} (NaCl), by using experimental (dashed line) and calculated (solid line) values of protonation constants. Species: **1**, $H_3(cit)^0$; **2**, $H_2(cit)^-$; **3**, $H(cit)^{2-}$; **4**, $(cit)^{3-}$; **5**, Σ.

extended to NaCl and KCl background electrolytes. The main results can be summarized as follows.

Table 8. Parameters for Dependence on Ionic Strength of Carboxylate Protonation Enthalpies (Equations 14 and 14a), together with the Temperature Gradients, in NaCl at 298 K[a]

	z^*	$\Delta\varepsilon'$	σ^b	σ^c	$10^4\ \partial\Delta\varepsilon/\partial T$
mal	4	−1.275	0.247	1.7	−7.50
	2	−0.718	0.180	0.9	−4.22
adip	4	−1.799	0.036	0.4	−10.0
	2	−1.587	0.036	0.2	−9.33
pim	4	−1.485	0.026	0.3	−8.73
	2	−1.622	0.026	0.1	−9.54
sub	4	−1.358	0.050	0.4	−7.98
	2	−1.369	0.050	0.2	−8.05
aze	4	−1.625	0.040	0.3	−9.55
	2	−1.120	0.040	0.3	−6.58
seb	4	−0.963	0.034	0.3	−5.66
	2	−1.329	0.034	0.2	−7.81
tca	6	−0.637	0.344	2.6	−3.75
	4	−0.613	0.207	1.2	−3.60
	2	−0.512	0.201	0.9	−3.01
cit	6	−0.431	0.057	1.0	−2.53
	4	−0.667	0.105	1.0	−3.92
	2	−0.259	0.043	0.4	−1.52
btc	8	−0.464	0.333	2.5	−2.73
	6	−0.235	0.287	1.9	−1.38
	4	−0.235	0.321	1.9	−1.38
	2	−0.483	0.264	1.2	−2.84

[a] Data from ref 13 and unpublished data from this laboratory. [b] Standard deviation on the value. [c] Standard deviation on the global fit.

Table 9. Polyelectrolytes Considered[a]

polyelectrolyte	effective charge	ionic medium
PAA 5.1 kDa	4.5	NaCl, KCl
PAA 20 kDa	4.6	NaCl, KCl
PMA 4 kDa	3.7	NaCl, KCl
PMA 5.4 kDa	4.4	NaCl, KCl
PAM 3 kDa	2.5	NaCl
PAM 70 kDa	2.5	NaCl
HA-S1	3.0	NaCl
HA-S2	3.0	NaCl
AA	3.5	NaCl, KCl
HA Fluka	2.0	NaCl
HA Pahokee peat	2.0	NaCl
HA "Ficuzza wood"	2.0	NaCl
HA "S. Cataldo"	2.1	NaCl
HA "Piano Zucchi"	2.0	NaCl
HA "Cefalu"	2.0	NaCl
HA Nordic Lake	2.1	NaCl
FA Elliot soil II	2.5	NaCl
FA "Ficuzza wood"	2.9	NaCl
FA Suwannee river II	2.6	NaCl

[a] Refs 16 and 17.

1. The data have been analyzed using an extended Debye−Hückel equation, a modified SIT equation, Pitzer equations, and simplified Pitzer equations. The goodness of fit observed by using different models is comparable.
2. With all equations each parameter value is proportional to the square of the charge on the anion, $x = \bar{x}z^2$. The proportionality constant, $\bar{x}$, is determined as a global average of individual values scaled to unit charge. This relationship, therefore, has excellent predictive power.
3. The strong correlation proposed previously between SIT parameters and Pitzer parameters has been confirmed. The two models may therefore be used with equivalent results.

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