

Protonation of carbonate in aqueous tetraalkylammonium salts at 25 °C

Francesco Crea^a, Concetta De Stefano^a, Antonio Gianguzza^b,
Daniela Piazzese^b, Silvio Sammartano^{a,*}

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

^b *Dipartimento di Chimica Inorganica e Analitica "Stanislao Cannizzaro", Università di Palermo, Viale delle Scienze, Parco d'Orleans, I-90128 Palermo, Italy*

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Abstract

Protonation constants of carbonate were determined in tetramethylammonium chloride ($\text{Me}_4\text{NCl}_{\text{aq}}$ $0.1 \leq I/\text{mol kg}^{-1} \leq 4$) and tetraethylammonium iodide ($\text{Et}_4\text{NI}_{\text{aq}}$ $0.1 \leq I/\text{mol kg}^{-1} \leq 1$) by potentiometric ($[\text{H}^+]$ -glass electrode) measurements. Dependence of protonation constants on ionic strength was taken into account by modified specific ion interaction theory (SIT) and by Pitzer models. Literature data on the protonation of carbonate in NaCl_{aq} ($0.1 \leq I/\text{mol kg}^{-1} \leq 6$) were also critically analysed. Both protonation constants of carbonate follow the trend $\text{Et}_4\text{NI} > \text{Me}_4\text{NCl} > \text{NaCl}$. An ion pair formation model designed to take into account the different protonation behaviours of carbonate in different supporting electrolytes was also evaluated.

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1. Introduction

The behaviour of carbonate systems in natural waters, and particularly in seawater, has been extensively investigated [1–8]. The main focus of research attention has been the determination of all the thermodynamic parameters relative to the carbon dioxide system in order to define the chemical and geochemical equilibrium data necessary for a better understanding of the alkalinity of seawater, and with the aim of identifying a relationship between a CO_2 gas–solution equilibrium and global climate change. The literature reports carbonate protonation constants in NaCl , KNO_3 and NaClO_4 media [9,15], mostly without considering the possible interaction of carbonate and bicarbonate with the supporting electrolyte cation. A select few data, reported by Harned and Bonner [16], Näsänen [17], Dyrssen and Hansson [18], Thurmond and Millero [19], and Patterson et al. [20], take into

account the effect of the sodium ion on carbonate protonation constants. The interaction of carbonate and bicarbonate with the magnesium ion in a mixed $\text{NaCl} + \text{MgCl}_2$ medium has also been examined by Millero and Thurmond [21] and many data are available on carbonate protonation constants in seawater at different salinities. Further selected data describing a complete model of interaction of carbonate with the major cation components of seawater have been published by Hansson [22], Pytkowicz [23], Pytkowicz and Hawley [24], Whitfield [25] and more recently, by Roy et al. [8], Mojica Prieto and Millero [26–32]. A potentiometric investigation of weak $\text{CO}_3^{2-} - \text{Na}^+$ association has been reported by Capewell et al. [33]. Millero and Roy [34] provided a Pitzer equation for a chemical model for the carbonate system in natural waters.

The object of our study is to establish a “baseline” for protonation constants in non-interacting supporting electrolytes and to compare the values obtained with carbonate protonation constants determined in NaCl or in mixed electrolyte media in order to quantitatively define cation effects on the carbon dioxide protonation system. Moreover, we

* Corresponding author. Tel.: +39 090 393659; fax: +39 090 392827.
E-mail address: sammartano@chem.unime.it (S. Sammartano).

need suitable protonation constants of carbonate, in different media, in a wide ionic strength range, in any study devoted to the speciation of different elements, since this inorganic ligand is present in almost all natural fluids and interacts quite strongly with a large amount of inorganic and organic cations [9–13,35]. For this purpose, K_1^H and K_2^H values of carbonate were determined in tetraalkylammonium salts [(CH₃)₄NCl and (C₂H₅)₄NI] as representative of non-interacting supporting electrolytes. Investigations were performed by potentiometry ([H⁺]-glass electrode) at $T=25^\circ\text{C}$ in the ionic strength ranges $0.1 \leq I/\text{mol kg}^{-1} \leq 4$ and $0.1 \leq I/\text{mol kg}^{-1} \leq 1$ for Me₄NCl and Et₄NI, respectively. The dependence of protonation constants on ionic strength was taken into account using a modified specific ion interaction theory (SIT) model [36,37] and by Pitzer equations [38,39]. Literature data on the protonation of carbonate in NaCl(aq) ($0.1 \leq I/\text{mol kg}^{-1} \leq 6$) were also critically analysed. The differences between $\log K_1^H$ and $\log K_2^H$ in tetraalkylammonium salts and the corresponding values determined in NaCl medium are interpreted in terms of Na⁺-carbonate complex formation.

2. Experimental

2.1. Chemicals and solutions

The Me₄NCl (tetramethylammonium chloride, Fluka purum) and Et₄NI (tetraethylammonium iodide, Fluka purum) solutions were prepared by weighting the recrystallized salts from methanol–acetone and the solvent was completely removed before use. All solutions were prepared using analytical grade water (conductivity < 0.1 μS) and grade A glassware was employed. The solutions were boiled to eliminate CO₂. Reagent grade Na₂CO₃ and NaHCO₃ were added to each measurement solution so that total concentration was 10–16 mmol L⁻¹, with ratios C_{carbonate}/C_{bicarbonate} ranging from 0.1 to 0.8. Reagent concentrations were checked by least squares analysis.

2.2. Apparatus and measurements

Potentiometric measurements were carried out using potentiometric apparatus consisting of a Metrohm model 665 automatic titrant dispenser coupled with a Metrohm model 654 potentiometer and a combination Orion–Ross 8172 glass electrode. The estimated accuracy of the potentiometric system was ±0.15 mV and ±0.002 mL for emf and titrant volume readings, respectively. A volume of 25 mL solution containing Na₂CO₃ and NaHCO₃ together with the supporting electrolyte (Me₄NCl or Et₄NI) at different ionic strength values was titrated with hydrochloric acid up to pH ~ 5. For each experiment, independent titrations of HCl solutions were performed in the same experimental conditions of ionic strength and temperature as the systems under study in order to determine formal electrode potential E_{ext}° . Glass cells with

thermostated jacket, at a temperature of $25 \pm 0.1^\circ\text{C}$, were used. The free hydrogen ion concentration scale was used ($\text{pH} = -\log[\text{H}^+]$). All titrations were carried out by magnetically stirring and bubbling pure nitrogen through the solutions in order to avoid O₂ and CO₂ inside.

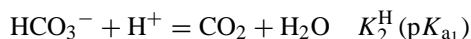
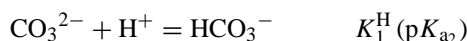
2.3. Calculations

Reagent concentrations and electrode system parameters (apparent standard potential slope and junction potential) were calculated by the ESAB2M [40] computer program. Protonation constants were calculated using both BSTAC and STACO computer programs [41]. The fitting of protonation constants to determine dependence on ionic strength was performed by the LIANA computer program [42] using different models. Weak complex formation constants were calculated using the ES2WC program [43]. All these programs are based on the least squares method coupled with the Levenberg–Marquardt damping algorithm. Speciation diagrams were plotted by the ES4EC program [41]. Details of calculation methods have been reported elsewhere [42]. The conversion from molar to molal scale for the different supporting electrolytes was obtained using the equation (at 25 °C; c = molar concentration; m = molal concentration) $c/m = d_0 + a_1c + a_2c^2$, with $d_0 = 0.99987$ and $a_1 = -0.017765$ (NaCl), -0.107951 (Me₄NCl), -0.184338 (Et₄NI), $a_2 = -6.525 \times 10^{-4}$ (NaCl), 4.833×10^{-4} (Me₄NCl), 8.112×10^{-4} (Et₄NI) [valid in the ranges: $0 \leq I(\text{NaCl})/\text{mol kg}^{-1} \leq 6$; $0 \leq I(\text{Me}_4\text{NCl})/\text{mol kg}^{-1} \leq 4.3$; $0 \leq I(\text{Et}_4\text{NI})/\text{mol kg}^{-1} \leq 1.2$].

3. Results and discussion

3.1. Experimental protonation constants

Protonation equilibria for carbonate are:



Carbonate protonation constants were determined at different ionic strengths in Me₄NCl_{aq} ($0.1 \leq I/\text{mol kg}^{-1} \leq 4$) and Et₄NI_{aq} ($0.1 \leq I/\text{mol kg}^{-1} \leq 1$) and values are reported in Table 1 in both molar and molal concentration scales. Significant differences can be observed in $\log K_i^H$ values for the two supporting electrolytes; as expected, the trend for all $\log K_i^H$ values is Et₄NI > Me₄NCl and this increases markedly with ionic strength. At $I = 1 \text{ mol kg}^{-1}$ these differences are apparent for both protonation steps > 0.1 log units. In turn, values of $\log K_i^H$ in tetraalkylammonium salts are significantly higher than in NaCl (see following sections). This behaviour is very similar to that shown by many inorganic (sulphate, phosphate) and organic (low molecular weight polycarboxylate) ligands [44–46].

Table 1

Experimental and smoothed protonation constants of carbonic acid in Et₄Ni and Me₄NCl (molar and molal concentration scales) at 25 °C

<i>I</i> /mol L ⁻¹	log <i>K</i> ₁ ^H	log <i>K</i> ₂ ^H	<i>I</i> /mol kg ⁻¹	log <i>K</i> ₁ ^H	log <i>K</i> ₂ ^H
Experimental values					
Et ₄ Ni					
0.063	10.073 ± 0.013 ^a	6.208 ± 0.005 ^a	0.064	10.066	6.202
0.108	10.060 ± 0.010	6.197 ± 0.008	0.111	10.050	6.187
0.250	10.100 ± 0.006	6.205 ± 0.016	0.263	10.078	6.183
0.480	10.208 ± 0.007	6.254 ± 0.027	0.528	10.166	6.213
0.860	10.370 ± 0.014	6.335 ± 0.038	1.025	10.294	6.259
Me ₄ NCl					
0.110	9.998 ± 0.011 ^a	6.145 ± 0.009 ^a	0.112	9.991	6.139
0.255	9.981 ± 0.006	6.094 ± 0.008	0.263	9.968	6.081
0.495	10.031 ± 0.003	6.075 ± 0.012	0.524	10.006	6.050
0.732	10.105 ± 0.003	6.072 ± 0.019	0.797	10.068	6.035
0.980	10.177 ± 0.011	6.092 ± 0.016	1.099	10.128	6.042
1.830	10.449 ± 0.004	6.187 ± 0.014	2.284	10.353	6.091
2.600	10.690 ± 0.024	6.281 ± 0.020	3.613	10.547	6.138
2.850	10.740 ± 0.018	6.286 ± 0.022	4.111	10.581	6.127
Smoothed values					
Et ₄ Ni					
0.10	10.054 ± 0.003 ^a	6.197 ± 0.003 ^a	0.10	10.044	6.189
0.25	10.100 ± 0.003	6.207 ± 0.002	0.25	10.073	6.184
0.50	10.222 ± 0.003	6.258 ± 0.002	0.50	10.164	6.209
1.00	10.417 ± 0.005	6.364 ± 0.002	1.00	10.289	6.257
Me ₄ NCl					
0.10	9.994 ± 0.004 ^a	6.143 ± 0.003 ^a	0.10	9.989	6.140
0.25	9.976 ± 0.003	6.091 ± 0.003	0.25	9.962	6.081
0.50	10.034 ± 0.003	6.072 ± 0.003	0.50	10.001	6.048
1.00	10.191 ± 0.003	6.098 ± 0.003	1.00	10.114	6.042
2.00	10.500 ± 0.003	6.206 ± 0.002	2.00	10.307	6.079
3.00	10.792 ± 0.009	6.308 ± 0.008	3.00	10.458	6.116
4.00	–	–	4.00	10.576	6.131

^a ±Standard deviation.

3.2. Dependence on ionic strength: smoothing function

Experimental protonation constants can be expressed as a function of ionic strength by a simple Debye–Hückel type equation:

$$\log K_i^H = \log K_i^{H^\circ} - 0.51 \cdot 2i \frac{\sqrt{I}}{1 + 1.5\sqrt{I}} + L(I) \quad (1)$$

where $\log K_i^{H^\circ}$ is the infinite dilution value and $L(I)$ is a linear function of ionic strength that can be formulated in different ways. The simplest expression for this linear term is $L(I) = CI$, where C is the only adjustable parameter. Often, this simple choice is sufficient to explain experimental data in a wide ionic strength range, generally <3 mol L⁻¹, when the supporting electrolyte is a 1:1 alkali metal salt. For higher ionic strengths and, in particular, when the supporting electrolyte is a tetraalkylammonium salt, a more complicated form of $L(I)$ must be used. Recently [47–49] we proposed the equation:

$$\frac{L(I)}{I} = c_\infty + \frac{c_0 - c_\infty}{I + 1} \quad (2)$$

which, for several systems (polycarboxylates, polyamines), can be used up to $I = 6$ mol kg⁻¹. In some cases, the parameter

c_∞ is, in turn, a function of ionic strength [50].

$$c_\infty = c_\infty^{(0)} + c_\infty^{(1)}I \quad (3)$$

The empirical parameters of Eqs. (2) and (3) for the protonation constants of carbonate in Et₄Ni and Me₄NCl are reported in Table 2. The values of $\log K_i^{H^\circ}$ in Eq. (1):

$$\log K_1^{H^\circ} = 10.3344$$

$$\log K_2^{H^\circ} = 6.3510$$

were obtained from a critical analysis of literature data (molar concentration scale), as reported in the next section and using

Table 2

Empirical parameters of Eqs. (2) and (3) for the dependence on ionic strength of carbonate protonation constants at 25 °C (molar concentration scale)

<i>i</i>	<i>c</i> ₀	<i>c</i> _∞	<i>c</i> _∞ ^a	σ ^a
Et ₄ Ni				
1	1.735	0.0646	–	0.005
2	0.704	0.1382	–	0.002
Me ₄ NCl				
1	1.054	0.297	–0.0027	0.007
2	0.1042	0.228	–0.0213	0.006

^a Standard deviation on the fit of Eqs. (2) and (3).

the protonation constants determined in the present study. Eqs. (1)–(3) can be used in both molar and molal concentration scales: smoothed $\log K_i^H$ values are reported in Table 1.

3.3. Thermodynamic protonation constants

A large numbers of thermodynamic parameters for the protonation of carbonate at different temperatures have been reported in literature [9–18,51]. Some of these data were collected and selected, and suitable calculation methods [42] allowed us to obtain the values:

$$\begin{aligned} \log K_1^{H^\circ} &= 10.333 \pm 0.0010; & \Delta H_1^0 &= -14.92 \pm 0.08; & \Delta Cp_1^0 &= 264 \pm 9 \\ \log K_2^{H^\circ} &= 6.3507 \pm 0.0006; & \Delta H_2^0 &= -9.07 \pm 0.07; & \Delta Cp_2^0 &= 395 \pm 8 \end{aligned}$$

at 25 °C ($\Delta H^0/\text{kJ mol}^{-1}$; $\Delta Cp^0/\text{J K}^{-1} \text{mol}^{-1}$) and in the molal concentration scale. These values are in quite good agreement with values reported by Harned and Scholes [52], Harned and Davis [53]: $\log K_1^{H^\circ} = 10.329$, $\Delta H_1^0 = -14.7$, $\Delta Cp_1^0 = 272$, $\log K_2^{H^\circ} = 6.3519$, $\Delta H_2^0 = -9.41$, $\Delta Cp_2^0 = 374$; Patterson et al. [20]: $\log K_1^{H^\circ} = 10.337$, $\Delta H_1^0 = -15.07$, $\Delta Cp_1^0 = 260$; Larson et al. [54]: $\log K_1^{H^\circ} = 10.329$, $\Delta H_1^0 = -14.7$, $\Delta Cp_1^0 = 250$.

3.4. Protonation constants in NaCl and Na⁺-carbonate ion pairs

Numerous data can also be found in literature for carbonate protonation constants in NaCl_{aq}. We selected the values reported by Harned and Bonner [16], Näsänen [17], Dyrssen and Hansson [18], Thurmond and Millero [19] and Patterson et al. [20]. These constants are plotted versus \sqrt{I} in Fig. 1. Using the smoothing function outlined in Section 3.2, we obtained reliable values in the range $0 \leq I/\text{mol kg}^{-1} \leq 6$, at 25 °C. Smoothed protonation constants are reported in Table 3. Mean literature values given in this work are in excellent agreement with those reported by Thurmond and Millero [19], with differences in $\log K_1^H$ and $\log K_2^H$ amounting to <0.01 and <0.008, respectively. By comparison, Fig. 2 plots the protonation constants of carbonate in NaCl, Et₄NI and Me₄NCl as a function of ionic strength. As can be seen, there

is a very sharp Et₄NI > Me₄NCl > NaCl trend; the differences in $\log K_i^H$, Δ_i (Et₄NI, NaCl) and Δ_i (Me₄NCl, NaCl) can be expressed by the simple equation (for $I \leq 1 \text{ mol kg}^{-1}$)

$$\Delta_i = a_i I^{2/3} \quad (4)$$

where a_i is an empirical parameter and i is the protonation step. For the two couples of supporting electrolytes, we have: (Et₄NI, NaCl), $a_1 = 0.83$ and $a_2 = 0.31$; (Me₄NCl, NaCl), $a_1 = 0.60$ and $a_2 = 0.08$. The effect of ionic media on the protonation constants of carbonate can be seen in Fig. 3,

where the formation percentages of species are reported in Et₄NI and NaCl aqueous solution. In the experimental conditions used to draw this speciation diagram, the formation curves for H₂CO₃⁰ and HCO₃⁻ shift by 0.2–0.4 and >0.5 pH units, respectively. These differences can be interpreted using different models: (a) models which take into account the differences in activity coefficients in different supporting electrolytes, such as SIT [36,37] or Pitzer equations [38,39], which will be examined in subsequent sections; (b) models which take into account the formation of ion pairs. The $\log K_i^H$ versus ionic strength function is quite different, as already seen, for different supporting electrolytes and the differences can be interpreted as Na⁺-carbonate complexes after choosing the baseline supporting electrolyte. In several

Table 3
Smoothed values of carbonate protonation constants at 25 °C (molal concentration scale) in NaCl_{aq}

$I/\text{mol kg}^{-1}$	$\log K_1^H$	$\log K_2^H$
0.10	9.880 ± 0.001 ^a	6.129 ± 0.001 ^a
0.50	9.589 ± 0.001	5.999 ± 0.002
0.70	9.530 ± 0.001	5.976 ± 0.003
1.00	9.476 ± 0.002	5.959 ± 0.003
1.50	9.435 ± 0.002	5.955 ± 0.003
2.00	9.426 ± 0.003	5.966 ± 0.003
3.00	9.457 ± 0.003	6.015 ± 0.003
4.00	9.523 ± 0.003	6.086 ± 0.003
5.00	9.611 ± 0.003	6.172 ± 0.004
6.00	9.715 ± 0.006	6.270 ± 0.007

^a ±Standard deviation.

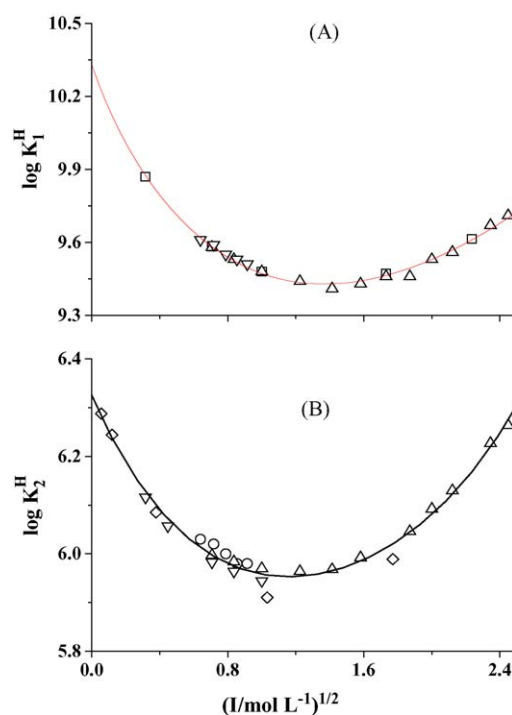


Fig. 1. Literature data for the protonation of carbonate at 25 °C. (A) □, Patterson et al.; △, Thurmond and Millero; ▽, Dyrssen and Hansson. (B) ◇, Näsänen; △, Thurmond and Millero; ▽, Harned and Bonner; ○, Dyrssen and Hansson.

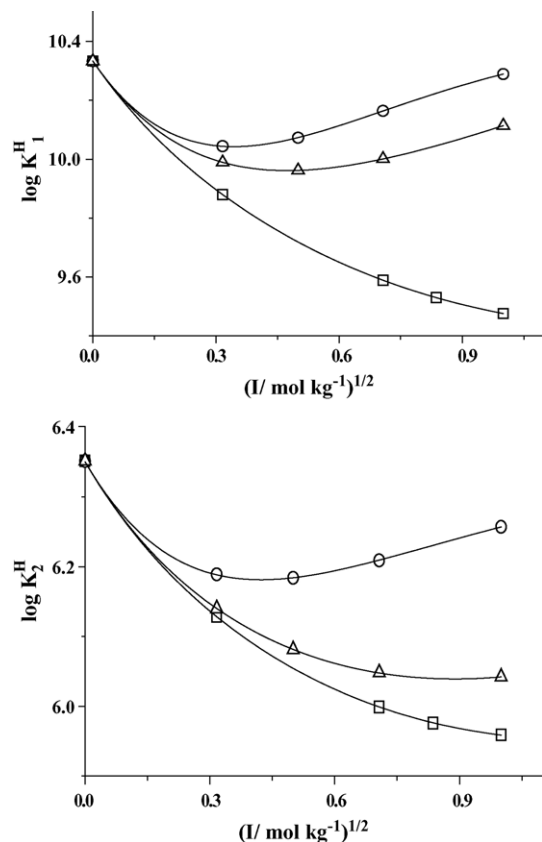


Fig. 2. $\log K_i^H$ vs. $(I/\text{mol kg}^{-1})^{1/2}$ in different supporting electrolytes at 25 °C. Symbol: \circ , Et_4NI ; \square , NaCl ; \triangle , Me_4NCl (full lines = theoretical curves).

previous works [44–46], we took Et_4NI as our baseline in determining weak alkali metal complex formation constants with low molecular weight inorganic and organic poly-anions (see also Section 4). According to a previously proposed simple model [43–46], it is possible to calculate weak complex formation constants from differences in protonation function

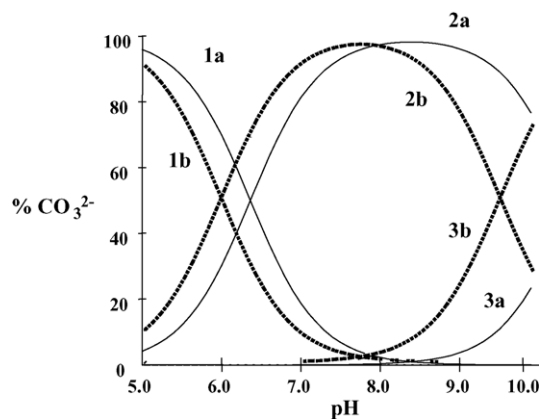


Fig. 3. Distribution diagram of carbonate species in different supporting electrolytes at $I = 1.0 \text{ mol kg}^{-1}$ and 25 °C (index: (a) Et_4NI ; (b) NaCl). Species: (1) H_2CO_3 ; (2) HCO_3^- ; (3) CO_3^{2-} . Concentration: $C_{\text{CO}_3^{2-}} = 1.0 \text{ mmol L}^{-1}$.

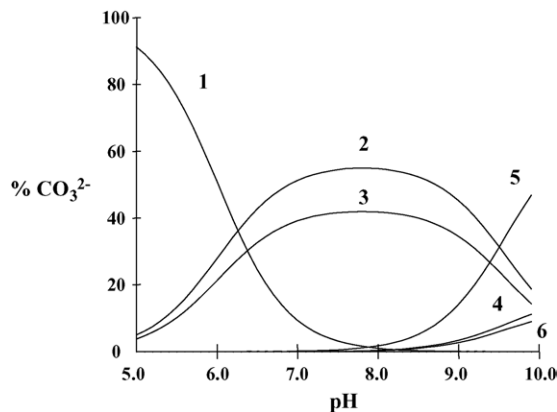


Fig. 4. Distribution diagram of carbonate species in NaCl at $I = 0.5 \text{ mol L}^{-1}$ at 25 °C. Species: (1) CO_2 ; (2) HCO_3^- ; (3) NaHCO_3 ; (4) Na_2CO_3 ; (5) NaCO_3^- ; (6) CO_3^{2-} . Concentration: $C_{\text{CO}_3^{2-}} = 1.0 \text{ mmol L}^{-1}$.

$$\bar{p} = \frac{\sum i\beta_i^H}{1 + \sum \beta_i^H} \quad (5)$$

($\beta^H = \Pi K^H$) for apparent and baseline protonation constants. Moreover, it is assumed that dependence on ionic strength is independent of the different ions and a function only of the stoichiometry of the reaction [44,45]:

$$\log K = \log K^\circ - \frac{z^*\sqrt{I}}{2 + 3\sqrt{I}} + CI + DI^{3/2} \quad (6)$$

($z^* = \sum z_{\text{react}}^2 - \sum z_{\text{prod}}^2$). K may be the protonation constant (K^H) or the weak complex formation constant (K^M) and C and D are empirical parameters, equal for all species obtained from reactants with the same charges. The model can be used at moderate ionic strength values, generally $I < 1 \text{ mol L}^{-1}$, and this study examines the range $0 \leq I/\text{mol L}^{-1} \leq 0.7$. By least squares refinement [42], we obtained the results reported in Table 4. The auto-consistency of this model is quite good: protonation constants calculated at infinite dilution agree to within 0.02 log units with those obtained from analysis of literature data, and mean deviations in $\log K_i^H$ are < 0.01 . Overall, in terms of agreement between experimental and calculated protonation constants the auto-consistency of the model is better than 5%. Fig. 4 shows the distribution diagram for Na^+ -carbonate species in NaCl aqueous solution at $I = 0.5 \text{ mol L}^{-1}$ and $T = 25 \text{ }^\circ\text{C}$. The maximum yield for NaHCO_3^0 is $\sim 40\%$ at $\text{pH } 7.5\text{--}8.5$, with NaCO_3^- yielding $\sim 50\%$ at $\text{pH } 10$ ($C_{\text{NaCl}} = 0.5 \text{ mol L}^{-1}$); small percentages ($< 10\%$) are observed for the very weak Na_2CO_3^0 species.

3.5. Dependence on ionic strength according to SIT

The protonation constants of carbonate can be expressed as a function of activity coefficients as follows:

$$\log K_1^H = \log K_1^{H^\circ} + \log \gamma_{\text{H}^+} + \log \gamma_{\text{CO}_3^{2-}} - \log \gamma_{\text{HCO}_3^-} \quad (7)$$

Table 4

Protonation and Na⁺ complex formation constants for carbonate at 25 °C (molar concentration scale, 0 ≤ I/mol L⁻¹ ≤ 1)

Equilibrium	log K ^c	C ^b	D ^b
CO ₃ ²⁻ + H ⁺ = HCO ₃ ^{-a}	10.356 ± 0.016	1.549 ± 0.018	-0.626 ± 0.015
CO ₃ ²⁻ + Na ⁺ = NaCO ₃ ⁻	1.15 ± 0.03		
CO ₃ ²⁻ + H ⁺ = CO ₂ + H ₂ O ^a	6.338 ± 0.008	0.755 ± 0.012	-0.313 ± 0.010
HCO ₃ ⁻ + Na ⁺ = NaHCO ₃	0.26 ± 0.03		
NaCO ₃ ⁻ + Na ⁺ = Na ₂ CO ₃	-0.25 ± 0.05		

^a Mean deviations (log K_{exp}^H - log K_{calcd}^H) are <0.01 for both protonation steps.^b Empirical parameters for the dependence on ionic strength (Eq. (6)).

$$\log K_2^H = \log K_2^{H^0} + \log \gamma_{H^+} + \log \gamma_{HCO_3^-} - \log \gamma_{CO_2} - \log a_{H_2O} \quad (7a)$$

where a_{H_2O} is the activity of water that can be calculated from the osmotic coefficients ϕ of different supporting electrolytes [55,56] at different concentrations:

$$\log a_{H_2O} = -0.007824 \phi \nu m$$

(ν is the number of ions in the electrolyte and m is the molality). Using literature values of ϕ [56–58], we calculated:

$$10^3 \log a_{H_2O} (\text{NaCl}) = -13.04m - 1.124m^2 \quad (8)$$

$$10^3 \log a_{H_2O} (\text{Me}_4\text{NCl}) = -14.50m - 0.58m^2 \quad (8a)$$

$$10^3 \log a_{H_2O} (\text{Et}_4\text{NI}) = -11.73m + 2.287m^2 \quad (8b)$$

From the work on solubility by Harned and Davis [53], Thurmond and Millero [19] obtained:

$$\ln \gamma_{CO_2} = 0.242m_{(\text{NaCl})} - 0.0106m_{(\text{NaCl})}^2 \quad (9)$$

or

$$10^3 \log \gamma_{CO_2} = 105.1m_{(\text{NaCl})} - 4.60m_{(\text{NaCl})}^2 \quad (9a)$$

for the activity coefficient of CO₂ in NaCl.

The equation used in SIT treatment of protonation constants at different ionic strengths assumes the form of Eq. (1) with:

$$L(I) = I\Delta\varepsilon_i + j \log a_{H_2O}$$

i is the protonation step, j the number of water molecules involved in the equilibrium, ε the specific interaction coefficients and for the protonation of carbonate we have (MX = supporting electrolyte)

$$\Delta\varepsilon_1 = \varepsilon(H^+, X^-) + \varepsilon(M^+, CO_3^{2-}) - \varepsilon(M^+, HCO_3^-) \quad (10)$$

$$\Delta\varepsilon_2 = \varepsilon(H^+, X^-) + \varepsilon(M^+, HCO_3^-) - \lambda_{CO_2} \quad (10a)$$

with

$$\lambda_{CO_2} = \frac{\log \gamma_{CO_2}}{m_{MX}} \quad (11)$$

The interaction coefficients ε are not constant for wide ionic strength ranges, and can be expressed as a function of I by the equation:

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{I + 1} \quad (12)$$

and

$$\varepsilon_\infty = \varepsilon_\infty^{(0)} + \varepsilon_\infty^{(1)}I \quad (13)$$

[note that Eqs. (12) and (13) are identical to Eqs. (2) and (3)]. Protonation data in NaCl from Thurmond and Millero [19] and from Bretti et al. [47] are

$$\lambda_{CO_2} = (105.1 - 4.60m_{\text{NaCl}})10^{-3} \quad (14)$$

$$\varepsilon(H^+, Cl^-) = 0.136 + \frac{0.0839 - 0.136}{I + 1} \quad (15)$$

Using Eqs. (8), (14) and (15) we determined (least squares calculations) the interaction coefficients of carbonate and bicarbonate with Na⁺ (see Table 5) from protonation constants of carbonate in NaCl reported in Table 3; the standard deviations on the fit of $\sigma(\log K_i^H)$ were: $\sigma(\log K_1^H) = 0.008$ and $\sigma(\log K_2^H) = 0.021$. For interaction coefficients in Me₄NCl_{aq} and Et₄NI_{aq} we have, from [50]:

$$\varepsilon(H^+, I^-) = 0.173 + \frac{0.204 - 0.173}{I + 1} \quad (16)$$

No value for λ_{CO_2} in either of the tetraalkylammonium supporting electrolytes is available. Long and McDevit's [59]

Table 5

Specific interaction coefficients of carbonate and bicarbonate in NaCl, Me₄NCl and Et₄NI at 25 °C according to the modified SIT model

	NaCl	Me ₄ NCl	Et ₄ NI
CO ₃ ²⁻ , M ⁺			
ε_0	-0.2833	0.7538	1.5951
$\varepsilon_\infty^{(0)}$	-0.0026	0.1038	-1.1761
$\varepsilon_\infty^{(1)}$	0.00115	-0.0304	0.2778
σ^a	0.004	0.006	0.003
HCO ₃ ⁻ , M ⁺			
ε_0	-0.0174	-0.1717	0.0566
$\varepsilon_\infty^{(0)}$	0.0362	-0.1633	-0.5237
$\varepsilon_\infty^{(1)}$	-0.0023	-0.0171	0
σ^a	0.003	0.005	0.001
I/mol kg ⁻¹ max.	6	4	1

^a Standard deviation on the fit.

Table 6
Pitzer parameters [38] used in this work for single electrolytes

Electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
NaCl	0.0765	0.2664	0.00127
Me ₄ NCl	0.043	-0.029	0.0078
Et ₄ NI	-0.179	-0.571	0.0412
HCl	0.1775	0.2945	0.00080
HI	0.2211	0.4907	0.00482

reported several data relative to the activity coefficients of CO₂ in different electrolytes, and Bergen and Long [60] have shown the effect of large ion on the same acidic substituted benzenes. From these reports, it is evident a quite strong lowering of γ in large ion salt solutions. Moreover, this effect was observed in our laboratory for a series of O-ligands, whose solubility was studied in NaCl_{aq}, Me₄NCl_{aq} and Et₄NI_{aq} (this laboratory, unpublished results). Estimates for activity coefficients of carbon dioxide are:

$$\log \gamma_{\text{CO}_2} = (-0.15 \pm 0.05) \quad (\text{Me}_4\text{NCl}) \quad (17)$$

$$\log \gamma_{\text{CO}_2} = (-0.35 \pm 0.08) \quad (\text{Et}_4\text{NI}) \quad (17a)$$

These may be reasonable values for our calculations, and the least squares calculations carried out on our experimental data gave the interaction coefficients for carbonate in Me₄NCl and Et₄NI (see Table 5, second and third column, respectively).

3.6. Dependence on ionic strength according to Pitzer equation

For the proton carbonate system, Pitzer equations can be written as follows:

$$\log K_1^{\text{H}} = \log K_1^{\text{H}^\circ} + \frac{4f^\gamma + F_1(p)}{\ln 10} \quad (18)$$

$$\log K_2^{\text{H}} = \log K_2^{\text{H}^\circ} + \frac{2f^\gamma + F_2(p)}{\ln 10} - \log \gamma_{\text{CO}_2} - \log a_{\text{H}_2\text{O}} \quad (18a)$$

where

$$f^\gamma = -0.391 \left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} \right] + 1.667 \ln (1 + 1.2\sqrt{I})$$

$$F_1(p) = p_{11}I + p_{12}f + p_{13}I^2 + 4g\beta^{(1)}I \quad (19)$$

Table 7
Parameters p_{11} , p_{12} , p_{13} of Eqs. (19) and (19a) at 25 °C

	p_{11}	p_{12}	p_{13}	p_{21}	p_{22}	p_{23}	σ^a
Et ₄ NI	-0.1244	5.142	0.0452	0.3529	2.019	-0.0664	0.002
Me ₄ NCl	0.7553	2.627	-0.0455	0.5682	0.5138	-0.0375	0.005
NaCl	0.5178	0.2382	-0.0072	0.5178	0.1747	-0.0115	0.003

^a Standard deviation on the fit.

Table 8
Pitzer parameters for carbonate in tetraalkylammonium salts at 25 °C

	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
M ⁺ , CO ₃ ²⁻			
Et ₄ NI	-0.82 ± 0.10 ^a	4.47 ± 0.18	-0.16 ± 0.14
Me ₄ NCl	0.04 ± 0.02	2.46 ± 0.05	-0.142 ± 0.008
M ⁺ , HCO ₃ ²⁻			
Et ₄ NI	-0.54 ± 0.08	0.96 ± 0.14	-0.11 ± 0.08
Me ₄ NCl	-0.16 ± 0.01	0.19 ± 0.04	-0.046 ± 0.004

^a ±Standard deviation.

$$F_2(p) = p_{21}I + p_{22}f + p_{23}I^2 + 2g\beta^{(1)}I \quad (19a)$$

$$f = [1 - (1 + 2\sqrt{I})g]$$

$$g = \exp(-2\sqrt{I})$$

Parameters for $\beta^{(1)}$ in different ionic media have been reported by Pitzer and are given in Table 6. The values of parameters p_{11} , p_{12} and p_{13} are reported in Table 7. For comparison, the values of these parameters in NaCl are reported in the same Table. Parameters p_{11} , p_{12} and p_{13} are, in turn, a function of Pitzer parameters

$$\frac{1}{2}p_{11} = \beta_{\text{MCO}_3}^{(0)} + \beta_{\text{HX}}^{(0)} - \beta_{\text{MHCO}_3}^{(0)}$$

$$\frac{1}{2}p_{21} = \beta_{\text{MHCO}_3}^{(0)} + \beta_{\text{HX}}^{(0)}$$

$$p_{12} = \beta_{\text{MCO}_3}^{(1)} + \beta_{\text{HX}}^{(1)} - \beta_{\text{MHCO}_3}^{(1)} - 2\beta_{\text{MX}}^{(1)}$$

$$p_{22} = \beta_{\text{HX}}^{(1)} + \beta_{\text{MHCO}_3}^{(1)} - \beta_{\text{MX}}^{(1)}$$

$$p_{13} = C_{\text{HX}}^\phi + \frac{C_{\text{MCO}_3}^\phi}{\sqrt{2}} - C_{\text{MHCO}_3}^\phi + C_{\text{MX}}^\phi$$

$$p_{23} = C_{\text{HX}}^\phi + C_{\text{MHCO}_3}^\phi + C_{\text{MX}}^\phi$$

where the mixed parameters Φ and Ψ are neglected. Using the coefficients of the supporting electrolyte (shown in Table 6), it is possible to compute coefficients $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ for carbonate in Me₄NCl and Et₄NI; these are given in Table 8.

Extensive treatment of the activity coefficients of carbonate in NaCl using Pitzer equations has been described by Thurmond and Millero [19], and by Millero and Roy [34].

4. Discussion

4.1. SIT parameters in different supporting electrolytes

Specific interaction coefficients (Section 3.5, Table 5) are quite different for different electrolytes, in particular for the interaction (M^+ , CO_3^{2-}). This is due mainly to the different effects of Na^+ , $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ cations on the structure of water [61]. No comparisons with literature can be made since our data on ϵ values are presented here for the first time. It is also worth mentioning that the use of a modified SIT equation allows the ionic strength range for alkali metal electrolytes ($I > 3 \text{ mol kg}^{-1}$) to be extended and permits interaction coefficients for tetraalkylammonium salts to be calculated too. Fitting $\log K_i^H$ in NaCl using the classic one-parameter SIT equation gives significantly worse results, with $\sigma_0^2/\sigma^2 = 2.3$ and 2 for $\log K_1^H$ and $\log K_2^H$, respectively. The same equation also gives quite unreliable results for protonation constants in Me_4N^+ and Et_4N^+ , even at low ionic strength values.

4.2. Pitzer parameters in different supporting electrolytes

No comparisons with literature data can be made, because Pitzer parameters for tetraalkylammonium electrolytes are reported here for the first time. However, if we compare our results (see Table 8) for tetraalkylammonium electrolytes with those reported by Thurmond and Millero [19] in NaCl [as an example for $Na^+CO_3^{2-}$, $\beta^{(0)} = 0.0362$, $\beta^{(1)} = 1.510$, $C^\Phi = 0.0052$], we can conclude that Pitzer parameters also differ noticeably depending on the supporting electrolyte under consideration. Data reported for tetraalkylammonium electrolytes are valid if (a) the approximation [Eqs. (17) and (17a)] for the activity coefficient of CO_2 is suitable, and (b) neglecting Φ and Ψ terms does not significantly alter the results. At the moment, there is no way to verify these assumptions but p_i values for Eqs. (19) and (19a) are valid since they are independent of the above assumptions. When γ_{CO_2} (in Me_4NCl and Et_4NI), Φ and Ψ parameters become available, new $\beta^{(0)}$, $\beta^{(1)}$ and C^Φ values can be calculated.

4.3. Comparisons between SIT and Pitzer treatment of protonation data

Both models work very well for the protonation of carbonate in tetraalkylammonium electrolytes. All the results obtained in this work show that there is no significant difference in fitting ability between SIT and Pitzer treatment of protonation data, as can be seen in Fig. 5a and b, where some residual plots of $\log K_i^H$ ($i = 1, 2$) in Et_4NI and Me_4NCl are reported in a wide ionic strength range. The SIT model is very simple to use and gives good results for protonation and formation equilibria in single or mixed supporting electrolytes by taking into account only interactions between opposite charges. However, the model proposed by Pitzer,

although more complicated, is more appropriate than the SIT model in mixed supporting electrolytes such as natural fluids, especially hyper saline water. This is due to the fact that it also considers the interactions of ions with the same charge or triple ion interactions, which can be quite significant at $I > 1 \text{ mol L}^{-1}$ [38,39].

4.4. Ion pair formation model

The model which uses the formation of alkali metal ion pairs to explain dependence on medium suffers from two weaknesses: (i) the arbitrary choice of a baseline background electrolyte and (ii) the implicit assumption that $\gamma_A = \gamma_{A'}$ and $\gamma_{HA} = \gamma_{HA'}$, where γ_A and γ_{HA} are the activity coefficients of A and HA in the baseline electrolyte, and $\gamma_{A'}$ and $\gamma_{HA'}$ are the same quantities in the interacting electrolyte, corrected for ion pair formation. The first issue has been discussed in many papers, where a consistently $Et_4N^+ > Me_4N^+ \gg K^+ > (\text{or } \approx) Na^+ > Li^+$ [44,45,48,62–69] trend is observed for the protonation of carboxylic and inorganic acids, and these differences, in turn, are an increasing function of poly-anion charge. Moreover, a study of weak alkali metal complexes using M^+ -ISE electrodes [70] showed that consistent results are obtained from the $\Delta \log K^H$ (Et_4NI) method and direct ISE measurements. Therefore, it would seem reasonable to assume Et_4NI to be the baseline, though not an absolute one. The second assumption is more difficult to justify, but here again empirical evidence is of help. First of all, it is necessary to define an ionic strength range in which the assumption may be valid, and this was indicated in previous works [43–45,62,66] to be $0 \leq I/\text{mol L}^{-1} \leq 1$. In this range, the results obtained using $\Delta \log K^H$ (Et_4NI) and M^+ -ISE methods are quite consistent; in addition, all alkali metal –O– ligands behave in a very similar way. Even if these factors do not unambiguously demonstrate the validity of the method, they furnish two important pieces of information: (a) an estimate of the formation constants of M^+A^{c-} ion pairs and (b) a comparison of the strengths of different weak complexes for different alkali metal –O– ligand systems. In particular, point (b) must be affected by the above assumptions to a lesser extent.

Several investigations have reported on the formation of weak complexes based on differences in protonation constants when tetramethylammonium chloride [64,71,72] or, in a few cases, CsCl ([73] and references therein) is used as the baseline salt. This approach may be correct in principle but can lead to some difficulties in interpretation. If, on the one hand, all tetraalkylammonium cations (and Cs^+) are considered incapable of interacting significantly with carboxylic anions, on the other there is abundant evidence that Me_4N^+ and Cs^+ have a lowering effect on carboxylate protonation constants [62]. Recently, Capewell et al. [33] reported formation constants for Na^+ -carbonate weak complexes using protonation constants in $CsCl_{aq}$, Me_4NCl_{aq} and $NaCl_{aq}$ media, and ISE- Na^+ potentiometric measurements. They found $\log K^{Na} = 0.40 \pm 0.05$ ($I = 1.0 \text{ mol L}^{-1}$,

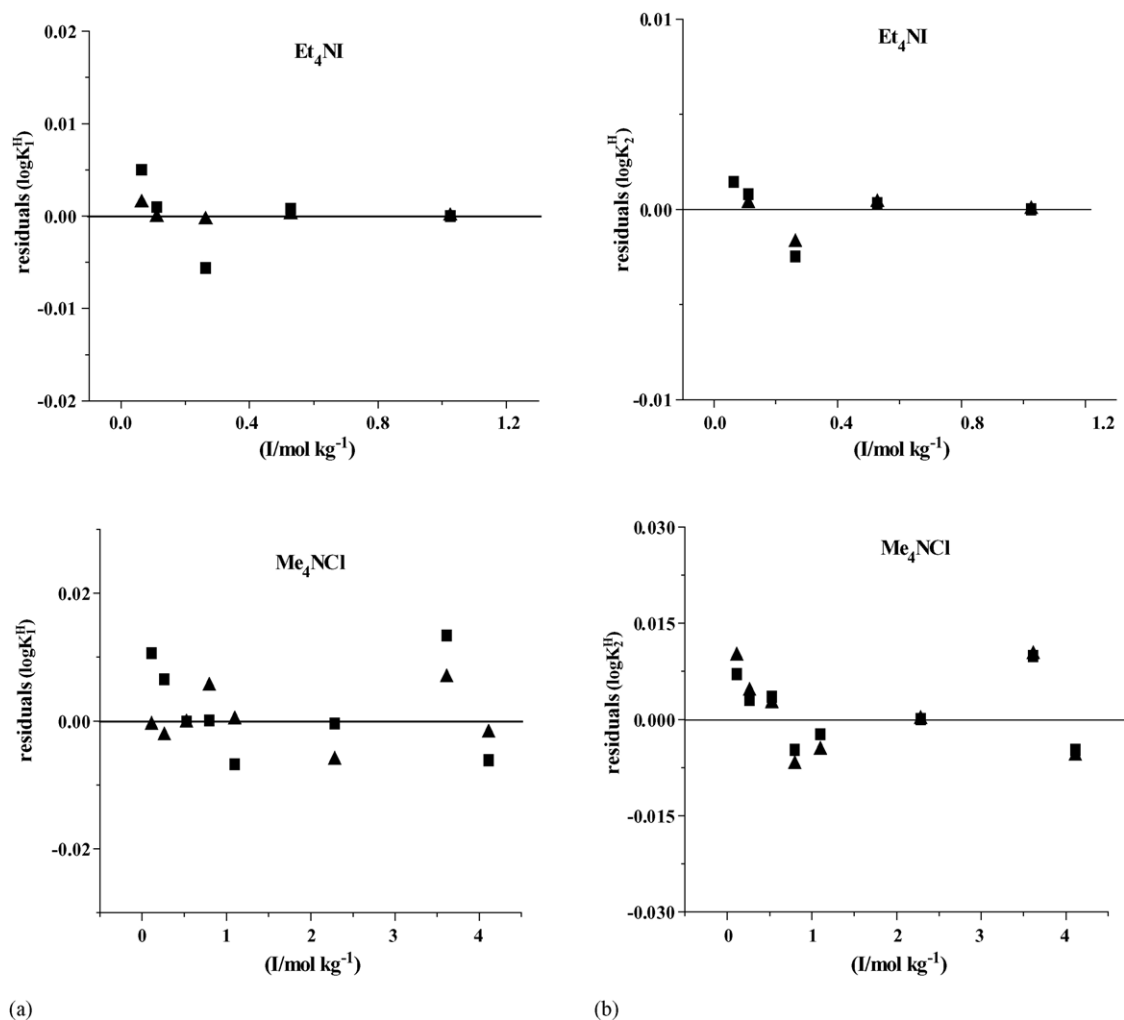


Fig. 5. (a) Residual plots for comparison of SIT and Pitzer treatment of protonation data ($\log K_1^H$) at different ionic strength values and $T=25^\circ\text{C}$ (symbol: ■, SIT; ▲, Pitzer). (b) Residual plots for comparison of SIT and Pitzer treatment of protonation data ($\log K_2^H$) at different ionic strength values and $T=25^\circ\text{C}$ (symbol: ■, SIT; ▲, Pitzer).

Me_4NCl) and $\log K^{\text{Na}} = 1.29 \pm 0.05$ ($I=0 \text{ mol L}^{-1}$, extrapolation of data obtained in CsCl_{aq} medium). By performing analogous calculations using our data (protonation constants in NaCl_{aq} from literature analysis and in Me_4NCl), we found $\log K^{\text{Na}} = 0.96 \pm 0.15$ and 0.79 ± 0.12 at $I/\text{mol L}^{-1} = 0$ and 1, respectively. The order of magnitude of formation constants is comparable but calculation of formation percentages allowed significant discrepancies to be observed. Butler and Huston [74], employing both sodium amalgam and ISE- Na^+ electrodes found $\log K^{\text{Na}} = 0.96$ at $I=0 \text{ mol kg}^{-1}$. Garrels et al. [75] reported (pH-activity measurements, $I=0 \text{ mol L}^{-1}$) $\log K^{\text{Na}} = 1.27$, and Pytkowicz and Hawley [24] obtained (ISE- H^+ measurements in artificial seawater, $I=0.7 \text{ mol L}^{-1}$) $\log K^{\text{Na}} = 0.63$. The latter data from literature are also quite consistent, but the problem of interpretation remains and we need further (and independent) experimental evidence and in-depth analysis of literature data.

Our research group has already published some papers dealing with the determination of weak formation con-

stants of some Na^+ -organic and inorganic ligand species using the $\Delta \log K^H$ (Et_4NI) method, and some results are reported in Table 9. The formation constants of carbonate complexes are fairly close to those of the other systems, and for the data shown in Table 9 we have average values of $\log K$ ($\text{Na}^+ + \text{L}^{2-} = \text{NaL}^-$) = 0.95 ± 0.15 and $\log K$ ($\text{Na}^+ + \text{HL}^- = \text{NaHL}^0$) = 0.15 ± 0.15 , indicating that these weak interactions are not specific in nature.

4.5. Final remarks

This work is the first to report carbonate protonation data in aqueous tetraalkylammonium salts in a wide ionic strength range, and results and literature data are discussed. Different models were used to express the function $\log K^H$ versus ionic strength. We must stress the importance of providing thermodynamic data for the protonation of poly-anions of analytical and environmental interest in different electrolyte solutions, since both dependence on ionic strength and (to an

Table 9

Formation constants of Na–L systems, with L = dicarboxylates, phosphates and sulphates at $I=0 \text{ mol L}^{-1}$ and $T=25^\circ\text{C}$

System	$\log K^M$
Na(succinate) ^{−a}	0.85
Na(Hsuccinate) ^{0a}	0.15
Na(malonate) ^{−a}	0.91
Na(Hmalonate) ^{0a}	−0.04
Na(malate) ^{−a}	0.66
Na(Hmalate) ^{0a}	0.15
Na(maleate) ^{−a}	1.18
Na(Hmaleate) ^{0a}	0.10
Na(HPO ₄) ^{−b}	1.07
Na(H ₂ PO ₄) ^{0b}	0.28
Na(SO ₄) ^{−c}	0.80
Na(SO ₄) ^{−d}	0.73
Na(CO ₃) ^{−e}	1.15
Na(HCO ₃) ^{0e}	0.26

^a Daniele et al. [44].

^b Daniele et al. [76].

^c De Robertis et al. [70].

^d Martell and Smith [9].

^e This work.

even greater degree) dependence on ionic media are of fundamental importance. SIT and Pitzer interaction parameters, together with formation constants for weak Na⁺ ion pairs, are a contribution to the building of databases of analytical, biological and environmental interest.

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