# Medium Effects on the Protonation of Carboxylic Acids at Different Temperatures

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Here we report a potentiometric study ($H^+$-glass electrode) relative to the protonation of carboxylic acids in different background salts (NaCl, KCl, $Me_4NCl$), at different temperatures ($5 \le t \le 45$ °C) and ionic strengths (NaCl, $0.1 \le I \le 5$; KCl, $0.1 \le I \le 4.5$; $Me_4NCl$, $0.1 \le I \le 3$ mol kg$^{-1}$). Dependence on ionic strength was considered using both a Debye−Hückel type equation and the Pitzer equations. Parameters for the dependence on ionic strength of protonation constants (and of activity coefficients) are reported. From the dependence on temperature of protonation constants, the enthalpy formations $\Delta H°$ were obtained. Some general relationships for the dependence on medium and on temperature of protonation constants are reported.

## Introduction

In our studies of the complexing ability of carboxylic ligands toward metal ions and polyammonium cations [Daniele et al., 1985a, 1990, 1997a (and references cited therein); De Robertis et al., 1996; De Stefano et al., 1993a], we had to determine the protonation constants of these in various ionic media and at various temperatures. It was necessary to work with different ionic media in order to find one that can be considered not to interact with the carboxylic anion and in order to obtain formation constants for cations which interact (Daniele et al., 1994). In particular, the determination of protonation constants at different ionic strengths (different media) allows us to obtain the ionic strength dependence parameters (or specific interaction parameters) for some equations proposed for the dependence on $I$ of log $K^H$ and/or activity coefficients. In the past decade we have carried out several investigations dealing with the dependence on ionic strength of protonation and formation constants [Daniele et al., 1985a,b, 1991; 1997b (and references cited therein); De Stefano et al., 1993b] by using a simple Debye−Hückel type model (DHT), and recently we have extended our interest to other models (Foti et al., 1997, 1998), such as those of Bromley (1973) and Pitzer (1973, 1991). These models have been extensively checked (Borge et al., 1996; Fiol et al., 1993; Millero, 1992; Partenen, 1998) and reviewed (Daniele et al., 1997b; Sastre de Vicente, 1997).

This work reports a potentiometric study of the protonation of malic (mala), tartaric (tar), 1,2,3-propanetricarboxylic (tricarballylic, tca), and 1,2,3,4-butanetetracarboxylic (btc) acids in sodium chloride ($0 \le I \le 5$ mol kg$^{-1}$), potassium chloride ($0 \le I \le 4.5$ mol kg$^{-1}$) and tetramethylammonium chloride ($0 \le I \le 3$ mol kg$^{-1}$) aqueous solutions, at different temperatures ($5 \le t \le 45$ °C). At $t = 25$ °C, and in NaCl and KCl aqueous solutions, acetic (ac), malonic (mal), and citric (cit) acids have also been considered.

## Experimental Section

***Chemicals.*** Carboxylic acids (Fluka products) were used without further purification, and their purity, checked alkalimetrically, was found to be >99%. Sodium and potassium chloride solutions were prepared by weighing pure salt (Fluka, p.a.) previously dried in an oven at 110 °C. Tetramethylammonium chloride, $Me_4NCl$, and tetramethylammonium hydroxide, $Me_4NOH$ (Fluka, purum), were recrystallized from methanol. Sodium hydroxide, potassium hydroxide, and hydrochloric acid solutions were prepared from concentrated ampules (Fluka). Hydroxide solutions and hydrochloric acid solutions were standardized against potassium biphthalate and sodium carbonate, respectively. All solutions were preserved from atmospheric $CO_2$ by means of soda lime traps. For the preparation of all the solutions grade A glassware and twice-distilled water were employed.

***Apparatus.*** The free hydrogen-ion concentration was measured with a Metrohm model 654 potentiometer (resolution, ±0.1 mV; reproducibility, ±0.15 mV) connected with a Metrohm 665 automatic buret and coupled with an Orion combination electrode Ross type 8102. The potentiometer and the buret were connected to a personal computer which, using suitable software, allows the automatic acquisition of data. The measurement cells were thermostated at $t \pm 0.2$, in the range $5 \le t \le 45$ °C. Purified $N_2$ was bubbled into the solutions in order to exclude the presence of $CO_2$ and $O_2$.

***Procedure.*** A 25 mL aliquot of the solution containing the acid under study, an excess of HCl (in order to have the full protonated ligand), and the background salt (in order to have the preestablished value of ionic strength) was titrated with standard hydroxide solution up to 90% neutralization. Details of experimental measurements are reported in Table 1. Separate titrations of HCl at the same ionic strength as the sample under study were carried to determine the standard electrode potential $E°$, and the junction potential coefficient $j_a$ ($E_j = j_a[H^+]$). The procedure followed for all the measurements was that suggested by Braibanti et al. (1987).

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**Table 1. Experimental Details of Potentiometric Measurements**

| acid[a] | $C_{acid}$/ (mmol L$^{-1}$) | salt | $C_{salt}$/ (mol L$^{-1}$) | $t$/°C | titrant |
|---|---|---|---|---|---|
| ac | 6, 12 | NaCl | 0.1−5 | 25 | NaOH |
| | | KCl | 0.1−4 | 25 | KOH |
| mal | 6, 12 | NaCl | 0.1−5 | 25 | NaOH |
| mala | 5, 7.5, 10 | NaCl | 0.1−5 | 5−45 | NaOH |
| | | KCl | 0.1−4 | 25 | KOH |
| | | Me$_4$NCl | 0.1−3 | 15−45 | Me$_4$NOH |
| tar | 5, 7.5 | NaCl | 0.1−5 | 15−45 | NaOH |
| | | Me$_4$NCl | 0.1−3 | 15−45 | Me$_4$NOH |
| cit | 5, 10 | NaCl | 0.1−5 | 25 | NaOH |
| | | KCl | 0.1−4 | 25 | KOH |
| tca | 5, 10 | NaCl | 0.1−5 | 5−45 | NaOH |
| | | KCl | 0.1−4 | 25 | KOH |
| | | Me$_4$NCl | 0.1−1 | 5−45 | Me$_4$NOH |
| btc | 5, 10 | NaCl | 0.1−5 | 5−45 | NaOH |
| | | KCl | 0.1−4 | 25 | KOH |
| | | Me$_4$NCl | 0.1−1 | 5−45 | Me$_4$NOH |

[a] ac = acetic, mal = malonic, mala = malic, tar = tartaric, cit = citric, tca = 1,2,3-propanetricarboxylic, and btc = 1,2,3,4-butanetetracarboxylic acids.

***Calculations.*** The nonlinear least squares computer program ESAB2M (De Stefano et al., 1987) was used to calculate all parameters of an acid−base titration (analytical concentration of reagents, $E°$, $K_w$, junction potential coefficient) and the conditional protonation constants; BSTAC (De Stefano et al., 1993b) and STACO (De Stefano et al., 1996) programs were used to calculate the protonation constants from measurements carried out at different ionic strengths; TDA and LIANA (De Stefano et al., 1997) programs were used to test the dependence of log $K$ on ionic strength by different equations.

The ionic strength dependence of formation constants was taken into account by using a Debye−Hückel type equation and the Pitzer equations. In a series of papers, concerning the dependence on ionic strength of protonation constants and of metal complex formation constants (Daniele et al., 1985a,b, 1991, 1997a; De Stefano et al., 1993b), we showed that it is possible to use a simple Debye−Hückel type (DHT) equation:

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

where

$$C = c_0 p^* + c_1 z^*; \quad D = d_0 p^* + d_1 z^*; \quad E = e_0 p^* + e_1 z^* \tag{2}$$

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

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

($K$ = formation constants; ${}^{T}K$ = formation constant at zero ionic strength; $c_0$, $c_1$, $d_0$, $d_1$, $e_0$, $e_1$ = empirical parameters). At $I \le 1$ mol L$^{-1}$, the $EI^2$ term can be neglected.

According to the specific interaction theory, Pitzer equations (Pitzer, 1973, 1991) estimate the activity coefficients in terms of interactions between ions. If we consider the protonation of a carboxylic anion in a 1:1 salt MX, the thermodynamic constant for a protonation step can be expressed (if $C_{MX} \gg C_A$; $C_{MX}$ = total concentration of background salt, and $C_A$ = total concentration of carboxylic acid) by

$$\begin{aligned} \ln K_j = {} & \ln {}^{T}K_j + 2z_A f^{\gamma} + 2I(\beta_{H,X}{}^{(0)} + \beta_{M,A}{}^{(0)} - \beta_{M,HA}{}^{(0)} + \\ & \Theta_{H,M} + \Theta_{A,X} - \Theta_{HA,X}) + I^2[C_{H,X}{}^{(\phi)} + C_{M,A}{}^{(\phi)}(|z_A|^{1/2})^{-1} - \\ & C_{M,HA}{}^{(\phi)}(|z_{HA}|^{1/2})^{-1} + C_{M,X}{}^{(\phi)} + \Psi_{H,M,X} + \Psi_{A,M,X} - \\ & \Psi_{HA,M,X}] + (\beta_{H,X}{}^{(1)} + \beta_{M,A}{}^{(1)} - \beta_{M,HA}{}^{(1)})f_1 + z_A \beta_{M,X}{}^{(1)} f_2 \end{aligned} \tag{3}$$

in general $A = A^{z-}$, $HA^{(z-1)-}$, ..., $H_{n-1}A^{(z-n+1)-}$ (A = carboxylic anion; $z$ = anion charge; $j = 1...n$; $n$ = maximum number of carboxylic groups). For $j = n$, eq 3 becomes ($\beta_{M,H_{n-1}A}{}^{(0)} = \lambda_{M,H_nA}$):

$$\begin{aligned} \ln K_n = {} & \ln {}^{T}K_n + 2f^{\gamma} + 2I(\beta_{H,X}{}^{(0)} + \beta_{M,H_{n-1}A}{}^{(0)} - \lambda_{M,H_nA} + \\ & \Theta_{H,M} + \theta_{H_{n-1}A,X}) + I^2[C_{H,X}{}^{(\phi)} + C_{M,H_{n-1}A}{}^{(\phi)} + C_{M,X}{}^{(\phi)} + \\ & \Psi_{H,M,X} + \Psi_{H_{n-1}A,M,X}] + (\beta_{H,X}{}^{(1)} + \beta_{M,H_{n-1}A}{}^{(1)})f_1 + \beta_{M,X}{}^{(1)} f_2 \end{aligned} \tag{4}$$

with

$$f^{\gamma} = -A_{\phi}[I^{1/2}(1 + 1.2I^{1/2})^{-1} + 1.667 \ln(1 + 1.2I^{1/2})] \tag{5}$$

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

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

where $I$ is the ionic strength in the molal scale, $\beta^{(0)}$, $\beta^{(1)}$, $C^{(\phi)}$ represent interaction parameters between two ions of opposite sign, $\Theta$ is the interaction parameter between two ions of the same sign (+ +, − − interactions), $\Psi$ is the triplet interaction parameter (+ − +, − + −), $\lambda$ is the interaction parameter of the neutral species; $A_\phi$ is the Debye−Hückel coefficient [$A_\phi = 0.3912 + 6.636 \times 10^{-4}((t/°C) - 25) + 3.562 \times 10^{-6}((t/°C) - 25)$; Pitzer, 1991]. At $I \le 3$ mol kg$^{-1}$, $\Theta$ and $\Psi$ parameters can be neglected. Literature interaction parameters of some inorganic acids and salts have been used in this work for [HCl, $\beta^{(0)} = 0.1775 - 3.081 \times 10^{-4}((t/°C) - 25)$, $C^{(\phi)} = 0.00080 - 6.213 \times 10^{-5}((t/°C) - 25)$, $\beta^{(1)} = 0.2945 + 1.419 \times 10^{-4}((t/°C) - 25)$; for NaCl, $C^{(\phi)} = 0.00127 - 10.54 \times 10^{-5}((t/°C) - 25)$, $\beta^{(1)} = 0.2664 + 7.005 \times 10^{-4}((t/°C) - 25)$; for KCl, $C^{(\phi)} = -0.000\,84$, $\beta^{(1)} = 0.2122$; for Me$_4$NCl, $C^{(\phi)} = 0.0078 - 7.66 \times 10^{-5}((t/°C) - 25)$, $\beta^{(1)} = -0.029 + 49.0 \times 10^{-4}((t/°C) - 25)$; $\Theta_{H,Na} = 0.036$; $\Theta_{H,K} = 0.005$; $\Psi_{H,Na,Cl} = -0.004$; $\Psi_{H,K,Cl} = -0.007$ (Pitzer, 1991)].

The temperature dependence of protonation constants can be taken into account by the Clarke−Glew ( Clarke and Glew, 1966) equation:

$$\log K_T = \log K_\theta + [\Delta H°_\theta(1/\theta - 1/T) + \Delta C°_{p,\theta}((\theta/T) + \ln(T/\theta) - 1)](R \ln 10)^{-1} \tag{8}$$

($\theta$ = reference temperature; $T$, $\theta$/K).

## Results and Discussion

***Protonation Constants.*** By potentiometric measurements, protonation constants of acetate, malate, malonate, tartrate, citrate, tricarballylate, and butanetetracarboxylate were determined in different ionic media, in the experimental conditions reported in Table 1. Protonation constants in the molal scale in NaCl, KCl, and Me$_4$NCl at different ionic strengths and at $t$ = 25 °C are reported in Tables 2−4. For all carboxylic acids considered, protonation constants are strongly dependent on ionic strength, as shown in Figure 1, where, as an example, the first protonation constant of butanetetracarboxylate is reported

**Table 2. Protonation Constants of Carboxylic Acids in NaCl at 25 °C**

| acid[a] | $I$/(mol kg$^{-1}$) | log $K_{1m}$ | log $K_{2m}$ | log $K_{3m}$ | log $K_{4m}$ |
|---|---|---|---|---|---|
| | | (±0.005)[b] | | | |
| ac | 0.5 | 4.483 | | | |
| | 1.0 | 4.501 | | | |
| | 2.0 | 4.606 | | | |
| | 3.0 | 4.749 | | | |
| | 5.0 | 5.097 | | | |
| | | (±0.002)[b] | (±0.003)[b] | | |
| mal | 0.1 | 5.290 | 2.635 | | |
| | 0.5 | 5.071 | 2.544 | | |
| | 1.0 | 5.009 | 2.538 | | |
| | 2.0 | 5.014 | 2.595 | | |
| | 3.0 | 5.080 | 2.690 | | |
| | 5.0 | 5.293 | 2.942 | | |
| | | (±0.002)[b] | (±0.002)[b] | | |
| mala | 0.1 | 4.682 | 3.252 | | |
| | 0.5 | 4.483 | 3.158 | | |
| | 1.0 | 4.445 | 3.147 | | |
| | 2.0 | 4.497 | 3.196 | | |
| | 3.0 | 4.610 | 3.282 | | |
| | 5.0 | 4.918 | 3.517 | | |
| | | (±0.002)[b] | (±0.002)[b] | | |
| tar | 0.1 | 3.949 | 2.828 | | |
| | 0.5 | 3.741 | 2.726 | | |
| | 1.0 | 3.691 | 2.705 | | |
| | 2.0 | 3.721 | 2.734 | | |
| | 3.0 | 3.811 | 2.800 | | |
| | 5.0 | 4.074 | 2.994 | | |
| | | (±0.003)[b] | (±0.003)[b] | (±0.005)[b] | |
| cit | 0.1 | 5.773 | 4.351 | 2.921 | |
| | 0.5 | 5.412 | 4.137 | 2.817 | |
| | 1.0 | 5.275 | 4.079 | 2.794 | |
| | 2.0 | 5.190 | 4.093 | 2.818 | |
| | 3.0 | 5.189 | 4.167 | 2.880 | |
| | 5.0 | 5.287 | 4.397 | 3.065 | |
| | | (±0.003)[b] | (±0.004)[b] | (±0.004)[b] | |
| tca | 0.1 | 5.859 | 4.502 | 3.473 | |
| | 0.5 | 5.528 | 4.319 | 3.371 | |
| | 1.0 | 5.429 | 4.301 | 3.351 | |
| | 2.0 | 5.419 | 4.393 | 3.380 | |
| | 3.0 | 5.492 | 4.546 | 3.446 | |
| | 5.0 | 5.740 | 4.934 | 3.642 | |
| | | (±0.003)[b] | (±0.004)[b] | (±0.004)[b] | (±0.005)[b] |
| btc | 0.1 | 6.342 | 5.204 | 4.118 | 3.171 |
| | 0.5 | 5.912 | 4.889 | 3.932 | 3.065 |
| | 1.0 | 5.793 | 4.809 | 3.910 | 3.039 |
| | 2.0 | 5.802 | 4.838 | 3.996 | 3.058 |
| | 3.0 | 5.917 | 4.951 | 4.142 | 3.114 |
| | 5.0 | 6.269 | 5.277 | 4.517 | 3.289 |

[a] ac = acetate, mal = malonate, mala = malate, tar = tartrate, cit = citrate, tca = 1,2,3-propanetricarboxylate, and btc = 1,2,3,4-butanetetracarboxylate acids. [b] Mean values of standard deviations.

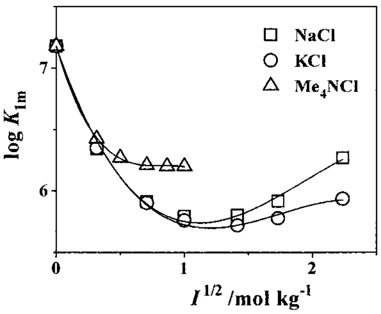

**Figure 1.** log $K_{1m}$ of 1,2,3,4-butanetetracarboxylate vs $I_m^{1/2}$/(mol kg$^{-1}$), in different salts and at $t$ = 25 °C, by using the EDH model (eq 1).

**Table 3. Protonation Constants of Carboxylic Acids in KCl at 25 °C**

| acid[a] | $I$/(mol kg$^{-1}$) | log $K_{1m}$ | log $K_{2m}$ | log $K_{3m}$ | log $K_{4m}$ |
|---|---|---|---|---|---|
| | | (±0.004)[b] | | | |
| ac | 0.1 | 4.556 | | | |
| | 0.5 | 4.491 | | | |
| | 1.0 | 4.516 | | | |
| | 2.0 | 4.634 | | | |
| | 3.0 | 4.787 | | | |
| | 4.5 | 5.052 | | | |
| | | (±0.004)[b] | (±0.004)[b] | | |
| mal | 0.1 | 5.292 | 2.636 | | |
| | 0.5 | 5.084 | 2.550 | | |
| | 1.0 | 5.033 | 2.549 | | |
| | 2.0 | 5.057 | 2.614 | | |
| | 3.0 | 5.136 | 2.715 | | |
| | 4.5 | 5.300 | 2.901 | | |
| | | (±0.003)[b] | (±0.003)[b] | (±0.005)[b] | |
| cit | 0.1 | 5.778 | 4.354 | 2.922 | |
| | 0.5 | 5.439 | 4.151 | 2.822 | |
| | 1.0 | 5.327 | 4.106 | 2.803 | |
| | 2.0 | 5.288 | 4.142 | 2.833 | |
| | 3.0 | 5.324 | 4.233 | 2.898 | |
| | 4.5 | 5.432 | 4.415 | 3.030 | |
| | | (±0.003)[b] | (±0.004)[b] | (±0.004)[b] | |
| tca | 0.1 | 5.863 | 4.500 | 3.476 | |
| | 0.5 | 5.546 | 4.310 | 3.387 | |
| | 1.0 | 5.462 | 4.280 | 3.382 | |
| | 2.0 | 5.477 | 4.348 | 3.440 | |
| | 3.0 | 5.569 | 4.470 | 3.532 | |
| | 4.5 | 5.760 | 4.699 | 3.706 | |
| | | (±0.003)[b] | (±0.004)[b] | (±0.004)[b] | (±0.005)[b] |
| btc | 0.1 | 6.349 | 5.241 | 4.124 | 3.183 |
| | 0.5 | 5.902 | 4.913 | 3.919 | 3.087 |
| | 1.0 | 5.760 | 4.816 | 3.871 | 3.072 |
| | 2.0 | 5.719 | 4.804 | 3.903 | 3.112 |
| | 3.0 | 5.778 | 4.869 | 3.990 | 3.186 |
| | 4.5 | 5.936 | 5.019 | 4.165 | 3.332 |

[a] ac = acetate, mal = malonate, cit = citrate, tca = 1,2,3-propanetricarboxylate, and btc = 1,2,3,4-butanetetracarboxylate acids. [b] Mean values of standard deviations.

**Table 4. Protonation Constants of Malate (mala) and Tartrate (tar) in Me$_4$NCl at Different Temperatures and Ionic Strengths**

| | | mala | | tar | |
|---|---|---|---|---|---|
| $t$/°C | $I$/(mol kg$^{-1}$) | log $K_{1m}$ (±0.005)[a] | log $K_{2m}$ (±0.005)[a] | log $K_{1m}$ (±0.004)[a] | log $K_{2m}$ (±0.005)[a] |
| 15 | 0.1 | 4.710 | 3.293 | 3.994 | 2.867 |
| | 0.5 | 4.571 | 3.241 | 3.850 | 2.812 |
| | 1.0 | 4.562 | 3.258 | 3.835 | 2.824 |
| | 2.0 | 4.631 | 3.336 | 3.891 | 2.893 |
| | 3.0 | 4.773 | 3.450 | 4.021 | 2.999 |
| 25 | 0.1 | 4.710 | 3.269 | 3.978 | 2.846 |
| | 0.5 | 4.567 | 3.215 | 3.831 | 2.788 |
| | 1.0 | 4.552 | 3.229 | 3.811 | 2.798 |
| | 2.0 | 4.611 | 3.301 | 3.858 | 2.861 |
| | 3.0 | 4.744 | 3.411 | 3.979 | 2.962 |
| 35 | 0.1 | 4.717 | 3.256 | 3.978 | 2.828 |
| | 0.5 | 4.572 | 3.197 | 3.828 | 2.765 |
| | 1.0 | 4.556 | 3.206 | 3.804 | 2.769 |
| | 2.0 | 4.610 | 3.268 | 3.843 | 2.821 |
| | 3.0 | 4.738 | 3.366 | 3.955 | 2.910 |
| 45 | 0.1 | 4.745 | 3.255 | 3.990 | 2.828 |
| | 0.5 | 4.597 | 3.193 | 3.837 | 2.764 |
| | 1.0 | 4.577 | 3.198 | 3.809 | 2.766 |
| | 2.0 | 4.624 | 3.251 | 3.840 | 2.813 |
| | 3.0 | 4.745 | 3.340 | 3.946 | 2.897 |

[a] Mean values of standard deviations.

vs $I^{1/2}$ in different salts. The protonation constants of malate, tartrate, tricarballylate, and butanetetracarboxylate in NaCl and Me$_4$NCl were also determined in the temperature range 5 ≤ $t$ ≤ 45 °C. The results obtained (Tables 4−7) also showed a fair dependence of protonation constants on temperature (as can be seen in Figure 2,

**Table 5. Protonation Constants of Malate (mala) and Tartrate (tar) in NaCl at Different Temperatures and Ionic Strengths**

| | | mala | | tar | |
|---|---|---|---|---|---|
| $t$/°C | $I$/(mol kg$^{-1}$) | log $K_{1m}$ (±0.002)[a] | log $K_{2m}$ (±0.002)[a] | log $K_{1m}$ (±0.002)[a] | log $K_{2m}$ (±0.002)[a] |
| 5 | 0.1 | 4.697 | 3.314 | | |
| | 0.5 | 4.511 | 3.223 | | |
| | 1.0 | 4.490 | 3.215 | | |
| | 2.0 | 4.577 | 3.269 | | |
| | 3.0 | 4.724 | 3.361 | | |
| | 5.0 | 5.101 | 3.607 | | |
| 15 | 0.1 | 4.683 | 3.276 | 3.964 | 2.850 |
| | 0.5 | 4.489 | 3.184 | 3.754 | 2.751 |
| | 1.0 | 4.457 | 3.176 | 3.703 | 2.735 |
| | 2.0 | 4.523 | 3.229 | 3.730 | 2.772 |
| | 3.0 | 4.650 | 3.320 | 3.818 | 2.846 |
| | 5.0 | 4.985 | 3.564 | 4.075 | 3.058 |
| 35 | 0.1 | 4.688 | 3.239 | 3.948 | 2.810 |
| | 0.5 | 4.484 | 3.141 | 3.732 | 2.704 |
| | 1.0 | 4.439 | 3.125 | 3.673 | 2.679 |
| | 2.0 | 4.479 | 3.164 | 3.684 | 2.699 |
| | 3.0 | 4.580 | 3.240 | 3.755 | 2.756 |
| | 5.0 | 4.863 | 3.454 | 3.980 | 2.932 |
| 45 | 0.1 | 4.716 | 3.240 | 3.960 | 2.810 |
| | 0.5 | 4.508 | 3.136 | 3.740 | 2.701 |
| | 1.0 | 4.458 | 3.116 | 3.676 | 2.672 |
| | 2.0 | 4.489 | 3.146 | 3.676 | 2.683 |
| | 3.0 | 4.580 | 3.214 | 3.737 | 2.732 |
| | 5.0 | 4.843 | 3.411 | 3.941 | 2.891 |

[a] Mean values of standard deviations.

where the first protonation constant of propanetricarboxylate is reported vs $t$/°C), both in NaCl and Me$_4$NCl aqueous solutions. Values of Tables 2−7 were extrapolated at zero ionic strength by using eq 1 and gave the results reported in Table 8. With respect to malate, tartrate, tricarballylate, and butanetetracarboxylate, $\Delta H°$ and $\Delta C°_p$ values were also determined (using eq 8), and results are reported in Table 9.

***Ionic Strength Dependence.*** In previous works, concerning the protonation constants of carboxylic acids in Me$_4$NCl (Foti et al., 1997) and Et$_4$NI (Foti et al., 1998), we showed how it is possible to express parameters of DHT and Pitzer equations for dependence on ionic strength, by some general equations depending only on anion charge, and independent of the acid considered. Here, we consider other ionic media, NaCl and KCl, at $t = 25$ °C, and we also test dependence on temperature ($5 \le t \le 45$ °C) in NaCl and Me$_4$NCl aqueous solutions.

By using the protonation constants of Tables 2−8, we calculated the empirical $C$, $D$, and $E$ parameters of eq 1. For all acids and in each medium considered, empirical parameters proved independent of the acid and dependent only on anion charge. The values of parameter $C$ obtained in NaCl and KCl medium are reported in Table 10, both in molar and molal scale and at $t = 25$ °C. From the protonation constants of Tables 5 and 6, we calculated parameters in the range $5 \le t \le 45$ °C, and molal values of parameter $C$ in NaCl are reported in Table 11. As shown in previous works (Foti et al., 1997, 1998), in NaCl and KCl, too, the parameters of the DHT equation proved linearly dependent on $z^*$, and it was possible to express the linear dependence by the following relationships [both in the molar and molal scales]:

molar scale

$$\text{NaCl:}\quad C = (0.076 \pm 0.006) + (0.0068 \pm 0.0014)z^*$$

$$E = (0.0130 \pm 0.0007) - (0.00050 \pm 0.00020)z^*$$

$$\text{KCl:}\quad C = (0.089 \pm 0.005) + (0.0108 \pm 0.0010)z^*$$

$$E = (0.0130 \pm 0.0007) - (0.00063 \pm 0.00016)z^*$$

molal scale

$$\text{NaCl:}\quad C = (0.079 \pm 0.003) + [(0.0065 \pm 0.0012) - (0.00035 \pm 0.00007)((t/°\text{C}) - 25)]z^*$$

$$E = (0.0072 \pm 0.0008) - (0.00043 \pm 0.00022)z^*$$

$$\text{KCl:}\quad C = (0.082 \pm 0.004) + (0.0111 \pm 0.0012)z^*$$

$$E = (0.0072 \pm 0.0008) - (0.00099 \pm 0.00022)z^*$$

**Table 6. Protonation Constants of 1,2,3-Propanetricarboxylate (tca) and 1,2,3,4-Butanetetracarboxylate (btc) in NaCl at Different Temperatures and Ionic Strengths**

| | | tca | | | btc | | | |
|---|---|---|---|---|---|---|---|---|
| $t$/°C | $I$/(mol kg$^{-1}$) | log $K_{1m}$ (±0.004)[a] | log $K_{2m}$ (±0.004)[a] | log $K_{3m}$ (±0.005)[a] | log $K_{1m}$ (±0.003)[a] | log $K_{2m}$ (±0.004)[a] | log $K_{3m}$ (±0.004)[a] | log $K_{4m}$ (±0.004)[a] |
| 5 | 0.10 | 5.886 | 4.557 | 3.574 | 6.341 | 5.284 | 4.193 | 3.266 |
| | 0.25 | 5.723 | 4.463 | 3.517 | 6.124 | 5.121 | 4.095 | 3.209 |
| | 0.50 | 5.601 | 4.405 | 3.473 | 5.961 | 5.000 | 4.030 | 3.163 |
| | 0.75 | 5.517 | 4.374 | 3.441 | 5.852 | 4.919 | 3.992 | 3.130 |
| | 1.00 | 5.439 | 4.345 | 3.411 | 5.750 | 4.842 | 3.957 | 3.098 |
| 15 | 0.10 | 5.879 | 4.531 | 3.518 | 6.351 | 5.247 | 4.154 | 3.212 |
| | 0.25 | 5.712 | 4.434 | 3.463 | 6.129 | 5.082 | 4.054 | 3.156 |
| | 0.50 | 5.583 | 4.372 | 3.420 | 5.958 | 4.956 | 3.985 | 3.111 |
| | 0.75 | 5.493 | 4.336 | 3.390 | 5.840 | 4.871 | 3.944 | 3.080 |
| | 1.00 | 5.408 | 4.303 | 3.361 | 5.729 | 4.790 | 3.905 | 3.050 |
| 35 | 0.10 | 5.913 | 4.530 | 3.465 | 6.421 | 5.232 | 4.136 | 3.167 |
| | 0.25 | 5.738 | 4.428 | 3.411 | 6.188 | 5.062 | 4.031 | 3.112 |
| | 0.50 | 5.595 | 4.357 | 3.372 | 5.999 | 4.927 | 3.956 | 3.071 |
| | 0.75 | 5.492 | 4.312 | 3.345 | 5.864 | 4.833 | 3.907 | 3.043 |
| | 1.00 | 5.393 | 4.270 | 3.320 | 5.735 | 4.743 | 3.862 | 3.017 |
| 45 | 0.10 | 5.949 | 4.551 | 3.462 | 6.476 | 5.249 | 4.151 | 3.170 |
| | 0.25 | 5.770 | 4.446 | 3.410 | 6.238 | 5.076 | 4.045 | 3.116 |
| | 0.50 | 5.621 | 4.370 | 3.372 | 6.041 | 4.937 | 3.966 | 3.077 |
| | 0.75 | 5.511 | 4.321 | 3.347 | 5.896 | 4.838 | 3.914 | 3.050 |
| | 1.00 | 5.406 | 4.274 | 3.324 | 5.759 | 4.744 | 3.865 | 3.026 |

[a] Mean values of standard deviations.

**Table 7. Protonation Constants of 1,2,3-Propanetricarboxylate (tca) and 1,2,3,4-Butanetetracarboxylate (btc) in $Me_4NCl$ at Different Temperatures and Ionic Strengths**

| | | tca | | | btc | | | |
|---|---|---|---|---|---|---|---|---|
| t/°C | I/(mol kg$^{-1}$) | log $K_{1m}$ (±0.005)[a] | log $K_{2m}$ (±0.005)[a] | log $K_{3m}$ (±0.006)[a] | log $K_{1m}$ (±0.004)[a] | log $K_{2m}$ (±0.005)[a] | log $K_{3m}$ (±0.005)[a] | log $K_{4m}$ (±0.005)[a] |
| 5 | 0.10 | 5.918 | 4.573 | 3.590 | 6.385 | 5.312 | 4.211 | 3.284 |
| | 0.25 | 5.802 | 4.502 | 3.558 | 6.234 | 5.191 | 4.140 | 3.254 |
| | 0.50 | 5.759 | 4.483 | 3.553 | 6.181 | 5.140 | 4.120 | 3.252 |
| | 0.75 | 5.754 | 4.491 | 3.562 | 6.182 | 5.129 | 4.127 | 3.264 |
| | 1.00 | 5.754 | 4.502 | 3.573 | 6.189 | 5.123 | 4.137 | 3.277 |
| 15 | 0.10 | 5.912 | 4.546 | 3.532 | 6.397 | 5.276 | 4.172 | 3.228 |
| | 0.25 | 5.794 | 4.472 | 3.498 | 6.243 | 5.154 | 4.098 | 3.195 |
| | 0.50 | 5.746 | 4.448 | 3.490 | 6.187 | 5.099 | 4.074 | 3.190 |
| | 0.75 | 5.737 | 4.451 | 3.495 | 6.183 | 5.085 | 4.076 | 3.199 |
| | 1.00 | 5.733 | 4.456 | 3.502 | 6.186 | 5.076 | 4.082 | 3.209 |
| 35 | 0.10 | 5.947 | 4.545 | 3.475 | 6.470 | 5.262 | 4.153 | 3.178 |
| | 0.25 | 5.824 | 4.464 | 3.436 | 6.311 | 5.136 | 4.073 | 3.141 |
| | 0.50 | 5.767 | 4.430 | 3.420 | 6.246 | 5.076 | 4.041 | 3.129 |
| | 0.75 | 5.749 | 4.422 | 3.418 | 6.234 | 5.057 | 4.034 | 3.130 |
| | 1.00 | 5.736 | 4.417 | 3.417 | 6.229 | 5.042 | 4.032 | 3.133 |
| 45 | 0.10 | 5.985 | 4.566 | 3.470 | 6.527 | 5.280 | 4.168 | 3.180 |
| | 0.25 | 5.859 | 4.482 | 3.429 | 6.366 | 5.152 | 4.086 | 3.140 |
| | 0.50 | 5.797 | 4.442 | 3.410 | 6.297 | 5.089 | 4.049 | 3.125 |
| | 0.75 | 5.775 | 4.429 | 3.404 | 6.280 | 5.067 | 4.038 | 3.122 |
| | 1.00 | 5.758 | 4.419 | 3.399 | 6.271 | 5.049 | 4.031 | 3.122 |

[a] Mean values of standard deviations.

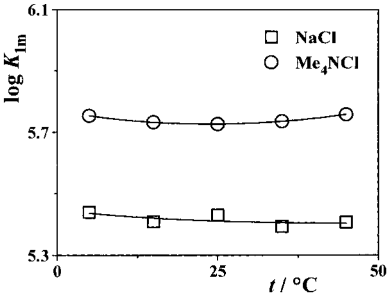

**Figure 2.** log $K_{1m}$ of 1,2,3-propanetricarboxylate vs *t*, in NaCl and $Me_4NCl$, at $I = 1$ mol kg$^{-1}$.

**Table 8. Protonation Constants[a] of Malate (mala), Tartrate (tar), 1,2,3-Propanetricarboxylate (tca), and 1,2,3,4-Butanetetracarboxylate (btc) at Different Temperatures and $I = 0$ mol kg$^{-1}$**

| | | log $K_j^{H}$ [b] | | | |
|---|---|---|---|---|---|
| t/°C | j | mala | tar | tca | btc |
| 5 | 1 | 5.108 | | 6.481 | 7.135 |
| | 2 | 3.520 | | 4.944 | 5.879 |
| | 3 | | | 3.774 | 4.583 |
| | 4 | | | | 3.467 |
| 15 | 1 | 5.096 | 4.381 | 6.477 | 7.149 |
| | 2 | 3.482 | 3.057 | 4.920 | 5.844 |
| | 3 | | | 3.717 | 4.546 |
| | 4 | | | | 3.412 |
| 25 | 1 | 5.097 | 4.366 | 6.489 | 7.179 |
| | 2 | 3.458 | 3.036 | 4.913 | 5.830 |
| | 3 | | | 3.681 | 4.529 |
| | 4 | | | | 3.379 |
| 35 | 1 | 5.104 | 4.367 | 6.516 | 7.225 |
| | 2 | 3.446 | 3.019 | 4.922 | 5.833 |
| | 3 | | | 3.663 | 4.530 |
| | 4 | | | | 3.365 |
| 45 | 1 | 5.133 | 4.38 | 6.555 | 7.284 |
| | 2 | 3.446 | 3.02 | 4.945 | 5.851 |
| | 3 | | | 3.659 | 4.547 |
| | 4 | | | | 3.368 |

[a] Stepwise: $H^+ + H_{j-1}A^{(z-j+1)-} = H_jA^{(z-j)-}$. [b] Standard deviations for these extrapolated (by eq 1) values range between 0.002 and 0.005.

(the parameter *D* can be neglected, both in the molar and molal scales).

**Table 9. Thermodynamic Parameters[a] for the Protonation of Malate (mala), Tartrate (tar), 1,2,3-Propanetricarboxylate (tca), and 1,2,3,4-Butanetetracarboxylate (btc), at $I = 0$ mol L$^{-1}$ and $t = 25$ °C**

| acid | j | $\Delta G°_j$/(kJ mol$^{-1}$) | $\Delta H°_j$/(kJ mol$^{-1}$) | $T\Delta S°_j$/(kJ mol$^{-1}$) | $\Delta C°_{p,j}$/(J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|
| mala | 1 | 29.09 ± 0.01 [b] | 1.18 ± 0.16 [b] | 30.3 ± 0.2 [b] | 187 ± 16 [b] |
| | 2 | 19.74 ± 0.02 | −2.92 ± 0.14 | 16.8 ± 0.2 | 149 ± 12 |
| tar | 1 | 24.92 ± 0.01 | −0.76 ± 0.07 | 24.2 ± 0.1 | 243 ± 10 |
| | 2 | 17.33 ± 0.02 | −2.82 ± 0.09 | 14.5 ± 0.1 | 172 ± 12 |
| tca | 1 | 37.04 ± 0.02 | 3.5 ± 0.2 | 40.5 ± 0.2 | 227 ± 20 |
| | 2 | 28.04 ± 0.03 | 0.4 ± 0.3 | 28.4 ± 0.3 | 234 ± 25 |
| | 3 | 21.01 ± 0.03 | −4.5 ± 0.3 | 16.5 ± 0.3 | 241 ± 40 |
| btc | 1 | 40.98 ± 0.02 | 6.7 ± 0.4 | 47.7 ± 0.4 | 250 ± 25 |
| | 2 | 33.29 ± 0.02 | −0.8 ± 0.4 | 32.5 ± 0.4 | 256 ± 25 |
| | 3 | 25.86 ± 0.03 | −1.1 ± 0.5 | 24.8 ± 0.5 | 268 ± 40 |
| | 4 | 19.22 ± 0.03 | −3.8 ± 0.5 | 15.4 ± 0.5 | 270 ± 40 |

[a] Refer to the reaction $H^+ + H_{j-1}A^{(z-j+1)-} = H_jA^{(z-j)-}$. [b] ±std dev.

The temperature gradient in NaCl is reported for molal *C* values only; for the other parameters it can be neglected. With respect to parameters in $Me_4NCl$, they were reported in a previous work, at $t = 25$ °C (Foti et al., 1997):

$Me_4NCl$

molar scale:
$$C = 0.093 + 0.013n + 0.130z^*$$
$$D = -0.10z^*$$
$$E = 0.030z^*$$

molal scale:
$$C = 0.030 + 0.010n + 0.136z^*$$
$$D = -0.10z^*$$
$$E = 0.025z^*$$

($n$ = number of carboxylic groups).

Pitzer interaction parameters (eq 4) in $Me_4NCl$ can also be calculated by some general equations linearly, depending on anion charge and independent of the acid considered (Foti et al., 1997):

**Table 10. Values of the *C* Parameter (Equation 1)[a] of Carboxylate Ligands in NaCl and KCl, Both in Molar and Molal Scale, at 25 °C**

| | | | NaCl | | KCl | |
|---|---|---|---|---|---|---|
| acid[b] | *j* | *z** | *C*[c] | *C*[d] | *C*[c] | *C*[d] |
| ac | 1 | 2 | 0.143 ± 0.002 [e] | 0.140 ± 0.001 [e] | 0.169 ± 0.001 [e] | 0.156 ± 0.001 [e] |
| mal | 1 | 4 | 0.092 ± 0.005 | 0.095 ± 0.004 | 0.122 ± 0.004 | 0.121 ± 0.004 |
| | 2 | 2 | 0.091 ± 0.002 | 0.092 ± 0.002 | 0.111 ± 0.003 | 0.104 ± 0.003 |
| mala | 1 | 4 | 0.145 ± 0.002 | 0.142 ± 0.002 | | |
| | 2 | 2 | 0.081 ± 0.008 | 0.083 ± 0.001 | | |
| tar | 1 | 4 | 0.110 ± 0.002 | 0.120 ± 0.003 | | |
| | 2 | 2 | 0.059 ± 0.003 | 0.063 ± 0.003 | | |
| cit | 1 | 6 | 0.054 ± 0.009 | 0.060 ± 0.009 | 0.113 ± 0.003 | 0.116 ± 0.003 |
| | 2 | 4 | 0.102 ± 0.001 | 0.103 ± 0.001 | 0.136 ± 0.002 | 0.133 ± 0.003 |
| | 3 | 2 | 0.054 ± 0.002 | 0.058 ± 0.002 | 0.069 ± 0.013 | 0.068 ± 0.004 |
| tca | 1 | 6 | 0.132 ± 0.001 | 0.135 ± 0.002 | 0.173 ± 0.001 | 0.172 ± 0.001 |
| | 2 | 4 | 0.143 ± 0.001 | 0.146 ± 0.001 | 0.172 ± 0.003 | 0.164 ± 0.003 |
| | 3 | 2 | 0.084 ± 0.001 | 0.088 ± 0.001 | 0.101 ± 0.002 | 0.096 ± 0.002 |
| btc | 1 | 8 | 0.126 ± 0.004 | 0.125 ± 0.003 | 0.174 ± 0.004 | 0.169 ± 0.003 |
| | 2 | 6 | 0.123 ± 0.003 | 0.121 ± 0.002 | 0.157 ± 0.002 | 0.145 ± 0.004 |
| | 3 | 4 | 0.115 ± 0.003 | 0.113 ± 0.001 | 0.135 ± 0.002 | 0.128 ± 0.002 |
| | 4 | 2 | 0.073 ± 0.001 | 0.072 ± 0.001 | 0.083 ± 0.003 | 0.077 ± 0.006 |

[a] Refer to the reaction $H^+ + H_{j-1}A^{(z-j+1)-} = H_jA^{(z-j)-}$. [b] ac = acetate, mal = malonate, mala = malate, tar = tartrate, cit = citrate, tca = 1,2,3-propanetricarboxylate, and btc = 1,2,3,4-butanetetracarboxylate acids. [c] Molar scale. [d] Molal scale. [e] ±std dev.

**Table 11. Molal Values of the *C* Parameter (Equation 1)[a] of Carboxylate Ligands in NaCl and Me₄NCl, at Different Temperatures (°C)**

| acid[b] | *j* | 5 °C | 15 °C | 35 °C | 45 °C |
|---|---|---|---|---|---|
| | | | NaCl | | |
| mala | 1 | 0.176 ± 0.002 [c] | 0.156 ± 0.002 [c] | 0.130 ± 0.001 [c] | 0.120 ± 0.003 [c] |
| | 2 | 0.089 ± 0.002 | 0.088 ± 0.001 | 0.073 ± 0.001 | 0.064 ± 0.002 |
| tar | 1 | | 0.117 ± 0.002 | 0.100 ± 0.002 | 0.090 ± 0.002 |
| | 2 | | 0.071 ± 0.002 | 0.054 ± 0.002 | 0.045 ± 0.002 |
| tca | 1 | 0.206 ± 0.003 | 0.178 ± 0.029 | 0.125 ± 0.029 | 0.099 ± 0.029 |
| | 2 | 0.231 ± 0.020 | 0.213 ± 0.020 | 0.178 ± 0.020 | 0.159 ± 0.020 |
| | 3 | 0.049 ± 0.010 | 0.057 ± 0.011 | 0.069 ± 0.010 | 0.077 ± 0.010 |
| btc | 1 | 0.279 ± 0.038 | 0.244 ± 0.038 | 0.174 ± 0.042 | 0.139 ± 0.038 |
| | 2 | 0.210 ± 0.029 | 0.193 ± 0.029 | 0.157 ± 0.029 | 0.140 ± 0.029 |
| | 3 | 0.204 ± 0.020 | 0.189 ± 0.020 | 0.161 ± 0.019 | 0.148 ± 0.020 |
| | 4 | 0.043 ± 0.010 | 0.050 ± 0.010 | 0.064 ± 0.010 | 0.069 ± 0.010 |
| | | | $Me_4NCl$ | | |
| mala | 1 | | 0.546 ± 0.007 [c] | 0.532 ± 0.006 [c] | 0.524 ± 0.005 [c] |
| | 2 | | 0.316 ± 0.003 | 0.300 ± 0.002 | 0.292 ± 0.003 |
| tar | 1 | | 0.534 ± 0.007 | 0.517 ± 0.005 | 0.509 ± 0.005 |
| | 2 | | 0.307 ± 0.003 | 0.291 ± 0.003 | 0.286 ± 0.004 |
| tca | 1 | 0.914 ± 0.011 [b] | 0.897 ± 0.011 | 0.861 ± 0.011 | 0.844 ± 0.011 |
| | 2 | 0.352 ± 0.007 | 0.630 ± 0.007 | 0.589 ± 0.007 | 0.568 ± 0.007 |
| | 3 | 0.345 ± 0.003 | 0.332 ± 0.004 | 0.301 ± 0.004 | 0.288 ± 0.007 |
| btc | 1 | 1.240 ± 0.014 | 1.223 ± 0.014 | 1.190 ± 0.014 | 1.173 ± 0.014 |
| | 2 | 0.883 ± 0.010 | 0.872 ± 0.010 | 0.848 ± 0.010 | 0.838 ± 0.010 |
| | 3 | 0.648 ± 0.007 | 0.629 ± 0.007 | 0.595 ± 0.007 | 0.577 ± 0.007 |
| | 4 | 0.357 ± 0.004 | 0.344 ± 0.003 | 0.315 ± 0.003 | 0.300 ± 0.003 |

[a] Refer to the reaction $H^+ + H_{j-1}A^{(z-j+1)-} = H_jA^{(z-j)-}$. [b] Mala = malate, tar = tartrate, tca = 1,2,3-propanetricarboxylate, and btc = 1,2,3,4-butanetetracarboxylate acids. [c] ±std dev.

$$\text{Me}_4\text{NCl:}\qquad \beta_{\text{Me}_4\text{N},A}{}^{(0)} = 0.023z^2$$

$$C_{\text{Me}_4\text{N},A}{}^{(\phi)} = 0.006 - 0.0055z^2$$

$$\beta_{\text{Me}_4\text{N},A}{}^{(1)} = 0.046 + 0.532z^2$$

($A = \text{A}^{z-}$, $\text{HA}^{(z-1)-}$, ..., $\text{H}_{n-1}\text{A}^{(z-n+1)-}$, A = carboxylic anion; $z$ = carboxylic anion charge; $n$ = maximum number of carboxylic groups). [*Note*: In the calculations relative to Pitzer equations we kept $\lambda_{\text{Na},\text{H}_n\text{A}} = 0.091$, $\lambda_{\text{K},\text{H}_n\text{A}} = 0.094$, and $\lambda_{\text{Me}_4\text{N},\text{H}_n\text{A}} = 0.035 + 0.011n$. These values were calculated as previously described (Foti et al., 1997, 1998). Moreover, we kept $\Theta_{A,\text{X}} = 0$ and $\Psi_{A,\text{M},\text{X}} = 0$. This assumption does not affect the goodness of fit, but we must consider that refined interaction parameters are $\beta_{\text{M},A}{}^{(0)} = \beta_{\text{M},A}{}^{(0)}$(effective) + $\Theta_{A,\text{X}}$ and $C_{\text{M},A}{}^{(\phi)} = C_{\text{M},A}{}^{(\phi)}$(effective) + $\Psi_{A,\text{M},\text{X}}$. These assumptions can be made only if $C_{\text{MX}} \gg C_{\text{A}}$, and therefore reported interaction parameters can be used only under these assumptions.] Pitzer parameters here obtained for malate and tartrate, at 25 °C, fitted quite well with previous equations (for mala, $\beta_{\text{Me}_4\text{N}^+,\text{HA}^-}{}^{(0)} = 0.024$, $\beta_{\text{Me}_4\text{N}^+,\text{A}^{2-}}{}^{(0)} = 0.066$, $\beta_{\text{Me}_4\text{N}^+,\text{HA}^-}{}^{(1)} = 0.68$, and $\beta_{\text{Me}_4\text{N}^+,\text{A}^{2-}}{}^{(1)} = 2.30$; for tar, $\beta_{\text{Me}_4\text{N}^+,\text{HA}^-}{}^{(0)} = 0.005$, $\beta_{\text{Me}_4\text{N}^+,\text{A}^{2-}}{}^{(0)} = 0.057$, $\beta_{\text{Me}_4\text{N}^+,\text{HA}^-}{}^{(1)} = 0.74$, and $\beta_{\text{Me}_4\text{N}^+,\text{A}^{2-}}{}^{(1)} = 2.21$). By using the protonation constants of Tables 2−8, we showed how it is also possible to obtain linear relationships on charge for interaction parameters in NaCl and KCl. Calculations performed first by considering all the interaction parameters of eq 4 showed it was possible to express $C^{(\phi)}$ by the general equations

$$\text{NaCl:}\qquad C_{\text{Na},A}{}^{(\phi)} = (0.0057 \pm 0.0013)z^2$$

$$\text{KCl:}\qquad C_{\text{K},A}{}^{(\phi)} = -(0.0084 \pm 0.0016)z^2$$

**Table 12. Pitzer Interaction Parameters (Equations 3 and 4)[a] of Carboxylate Ligands in NaCl, at 25 °C**

| | $\beta^{(0)}$ | | | | $\beta^{(1)}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| acid[b] | $Na^+,A^-$ | $Na^+,A^{2-}$ | $Na^+,A^{3-}$ | $Na^+,A^{4-}$ | $Na^+,A^-$ | $Na^+,A^{2-}$ | $Na^+,A^{3-}$ | $Na^+,A^{4-}$ | std dev[c] |
| ac | 0.133 | | | | 0.286 | | | | 0.007 |
| mal | 0.071 | 0.129 | | | 0.347 | 1.118 | | | 0.019 |
| mala | 0.064 | 0.104 | | | 0.319 | 1.707 | | | 0.011 |
| tar | 0.046 | 0.087 | | | 0.270 | 1.347 | | | 0.021 |
| cit | 0.050 | 0.081 | 0.170 | | 0.201 | 1.309 | 2.694 | | 0.003 |
| tca | 0.075 | 0.118 | 0.201 | | 0.280 | 1.686 | 3.760 | | 0.013 |
| btc | 0.054 | 0.067 | 0.131 | 0.220 | 0.282 | 1.634 | 3.720 | 6.760 | 0.011 |

[a] Calculated by considering $C^{(\phi)} = 0.0057z^2$. [b] ac = acetate, mal = malonate, mala = malate, tar = tartrate, cit = citrate, tca = 1,2,3-propanetricarboxylate, and btc = 1,2,3,4-butanetetracarboxylate acids. [c] Standard deviation of the eqs 3 and 4 fits.

**Table 13. Pitzer Interaction Parameters (Equations 3 and 4)[a] of Carboxylate Ligands in KCl at 25 °C**

| | $\beta^{(0)}$ | | | | $\beta^{(1)}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| acid[b] | $K^+, A^-$ | $K^+, A^{2-}$ | $K^+, A^{3-}$ | $K^+, A^{4-}$ | $K^+, A^-$ | $K^+, A^{2-}$ | $K^+, A^{3-}$ | $K^+, A^{4-}$ | std dev[c] |
| ac | 0.228 | | | | 0.143 | | | | 0.012 |
| mal | 0.159 | 0.345 | | | 0.226 | 0.812 | | | 0.006 |
| cit | 0.154 | 0.306 | 0.526 | | −0.032 | 0.924 | 2.365 | | 0.013 |
| tca | 0.162 | 0.332 | 0.576 | | 0.130 | 1.234 | 2.959 | | 0.008 |
| btc | 0.145 | 0.307 | 0.556 | 0.876 | 0.095 | 0.942 | 2.464 | 4.732 | 0.013 |

[a] Calculated by considering $C^{(\phi)} = -0.0084z^2$. [b] ac = acetate, mal = malonate, cit = citrate, tca = 1,2,3-propanetricarboxylate, and btc = 1,2,3,4-butanetetracarboxylate acids. [c] Standard deviation of the eqs 3 and 4 fits.

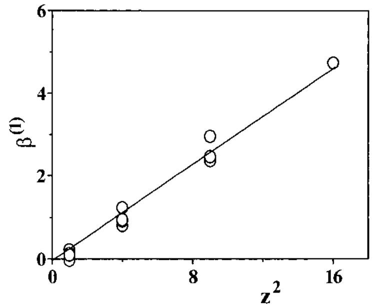

**Figure 3.** $\beta^{(1)}$ (eq 3) of carboxylate ligands in KCl vs $z^2$ ($z$ = anion charge) at $t$ = 25 °C.

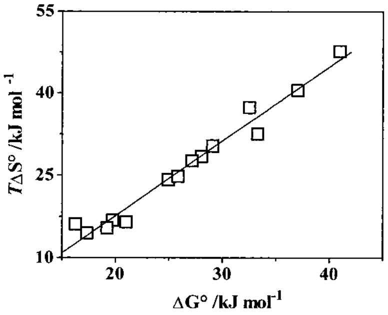

**Figure 4.** $T\Delta S°$ vs $\Delta G°$ for the protonation of carboxylate ligands at $I = 0$ mol L$^{-1}$ and 25 °C.

By considering these values of $C^{(\phi)}$, we calculated the interaction parameters $\beta_{M,A}{}^{(0)}$ and $\beta_{M,A}{}^{(1)}$ (M = cation of salt). Results are reported in Tables 12 and 13, for $Na^+$ and $K^+$, respectively. In this case, too, parameters proved linearly dependent on anion charge, as we can see in Figure 3, where values of $\beta_{M,A}(1)$ in KCl are reported vs $z^2$. The linear dependence on $z^2$ can be expressed by the following relationships:

$$\text{NaCl:}\quad \beta_{Na,A}{}^{(0)} = (0.059 \pm 0.004) + (0.0107 \pm 0.0010)z^2$$

$$\beta_{Na,A}{}^{(1)} = (0.402 \pm 0.010)z^2$$

$$\text{KCl:}\quad \beta_{K,A}{}^{(0)} = (0.121 \pm 0.008) + (0.0476 \pm 0.0009)z^2$$

$$\beta_{K,A}{}^{(1)} = (0.283 \pm 0.008)z^2$$

***Temperature Dependence of Protonation Constants.*** From the temperature dependence of protonation constants we have obtained $\Delta H°$ and $\Delta C°_p$ values reported in Table 9, together with $\Delta G°$ and $T\Delta S°$. The dependence on temperature is quite small, and therefore the main contribution to the stability of protonated species arises from the $T\Delta S°$ term. Moreover, we can observe a linear correlation between $T\Delta S°$ and $\Delta G°$, as shown in Figure 4. The linear relationship can be written [by also considering the protonation of acetate, $-\Delta G° = 27.5$, $T\Delta S° = 27.6$, and malonate, at first step $-\Delta G° = 32.51$, $T\Delta S° = 37.4$ and second step $-\Delta G° = 16.25$, $T\Delta S° = 16.1$ (Martell and Smith, 1997)]:

$$\frac{T\Delta S° - 9.5}{\Delta G°} = 1.337 \pm 0.025$$

with a linear correlation coefficient, $r = 0.985$. This equation can also be written as $-\Delta G° = a + b\Delta S°$, and in this case we have $a = 0.76$ and $b = 213$. The slope of the line is very close to the value of 218 predicted by Bierrum theory (King, 1965). A similar trend, with a close value of the slope $b$, has been found by different authors (Eberson and Wadsö, 1963; Christensen et al., 1967; Purdie et al., 1972). By considering that $\Delta C°_p$ values are affected by large errors, this parameter can be considered a constant; i.e. $\Delta C°_p \sim 230$ J K$^{-1}$ mol$^{-1}$, in accordance with previous findings (King, 1965; De Robertis et al., 1990). For protonation constants determined in NaCl and $Me_4NCl$ at different temperatures ($5 \leq t \leq 45$ °C) we calculated also the temperature gradients for the parameters of EDH and Pitzer equations. By using protonation constants of Tables 7 and 8, we obtained the temperature gradient, for the molal $C$ parameter (for the other parameters of EDH, the temperature gradient can be neglected):

$$\text{Me}_4\text{NCl:}\quad C = 0.030 + 0.010n + [0.136 - (0.00036 \pm 0.00003)((t/°C) - 25)]z^*$$

The temperature gradient of $C^{(\phi)}$ and $\beta^{(0)}$ (Pitzer equations) proved very low and could be neglected; the temper-

**Table 14. Temperature Gradient of Pitzer Interaction Parameters (Equation 3)[a] in NaCl and $Me_4NCl$**

| | | $\partial\beta^{(1)}/\partial t$ | | | |
|---|---|---|---|---|---|
| acid[b] | M | M, $A^-$ | M, $A^{2-}$ | M, $A^{3-}$ | M, $A^{4-}$ |
| mala | $Na^+$ | −0.006 ± 0.002 [c] | −0.015 ± 0.003 [c] | | |
| tar | | −0.014 ± 0.002 | −0.023 ± 0.002 | | |
| tca | | −0.0009 ± 0.0017 | −0.014 ± 0.004 | −0.034 ± 0.005 [c] | |
| btc | | −0.0010 ± 0.0018 | −0.013 ± 0.004 | −0.030 ± 0.006 | −0.057 ± 0.008 [c] |
| mala | $Me_4N^+$ | −0.024 ± 0.002 | −0.010 ± 0.003 | | |
| tar | | −0.028 ± 0.003 | −0.020 ± 0.003 | | |
| tca | | −0.006 ± 0.006 | −0.017 ± 0.009 | −0.027 ± 0.009 | |
| btc | | −0.006 ± 0.005 | −0.018 ± 0.007 | −0.027 ± 0.007 | −0.040 ± 0.008 |

[a] $\partial\beta^{(0)}/\partial t = 0$; $\partial C^{(\phi)}/\partial t = 0$. [b] mala = malate, tar = tartrate, tca = 1,2,3-propanetricarboxylate, and btc = 1,2,3,4-butanetetracarboxylate acids. [c] ±std dev.

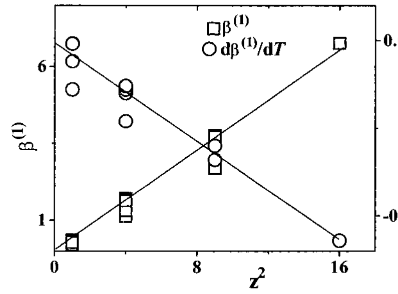

**Figure 5.** $\beta^{(1)}$ (eq 3) of carboxylate ligands in NaCl vs $z^2$ ($z$ = anion charge) at $t$ = 25 °C, together with the relative temperature gradient.

ature gradients of $\beta^{(1)}$ in NaCl and $Me_4NCl$ are reported in Table 14. As can be seen in Figure 5, they also are linearly dependent on $z^2$ and can be expressed by the following general equations:

$$\text{NaCl:}\quad \partial\beta_{\mathrm{Na},A}{}^{(1)}/\partial t = -(0.00360 \pm 0.00009)z^2$$

$$\text{Me}_4\text{NCl:}\quad \partial\beta_{\mathrm{Me_4N},A}{}^{(1)}/\partial t = -(0.00300 \pm 0.00008)z^2$$

***Final Remarks.*** In this work we have reported a large amount of protonation data for several carboxylic acids, in different ionic media and at different ionic strengths and temperatures. Results at low ionic strength fit quite well with literature reports (Pettit and Powell, 1993; Martell and Smith, 1997). Results at high ionic strength are in most cases reported for the first time here. Recently, some papers have reported on the protonation of carboxylic acids in different media and at $I < 1$ mol $L^{-1}$ (Jackson and Seymour, 1995; see also references reported by Daniele et al. (1997b)). For all the carboxylic acids considered here, we have determined parameters for dependence on ionic strength. The most interesting feature of these parameters (or interaction parameters) is the regular trend vs charge, as shown by the different relationships reported in the text, and in accordance with previous findings on the protonation of carboxylic acids in $Me_4NCl$ and in $Et_4NI$ (Foti et al., 1997, 1998). Some interaction parameters have been reported by Pitzer (1991) and Partanen (1998) for mono- and dicarboxylic acids. Values for $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ agree with the present ones, by taking into account the different assumptions (see Note given earlier). Activity coefficients for mono- and dicarboxylic acids were collected by Robinson and Stokes (1965). Also the dependence on temperature of both protonation constants and ionic strength parameters shows interesting (and useful) regularities. This is of great importance for predictive purposes, in particular when dealing with the speciation problems of multicomponent natural systems.

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## Literature Cited

Borge, G.; Etxebarria, N.; Fernadéz, L. A.; Olazabal, M. A.; Madariaga, J. M. Development of a Modified Bromley's Methodology (MDM) for the Estimation of Ionic Media Effects on Solution Equilibria. Part 2. Correlation of the Molar and Molal Interaction Parameters with the Charge and Crystal Radii of the Ions. *Fluid Phase Equilib.* **1996**, *121*, 99−109, and references cited therein.

Braibanti, A.; Ostacoli, G.; Paoletti, P.; Pettit, L. D.; Sammartano, S. Recommended Procedure for Testing the Potentiometric Apparatus and Technique for the pH-Metric Measurement of Metal-Complex Equilibrium Constants. *Pure Appl. Chem.* **1987**, *59*, 1721−1728.

Bromley, L. A. Themodynamic Properties of Strong Electrolytes in Aqueous Solutions. *AIChE J.* **1973**, *19*, 313−320.

Christensen, J. J.; Izatt, R. M.; Hansen, L. D. Thermodynamics of Proton Ionization in Dilute Aqueous Solution. VII. $\Delta H°$ and $\Delta S°$ Values for Proton Ionization from Carboxylic Acids at 25 °C. *J. Am. Chem. Soc.* **1967**, *89*, 213−222.

Clarke, E. C. W.; Glew, D. N. Evaluation of Thermodynamic Functions from Equilibrium Constants. *Trans. Faraday Soc.* **1966**, *134*, 539−547.

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

Daniele, P. G.; Rigano, C.; Sammartano, S. Ionic Strength Dependence of Formation Constants. 9. Alkali Metal Complexes of Ethylenediaminetetraacetate, Nitrilotriacetate, Diphosphate, and Tripolyphosphate in Aqueous Solution. *Anal. Chem.* **1985b**, *57*, 2956−2960.

Daniele, P. G.; De Robertis, A.; De Stefano, C.; Gianguzza, A.; Sammartano, S. Studies on Polyfunctional O-Ligands. Formation Thermodynamics of Simple and Mixed Alkali Metal Complexes with Citrate at Different Ionic Strengths in Aqueous Solution. *J. Chem. Res.* **1990**, (S) 300−301, (M) 2316−2350.

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

Daniele, P. G.; De Stefano, C.; Prenesti, E.; Sammartano, S. Weak Complex Formation in Aqueous Solution. *Curr. Top. Sol. Chem.* **1994**, *1*, 95−106.

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

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. Sol. Chem.* **1997b**, *2*, 253−274.

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* (6), 569−587.

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

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

De Stefano, C.; Gianguzza, A.; Sammartano, S. Mixed Proton Complexes of Amino Acids and Carboxylic Ligands in Aqueous Solution. *Talanta* **1993a**, *40*, 629−635.

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

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

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

Eberson, L.; Wadsö, I. Intramolecular Hydrogen Bonding as a Factor in Determining the $K_1/K_2$ Ratios of Dicarboxylic Acids. *Acta Chem. Scand.* **1963**, *17*, 1552−1562.

Fiol, S.; Brandariz, I.; Armesto, X. L.; Arce, F.; Sastre De Vicente, M. Pitzer's parameters calculated from stoichiometric equilibrium constants with commercial $H^+$ electrodes. *Ann. Chim. (Rome)* **1993**, *83*, 175−187, and references cited therein.

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

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.

Jackson, G. E.; Seymour, L. F. Formation Constants at High Ionic Strength I. Potentiometric Determination of Protonation Constants for Succinic, Propionic and Monomethyl Succinic Acid in Different Ionic Media. *Talanta* **1995**, *42* (1), 5−8.

King, E. J. *Acid−Base Equilibria*; Pergamon: New York, 1965.

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

Millero, F. J. Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength. *Geochim. Cosmochim. Acta* **1992**, *56*, 3123−3132, and references cited therein.

Partanen, J. I. Calculation of Stoichiometric Dissociation Constants of Formica, Acetic, Glycolic and Lactic Acids in Dilute Aqueous Potassium, Sodium or Lithium Chloride Solutions at 298.15 K. *Acta Chem. Scand.* **1998**, *52*, 985−994.

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

Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268−277.

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

Purdie, N.; Tomson, M. B.; Riemann, N. The Thermodynamics of Ionization of Polycarboxylic Acids. *J. Solution Chem.* **1972**, *1* (5), 465−476.

Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1955.

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

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