

Dependence on Ionic Strength of Protonation Enthalpies of Polycarboxylate Anions in NaCl Aqueous Solution

Concetta De Stefano, Claudia Foti, Ottavia Giuffrè, and Silvio Sammartano*

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

The protonation enthalpies of some polycarboxylate anions (malonate, citrate, 1,2,3-propanetricarboxylate, and 1,2,3,4-butanetetracarboxylate) were studied calorimetrically at different ionic strengths, $1 \leq I \leq 5$ mol kg⁻¹, in NaCl aqueous solutions. Some potentiometric measurements were also made at 15 and 55 °C. Both calorimetric and potentiometric data (including previously reported data) were used to obtain complete sets of ΔG , ΔH , and $T\Delta S$ values for the protonation of carboxylate anions. The dependence of ΔH on ionic strength was modeled by simple linear equations and using the Pitzer equations. Both ΔH values and their dependence on ionic strength follow regular trends as a function of the protonation steps, and general empirical relationships are proposed.

Introduction

Speciation studies require a knowledge of the dependence on ionic strength of protonation and complex formation constants (see, e.g., ref 1). In the past two decades several studies have been carried out in this field (ref 2 and references cited therein) in our laboratory. The dependence on ionic strength of the protonation constants of carboxylate ligands was studied at different temperatures and in different ionic media: Me₄NCl,³ Et₄NI,⁴ NaCl, and KCl.⁵ Although these papers reported some ΔH values and parameters for the dependence of ionic strength on temperature, no direct attention was paid to the problem of the dependence of ΔH protonation on I . This problem can be dealt with, however, (i) by studying the simultaneous dependence of $\log K^H$ on T and I or (ii) by performing direct calorimetric measurements at different values of I . Some recent studies of the effect of medium on the protonation thermodynamics of mono-, di-, and tricarboxylate anions were performed^{6–12} using the potentiometric technique alone. In this work we decided to use both methods (also using previously reported data) to build a complete picture of the dependence on I of ΔH protonation values for carboxylate ligands. The carboxylate anions taken into account were malonate (*mal*), citrate (*cit*), 1,2,3-propanetricarboxylate (tricarboxylate, *tca*), and 1,2,3,4-butanetetracarboxylate (*btc*). To correctly calculate ΔH values for the protonation of carboxylate anions at different ionic strengths, exact ΔH values for the ionization of water in the same conditions must be known. We therefore performed some ΔH_w measurements at high I values and systematically analyzed the data reported in the literature. We chose NaCl as the background salt because it is the most important salt in speciation studies of natural waters.

Experimental Section

Materials. Malonic acid (H₂*mal*, Fluka puriss.), citric acid (H₃*cit*, Fluka puriss.), 1,2,3-propanetricarboxylic acid (H₃*tca*, Fluka puriss.), and 1,2,3,4-butanetetracarboxylic

acid (H₄*btc*, Fluka purum) were used without further purification; their purity was checked alkalimetrically and was always $\geq 99.5\%$. Na₂(*mal*), Na₃(*cit*), Na₃(*tca*), and Na₄(*btc*) solutions were prepared by adding standard NaOH to H₂(*mal*), H₃(*cit*), H₃(*tca*), and H₄(*btc*) solutions up to neutralization. The purity of these reagents was tested by potentiometric titration. Sodium chloride solutions (Fluka puriss.) were prepared by weighing previously oven-dried pure salts at 110 °C. Standard solutions of NaOH and HCl were prepared by diluting concentrated Fluka ampules and were standardized against potassium hydrogen phthalate and sodium carbonate, respectively. Grade A glassware and twice-distilled water were used for all solutions.

Potentiometric Measurements. Potentiometric measurements were carried out with a Metrohm 654 potentiometer coupled with a combination Ross type electrode 8102; the titrant was delivered by a Metrohm dosimat 665 dispenser, and a computer program was used for the acquisition of potentiometric data. The titration program allows the evaluation of equilibrium potential values and determines the amount of titrant based on the actual buffering properties on the titrated solution, so that there is a difference in pH values of 0.05–0.08 between two successive readings; the emf was considered to be stable when the variation was $< \pm 0.1$ mV within 5 min. A volume of 25 mL of the solution containing *mal* or *cit* or *tca* or *btc* and the background salt was titrated with standard NaOH up to $\approx 90\%$ neutralization. Experimental conditions were as follows: $C_{\text{acid}} = 10$ mmol L⁻¹, $C_{\text{NaOH}} = 0.2$ mol L⁻¹, $1 \leq I(\text{NaCl}) \leq 5$ mol kg⁻¹, $T = 15$ and 55 °C. Separate titrations of HCl at about the same ionic strength value as the sample under study were carried out to calculate the standard electrode potential E° of the electrodic cell. A stream of purified and presaturated N₂ was bubbled through all solutions in order to exclude the presence of CO₂ and O₂.

Calorimetric Measurements. Calorimetric measurements were performed at (25.000 ± 0.001) °C using a Tronac isoperibol model 450 titration calorimeter coupled with a Keithley 196 system Dmm digital multimeter. The titrant was delivered by a 2.5 mL capacity model 1002TLL Hamilton syringe. A computer program was used for the

* Author to whom correspondence should be addressed [fax 0039 (0) 90 392827; e-mail sammartano@chem.unime.it].

Table 1. Experimental Values of Overall Protonation Constants of Carboxylate Anions at Different Temperatures and Ionic Strengths

T °C	I mol kg ⁻¹	$\log \beta_1^H \pm 3s^a$	$\log \beta_2^H \pm 3s^a$	$\log \beta_3^H \pm 3s^a$	$\log \beta_4^H \pm 3s^a$
<i>mal</i>					
15	1.00	4.99 ± 0.02	7.57 ± 0.02		
15	2.00	4.98 ± 0.02	7.58 ± 0.02		
15	3.05	5.09 ± 0.02	7.76 ± 0.04		
15	5.19	5.39 ± 0.02	8.38 ± 0.03		
55	0.99	5.05 ± 0.04	7.63 ± 0.05		
55	2.20	5.05 ± 0.02	7.65 ± 0.02		
55	3.08	5.08 ± 0.02	7.73 ± 0.02		
55	5.30	5.29 ± 0.02	8.24 ± 0.02		
<i>tca</i>					
15	0.98	5.46 ± 0.02	9.79 ± 0.02	13.18 ± 0.02	
15	1.47	5.44 ± 0.02	9.78 ± 0.02	13.20 ± 0.02	
15	1.97	5.46 ± 0.02	9.86 ± 0.02	13.31 ± 0.03	
15	3.00	5.55 ± 0.02	10.08 ± 0.02	13.64 ± 0.04	
15	5.13	5.84 ± 0.02	10.69 ± 0.02	14.54 ± 0.02	
55	0.99	5.60 ± 0.02	9.92 ± 0.02	13.32 ± 0.04	
55	1.47	5.55 ± 0.02	9.89 ± 0.02	13.26 ± 0.02	
55	1.98	5.53 ± 0.02	9.89 ± 0.03	13.28 ± 0.04	
55	3.01	5.60 ± 0.02	10.07 ± 0.02	13.55 ± 0.02	
55	5.14	5.77 ± 0.02	10.48 ± 0.02	14.20 ± 0.02	
<i>cit</i>					
15	0.98	5.18 ± 0.02	9.28 ± 0.02	12.09 ± 0.02	
15	1.46	5.12 ± 0.02	9.21 ± 0.02	12.02 ± 0.04	
15	1.97	5.10 ± 0.02	9.21 ± 0.04	12.04 ± 0.05	
15	2.98	5.13 ± 0.05	9.33 ± 0.05	12.23 ± 0.05	
15	5.06	5.36 ± 0.03	9.80 ± 0.04	12.92 ± 0.05	
55	0.98	5.20 ± 0.05	9.21 ± 0.05	11.90 ± 0.05	
55	1.46	5.12 ± 0.03	9.10 ± 0.05	11.76 ± 0.05	
55	1.97	5.08 ± 0.02	9.07 ± 0.03	11.76 ± 0.04	
55	3.03	5.08 ± 0.02	9.12 ± 0.02	11.86 ± 0.02	
55	5.11	5.25 ± 0.05	9.48 ± 0.05	12.40 ± 0.05	
<i>btc</i>					
15	0.97	5.76 ± 0.02	10.58 ± 0.02	14.49 ± 0.03	17.57 ± 0.03
15	1.45	5.72 ± 0.03	10.52 ± 0.02	14.45 ± 0.04	17.54 ± 0.03
15	1.95	5.72 ± 0.02	10.54 ± 0.03	14.50 ± 0.04	17.61 ± 0.03
15	2.94	5.78 ± 0.04	10.67 ± 0.06	14.71 ± 0.05	17.91 ± 0.05
15	4.95	6.04 ± 0.04	11.22 ± 0.05	15.57 ± 0.05	19.05 ± 0.05
55	0.98	5.88 ± 0.02	10.69 ± 0.02	14.58 ± 0.02	17.61 ± 0.02
55	1.45	5.80 ± 0.02	10.58 ± 0.02	14.47 ± 0.03	17.50 ± 0.05
55	1.96	5.80 ± 0.02	10.58 ± 0.02	14.50 ± 0.02	17.56 ± 0.01
55	2.87	5.85 ± 0.02	10.69 ± 0.04	14.69 ± 0.04	17.82 ± 0.05
55	4.96	5.96 ± 0.03	10.98 ± 0.05	15.18 ± 0.05	18.51 ± 0.05

^a s = standard deviation.

acquisition of calorimetric data. Its accuracy was checked by titrating a Tris [tris(hydroxymethyl)aminomethane] buffer with HCl. Calorimetric experiments were performed by titrating 50 mL of the solution (i) of *mal* or *cit* or *tca* or *btc* and the background salt with standard NaOH [experimental conditions: $C_{\text{acid}} = 10 \text{ mmol L}^{-1}$, $C_{\text{NaOH}} = 1.2 \text{ mol L}^{-1}$, $1 \leq I (\text{NaCl}) \leq 5 \text{ mol kg}^{-1}$] and (ii) of $\text{Na}_2(\text{mal})$ or $\text{Na}_3(\text{cit})$ or $\text{Na}_3(\text{tca})$ or $\text{Na}_4(\text{btc})$ and the background salt with standard HCl [experimental conditions: $C_{\text{Na}(\text{carbox})} = 10 \text{ mmol L}^{-1}$, $C_{\text{HCl}} = 1.2 \text{ mol L}^{-1}$, $1 \leq I (\text{NaCl}) \leq 5 \text{ mol kg}^{-1}$]. Measurements for water ionization were performed by adding standard NaOH to 50 mL of HCl solution and the background salt [experimental conditions: $C_{\text{HCl}} = 25 \text{ mmol L}^{-1}$, $C_{\text{NaOH}} = 1.0 \text{ mol L}^{-1}$, $I (\text{NaCl}) = 4.32, 5.54 \text{ mol kg}^{-1}$]. The heat of dilution was measured in separate experiments at each ionic strength.

Calculations. The computer program BSTAC¹³ was used to calculate protonation constants from measurements carried out at variable ionic strengths. Calorimetric titration data were analyzed by the computer program ES5CMI.¹⁴ Using the computer program LIANA,¹⁵ we were able to calculate the thermodynamic parameter values of the carboxylate ligands at $I = 0 \text{ mol kg}^{-1}$, starting from the relative conditional thermodynamic parameters using different equations.

Table 2. Experimental Values of Overall Protonation Enthalpies^a at $T = 25 \text{ }^\circ\text{C}$ and at Different Ionic Strengths (NaCl)

I mol kg ⁻¹	ΔH_1 kJ mol ⁻¹	ΔH_2 kJ mol ⁻¹	ΔH_3 kJ mol ⁻¹	ΔH_4 kJ mol ⁻¹
<i>mal</i>				
1.03	3.42	3.02		
1.54	2.38	0.78		
2.09	0.61	-2.12		
3.26	-1.3	-4.4		
5.42	-7.79	-14.72		
<i>tca</i>				
1.04	2.46	1.96	-2.14	
1.55	1.35	0.14	-5.13	
2.08	0.36	-1.72	-7.49	
3.17	-2.17	-6.25	-13.41	
5.39	-8.72	-16.25	-26.21	
<i>cit</i>				
1.03	0.94	-2.86	-7.46	
1.55	0.00	-4.60	-10.09	
2.08	-0.81	-6.23	-12.00	
3.17	-3.00	-10.04	-16.28	
5.41	-4.16	-14.37	-21.91	
<i>btc</i>				
1.05	4.28	2.75	1.27	-2.72
2.09	1.92	-1.77	-4.86	-10.28
3.21	0.25	-5.36	-9.88	-16.35
5.46	-6.14	-15.18	-23.98	-34.07

^a In all cases the fitting standard deviation ranges between 0.05 and 0.3 kJ mol⁻¹.

Results and Discussion

Experimental Protonation Constants and Protonation Enthalpies. The experimental results of potentiometric and calorimetric measurements are shown in Tables 1 and 2, respectively. Three examples of the effects of ionic strength on $\log \beta^H$ and ΔH are reported in Figure 1. As can be seen, protonation constants are strongly dependent on ionic strength and, in turn, this dependence is a function of temperature.

Potentiometric and calorimetric data (including previous potentiometric values⁵) were fitted collectively using different equations for dependence on temperature and on ionic strength. Temperature dependence was accounted for using the Clarke and Glew¹⁶ equation

$$\log K = \log K_\theta + \Delta H_\theta \left(\frac{1}{\theta} - \frac{1}{T} \right) 52.23 + \Delta C_p \left(\frac{\theta}{T} - 1 + \ln \left(\frac{T}{\theta} \right) \right) / 19.145 \quad (1)$$

($\Delta H/\text{kJ mol}^{-1}$; $\Delta C_p/\text{J K}^{-1} \text{ mol}^{-1}$; θ = reference temperature/K) or by the polynomial-like equation

$$G(T) = a_0 \ln T + \sum_{i=-2}^n a_i T^i \quad (2)$$

Debye–Hückel type² and Pitzer¹⁷ equations were used to describe ionic strength dependence. Mean smoothed ΔG , ΔH , and $T\Delta S$ values (using different equations) are reported in Tables 3–6 for malonate, citrate, 1,2,3-propanetricarboxylate, and 1,2,3,4-butanetetracarboxylate, respectively.

Debye–Hückel Type Equation (DHT). The Debye–Hückel type equation² used in this work is ($I/\text{mol kg}^{-1}$)

$$\log K = \log K^0 - z^* A I^{1/2} / (1 + 1.5 I^{1/2}) + CI + EI^2 \quad (3)$$

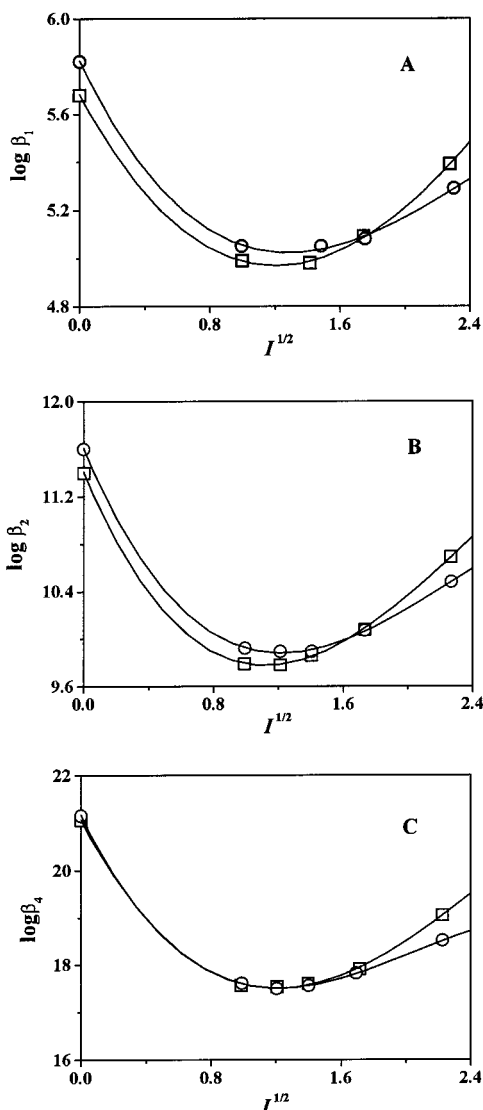


Figure 1. Dependence on ionic strength of protonation constants of (A) malonate (first step), (B) 1,2,3-propanetricarboxylate (second step), and (C) 1,2,3,4-butanetetracarboxylate (fourth step) at (□) 15 °C and (○) 55 °C.

with

$$A = 0.51 + 9.1 \times 10^{-4}(T - 25) + 5.0 \times 10^{-6}(T - 25)^2$$

and

$$z^* = \sum z_{\text{reactants}}^2 - \sum z_{\text{products}}^2$$

(K = formation constant; K^0 = formation constant at infinite dilution; C and E = empirical parameters, z = charge). Preliminary calculations showed that C is a function of z^* for all of the carboxylate anions studied in this work:

$$C = [(0.0204 \pm 0.0029) + (1.56 \pm 0.069) \times 10^{-4}(T - 25)]z^* + (0.031 \pm 0.013) \quad (4)$$

A similar equation can also be considered for E :

$$E = [e_1 + e_2(T - 25)]z^* + e_0 \quad (5)$$

Values for empirical parameters e_1 , e_2 , and e_0 are reported in Table 7. The same order of magnitude (quite low) is observed for these parameters, and a general equation can

be written for all of the carboxylate anions:

$$E = [-(1.7 \pm 0.2) \times 10^{-3} - (5.1 \pm 0.7) \times 10^{-5}(T - 25)]z^* + (0.0127 \pm 0.0009) \quad (6)$$

Pitzer Equations. The Pitzer equations¹⁷ for the systems studied here can be written as³⁻⁵

$$\begin{aligned} \ln K_j = & \ln {}^T K_j + 2z_A f^\gamma + 2I(\beta_{\text{H,Cl}}^{(0)} + \beta_{\text{Na,A}}^{(0)} - \\ & \beta_{\text{Na,HA}}^{(0)} + \Theta_{\text{H,Na}} + \Theta_{\text{A,Cl}} - \Theta_{\text{HA,Cl}}) + I^2 [C_{\text{H,Cl}}^{(\phi)} + \\ & C_{\text{Na,A}}^{(\phi)} (|z_A|^{1/2})^{-1} - C_{\text{Na,HA}}^{(\phi)} (|z_{\text{HA}}|^{1/2})^{-1} + C_{\text{Na,Cl}}^{(\phi)} + \\ & \Psi_{\text{H,Na,Cl}} + \Psi_{\text{A,Na,Cl}} - \Psi_{\text{HA,Na,Cl}}] + (\beta_{\text{H,Cl}}^{(1)} + \beta_{\text{Na,A}}^{(1)} - \\ & \beta_{\text{Na,HA}}^{(1)})f_1 + z_A \beta_{\text{Na,Cl}}^{(1)} f_2 \quad (7) \end{aligned}$$

In general $A = A^{z-}$, $HA^{(z-1)-}$, ..., $H_{n-1}A^{(z-n+1)-}$ (A = carboxylate anion; z = anion charge; $j = 1, \dots, n$; n = maximum number of carboxylic groups). For $j = n$, the eq 7 becomes ($\beta_{\text{Na,H}_{n-1}A}^{(0)} = \lambda_{\text{Na,H}_{n-1}A}$)

$$\begin{aligned} \ln K_n = & \ln {}^T K_n + 2f^\gamma + 2I(\beta_{\text{H,Cl}}^{(0)} + \beta_{\text{Na,H}_{n-1}A}^{(0)} - \\ & \lambda_{\text{Na,H}_{n-1}A} + \Theta_{\text{H,Na}} + \Theta_{\text{H}_{n-1},\text{A,Cl}}) + I^2 [C_{\text{H,Cl}}^{(\phi)} + C_{\text{Na,H}_{n-1}A}^{(\phi)} + \\ & C_{\text{Na,Cl}}^{(\phi)} + \Psi_{\text{H,Na,Cl}} + \Psi_{\text{H}_{n-1},\text{A,Na,Cl}}] + \\ & + (\beta_{\text{H,Cl}}^{(1)} + \beta_{\text{Na,H}_{n-1}A}^{(1)})f_1 + \beta_{\text{Na,Cl}}^{(1)} f_2 \quad (7a) \end{aligned}$$

with

$$f^\gamma = -A_\phi [I^{1/2}(1 + 1.2I^{1/2})^{-1} + 1.667 \ln(1 + 1.2I^{1/2})] \quad (7b)$$

$$f_1 = 1 - (1 + 2I^{1/2}) \exp(-2I^{1/2}) \quad (7c)$$

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

where I is ionic strength in the molal scale, $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters between two ions of opposite signs, Θ is the interaction parameter between two ions of the same sign (+ +, - - interactions), Ψ is the triplet interaction parameter (+ - +, - + -), λ is the interaction parameter of neutral species, and A_ϕ is the Debye-Hückel coefficient [$A_\phi = 0.3912 + 6.636 \times 10^{-4}(T - 25) + 3.562 \times 10^{-6}(T - 25)$].¹⁷ At $I \leq 3$ mol kg⁻¹, Θ and Ψ parameters can be neglected. Literature interaction parameters for HCl and NaCl were used in these calculations [$\beta_{\text{H,Cl}}^{(0)} = 0.1775 - 3.081 \times 10^{-4}(T - 25)$, $C_{\text{H,Cl}}^{(\phi)} = 0.00080 - 6.213 \times 10^{-5}(T - 25)$, $\beta_{\text{H,Cl}}^{(1)} = 0.2945 + 1.419 \times 10^{-4}(T - 25)$; $C_{\text{Na,Cl}}^{(\phi)} = 0.00127 - 10.54 \times 10^{-5}(T - 25)$, $\beta_{\text{Na,Cl}}^{(1)} = 0.2664 + 7.005 \times 10^{-4}(T - 25)$; $\Theta_{\text{H,Na}} = 0.036$; $\Psi_{\text{H,Na,Cl}} = -0.004$].¹⁷ Preliminary calculations showed that, for all of the carboxylate anions, $\beta^{(0)}$ is a function of z^2 , according to the relationship

$$\beta_{\text{Na,A}}^{(0)} = (-0.06 \pm 0.03) + (0.043 \pm 0.002)z^2 \quad (8)$$

(fairly independent of temperature). Parameters $C^{(\phi)}$ and $\beta^{(1)}$ can be expressed as a function of $T/^\circ\text{C}$ and z^2 by the simple relationships:

$$C_{\text{Na,A}}^{(\phi)} = [c_1 + c_2(T - 25)]z^2 + c_0 \quad (9)$$

$$\beta_{\text{Na,A}}^{(1)} = [b_1 + b_2(T - 25)]z^2 \quad (10)$$

where c_i and b_i are the empirical parameters reported in Table 8. These parameters are fairly similar for all of the

Table 3. Thermodynamic Parameters^a of Malonate Anion at Different Temperatures and Ionic Strengths

T °C	I mol kg ⁻¹	$-\Delta G_1$ kJ mol ⁻¹	$-\Delta G_2$ kJ mol ⁻¹	ΔH_1 kJ mol ⁻¹	ΔH_2 kJ mol ⁻¹	$T\Delta S_1$ kJ mol ⁻¹	$T\Delta S_2$ kJ mol ⁻¹
10	0	32.3	48.0	1.3	-2.8	33.6	45.2
25	0	32.5	48.0	5.0	4.9	37.5	52.9
40	0	32.8	48.4	8.7	12.5	41.5	60.9
50	0	33.1	48.9	11.2	17.6	44.3	66.5
10	0.1	29.9	45.5	1.2	-3.0	31.1	42.5
25	0.1	30.1	45.5	4.9	4.6	35.0	50.2
40	0.1	30.4	45.9	8.6	12.3	39.0	58.2
50	0.1	30.7	46.4	11.0	17.4	41.7	63.8
10	1	28.4	43.4	-0.3	-5.2	28.1	38.2
25	1	28.5	43.3	3.4	2.5	31.9	45.8
40	1	28.7	43.6	7.1	10.1	35.8	53.7
50	1	28.9	44.0	9.6	15.2	38.6	59.2
10	2	28.5	43.3	-2.2	-8.1	26.3	35.2
25	2	28.5	43.1	1.5	-0.5	30.0	42.6
40	2	28.6	43.3	5.2	7.2	33.8	50.4
50	2	28.8	43.6	7.7	12.3	36.5	55.8
10	3	29.0	44.2	-4.5	-11.7	24.5	32.5
25	3	28.9	43.8	-0.8	-4.0	28.1	39.8
40	3	28.9	43.7	2.9	3.6	31.8	47.4
50	3	29.0	43.9	5.4	8.7	34.4	52.7
10	5	30.7	47.9	-10.2	-20.4	20.5	27.4
25	5	30.3	47.0	-6.5	-12.8	23.8	34.2
40	5	30.0	46.5	-2.8	-5.2	27.2	41.4
50	5	30.0	46.5	-0.3	-0.1	29.7	46.4

^a Errors, expressed as 3 standard deviations, are as follows: for ΔG , ± 0.05 – 0.1 ; for ΔH , ± 0.5 – 2.5 , for $T\Delta S$, ± 1 – 3 .

Table 4. Thermodynamic Parameters^a of Citrate Anion at Different Temperatures and Ionic Strengths

T °C	I mol kg ⁻¹	$-\Delta G_1$ kJ mol ⁻¹	$-\Delta G_2$ kJ mol ⁻¹	$-\Delta G_3$ kJ mol ⁻¹	ΔH_1 kJ mol ⁻¹	ΔH_2 kJ mol ⁻¹	ΔH_3 kJ mol ⁻¹	$T\Delta S_1$ kJ mol ⁻¹	$T\Delta S_2$ kJ mol ⁻¹	$T\Delta S_3$ kJ mol ⁻¹
10	0	36.4	63.8	81.9	-0.1	-4.8	-10.8	36.3	59.0	71.2
25	0	36.5	63.7	81.5	3.3	1.0	-3.3	39.8	64.7	78.2
40	0	36.7	63.9	81.6	6.6	6.8	4.1	43.4	70.7	85.7
50	0	37.0	64.1	81.7	8.8	10.7	9.1	45.8	74.8	90.8
10	0.1	32.7	57.7	74.6	-0.4	-5.3	-11.3	32.4	52.4	63.3
25	0.1	32.8	57.6	74.2	3.0	0.5	-3.9	35.8	58.1	70.4
40	0.1	33.0	57.8	74.2	6.3	6.4	3.6	39.4	64.1	77.8
50	0.1	33.3	58.0	74.4	8.6	10.3	8.5	41.8	68.2	82.9
10	1	29.6	53.1	69.1	-2.7	-9.1	-15.9	26.9	43.9	53.2
25	1	29.6	52.7	68.5	0.6	-3.3	-8.5	30.2	49.4	60.0
40	1	29.7	52.7	68.2	4.0	2.5	-1.0	33.7	55.2	7.2
50	1	29.8	52.8	68.3	6.2	6.4	3.9	36.1	59.2	72.2
10	2	29.0	52.6	68.7	-4.7	-12.7	-20.2	24.3	39.9	48.5
25	2	28.9	52.0	67.8	-1.4	-6.9	-12.8	27.5	45.2	55.1
40	2	28.9	51.8	67.4	2.0	-1.0	-5.3	30.9	50.8	62.1
50	2	29.0	51.9	67.3	4.2	2.9	-0.4	33.2	54.7	66.9
10	3	29.1	53.1	69.6	-6.1	-15.5	-23.6	23.1	37.6	46.0
25	3	28.9	52.4	68.6	-2.7	-9.7	-16.2	26.2	2.8	52.4
40	3	28.8	52.1	68.0	0.6	-3.9	-8.8	29.5	48.3	59.2
50	3	28.9	52.1	67.8	2.9	0	-3.8	31.8	52.1	64.0
10	5	30.5	55.9	73.8	-6.9	-19	-27.9	23.6	37.0	45.9
25	5	30.2	55.1	72.5	-3.5	-13.1	-20.5	26.7	42.0	52.0
40	5	30.1	54.6	71.7	-0.2	-7.3	-13.0	29.9	47.3	58.7
50	5	30.1	54.4	71.4	2.0	-3.4	-8.1	32.2	51.0	63.3

^a See footnote to Table 3.

carboxylate anions, and we can calculate mean values as follows:

$$C_{\text{Na},A}^{(\phi)} = [-(4.8 \pm 0.4) \times 10^{-3} - (8.4 \pm 1.5) \times 10^{-5}(T - 25)]z^2 + (0.0156 \pm 0.0024) \quad (11)$$

$$\beta_{\text{Na},A}^{(1)} = [(0.345 \pm 0.005) - (0.0026 \pm 0.003)(T - 25)]z^2 \quad (12)$$

We demonstrated in previous papers that it is possible to define Pitzer interaction parameters for carboxylate versus charge,³⁻⁵ and Sastre de Vicente and co-workers¹⁸ analyzed the acid–base equilibria of monocarboxylate anions in various ionic media, obtaining very similar Pitzer parameter values for all of the acids.

Dependence of ΔH on Ionic Strength. The dependence on ionic strength of enthalpy changes can be obtained from the temperature coefficients of eqs 4 and 6 or 8–10 or by fitting ΔH values to an empirical polynomial equation:

$$\Delta H_j = \Delta H_j^0 + \sum a_{ij}I^i \quad (13)$$

As a first approximation, a single term is sufficient to fit calorimetric data to eq 13, i.e., $i = 1$, or, at the most, two terms are needed ($i = 1, 2$). These empirical coefficients are very similar for the same protonation step of different anions and are linearly proportional to z^* . Therefore, general empirical equations can be written as follows:

$$\Delta H_j = \Delta H_j^0 + \sum z_j^* a_j I^i \quad (14)$$

Table 5. Thermodynamic Parameters^a of 1,2,3-Propanetricarboxylate Anion at Different Temperatures and Ionic Strengths

T °C	I mol kg ⁻¹	$-\Delta G_1$ kJ mol ⁻¹	$-\Delta G_2$ kJ mol ⁻¹	$-\Delta G_3$ kJ mol ⁻¹	ΔH_1 kJ mol ⁻¹	ΔH_2 kJ mol ⁻¹	ΔH_3 kJ mol ⁻¹	$T\Delta S_1$ kJ mol ⁻¹	$T\Delta S_2$ kJ mol ⁻¹	$T\Delta S_3$ kJ mol ⁻¹
10	0	37.1	65.3	86.7	-3.2	-3.4	-13.6	33.9	61.9	73.1
25	0	37.1	65.3	86.3	3.5	4.2	0	40.6	69.4	86.3
40	0	37.4	65.7	86.6	10.2	11.7	13.7	47.6	77	100.3
50	0	37.8	66.1	87.1	14.6	16.8	22.7	52.4	82.9	109.9
10	0.1	33.5	59.3	79.5	-3.3	-3.6	-13.8	30.2	55.7	65.7
25	0.1	33.5	59.3	79.2	3.4	4.0	-0.2	36.9	63.3	78.9
40	0.1	33.8	59.7	79.5	10.1	11.5	13.4	43.9	71.2	92.9
50	0.1	34.2	60.1	80.0	14.6	16.6	22.5	48.7	76.7	102.5
10	1	31.1	55.8	75.4	-4.2	-5.8	-16.6	26.9	50.1	58.8
25	1	31.0	55.7	74.8	2.5	1.8	-3.0	33.5	57.5	71.9
40	1	31.3	56.0	75.0	9.2	9.4	10.6	40.5	65.4	85.7
50	1	31.7	56.3	75.5	13.6	14.4	19.7	45.3	70.8	95.2
10	2	31.1	56.4	76.2	-5.8	-8.8	-20.5	25.3	47.6	55.7
25	2	31.0	56.1	75.4	0.9	-1.2	-6.8	31.9	54.9	68.6
40	2	31.2	56.2	75.4	7.6	6.4	6.8	38.8	62.6	82.2
50	2	31.5	56.5	75.8	12.0	11.4	15.8	43.5	67.9	91.6
10	3	31.7	57.7	78.0	-8.0	-12.4	-25.2	23.7	45.2	52.9
25	3	31.4	57.2	77.1	-1.3	-4.9	-11.6	30.1	52.3	65.5
40	3	31.5	57.2	76.8	5.3	2.7	2.0	36.9	59.9	78.9
50	3	31.7	57.3	77.0	9.8	7.8	11.1	41.6	65.1	88.1
10	5	33.4	61.3	83.3	-14.2	-21.8	-37.2	19.2	39.5	46.1
25	5	32.9	60.3	81.7	-7.5	-14.2	-23.6	25.3	46.1	58.1
40	5	32.7	59.8	80.9	-0.8	-6.7	-10.0	31.8	53.2	70.9
50	5	32.7	59.7	80.7	3.6	-1.6	-0.9	36.3	58.1	79.8

^a See footnote to Table 3.**Table 6. Thermodynamic Parameters^a of 1,2,3,4-Butanetetracarboxylate Anion at Different Temperatures and Ionic Strengths**

T °C	I mol kg ⁻¹	$-\Delta G_1$ kJ mol ⁻¹	$-\Delta G_2$ kJ mol ⁻¹	$-\Delta G_3$ kJ mol ⁻¹	$-\Delta G_4$ kJ mol ⁻¹	ΔH_1 kJ mol ⁻¹	ΔH_2 kJ mol ⁻¹	ΔH_3 kJ mol ⁻¹	ΔH_4 kJ mol ⁻¹	$T\Delta S_1$ kJ mol ⁻¹	$T\Delta S_2$ kJ mol ⁻¹	$T\Delta S_3$ kJ mol ⁻¹	$T\Delta S_4$ kJ mol ⁻¹
10	0	40.9	74.5	100.6	120.2	2.6	-1.7	-6.9	-14.7	43.5	72.7	93.7	105.6
25	0	41.2	74.7	100.8	120.1	6.4	5.9	4.8	1.1	47.6	80.7	105.6	121.2
40	0	41.6	75.1	101.1	120.3	10.1	13.6	16.5	16.8	51.7	88.6	117.6	137.2
50	0	41.8	75.3	101.3	120.6	12.6	18.7	24.3	27.3	54.4	94.0	125.6	148.0
10	0.1	36.1	66.1	89.8	108.3	2.4	-2.0	-7.2	-15.0	38.6	64.1	82.7	93.3
25	0.1	36.4	66.3	90.0	108.2	6.2	5.6	4.5	0.8	42.6	72.0	94.5	108.9
40	0.1	36.8	66.7	90.3	108.4	9.9	13.3	16.2	16.5	46.7	79.9	106.5	124.9
50	0.1	37.0	66.9	90.5	108.6	12.4	18.4	24.0	27.0	49.4	85.3	114.5	135.7
10	1	32.9	60.4	82.9	100.6	0.8	-4.9	-10.4	-18.5	33.6	55.5	72.4	82.0
25	1	33.1	60.5	82.9	100.2	4.5	2.7	1.3	-2.8	37.6	63.3	84.1	97.5
40	1	33.3	60.7	83.0	100.3	8.3	10.4	13.0	13.0	41.6	71.1	96.0	113.2
50	1	33.5	60.9	83.1	100.4	10.8	15.5	20.8	23.5	44.2	76.4	103.9	123.9
10	2	32.7	60.4	83.1	101.0	-1.3	-8.4	-14.8	-23.6	31.5	52.0	68.3	77.5
25	2	32.9	60.3	82.9	100.4	2.5	-0.8	-3.1	-7.8	35.3	59.5	79.8	92.6
40	2	33.0	60.3	82.8	100.2	6.2	6.9	8.6	7.9	39.2	67.2	91.4	108.1
50	2	33.1	60.4	82.8	100.2	8.7	12.0	16.4	18.4	41.8	72.3	99.2	118.7
10	3	33.2	61.4	84.8	103.2	-3.5	-12.2	-19.9	-29.8	29.7	49.2	64.9	73.4
25	3	33.2	61.1	84.3	102.3	0.2	-4.6	-8.2	-14.0	33.4	56.5	76.1	88.2
40	3	33.2	60.9	84.0	101.8	4.0	3.1	3.5	1.7	37.2	64.0	87.5	103.5
50	3	33.3	60.9	83.8	101.6	6.5	8.2	11.3	12.2	39.7	69.1	95.1	113.8
10	5	34.8	64.7	89.9	109.9	-8.6	-20.7	-32.5	-45.7	26.3	44.0	57.4	64.2
25	5	34.6	64.0	88.8	108.2	-4.8	-13.1	-20.8	-30.0	29.7	50.9	68.0	78.2
40	5	34.4	63.4	87.8	106.9	-1.1	-5.4	-9.1	-14.2	33.3	58.0	78.7	92.7
50	5	34.2	63.1	87.3	106.3	1.4	-0.3	-1.3	-3.7	35.6	62.8	86.0	102.5

^a See footnote to Table 3.**Table 7. Empirical Parameters for Equation 5**

anion	$e_1 \times 10^3$	$e_2 \times 10^5$	e_0
mal	-2.7 ± 0.5^a	8.0 ± 2.3	0.0160 ± 0.0013^b
tca	-4.8 ± 0.4	4.3 ± 1.5	
cit	-1.9 ± 0.4	5.4 ± 1.7	
btc	-2.1 ± 0.2	4.4 ± 0.4	

^a ± standard deviation. ^b The parameter e_0 was made equal for all of the carboxylate anions.

Different types of calculations are reported in Table 9: (1) Parameters a_1 and a_2 are calculated for each protonation step of each acid: the mean deviation on the fit ranges between 0.08 and 0.54 (on average = 0.28), which is comparable with experimental errors, indicating, moreover, that the simple eq 13 is sufficient to fit ΔH versus I . (2) Parameter a_1 is calculated as before while $a_2 = 0$: in this case the mean deviation ranges between 0.07 and 0.67 (on

Table 8. Empirical Parameters for Equations 9 and 10

anion	$c_1 \times 10^3$	$c_2 \times 10^4$	c_0
mal	-6.7 ± 0.4^a	-2.2 ± 0.2^a	$0.017 \pm 0.08^{a,b}$
cit	-7.41 ± 0.15	0	
tca	-3.1 ± 0.2	-1.2 ± 0.1	
btc	-4.9 ± 0.2	-0.9 ± 0.1	

anion	b_1	$b_2 \times 10^3$
mal	0.423 ± 0.013^a	-2.8 ± 0.8^a
cit	0.226 ± 0.004	-3.7 ± 0.3
tca	0.370 ± 0.004	-2.6 ± 0.2
btc	0.350 ± 0.002	-2.6 ± 0.1

^a ± standard deviation. ^b The parameter c_0 was made equal for all of the carboxylate anions.

average = 0.34); that is, the introduction of a quadratic term into eq 13 takes into account a very small proportion of experimental data. (3–5) Successive calculations were

Table 9. Empirical Parameters for the Dependence on Ionic Strength of ΔH (Equation 13)

anion	i	1			2			3			4			5		
		a_1	a_2	ϵ^a	a_1	ϵ^a	a_1/z^*	ϵ^a	a_1/z^*	a_2/z^*	ϵ^a	a_1/z^*	a_2/z^*	ϵ^a		
mal	1	-1.46 ± 0.14^b	-0.17 ± 0.03^b	0.19	-1.93 ± 0.05^b	0.28	-0.29 ± 0.01^b	1.44	-0.25 ± 0.01^b	-0.26 ± 0.02^b	0.47	-0.26 ± 0.01^b	-0.01 ± 0.01^b	2.33		
	2	-2.28 ± 0.10	-0.25 ± 0.02	0.54	-2.85 ± 0.08	0.60		2.15		-0.40 ± 0.02	0.70			3.57		
tca	1	-1.03 ± 0.06	-0.23 ± 0.01	0.08	-1.59 ± 0.11	0.43		0.48		-0.13 ± 0.02	0.49			0.68		
	2	-2.24 ± 0.07	-0.29 ± 0.02	0.20	-2.97 ± 0.14	0.67		0.64		-0.24 ± 0.02	0.31			1.02		
	3	-2.76 ± 0.11	-0.39 ± 0.03	0.42	-3.75 ± 0.17	0.07		1.10		-0.34 ± 0.02	0.49			1.86		
cit	1	-2.50 ± 0.11	0.21 ± 0.02	0.15	-2.00 ± 0.06	0.15		0.63		0.01 ± 0.03	0.97			1.12		
	2	-3.99 ± 0.13	0.21 ± 0.03	0.16	-3.50 ± 0.06	0.13		1.28		-0.08 ± 0.04	1.43			1.46		
	3	-4.73 ± 0.09	0.24 ± 0.02	0.20	-4.15 ± 0.07	0.18		1.38		-0.10 ± 0.04	1.57			1.59		
btc	1	-1.82 ± 0.20	-0.09 ± 0.04	0.26	-1.99 ± 0.08	0.20		0.64		0.05 ± 0.02	0.24			0.85		
	2	-3.12 ± 0.19	-0.14 ± 0.04	0.25	-3.51 ± 0.04	0.29		1.19		0.06 ± 0.03	0.35			1.77		
	3	-3.65 ± 0.19	-0.30 ± 0.04	0.37	-4.57 ± 0.10	0.46		1.71		0.12 ± 0.03	0.81			1.98		
	4	-4.08 ± 0.21	-0.43 ± 0.04	0.50	-5.41 ± 0.12	0.67		1.34		0.24 ± 0.03	0.90			1.01		

¹ Parameters a_1 and a_2 are calculated for each carboxylate anion. ² Only parameter a_1 is calculated for each carboxylate anion. ³ Parameter a_1/z^* (eq) was made equal for all of the carboxylate anions. ⁴ Calculation of a_1/z^* (forced) and a_1/z^* for each carboxylate anion. ⁵ Both a_1/z^* and a_2/z^* made equal for all of the carboxylate anions. ^a ϵ = mean deviation. ^b \pm standard deviation.

performed considering the a/z^* parameters, which, in some cases, were made equal for all of the protonation steps of all the acids. In these calculations mean deviations become significantly higher, but, considering the drastic approximation used, are still reasonable. In accordance with previous findings, these calculations also demonstrate that under the same conditions (temperature, medium) the most important factor governing I dependence is the charge parameter z^* .

Other Empirical Relationships. As observed in this paper, and as previously reported by ourselves and others,^{3-5,18,19} thermodynamic parameters for the protonation of low molecular weight ligands (such as the formation of different classes of complexes) show interesting regularities. These are of three types, summarized as follows: (i) dependence of one thermodynamic parameter on another parameter, or constancy of a parameter in different conditions for different ligands; (ii) empirical relationships between thermodynamic parameters and different features of different ligands taken into consideration; (iii) empirical relationships between ionic strength parameters and anion charge.

In some cases thermodynamic parameters may show good constancy in the investigated range. For example, ΔG for the first protonation step of malonate has a mean value of -29.9 ± 1.5 , with a fairly low standard deviation (in the range $0 \leq I/\text{mol kg}^{-1} \leq 5$, $10 \leq T/^\circ\text{C} \leq 50$), and all of the carboxylate anions behave in the same way: in general, $\sigma < 7 \text{ kJ mol}^{-1}$. $T\Delta S$ variation, however, is quite considerable. Quite the opposite is true of the behavior of amines for which $T\Delta S$ is the constant parameter (or the parameter least subject to variation). The strict relationship between ΔG and $T\Delta S$, already observed by many authors,^{19,20} is particularly interesting. In a previous work⁵ for several carboxylate anions we found the relationship

$$\frac{T\Delta S + A}{\Delta G} = B \quad (15)$$

with $A = -9.5(\pm 0.2)$ and $B = -1.34(\pm 0.03)$, at $T/^\circ\text{C} = 25$ and $I = 0 \text{ mol kg}^{-1}$. Because in this work we obtained ΔG and $T\Delta S$ values at different temperatures and ionic strengths, we were able to investigate the dependence on I and T of the parameters of eq 15. By considering all of the data in Tables 3–6 we have

$$A = -9.5 + 0.25(T - 25) \quad (15a)$$

$$B = -1.37 - 0.12I^{1/2} + 0.11I \quad (15b)$$

with a standard deviation on the fit of $\sigma = 2.5 \text{ kJ mol}^{-1}$.

The empirical relationships (eqs 15a and 15b) indicate that parameter A depends only on temperature and parameter B depends only on ionic strength.

With regard to point ii, it may be observed that ΔH values, among other factors, depend on j (protonation step), n (maximum number of dissociable protons in the acid), and m (number of $-\text{OH}$ groups in the acid). By considering all of the data reported in this work as well as those for acetate, formate, benzoate, succinate, malate, and tartrate ligands,⁶⁻¹² we obtained the very simple relationship ($I = 0 \text{ mol kg}^{-1}$, $T = 25^\circ\text{C}$)

$$\Delta H^0 = 1 - a(j + m - n) \quad (16)$$

with $a = 2.4 \pm 0.3$ and a standard deviation on the fit of $\sigma = 1.5 \text{ kJ mol}^{-1}$.

Empirical relationships for ionic strength dependence parameters have already been discussed in this paper. In particular, we illustrated the strict dependence of these parameters in eqs 4–6, 8–12, and 14 and in Tables 7–9. A further empirical relationship can be obtained by simultaneously considering the dependence of ΔH on j , m , and n and the dependence of ΔH on I . This leads to the equation

$$\Delta H = \Delta H_c^0 + z^*(a_1I + a_2I^2) \quad (17)$$

where ΔH_c^0 is the value calculated by eq 16: $a_1 = -0.29 \pm 0.03$ and $a_2 = -(1.0 \pm 0.7) \times 10^{-3}$, with a standard deviation on the fit of $\sigma = 2.5 \text{ kJ mol}^{-1}$.

Literature Comparison. Protonation enthalpies for 1,2,3-propanetricarboxylate and 1,2,3,4-butanetetracarboxylate have already been reported by us⁵ and are in excellent agreement with the present results, the differences being $\ll 1 \text{ kJ mol}^{-1}$. ΔH values for the protonation of malonate have been reported by several authors^{8,21} and, at low ionic strengths, are very close to each other (differences $< 0.2 \text{ kJ mol}^{-1}$). Kettler et al.⁸ have also reported thermodynamic parameters for $I \leq 5 \text{ mol kg}^{-1}$ (NaCl) in a wide range of temperatures. Their ΔH values are quite close to those reported here for $I \leq 3 \text{ mol kg}^{-1}$, whereas significant differences can be observed at $I = 5 \text{ mol kg}^{-1}$ [$\Delta H_1 = -2.9$, $\Delta H_2 = -9.0 \text{ kJ mol}^{-1}$ (our values -6.5 and -12.8 , respectively)]. For citrate there is also good agreement on ΔH at low ionic strengths (differences $\leq 0.6 \text{ kJ mol}^{-1}$), whereas at $I = 1 \text{ mol kg}^{-1}$ there are significant differences: our values are $\Delta H_1 = 0.6$, $\Delta H_2 = -3.3$, $\Delta H_3 = -8.5$; ref 12: $\Delta H_1 = 3.9$, $\Delta H_2 = 2.4$, $\Delta H_3 = -2$; ref 21: $\Delta H_1 = -1.3$, $\Delta H_2 = -5.7$, $\Delta H_3 = -10.0 \text{ kJ mol}^{-1}$).

In general it may be observed that relatively few protonation enthalpies are reported at high ionic strength in the

Table 10. Molal Thermodynamic Parameters for the Ionization of Water at $I = 0$ mol kg⁻¹

$T/^\circ\text{C}$	$\log K_w^0 \pm 3s^a$	$\Delta H_w^0 \pm 3s^a$	$\Delta C_p \pm 3s^a$
0	14.944 ± 0.006	-62.56 ± 0.17	317 ± 9
5	14.732 ± 0.006	-61.03 ± 0.14	295 ± 9
10	14.532 ± 0.005	-59.60 ± 0.12	275 ± 7
15	14.343 ± 0.005	-58.27 ± 0.11	258 ± 6
20	14.165 ± 0.005	-57.02 ± 0.11	242 ± 5
25	13.997 ± 0.005	-55.85 ± 0.11	228 ± 4
30	13.837 ± 0.005	-54.74 ± 0.11	216 ± 4
35	13.685 ± 0.005	-53.69 ± 0.11	206 ± 4
40	13.541 ± 0.005	-52.68 ± 0.11	197 ± 5
45	13.404 ± 0.005	-51.72 ± 0.12	189 ± 5
50	13.274 ± 0.006	-50.79 ± 0.12	183 ± 6
55	13.150 ± 0.006	-49.89 ± 0.13	178 ± 7
60	13.032 ± 0.007	-49.01 ± 0.14	174 ± 8

^a s = standard deviation.

literature and most are obtained from the temperature gradients in potentiometric data. In our opinion more direct calorimetric determinations are needed.

In our results we did not explicitly report ΔC_p values for the protonation of the different acids, because they are affected by significant error. It is nevertheless possible, using some of our own previous results as well as those in the literature,^{20,22} to calculate mean values for each protonation step at 25 °C and $I = 0$ mol kg⁻¹:

$$\Delta C_{p1}^0 = 245 \pm 60 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta C_{p2}^0 = 405 \pm 40 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta C_{p3}^0 = 570 \pm 55 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta C_{p4}^0 = 730 \pm 90 \text{ JK}^{-1} \text{ mol}^{-1}$$

Final Remarks

This work reports ΔG , ΔH , and $T\Delta S$ values for the protonation of some polycarboxylate anions at different ionic strengths in NaCl aqueous solutions. Our main comments on the results are as follows:

(i) These are the first results reported in the literature based on calorimetric and potentiometric measurements in a wide ionic strength range.

(ii) No data relative to the protonation of tca and btc have ever previously been published either (in a previous paper only potentiometric data were reported⁵).

(iii) Both dependence on ionic strength and thermodynamic parameter values can be modeled by simple empirical equations (see eqs 4–6 and 8–12).

(iv) From careful analysis of literature data (together with a few calorimetric measurements) we calculated thermodynamic parameters for the ionization of water in the ranges $0 \leq T/^\circ\text{C} \leq 60$ and $0 < I/\text{mol kg}^{-1} \leq 5$.

Appendix I: Ionization of Water in NaCl Aqueous Media

Careful studies of the ionization of water were carried out using both potentiometric and calorimetric techniques. We systematically analyzed the literature relative to K_w and ΔH_w determinations in NaCl aqueous solutions and selected some 150 $\log K_w$, ΔH_w , and ΔC_{pW} values at different temperatures and ionic strengths.^{23–29} Generally, different authors' values are fairly consistent in the ranges $0 \leq T/^\circ\text{C} \leq 60$ and $I/\text{mol kg}^{-1} \leq 3$, whereas at higher ionic strengths differences are greater. We therefore made some calorimetric measurements, and the values obtained were $\Delta H(I = 4.32 \text{ mol kg}^{-1}) = -59.86 \pm 0.08$ and $\Delta H(I = 5.54$

Table 11. Molal Thermodynamic Parameters for the Ionization of Water at Different Temperatures and Ionic Strengths (NaCl)

T °C	I mol kg ⁻¹	$\log K_w \pm 3s^a$	$\Delta H_w^0 \pm 3s^a$ kJ mol ⁻¹	$\Delta C_p \pm 3s^a$ J K ⁻¹ mol ⁻¹
5	0.1	14.53 ± 0.01	-61.2 ± 0.1	272 ± 4
15	0.1	14.14 ± 0.01	-58.7 ± 0.1	235 ± 4
25	0.1	13.79 ± 0.01	-56.5 ± 0.1	205 ± 4
35	0.1	13.47 ± 0.01	-54.5 ± 0.1	183 ± 4
45	0.1	13.19 ± 0.01	-52.7 ± 0.1	166 ± 4
55	0.1	12.93 ± 0.01	-51.1 ± 0.1	155 ± 4
5	0.5	14.44 ± 0.02	-61.2 ± 0.3	244 ± 12
15	0.5	14.05 ± 0.02	-58.8 ± 0.3	207 ± 12
25	0.5	13.70 ± 0.02	-56.9 ± 0.2	177 ± 12
35	0.5	13.38 ± 0.02	-55.2 ± 0.2	155 ± 12
45	0.5	13.09 ± 0.02	-53.7 ± 0.2	138 ± 12
55	0.5	12.83 ± 0.02	-52.3 ± 0.2	127 ± 12
5	1	14.46 ± 0.02	-61.2 ± 0.4	226 ± 16
15	1	14.07 ± 0.02	-59.0 ± 0.3	189 ± 16
25	1	13.71 ± 0.02	-57.2 ± 0.3	159 ± 16
35	1	13.39 ± 0.02	-55.7 ± 0.3	137 ± 16
45	1	13.10 ± 0.02	-54.3 ± 0.3	120 ± 16
55	1	12.83 ± 0.02	-53.1 ± 0.3	109 ± 16
5	2	14.58 ± 0.02	-61.5 ± 0.4	204 ± 18
15	2	14.18 ± 0.02	-59.5 ± 0.4	166 ± 18
25	2	13.82 ± 0.02	-57.9 ± 0.3	137 ± 18
35	2	13.50 ± 0.02	-56.6 ± 0.3	114 ± 18
45	2	13.20 ± 0.02	-55.4 ± 0.3	97 ± 18
55	2	12.93 ± 0.02	-54.4 ± 0.3	86 ± 18
5	3	14.73 ± 0.02	-61.8 ± 0.4	185 ± 17
15	3	14.34 ± 0.02	-60.1 ± 0.3	148 ± 17
25	3	13.97 ± 0.02	-58.6 ± 0.3	118 ± 17
35	3	13.64 ± 0.02	-57.5 ± 0.3	95 ± 17
45	3	13.34 ± 0.02	-56.5 ± 0.3	79 ± 17
55	3	13.06 ± 0.02	-55.6 ± 0.3	68 ± 17
5	5	15.09 ± 0.03	-62.7 ± 0.5	146 ± 25
15	5	14.69 ± 0.03	-61.3 ± 0.5	108 ± 25
25	5	14.32 ± 0.03	-60.2 ± 0.4	79 ± 25
35	5	13.98 ± 0.03	-59.4 ± 0.4	56 ± 25
45	5	13.66 ± 0.03	-58.7 ± 0.4	40 ± 25
55	5	13.37 ± 0.03	-58.2 ± 0.4	29 ± 25

^a s = standard deviation.

mol kg⁻¹) = -61.3 ± 0.1 kJ mol⁻¹. These data were considered together with literature data. To fit $\log K_w$ and ΔH_w we used the equations:

$$\log K = \log K^0 + (-2AF + CI + Df_1 + Ef_2)/\ln(10) \quad (18)$$

$$\Delta H = \Delta H^0 + R/1000 [-2(-315.14 + 1.2544T)F + (-p_4 + p_7T)I + (-p_5 + p_8T)f_1 + (-p_6 + p_9T)f_2] \quad (19)$$

$$\Delta C_p = \Delta C_p^0 + R(1.2544 \times 2F + p_4f_1 + p_7f_2) \quad (20)$$

$$\log K^0 = (1595.3 - 81830/T + 5494500/T^2 - 250.56 \ln T + 0.25889T)/\ln 10 \quad (21)$$

$$\Delta H^0 = (81830 - 2 \times 5494500/T - 250.56T + 0.25889T^2)R/1000 \quad (22)$$

$$\Delta C_p^0 = (2 \times 5494500/T^2 - 250.56 + 2 \times 0.25889T)R \quad (23)$$

where

$$A = (-7.8135 + 315.14/T + 1.2544 \ln T)$$

$$F = I^{1/2}/(1 + 1.2I^{1/2}) + 1.667 \ln(1 + 1.2 I^{1/2})$$

$$f_1 = [1 - (1 + 2I^{1/2}) - 2I^{1/2}]$$

$$C = (p_1 + p_4/T + p_7 \ln T)$$

$$D = (p_2 + p_5/T + p_8 \ln T)$$

$$E = (p_3 + p_6/T + p_9 \ln T)$$

with

$$\begin{aligned} p_1 &= 1.7379; & p_2 &= 29.509; & p_3 &= 1.0465; & p_4 &= -6.0803; \\ p_5 &= -1447.1; & p_6 &= -44.037; & p_7 &= -0.21111; & p_8 &= -4.2692; \\ p_9 &= -0.15772; & R &= 8.31433 \end{aligned}$$

The fit of these data is quite good as shown by the low errors reported in Tables 10–11 together with thermodynamic parameters. The value of ΔH_W^0 ($T^\circ\text{C} = 25$, $I = 0$ mol kg^{-1}) can be compared with CODATA³⁰ recommended ones ($\Delta H_W^0 = -55.82 \pm 0.06$ kJ mol^{-1}) and with that proposed by NBS³¹ ($\Delta H_W^0 = -55.84$ kJ mol^{-1}). Other useful comparisons can be made with the values reported in refs 23–25 and 32–34.

Literature Cited

- Grenthe, I., Puigdomenech, I., Eds. *Modeling in Aquatic Chemistry*; OECD: 1997.
- 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.
- 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*, 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.
- 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.
- Mesmer, R. E.; Patterson, C. S.; Busey, R. H.; Holmes. Ionization of acetic acid in NaCl(aq) media: a potentiometric study to 573 K and 130 bar. *J. Phys. Chem.* **1989**, *93*, 7483–7490.
- Kettler, R. M.; Palmer, D. A.; Wesolowski, D. J. Dissociation quotients of oxalic acid in aqueous sodium chloride media to 175 °C. *J. Solution Chem.* **1991**, *20*, 905–927.
- Kettler, R. M.; Wesolowski, D. J.; Palmer, D. A. Dissociation quotients of malonic acid in aqueous sodium chloride media to 100 °C. *J. Solution Chem.* **1992**, *21*, 883–900.
- 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*, 65–87.
- 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*, 385–407.
- Bell, J. L. S.; Wesolowski, D. J.; Palmer, D. A. The dissociation quotients of formic acid in sodium chloride solutions to 200 °C. *J. Solution Chem.* **1993**, *22*, 125–136.
- Bénézech, 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*, 63–84.
- 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)* **1993**, *83*, 243–277.
- De Robertis, A.; De Stefano, C.; Rigano, C. Computer analysis of equilibrium data in solution. ES5CM fortran and basic programs for computing formation enthalpies from calorimetric measurements. *Thermochim. Acta* **1989**, *138*, 141–146.
- 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 Academic Publishers: Amsterdam, The Netherlands, 1997; pp 71–83.
- Clarke, E. C. W.; Glew, D. N. Evaluation of thermodynamic functions from equilibrium constants. *Trans. Faraday Soc.* **1966**, *134*, 539–547.
- Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.
- Barriada, J. L.; Brandariz, I.; Sastre de Vicente, M. E. Acid–base equilibria of monocarboxylic acids in various saline media: analysis of data using Pitzer equations. *J. Chem. Eng. Data* **2000**, *45*, 1173–1178.
- Ebersson, 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.
- King, E. J. *Acid–Base Equilibria*; Pergamon: New York, 1965.
- Martell, A. E.; Smith, R. M.; Motekaitis, R. J. *Critically Selected Stability Constants of Metal Complexes Database*, version 4.0; PC-based Database; NIST: Gaithersburg, MD, 1997.
- De Robertis, A.; De Stefano, C.; Rigano, C.; Sammartano, S. Thermodynamic Parameters for the Protonation of Carboxylic Acids in Aqueous Tetraethylammonium Iodide Solutions. *J. Solution Chem.* **1990**, *19*, 569–587.
- Harned, H. S.; Mannweiler, G. E. The thermodynamic of ionized water in sodium chloride solutions. *J. Am. Chem. Soc.* **1935**, *57*, 1873–1876.
- Busey, R. H.; Mesmer, R. E. Thermodynamic quantities for the ionization of water in sodium chloride media to 300 °C. *J. Chem. Eng. Data* **1978**, *23*, 175–176.
- Kron, I.; Marshall, S. L.; May, P. M.; Hefter, G.; Königsberger, E. The ionic product of water in highly concentrated aqueous electrolyte solutions. *Monatsch Chem.* **1995**, *126*, 819–837.
- Bender, P.; Biermann, W. J. Heat of neutralization studies at high acid–base concentrations. I. Sodium hydroxide–hydrochloric acid. *J. Am. Chem. Soc.* **1952**, *74*, 322–325.
- Lobanov, G. A.; Vasil'ev, V. P. Heat of water ionization is solutions of some 1-1 electrolytes at 25 °C. *Izv. Vysshikh. Uchebn. Zaved. SSSR Khimiya I Khim. Teknol.* **1969**, *12*, 740–743.
- Christensen, J. J.; Hansen, L. D.; Izatt, R. M. *Handbook of Proton Ionization Heats*; Wiley: New York, 1976.
- Maeda, M. Estimation of medium effect on enthalpy changes for ionization of water and ammonium ion in aqueous solution. *J. Phys. Chem.* **1986**, *90*, 1134–1137.
- Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing: New York, 1989.
- National Bureau of Standards. *Selected Values of Chemical Thermodynamic Properties*; Technical Note 270-3; U.S. Government Printing Office: Washington, DC, 1968.
- Murray, K.; May, P. M. *Joint Expert Speciation System*; Jess Primer, Murdoch: Western Australia, 2000.
- Pettit, L. D.; Powell, K. J. *IUPAC Stability Constants Database*; Academic Software: Otley, U.K., 1997.
- Sillén, L. G.; Martell, A. E. *Stability Constants of Metal–Ion Complexes*; Special Publication 17 and 25; The Chemical Society: London, U.K., 1964, 1971, respectively.

Received for review May 2, 2001. Accepted July 10, 2001. We thank MURST for financial support.

JE0101420