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Acid−Base Equilibria of Monocarboxylic Acids in Various Saline Media: Analysis of Data Using Pitzer Equations

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The protonation constants of acetic, chloroacetic, and phenylacetic acids in KNO_3 at 25 °C at several ionic strengths were determined by potentiometry with a glass electrode. pK^* versus I plots were fitted to Pitzer equations as well as reported pK^* data. The most salient conclusion reached is that all acid−electrolyte interaction parameters show roughly the same value irrespective of the particular carboxylic acid. On the basis of this finding, an average equation that reproduces the behavior of simple carboxylic acids in different saline media was developed.

Introduction

Carboxylic acids play prominent roles as basic acid−base functions in aqueous solutions. As a result, the thermodynamics of their protonation is a fundamental research subject of much interest. Also, organic acids related to human activities have a strong impact on the aquatic environment. Chelation of carboxylic and phenol groups is the principal form of metal complexation by humic substances.[1,2] In addition, organic acids play a central role in the fundamental acid−base functions of geochemical processes including soil formation, surface weathering, and pore and ore formation.[3]

Acid−base properties are known to be strongly affected by the nature and concentration of the ionic medium concerned. The results for relatively low molecular mass solutes might considerably help understanding of the properties of complex molecules in intricate media such as natural waters. The effects of ionic strength and ionic medium were recently reviewed by Daniele et al.[4] and Sastre de Vicente.[5]

In this work, the protonation constants of acetic, chloroacteic and phenylacetic acids in KNO_3 at 25 °C were determined potentiometrically. The results thus obtained were analyzed in light of Pitzer equations and compared with those reported for many other acids. This research is complementary to previous studies on carboxylic acids in saline media conducted in the past few years by Foti et al.,[6,7] De Robertis et al.,[8] De Stefano et al.,[9] Partanen et al.,[10−13] Wesolowski et al.,[14−17] and Barriada et al.[18]

Theory

The chemical equilibrium of a carboxylic acid can be represented by

$$\mathrm{AH} \rightleftharpoons \mathrm{A}^- + \mathrm{H}^+ \qquad (1)$$

so the corresponding equilibrium constant will be given by

$$K^{\mathrm{T}} = \frac{(\mathrm{A}^-)(\mathrm{H}^+)}{(\mathrm{AH})} = \frac{[\mathrm{A}^-][\mathrm{H}^+]}{[\mathrm{AH}]}\frac{\gamma_{\mathrm{A}^-}\gamma_{\mathrm{H}^+}}{\gamma_{\mathrm{AH}}} = K^*\frac{\gamma_{\mathrm{A}^-}\gamma_{\mathrm{H}^+}}{\gamma_{\mathrm{AH}}} \qquad (2)$$

where K^* is the stoichiometric constant and γ_i the molal activity coefficient of species i. If the activity coefficients for the species involved in the equilibrium are substituted by their expressions in the Pitzer equations,[19] then, in the presence of an inert electrolyte MX of molality I,[20]

$$\mathrm{p}K^* = \mathrm{p}K^{\mathrm{T}} + \frac{2}{\ln 10}f^{\gamma} + \frac{2\beta^1_{\mathrm{MX}}}{\ln 10}I\mathrm{e}^{-2\sqrt{I}} + AI + B[1 - (1 + 2\sqrt{I})\mathrm{e}^{-2\sqrt{I}}] \qquad (3)$$

where

$$f^{\gamma} = -0.3910\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2}\ln(1 + 1.2\sqrt{I})\right]$$
$$A = 2\frac{(\beta^0_{\mathrm{HX}} + \beta^0_{\mathrm{MA}} - \lambda_{\mathrm{AH,MX}})}{\ln 10} \qquad (4)$$
$$B = \frac{(\beta^1_{\mathrm{HX}} + \beta^1_{\mathrm{AM}} - \beta^1_{\mathrm{MX}})}{\ln 10}$$

The parameter β^1_{MX} corresponds to the inert electrolyte and is tabulated for a variety of compounds; specifically, $\beta^1_{\mathrm{MX}} = 0.0494$ for KNO_3. In theory, constants A and B depend on both the acid and the inert electrolyte concerned. The θ, ψ, and C^{ϕ} terms were discarded as the ionic strengths studied were all moderate ($m < 2$).[19]

Experimental Section

The carboxylic acids studied were reagent-grade chemicals from Merck, and the KNO_3 used was a Merck p.a. reagent. Potentiometric titrations were carried out in a glass cell furnished with a thermostating jacket and inlets for the electrode, a buret, and a nitrogen stream intended to remove O_2 and CO_2 and also to homogenize the solution. Merck p.a. KOH was added from a Crison microBU 2031 automatic buret to a 0.01 M solution of the corresponding acid. Electromotive force measurements were made with a Crison micropH 2000 pH-meter equipped with a Radiometer GK2401C combined glass membrane electrode, using Ag/AgCl as reference. All solutions were adjusted to the desired ionic strength by adding an inert electrolyte.

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Table 1. Calibration Parameters for the Electrodes Used

	acetic		chloroacetic		phenylacetic	
I/mol·dm^{-3}	$E°$/mV	s/mV	$E°$/mV	s/mV	$E°$/mV	s/mV
0.10	358.70	58.74	361.84	58.90	363.20	59.21
0.30	358.93	59.11	362.02	59.02	363.06	59.14
0.50	358.84	59.02	362.55	58.97	364.15	59.34
0.70	360.08	59.01	363.04	58.87	364.31	59.31
0.90	361.05	59.12	364.20	59.02	365.37	59.14
1.10	361.47	59.22	365.38	59.05	366.80	59.40
1.30	362.70	59.33	365.96	58.87	368.31	59.54
1.50	362.65	59.07	366.95	58.84	368.88	59.28

Table 2. Stoichiometric Equilibrium Constants for Acetic, Chloroacetic, and Phenylacetic Acids in KNO_3 at 25 °C, Expressed on the Molality (m) Scale

	pK^*		
m/mol·kg^{-1} of KNO_3	acetic	chloroacetic	phenylacetic
0.10	4.566 (0.006)	2.640 (0.011)	4.109 (0.004)
0.30	4.511 (0.010)	2.618 (0.001)	4.070 (0.001)
0.51	4.499 (0.009)	2.595 (0.005)	4.051 (0.003)
0.72	4.483 (0.007)	2.583 (0.011)	4.043 (0.002)
0.94	4.491 (0.004)	2.607 (0.007)	4.066 (0.001)
1.15	4.502 (0.004)	2.615 (0.002)	4.077 (0.005)
1.37	4.521 (0.005)	2.614 (0.004)	4.090 (0.006)
1.60	4.546 (0.013)	2.653 (0.002)	4.118 (0.003)

Stoichiometric equilibrium constants were calculated from data obtained in the potentiometric titrations, using the software MINIQUAD.[21]

The electrode was first calibrated on the proton concentration scale in order to determine the formal potential for each experiment. Calibrations were done over the pH range from 2.3 to 2.9,[22,23] where the electrode response was optimal. Known volumes of a 0.1 M solution of HCl at the desired ionic strength were added to a solution of the background electrolyte at the same ionic strength, and the potential of the mixed solution was measured upon each addition.

Proton concentration−potential data pairs were fitted to the equation $E = E° + s \log [H^+]$, where $[H^+]$ is the hydrogen ion concentration, expressed in molar units. Calibrations provided the value of the reference potential, $E°$, and allowed us to check for Nernstian behavior in the electrode through the Nernst slope, s.

Results and Discussion

Table 1 lists the formal potential, $E°$, and slope, s, obtained using the different electrodes tested. As can be seen, the electrode used to determine the constants for chloroacetic acid deviated markedly from Nernstian behavior; in fact, all slope values were smaller than 59.16 mV (the average was 58.9 mV). For this reason, the electrode slope values in the MINIQUAD listing were corrected, which introduced a virtually constant shift of about 0.02 units in the pK^* values.

The equilibrium constants initially obtained on the molarity scale were converted into molal units through the solution density.[24] Table 2 gives the pK^*_m values obtained as a function of m. Table 3 shows the results of the fitting of these values to eq 3 as well as to the reported values for benzoic, m-nitrobenzoic, and o-chlorobenozic acids in KNO_3 at different ionic strengths.[18] As can be seen, the parameters A and B are virtually the same—within experimental error—for all the acids, suggesting that neither $(\beta^0_{MA} - \lambda)$ nor β^1_{MA} for each electrolyte depends on the particular acid.

Kiss and Urmánczy[25] determined the stoichiometric constant for acetic and formic acids in KNO_3 and other electrolytes at 25 °C. Table 4 shows the results obtained by fitting their data to eq 3; we used the thermodynamic constant, at infinite dilution, reported by Harned and Owen[26] for each acid in the fitting function because the lowest ionic strength studied by the previous authors was 0.5 m. The lack of data for more dilute solutions detracted from the goodness of pK^T, which was obtained by extrapolation to $I = 0$. If, rather than fixing pK^T, this parameter was used as a fitting variable, the following results were obtained: p$K^T = 4.712 \pm 0.013$, $A = 0.143 \pm 0.005$, and $B = 0.474 \pm 0.030$. As can be seen, the thermodynamic constant differs markedly from the accepted value for the acetic acid equilibrium, 4.756.[26] Also, B is rather different from all the values for the acids in Table 3 and from those for KNO_3 in Table 4. This is not surprising taking into account that the variation and contribution of the exponential function, by which B is multiplied, are both maximal at the lower ionic strengths. In any case, the average A and B values obtained from the data of Kiss and Urmanczy[25] in KNO_3 coincide, within fitting error, with the calculated values for the acids studied in this work.

Larsson and Adell[27−29] determined the stoichiometric constants for a large number of carboxylic acids in KCl and NaCl at 18 °C. Because these data were not obtained at 25 °C (the temperature at which tabulated data for the interaction parameters in Pitzer equations were determined), both the constant A_ϕ (0.3910 at 25 °C) and β^1_{MX} had to be recalculated at the working temperature, as they were the two fixed parameters in eq 3. The corrected A_ϕ value was determined by fitting reported data[19] to a sixth-order interpolation polynomial; that for β^1_{MX} was determined from its temperature dependence in each electrolyte[19] ($\beta^1_{NaCl} = 0.2615$ and $\beta^1_{KCl} = 0.2047$ at 18 °C). Table 5 shows the parameter values obtained by applying the Pitzer equations to the data of Larsson et al. As can be seen, both A and B were very similar for all the acids, and the similarity increases when the resemblance among the acids compared is greater; thus, simple carboxylic acids are more similar in their behavior and similarities between parameter values decrease as changes such as new functional groups or chain branching are introduced. Figure 1 shows a plot of (pK^* − pK^T) versus I for the acids in the different media. As can be seen, all the acids behave very similarly. The figure also shows the function for the average of A and B for the first nine carboxylic acids, seven of which have a straight chain—in the other two, isobutyric and isocaproic acid, there is a branched chain. These nine acids exhibit a much more similar behavior. Others possess functional groups (many at positions next to the carboxylate group); although their behavior deviates slightly from that of the previous acids, the trend continues to be very similar. Figure 1 also shows the function corresponding to the average for all the acids examined. The deviation from the curve for the most simple carboxylic acids is apparent but relatively small.

Studies involving a large number of acids in various saline media led to the same conclusion, viz. a high similarity among fitting parameters in the same medium.[6−8,30−32]

On the other hand, provided all the parameters in eq 3 are known, a pK^* versus I plot can be constructed. For example, to be able to calculate the curve for acetic acid in KCl, one must know the interaction parameters for the following electrolytes: HCl (β^0_{HCl}, β^1_{HCl}), KCl (β^1_{KCl}), and potassium acetate (β^0_{KAc}, β^1_{KAc}), which can be obtained from activity and/or osmotic coefficients. Besides, one must also know the salting coefficient of acetic acid in KCl (eqs 3 and

Table 3. Parameter Values Obtained by Fitting the Data of Table 2 and Those for Benzoic, *m*-Nitrobenzoic, and *o*-Chlorobenzoic Acid in Ref 18, All at 25 °C, to Eq 3[a]

	pK^T	*A*	*B*	$\beta^0_{AK} - \lambda_{AH,KNO_3}$	β^1_{AK}
acetic	4.78 ± 0.01	0.18 ± 0.02	0.22 ± 0.05	0.095(0.023)	0.235(0.11)
chloroacetic	2.84 ± 0.02	0.14 ± 0.04	0.37 ± 0.09	0.049(0.046)	0.581(0.21)
phenylacetic	4.32 ± 0.01	0.17 ± 0.02	0.29 ± 0.05	0.084(0.023)	0.397(0.11)
benzoic	4.21 ± 0.01	0.13 ± 0.01	0.35 ± 0.04	0.038(0.012)	0.535(0.09)
m-nitrobenzoic	3.49 ± 0.02	0.16 ± 0.03	0.35 ± 0.08	0.072(0.034)	0.535(0.18)
o-chlorobenzoic	2.96 ± 0.02	0.19 ± 0.03	0.21 ± 0.08	0.107(0.034)	0.212(0.18)
average		*0.16 ± 0.02*	*0.30 ± 0.07*		

[a] The error in the average value corresponds to the standard deviation of the data.

Table 4. Parameter Values Obtained by Fitting the Data of Kiss and Urmánczy[25] for Formic and Acetic Acids in Four Different Electrolytes, All at 25 °C, to Eq 3[a]

	A	*B*
	NaCl	
formic acid	0.210 ± 0.007	0.151 ± 0.030
acetic acid	0.224 ± 0.005	0.168 ± 0.022
	KCl	
formic acid	0.221 ± 0.007	0.204 ± 0.026
acetic acid	0.223 ± 0.003	0.221 ± 0.010
	KNO_3	
formic acid	0.160 ± 0.006	0.330 ± 0.017
acetic acid	0.156 ± 0.006	0.377 ± 0.016
average	*0.158*	*0.354*
	$NaNO_3$	
formic acid	0.151 ± 0.014	0.258 ± 0.052
acetic acid	0.167 ± 0.009	0.274 ± 0.033

[a] The pK^T values for the acids (3.752 for formic and 4.756 for acetic acid) were taken from Harned and Owen.[26]

Table 5. Parameter Values Obtained by Fitting the Data of Larsson and Adell[27−29] for Various Carboxylic Acids in KCl and NaCl, All at 18 °C, to Eq 3[a]

	pK^T	*A*	*B*
	NaCl		
formic	3.750 ± 0.006	0.216 ± 0.005	0.123 ± 0.022
acetic	4.777 ± 0.001	0.228 ± 0.001	0.126 ± 0.005
propionic	4.878 ± 0.005	0.218 ± 0.004	0.166 ± 0.017
butyric	4.816 ± 0.004	0.216 ± 0.004	0.166 ± 0.015
valeric	4.832 ± 0.004	0.221 ± 0.004	0.138 ± 0.015
caproic	4.860 ± 0.006	0.216 ± 0.005	0.158 ± 0.021
heptanoic	4.857 ± 0.005	0.219 ± 0.004	0.152 ± 0.017
isobutyric	4.843 ± 0.003	0.209 ± 0.003	0.168 ± 0.010
isocaproic	4.843 ± 0.004	0.211 ± 0.003	0.189 ± 0.013
average for first 9 acids		*0.217 ± 0.006*	*0.154 ± 0.022*
trimethylacetic	5.037 ± 0.004	0.210 ± 0.004	0.110 ± 0.014
benzoic	4.226 ± 0.009	0.196 ± 0.014	0.154 ± 0.044
glycolic	3.836 ± 0.005	0.189 ± 0.004	0.132 ± 0.018
lactic	3.876 ± 0.003	0.191 ± 0.002	0.132 ± 0.010
ethylmethylglycolic	3.996 ± 0.004	0.196 ± 0.003	0.159 ± 0.012
levulinic	4.652 ± 0.004	0.204 ± 0.003	0.115 ± 0.013
chloroacetic	2.841 ± 0.003	0.198 ± 0.003	0.161 ± 0.011
crotonic	4.705 ± 0.004	0.210 ± 0.004	0.139 ± 0.015
phenylacetic	4.313 ± 0.003	0.209 ± 0.002	0.147 ± 0.009
β-phenylpropionic	4.681 ± 0.003	0.221 ± 0.002	0.125 ± 0.009
phenylglycolic	3.396 ± 0.003	0.180 ± 0.003	0.141 ± 0.011
diphenylglycolic	3.075 ± 0.002	0.168 ± 0.003	0.212 ± 0.010
salicylic	3.025 ± 0.002	0.185 ± 0.003	0.191 ± 0.010
m-hydroxybenzoic	4.169 ± 0.007	0.206 ± 0.006	0.101 ± 0.025
γ-hydroxyvaleric	4.695 ± 0.003	0.217 ± 0.003	0.166 ± 0.012
average for all acids		*0.206 ± 0.015*	*0.149 ± 0.027*
	KCl		
formic	3.745 ± 0.004	0.215 ± 0.003	0.205 ± 0.012
acetic	4.774 ± 0.002	0.225 ± 0.002	0.189 ± 0.007
propionic	4.880 ± 0.002	0.218 ± 0.002	0.212 ± 0.007
butyric	4.818 ± 0.004	0.216 ± 0.003	0.215 ± 0.015
valeric	4.828 ± 0.002	0.217 ± 0.002	0.200 ± 0.008
caproic	4.851 ± 0.004	0.213 ± 0.003	0.214 ± 0.012
heptanoic	4.856 ± 0.004	0.214 ± 0.003	0.207 ± 0.013
isobutyric	4.853 ± 0.004	0.212 ± 0.003	0.191 ± 0.014
isocaproic	4.840 ± 0.003	0.209 ± 0.003	0.230 ± 0.011
average for first 9 acids		*0.215 ± 0.005*	*0.207 ± 0.013*
trimethylacetic	5.037 ± 0.004	0.201 ± 0.004	0.162 ± 0.015
benzoic	4.217 ± 0.002	0.193 ± 0.003	0.178 ± 0.009
glycolic	3.847 ± 0.003	0.210 ± 0.003	0.176 ± 0.011
lactic	3.876 ± 0.003	0.204 ± 0.002	0.183 ± 0.009
ethylmethylglycolic	3.999 ± 0.003	0.194 ± 0.002	0.204 ± 0.010
levulinic	4.645 ± 0.004	0.198 ± 0.003	0.190 ± 0.014
chloroacetic	2.846 ± 0.003	0.194 ± 0.002	0.213 ± 0.010
crotonic	4.712 ± 0.003	0.205 ± 0.003	0.190 ± 0.011
phenylacetic	4.314 ± 0.002	0.211 ± 0.002	0.191 ± 0.007
β-phenylpropionic	4.676 ± 0.002	0.211 ± 0.001	0.202 ± 0.006
phenylglycolic	3.401 ± 0.001	0.182 ± 0.001	0.182 ± 0.004
diphenylglycolic	3.073 ± 0.008	0.164 ± 0.011	0.215 ± 0.035
salicylic	3.049 ± 0.008	0.187 ± 0.006	0.153 ± 0.027
m-hydroxybenzoic	4.174 ± 0.006	0.192 ± 0.005	0.155 ± 0.021
γ-hydroxyvaleric	4.692 ± 0.004	0.209 ± 0.004	0.242 ± 0.016
average for all acids		*0.204 ± 0.014*	*0.196 ± 0.022*

[a] The error in the average value corresponds to the standard deviation of the data.

4). In this way, we reconstructed the curves for acetic acid in three different media (KCl, NaCl, and KNO_3), which are shown in Figure 2 together with experimental data reported elsewhere.[18,25] We used the osmotic coefficients reported by Robinson and Stokes[33] to calculate the parameters for simple electrolytes, viz. hydrochloric acid, potassium chloride, sodium chloride, nitric acid, potassium nitrate, potassium acetate, and sodium acetate, using the following equation

$$\phi = 1 - 0.391\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \beta^0_{MX}I + \beta^1_{MX}Ie^{-2\sqrt{I}} + C^{\phi}_{MX}I^2 \qquad (5)$$

which included the parameter C^{ϕ}_{MX} as experimental values reached high ionic strengths (above 2 molal). The values of the Pitzer interaction parameters are given in Table 6. The salting coefficients in the previous three media were taken from Brandariz et al.[34] The errors in the abovementioned parameters allowed the upper and lower bounds of the fitting to be represented at a confidence level of 95% (see Figure 2). The fitting of the experimental data of Kiss and Urmánczy[25] in KCl and NaCl is very good up to 2 m, above which slight deviations are observed—particularly for KCl. Unfortunately, the interaction parameters θ, ψ, and C^{ϕ} were unavailable, which precluded extending the curves to those situations where interactions among species are crucial by virtue of their high concentrations. Kron et al.[35] also used Pitzer equations to express the stoichiometric constant of water as a function of ionic strength. With KCl or NaCl as the electrolyte, the curves accurately reproduce experimental data when the values for the parameters θ, ψ, and C^{ϕ} are included. In KNO_3, however, the behavior is identical with that for acetic acid in KNO_3 observed in this work (see Figure 2c); that is, the Pitzer equations developed

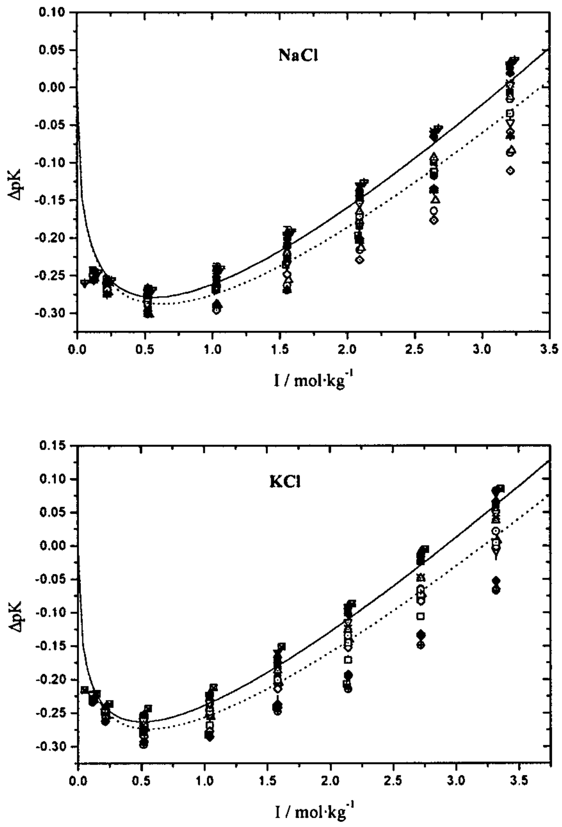

Figure 1. Δp*K* (=p*K** − p*K*^{T}) for various carboxylic acids in NaCl and KCl at 18 °C: (—) Δp*K* using the averaged *A* and *B* values from formic, acetic, propionic, butyric, valeric, caproic, heptanoic, isobutyric, and isocaproic acids in eq 3; (···) Δp*K* as obtained using the averaged *A* and *B* values from all the acids in eq 3; (■) formic; (●) acetic; (▲) propionic; (▼) butyric; (◆) valeric + caproic; (×) heptanoic; (∗) isobutyric; (—) isocaproic; (|) trimethylacetic; (□) benzoic; (○) glycolic; (△) lactic; (▽) ethylmethylglycolic; (◇) levulinic; (⊡) chloroacetic; (⊙) crotonic; (dotted up triangle) phenylacetic; (▽) *β*-pheylpropionic; (dotted diamond) phenylglycolic; (plus in a box) diphenylglycolic; (plus in a circle) salicylic; (plus in an up triangle) *m*-hydroxybenzoic; (plus in a down triangle) *γ*-hydroxyvaleric.

in a similar manner do not fit the experimental data—not even at low ionic strengths. Consistent with the results of Kron et al., only a fitting involving all the parameters accurately reproduces the experimental data. This suggests the presence of some error in the parameters for KNO_3. Although the tabulated Pitzer data were not exactly the same as those calculated in this work, they are identical if the fitting error (Table 6) is considered; consequently, the graphs for KNO_3 suggest that the error lies in the experimental data used to calculate the interaction parameters in this medium. The dotted line in Figure 2c shows the upper and lower bounds for a fitting performed using the model of Guggenheim. The fitting function used was of the form

$$pK^* = pK^T - \frac{A\sqrt{I}}{1 + B_{H,NO_3}\sqrt{I}} - \frac{A\sqrt{I}}{1 + B_{K,Ac}\sqrt{I}} + (C_{H,NO_3} + C_{K,Ac} - \lambda_{HAc,KNO_3})I \quad (6)$$

where *A*, B_i, and C_i were taken from Meier,[36] and *λ* was taken from Brandariz et al.[34] Because Meier made no mention of errors in his parameters, we assumed the lowest possible error based on the number of significant figures used in his work. As can be seen from Figure 2, the fitting, while still departing from the experimental data, was significantly better. Because no data for potassium nitrate other than its salting coefficient were used, the results further support the possibility of an error in the experimental activity coefficients for this electrolyte. Some error in the other two electrolytes (nitric acid and potassium acetate) cannot be excluded, however.

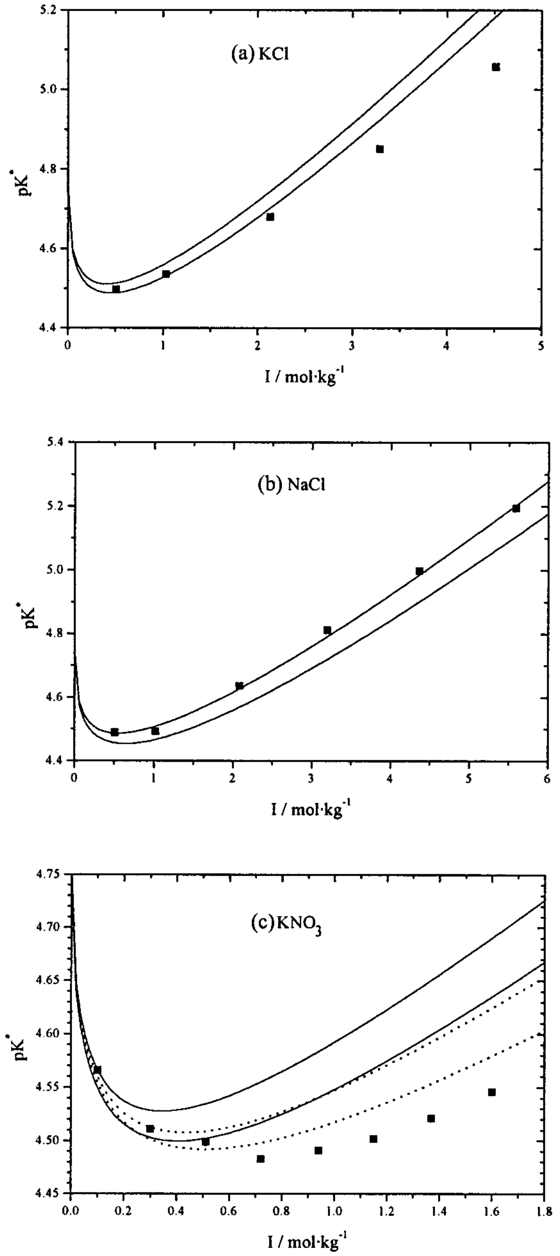

Figure 2. Experimental data for acetic acid in KCl (a), NaCl (b), and KNO_3 (c) at 25 °C. Solid lines are the upper and lower bands corresponding to a 95% confidence level in the fitting function (eq 3) obtained using Pitzer parameter values calculated from bibliography osmotic coefficients.[33] Dashed lines in part c are the upper and lower error bands using the Guggenheim model.

Finally, because the salting coefficients for neutral species are very often ignored on the assumption of a unity activity coefficient, we examined the effect on p*K** of discarding the contribution of the neutral species, that is of removing the parameter $\lambda_{AH,MX}$ from eq 4. Figure 3 illustrates the change in the fitting function for benzoic acid in KNO_3 resulting from removal of the contribution of the neutral molecule, using the salting coefficient reported by

Table 6. Interaction Parameters in Pitzer Equations with Errors Calculated at the 95% Confidence Level[a]

	fitting	Pitzer
	HNO_3	
β^0	0.112 ± 0.002	0.1119
β^1	0.317 ± 0.012	0.3206
C^ϕ	0.00096 ± 0.00078	0.0010
	KNO_3	
β^0	−0.075 ± 0.003	−0.0816
β^1	0.027 ± 0.014	0.0494
C^ϕ	0.00507 ± 0.00071	0.00660
	potassium acetate	
β^0	0.159 ± 0.002	0.1587
β^1	0.322 ± 0.011	0.3251
C^ϕ	−0.00662 ± 0.00059	−0.00660
	HCl	
β^0	0.183 ± 0.002	0.1775
β^1	0.252 ± 0.014	0.2945
C^ϕ	−0.00058 ± 0.00031	0.00080
	KCl	
β^0	0.048 ± 0.001	0.04835
β^1	0.208 ± 0.004	0.2122
C^ϕ	−0.00066 ± 0.00015	−0.00084
	NaCl	
β^0	0.076 ± 0.001	0.0765
β^1	0.265 ± 0.008	0.2664
C^ϕ	0.00130 ± 0.00018	0.00127
	sodium acetate	
β^0	0.143 ± 0.003	0.1426
β^1	0.320 ± 0.015	0.3237
C^ϕ	−0.00630 ± 0.00080	−0.00629

[a] The error in the Pitzer tabulated parameters was unavailable.

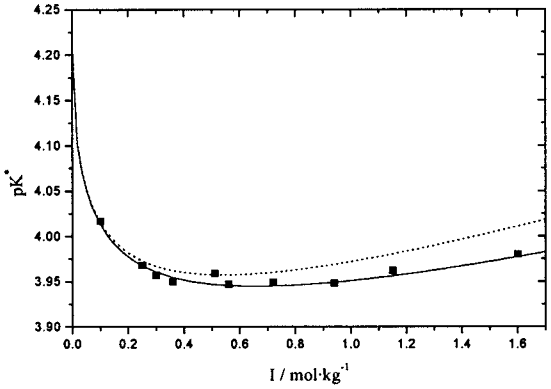

Figure 3. Effect of the activity of the neutral species upon equilibrium, eq 1, for benzoic acid in KNO_3 at 25 °C: (—) complete fitting function (eqs 3 and 4); (···) fitting function without $\lambda_{AH,MX}$, taken from Brandariz et al.;[34] (■) experimental points taken from ref 18.

Brandariz et al.[34] Although the salting coefficient, λ, is relatively small compared to those of other electrolytes (0.024 in KNO_3 versus 0.144 in KCl and 0.199 in NaCl), the change is quite significant, even at moderate ionic strengths. Obviously, the influence of the salting coefficient depends not only on its magnitude but also on its contribution to the *A* term. As a result, assuming that the activity coefficient for a neutral species is close to unity may introduce sizable errors depending on the particular working concentration range.

Conclusions

As shown in this work, Pitzer parameters for carboxylic acids exhibit interesting similarities. An average equation that describes the generic behavior of a carboxylic acid in KNO_3 at 25 °C on the basis of data obtained in our laboratory, and also in KCl and NaCl at 18 °C from reported data, was developed.

The precision of the reconstructed p*K** versus *I* curves obtained from known Pitzer parameter values depends on the reliability of the parameters derived from the individual electrolytes. The results obtained in this work and in previous studies suggest that the data for KNO_3 are subject to some error.

The salting coefficient for a neutral species significantly influences the precision of the curves.

Literature Cited

(1) Morel, F. M. M.; Hering, J. G. In *Principles and applications of aquatic chemistry*; Wiley: New York, 1993; Chapter 6.

(2) Perdue, E. M.; Gjessing, E. T.; Glaze, W. *Organic acids in aquatic ecosystems: report of the Dahlem Workshop on Organic Acids in Aquatic Ecosystems, Berlin 1989, May 7−12*; Wiley: Chichester [England], New York, 1990.

(3) Pittman, E. D.; Lewan, M. D. *Organic acids in geological processes*; Springer-Verlag: Berlin, New York, 1994.

(4) Daniele, P. G.; De Stefano, C.; Foti, C.; Sammartano, S. The effect of ionic strength and ionic medium on the thermodynamic parameters of protonation and complex formation. *Curr. Top. Solution Chem.* **1997**, *2*, 253−274.

(5) Sastre de Vicente, M. E. Ionic strength effects on acid−base equilibria. A review. *Curr. Top. Solution Chem.* **1997**, *2*, 157−181.

(6) 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.

(7) 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 Equilibr.* **1998**, *149* (1−2), 91−101.

(8) 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.

(9) De Stefano, C.; Gianguzza, A.; Piazzese, D.; Sammartano, S. Speciation of low molecular weight carboxylic ligands in natural fluids: protonation constants and association with major components of seawater of oxydiacetic and citric acids. *Anal. Chim. Acta* **1999**, *398* (1), 103−110.

(10) Partanen, J. I. Determination of the molality scale dissociation constants of formic, propionic and *n*-butyric acids in aqueous sodium chloride solutions at 298.15 K. *Acta Chem. Scand.* **1996**, *50* (6), 492−498.

(11) Partanen, J. I. Calculation of stoichiometric dissociation constants of formic, acetic, glycolic and lactic acids in dilute aqueous potassium, sodium or lithium chloride solutions at 298.15 K. *Acta Chem. Scand.* **1998**, *52* (8), 985−994.

(12) Partanen, J. I.; Juusola, P. M.; Minkkinen, P. O. Determination of stoichiometric dissociation constants for propionic acid in aqueous sodium or potassium chloride solutions at 298.15 K. *Acta Chem. Scand.* **1999**, *53* (8), 547−556.

(13) Partanen, J. I.; Juusola, P. M. Determination of stoichiometric dissociation constants of formic acid in aqueous sodium or potassium chloride solutions at 298.15 K. *J. Chem. Eng. Data* **2000**, *45* (1), 110−115.

(14) Kettler, R. M.; Palmer, D. A.; Wesolowski, D. J. Dissociation quotients of succinic acid in aqueous sodium-chloride media to 225 °C. *J. Solution Chem.* **1995**, *24* (1), 65−87.

(15) Kettler, R. M.; Wesolowski, D. J.; Palmer, D. A. Dissociation quotient of benzoic-acid in aqueous sodium-chloride media to 250 °C. *J. Solution Chem.* **1995**, *24* (4), 385−407.

(16) Bénézeth, P.; Palmer, D. A.; Wesolowski, D. J. Dissociation quotients for citric acid in aqueous sodium chloride media to 150 °C. *J. Solution Chem.* **1997**, *26* (1), 63−84.

(17) Kettler, R. M.; Wesolowski, D. J.; Palmer, D. A. Dissociation constants of oxalic acid in aqueous sodium chloride and sodium trifluoromethanesulfonate media to 175 °C. *J. Chem. Eng. Data* **1998**, *43* (3), 337−350.

(18) Barriada, J. L.; Brandariz, I.; Armesto, X. L.; Herrero, R.; Sastre de Vicente, M. E. Trend and energetics of p*K** vs ionic strength for *o*-chlorobenzoic, *m*-nitrobenzoic and benzoic acids in aqueous KNO_3 solutions at 298 K. *J. Chem. Soc., Faraday Trans.* **1998**, *94* (20), 3093−3096.

(19) (a) Pitzer, K. S. *Activity coefficients in electrolyte solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991. (b) Pytkowicz, R. M. *Activity coefficients in electrolyte solutions*; CRC Press: Boca Raton, FL, 1979.

(20) Brandariz, I.; Arce, F.; Armesto, X. L.; Penedo, F.; Sastre de Vicente, M. E. Dependence of Equilibrium-Constants of L-Valine

on Ionic-Strength According to Guggenheim, Scatchard and Pitzer Models. *Monatsh. Chem.* **1993**, *124* (3), 249−257.

(21) Sabatini, A.; Vacca, A.; Gans, P. Miniquad − A general computer programme for the computation of formation constants from potentiometric data. *Talanta* **1974**, *21*, 53−77.

(22) May, P. M.; Williams, D. R.; Linder, P. W.; Torrington, R. G. The use of glass electrodes for the determination of formation constants I. *Talanta* **1982**, *29*, 249−256.

(23) May, P. M.; Murray, K.; Williams, D. R. The use of glass electrodes for the determination of formation constants II. *Talanta* **1985**, *32* (6), 483−489.

(24) Söhnel, O.; Novotný, P. *Densities of aqueous solutions of inorganic substances*; Elsevier: Distribution for the U.S.A. and Canada Elsevier Science Pub. Co.: Amsterdam, New York, 1985.

(25) Kiss, Á. v.; Urmánczy, A. Über die Dissoziationskonstanten von Ameisen- und Essigsäure in konzentrierten Salzlösungen. *Z. Phys. Chem. A* **1934**, *171*, 257−267.

(26) Harned, H. S.; Owen, B. B. *The physical chemistry of electrolytic solutions*, 3rd ed.; Reinhold Pub. Corp.: New York, 1958.

(27) Larsson, E.; Adell, B. Die elektrolytische Dissoziation von Säuren in Salzlösungen. I. Die Dissoziationskonstante der Essigsäure und die Aktivitätsverhältnisse ihrer Ionen in den Lösungen einiger Alkali- und Erdalkalichloride. *Z. Phys. Chem. A* **1931**, *156*, 352−379.

(28) Larsson, E.; Adell, B. Die elektrolytische Dissoziation von Säuren in Salzlösungen. II. Die Dissoziationskonstanten einiger Fettsäuren und die Aktivitätsverhältnisse ihrer Ionen in Natriumchlorid- und Kaliumchloridlösungen. *Z. Phys. Chem. A* **1931**, *156*, 381−396.

(29) Larsson, E.; Adell, B. Die elektrolytische Dissoziation von Säuren in Salzlösungen. III. Die Dissoziationskonstanten einiger Säuren und die Aktivitätsverhältnisse ihrer Ionen in Natriumchlorid- und Kaliumchloridlösungen. *Z. Phys. Chem. A* **1931**, *157*, 342−362.

(30) Daniele, P. G.; Rigano, C.; Sammartano, S. Ionic Strength Dependence of Formation Constants I. *Talanta* **1983**, *30* (2), 81−87.

(31) De Robertis, A.; De Stefano, C.; Rigano, C.; Sammartano, S. Thermodynamic Parameters for the Protonation of Carboxilic Acids in Aqueous Tetraethylammonium Iodide Solutions. *J. Solution Chem.* **1990**, *19* (6), 569−587.

(32) Fiol, S.; Brandariz, I.; Armesto, X. L.; Arce, F.; Sastre de Vicente, M. E. Pitzer parameters calculated from stoichiometric equilibrium constants with commercial H^+ electrodes. *Ann. Chim.* **1993**, *83* (3−4), 175−187.

(33) Robinson, R. A.; Stokes, R. H. *Electrolyte solutions, the measurement and interpretation of conductance, chemical potential, and diffusion in solutions of simple electrolytes*, 2nd ed.; Butterworth Scientific Publications: London, 1959.

(34) Brandariz, I.; Barriada, J. L.; Vilariño, T.; Sastre de Vicente, M. E. Submitted.

(35) Kron, I.; Marshall, S. L.; May, P. M.; Hefter, G.; Königsberger, E. The Ionic Product of Water in Highly Concentrated Aqueous Electrolyte Solutions. *Monatsh. Chem.* **1995**, *126*, 819−837.

(36) Meier, P. C. Two-parameter Debye−Hückel approximation for the evaluation of mean activity coefficients of 109 electrolytes. *Anal. Chim. Acta* **1982**, *136*, 363−368.

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