Potentiometric Study of the Protonation Equilibria of Tartaric Acid in Aqueous Sodium Perchlorate Solutions at 25 °C. Construction of a Thermodynamic Model

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The protonation equilibria of the tartrate ion have been studied using an automated potentiometric system. The temperature was kept constant at 25 °C and the ionic strength was 0.5, 1.0, 2.0 and 3.0 mol dm^{-3} in NaClO$_4$. The experimental constants, obtained at different ionic strengths, were correlated by means of the modified Bromley theory and the thermodynamic protonation constants found to be log $^\circ\beta_1 = 4.36 \pm 0.02$ and log $^\circ\beta_2 = 7.36 \pm 0.02$. The possibility of the formation of mixed sodium species is also discussed.

The hydrolysis of organic acids and bases has been thoroughly studied at various temperatures and ionic strengths and most of the protolytic data are collected in the different compilations of stability constants.[1,2] Among them the protolytic equilibria of polyoxoacids is of special interest due to their importance in different biochemical, environmental and industrial processes.[3-5]

One of the industrial processes in which carboxylic or hydroxycarboxylic acids, together with other organic substances such as aminocarboxylic acids, surfactants, substituted amines or gluconates, can be found is nickel plating. The electrolytic nickel baths generally contain small amounts of the mentioned organic substances together with NiSO$_4$, NiCl$_2$, and various bases in sodium form.[6-8] The most common treatment of waste waters containing nickel is precipitation with sodium or calcium hydroxides, decantation and filtration. The presence of some of the mentioned organic ligands avoids the complete precipitation of nickel hydroxide due to the formation of strong complexes. A general overview of this problem was presented by Ying *et al.*[9]

Although several authors have proposed different methods to eliminate the metal in wastes,[10-13] some of the methods are very complicated and need new reactants which could increase the toxicity of the effluent.

An alternative to developing new processes[14] to solve this problem is the modelling of the chemical system (the wastes) through knowledge of the equilibria involved (protonation, hydrolysis, complexation, precipitation and redox equilibria).[3] The protolytic equilibria involving the different organic substances present in the baths must be known, as well as the possible interactions between those reagents and the inert salts of the medium.

Only a few data concerning the protolysis equilibria of tartaric acid are available in the literature,[15-22] and fewer data in sodium media. Thus there is a need to study the acid–base equilibria of tartaric acid in sodium media. In this work a systematic potentiometric study of the protonation constants of tartrate ion at different ionic strengths has been performed using NaClO$_4$ as the ionic medium. The possible formation of weak complexes between the organic bases and the alkaline cations of the medium, which have been proposed in several other works,[16,21-24] also requires attention and special care in the analysis of the experimental results.

The protonation constants obtained in this work, together with data found in the literature will be used to obtain the thermodynamic protolysis constants of tartaric acid and to build a chemical model which explains the behaviour of this acid–base system in sodium salt media.

Experimental

Reagents and Solutions.—All reagents were used without further purification. The stock solution of sodium hydrogentartrate (Aldrich 98%) was standardized by acidimetric titration. Special care should be taken with this solution due to the formation of colonies of micro-organisms. It should be used soon after preparation and when stored (for one or two weeks) sterilization of the glassware is highly recommended. In this case the use of fungicides or related compounds was not considered.

Stock solutions of perchloric acid (Fluka puriss p.a.) and sodium hydroxide (Merck p.a.) were standardized against tris(hydroxymethyl)aminomethane (Merck p.a.) and potassium hydrogenphthalate (Merck p.a.) respectively. Sodium perchlorate monohydrate (Fluka p.a.) was employed as the ionic medium. The concentration of the stock solution was tested gravimetrically after evaporation of an aliquot at 110 °C.

Apparatus.—All the experiments were carried out with an automatic potentiometric system developed in this laboratory[25] which can control up to three titrations at the same time.

The glass electrode (Methrom 6.0101.100) and the double-junction reference electrode [Ag–AgCl(s), Methrom 6.0726.100] were connected to an operational preamplifier in order to adapt the electric signal to the voltmeter. The electromotive force measurement was carried out with a Hewlett-Packard HP3421A voltmeter connected to a computer. The titrant additions were performed with a Crison microBU 2031 burette with a minimum reading of 0.004 cm^3. The potentiometric measurements were made with the following cell (1) where I is the ionic strength of the solutions. In all titrations, N$_2$ was bubbled through the solution and the temperature was kept constant at 25.0 ± 0.1 °C with a thermostatted oil-bath. Additionally, magnetic stirring was employed during the titrations.

$$\text{Ag–AgCl}\left|\begin{array}{c} I\ \text{mol dm}^{-3}\text{NaClO}_4 \\ \text{saturated AgCl}\end{array}\right\|\begin{array}{c} I\ \text{mol dm}^{-3} \\ \text{NaClO}_4\end{array}\left\|\begin{array}{c}\text{Test} \\ \text{solution}\end{array}\right|\begin{array}{c}\text{Glass} \\ \text{electrode}\end{array} \qquad (1)$$

Procedure.—In order to study the protolytic behaviour of tartrate a solution (75–80 cm^3) containing sodium tartrate (10^{-2}–3.0×10^{-2} mol dm^{-3}) together with the necessary amount of NaClO$_4$ to keep the ionic strength constant was titrated with

$(Na^+,H^+)ClO_4$ solutions at the same ionic strength. An excess of NaOH was added at the beginning of each titration in order to avoid the presence of hydrogentartrate and to calculate the standard potential (E° value) of the electrolytic cell (1). For each addition it was considered that equilibrium was reached when the deviation of the last three measurements was less than ± 0.05 mV. The ionic strengths studied were 0.5, 1.0, 2.0 and 3.0 mol dm^{-3}. Lower values were not employed because their constancy could not be assured. Each titration took around 12 h and at least four titrations were carried out for each of the ionic strengths studied.

Determination of h. The free concentration of hydrogen ions (h) was calculated using the Nernst equation where the measured potential can be expressed as in equations (2) and (3).

$$E = E^\circ + g \log h + E_j(h) \qquad (2)$$

$$E_j(h) = j_{ac}h + j_{bas}k_w h^{-1} \qquad (3)$$

The values of the autoprotolysis constant of water (k_w), the acid and base liquid junction potential coefficients (j_{ac} and j_{bas}, respectively) were determined previously by means of potentiometric ionic media titrations. They were calculated by means of Gran's method[26] and were numerically refined by the non-linear least-squares computer program ESAB2M.[27] As their values depend on the ionic strength,[28] they can be considered to be constant in the latter potentiometric titrations with sodium tartrate.

Calculations and Results

The protonation equilibria of the tartrate ion can be written as in equation (4) where L^{2-} is the tartrate dianion. The stoichiometric protonation constants for a given medium of constant ionic strength can be expressed as in equation (5) where the superscript indicates the ionic strength. The data were treated by means of graphical and numerical methods. The numerical treatment was developed using the programs ESAB2M,[27] BSTAC,[29] and the NYTIT[30] version of LETAGROP.[31]

$$iH^+ + L^{2-} \rightleftharpoons H_iL^{i-2} \qquad (4)$$

$${}^I\beta_i = [H_iL^{i-2}]/[H^+]^i[L^{2-}] \qquad (5)$$

In a first approach to the stoichiometry and the values of the protonation constants a graphical treatment was carried out by means of function Z applied to equation (4).[32] This function can be defined as the average number of ligands bound to the central ion [equation (6)]. As expected, the Z values were not a function of the total tartrate concentration (see Fig. 1) so the above proposed reaction is in accord with the experimental data. On the other hand, the experimental Z values ranged between 0 and 2 in the interval $7 < \text{pH} < 1$, which suggests the presence of two protonation steps. Thus, the classical Z treatment was extended to the normalized variable and one-parameter treatment, so that equation (6) can be rewritten as (7) where U and r were defined as in equations (8) and (9). The experimental curves of Z *vs.* $-\log h$ can be compared with the theoretical plots of Z *vs.* $-\log U$ for different values of the constants and the values of the protonation constants are obtained from the best fit. This comparison is shown for $I = 0.5$ mol dm^{-3} in Fig. 1.

$$Z = \frac{[H]_{tot} - h + k_w h^{-1}}{[L]_{tot}} = \frac{\sum_{1}^{i} i\,{}^I\beta_i h^i}{1 + \sum_{1}^{i} {}^I\beta_i h^i} \qquad (6)$$

$$Z = \frac{\beta_1 h + 2\beta_2 h^2}{1 + \beta_1 h + \beta_2 h^2} = \frac{U + 2rU^2}{1 + U + rU^2} \qquad (7)$$

$$U = \beta_1 h \qquad (8)$$

$$r = \beta_2/\beta_1^2 \qquad (9)$$

The values obtained in the graphical treatment were numerically refined. For this purpose three computer programs were employed: ESAB2M, a non-linear least-squares program minimizing the absolute square error sum of the volume added (U_v), BSTAC, and the NYTIT version of LETAGROP minimizing the absolute square error sum of the measured potential (U_E). Besides the different experimental quantities minimized by these programs there are other differences among them which were taken into account in order to have a set of comparable constants. In this sense the same number of experimental measurements were considered in order to calculate the average values of the constants and their errors. The values obtained by each numerical treatment with the graphical one are listed in Table 1. As can be seen, the values from the different numerical treatments and the graphical one are equal within the limits of experimental error. As an example, Fig. 1 shows the fit between the experimental curves $Z = f(-\log h)$ and the theoretical plot of Z *vs.* $(-\log h)$ constructed with the protonation constants at 0.5 mol dm^{-3} $NaClO_4$ proposed in this work and listed in Table 2.

Discussion

There are several literature references to the protonation constants of tartrate anion at 25 °C.[15-22] Some of these correspond to mixed media[18,19] and only three[15,17,20] concern $NaClO_4$ as a medium (the first and last references give the same values). Thus, there is not enough information to build a suitable thermodynamic model from previous data.

As it has been mentioned before, several authors have proposed the formation of weak complexes between low-molecular-weight carboxylate ligands and alkali and alkaline-earth metals,[16,21-24] which should be critically considered. These mixed species have been proposed in order to explain the differences between values at the same ionic strength but in different ionic media. The explanations are uncertain in many cases and it is a matter of endless discussion as to whether there is sufficient experimental evidence for the formation of such mixed complexes.

The differences experimentally observed could also be attributed to the variation of the activity coefficients of the species involved in the equilibria. Both approaches could explain satisfactorily the experimental behaviour and could form the basis of different chemical models from completely different points of view.

As stated in the Introduction, the main aim of this work is to develop a thermodynamic model in order to explain the behaviour of the protolysis of tartrate ion in $NaClO_4$ media.

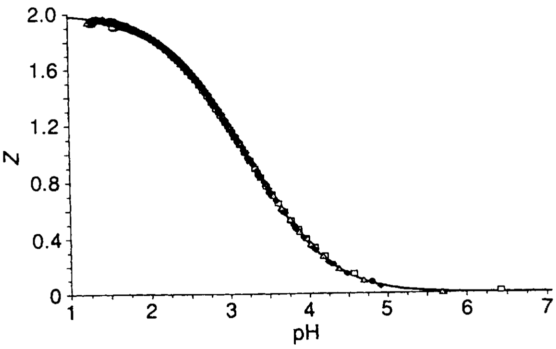

Fig. 1 Plot of Z as a function of $-\log h$ at different total tartrate concentrations and 0.5 mol dm^{-3} $NaClO_4$. (——), Theoretical function; (□) and (○), 0.1 mol dm^{-3} tartrate; (◇) and (△), 0.15 mol dm^{-3} tartrate

Table 1 Stoichiometric protonation constants for tartrate anion at different ionic strengths in $NaClO_4$ medium calculated by the different graphical and numerical methods[a]

	$\log \beta_1$				$\log \beta_2$			
I/mol dm^{-3}	Graphical	ESAB2M[b]	BSTAC[c]	NYTIT[c]	Graphical	ESAB2M	BSTAC	NYTIT
0.5	3.70 ± 0.01	3.69 ± 0.03	3.74 ± 0.01	3.71 ± 0.07	6.43 ± 0.02	6.43 ± 0.04	6.46 ± 0.01	6.38 ± 0.04
1.0	3.68 ± 0.03	3.70 ± 0.02	3.72 ± 0.01	3.67 ± 0.01	6.42 ± 0.02	6.41 ± 0.01	6.40 ± 0.01	6.42 ± 0.02
2.0	3.75 ± 0.03	3.74 ± 0.03	3.75 ± 0.01	3.74 ± 0.04	6.57 ± 0.02	6.56 ± 0.03	6.55 ± 0.01	6.56 ± 0.02
3.0	3.82 ± 0.03	3.80 ± 0.02	3.87 ± 0.01	3.81 ± 0.03	6.78 ± 0.03	6.77 ± 0.03	6.80 ± 0.01	6.79 ± 0.06

[a] Even if these programs work differently as has been pointed out in the text, the number of experimental measurements is the same in all the numerical treatments. In the case of ESAB2M and NYTIT the values of the constants and their standard deviations have been averaged. [b] Equation minimized: $U_v = \Sigma_i (v_i - v_{calc,i})^2$, where v_i is the volume added and $v_{calc,i}$ the volume calculated. [c] Equation minimized: $U_E = \Sigma_i (E_i - E_{calc,i})^2$ where E_i is the measured potential, and $E_{calc,i}$ the calculated potential.

Table 2 Protonation constants for tartrate anion at different ionic strengths in $NaClO_4$ medium calculated as a weighted average of the values given in Table 1.

I/mol dm^{-3}	$\log \beta_1$	$\log \beta_2$
0.5	3.71 ± 0.03	6.42 ± 0.03
1.0	3.69 ± 0.03	6.41 ± 0.02
2.0	3.75 ± 0.03	6.56 ± 0.02
3.0	3.82 ± 0.03	6.78 ± 0.03

This chemical model will be constructed by means of the modified Bromley theory[33,34] which has been successfully employed to explain the hydrolysis of Mo^{VI}, V^{V}, Nb^{V} and Ta^{V} [34,35] and the protolytic equilibria of 4-methylpyridine.[36]

In this work two approaches are considered: in the first the chemical model takes account only of the protonation equilibria defined above; in the second the formation of mixed complexes NaH_iL (i = 0 or 1) is considered, even if, as will be shown below, this assumption greatly increases the difficulties in the construction of the thermodynamic model.

In the first approach, equation (5) can be rewritten as (10)

$$^{\circ}\beta_i = \frac{\{H_iL^{i-2}\}}{\{H^+\}^i\{L^{2-}\}} = \frac{[H_iL^{i-2}]\gamma_{H_iL^{i-2}}}{[H^+]^i\gamma^i_{H^+}[L^{2-}]\gamma_{L^{2-}}} \qquad (10)$$

where $^{\circ}\beta_i$ is the thermodynamic protonation constant and γ the molar activity coefficient ({ } indicates activity). Combining equations (5) and (10) the expression to correlate the stoichiometric protonation constant can be written as (11).

$$\log {}^{I}\beta_i = \log {}^{\circ}\beta_i + i \log \gamma_{H^+} + \log \gamma_{L^{2-}} - \log \gamma_{H_iL^{i-2}} \qquad (11)$$

The individual activity coefficients, on the molar scale, of the charged species, γ_i, can be substituted by use of the Bromley equation (12) where $A = 0.5109$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$, I the ionic strength

$$\log \gamma_M = -\frac{AZ^2_M I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \sum_x \mathring{B}_{MX}(|Z_M| + |Z_X|)^2 \frac{c_X}{4} \qquad (12)$$

on the molar scale, Z_M the ionic charge of M, Z_X the charge of the ionic species with opposite sign to M and c_X its molarity. The parameter $\mathring{B}_{MX}$ can be expressed as in equation (13) where

$$\mathring{B}_{MX} = \frac{(0.06 + 0.6B_{MX})|Z_M Z_X|}{[1 + (1.5I/|Z_M Z_X|)]^2} + B_{MX} \qquad (13)$$

B_{MX} is the interaction parameter of the ion pair MX on the molar scale.

In the case of uncharged species the activity coefficient is expressed by means of the salt coefficient S proposed by Long and McDevit,[37] [equation (14)]. Rearranging equation (11)

$$\log \gamma_{MX} = S_{MX,\,\text{ionic medium}}\, c_{\text{ionic medium}} \qquad (14)$$

and making use of equations (12)–(14) it is possible to obtain expressions (15) and (16) to correlate the protonation constants

$$\log {}^{I}\beta_1 = \log {}^{\circ}\beta_1 - 4D + F_{H^+,ClO_4^-} + F_{L^{2-}Na^+} - F_{HL^-,Na^+} \qquad (15)$$

$$\log {}^{I}\beta_2 = \log {}^{\circ}\beta_2 - 6D + 2F_{H^+,ClO_4^-} + F_{L^{2-},Na^+} - S_{H_2L,NaClO_4}I \qquad (16)$$

at different ionic strengths in which the F functions are the corresponding terms of the Bromley equation (13). These expressions depend only on the values of the thermodynamic constants for the different equilibria taking place and the interaction parameters (B) or salt coefficients (S) of the different ionic or neutral species.

Daniele *et al.*[21] and De Robertis *et al.*[22] have proposed values for the protonation constants at different ionic strengths in NEt_4I as medium and calculated the thermodynamic protonation constants by means of a different correlation theory.[38] According to the interpretation given by these authors, those values are not affected by any side effect, so they should be considered strictly as stoichiometric constants. In order to validate the data and the thermodynamic constants proposed by those authors, Bromley's theory was employed to correlate their experimental data together with the experimental results in this work.

The value of B_{H^+,ClO_4^-} was previously determined[39] by making use of the literature (m, $\gamma_\pm$) data, while the thermodynamic constants and the rest of the interaction parameters have to be calculated. The correlation was made by means of the spreadsheet EXCEL 4.0.[40]

The results obtained are collected in Table 3 and Figs 2 and 3 show the fit between the experimental data and the theoretical curve. The thermodynamic constants obtained with the constants proposed in this work and in refs. 21 and 22 from the Bromley equation ($\log {}^{\circ}\beta_1 = 4.36 \pm 0.02$, $\log {}^{\circ}\beta_2 = 7.36 \pm 0.02$) are in good agreement with these proposed by Daniele *et al.*[21] and De Robertis *et al.*[22] from their data in NEt_4I. Thus this model can explain satisfactorily the protonation equilibria of tartrate ion in different ionic media without consideration of any mixed complex. However, it was decided to develop the second kind of correlation to show whether it is able to explain the experimental results in terms of the formation of weak complexes between sodium and tartrate ion.

According to Daniele *et al.*[21] and De Robertis *et al.*[22] the presence of NaL^- and $Na(HL)$ complexes can be considered so all the values of the experimental stoichiometric constants would be affected by those side reactions and the values of the proposed formation constants should be considered as conditional constants ($^{I}\beta'_i$) expressed as in equation (17) where

$$^{I}\beta'_i = \frac{[H_iL^{i-2}]'}{[H^+]^i[L^{2-}]'} = \frac{[H_iL^{i-2}]\alpha_{H_iL^{i-2}(Na^+)}}{[H^+]^i[L^{2-}]\alpha_{L^{2-}(Na^+)}} \qquad (17)$$

α is the side reaction coefficient defined as in equation (18) for

$$\alpha_{\mathrm{H}_i\mathrm{L}^{i-2}(\mathrm{Na}^+)} = 1 + {}^{I}K^{\mathrm{Na}^+}_{\mathrm{H}_i\mathrm{L}^{i-2}}[\mathrm{Na}^+] \qquad (18)$$

$i = 0$ to 1 and where ${}^{I}K^{\mathrm{Na}^+}_{\mathrm{H}_i\mathrm{L}^{i-2}}$ is the stoichiometric stepwise formation constant of the complex species.

Combining equations (5), (10) and (18), equation (15) can be rewritten as (19). Substituting the value of the side reaction coefficients as a function of the thermodynamic constants the activity coefficients, equation (19) becomes (20). In this

$$\log {}^{I}\beta'_i = \log {}^{\circ}\beta_i + i \log \gamma_{\mathrm{H}^+} + \log \gamma_{\mathrm{L}^{2-}} - \log \gamma_{\mathrm{H}_i\mathrm{L}^{i-2}} + \log \alpha_{\mathrm{H}_i\mathrm{L}^{i-2}(\mathrm{Na}^+)} - \log \alpha_{\mathrm{L}^{2-}(\mathrm{Na}^+)} \qquad (19)$$

$$\log {}^{I}\beta'_i = \log {}^{\circ}\beta_i + i \log \gamma_{\mathrm{H}^+} + \log \gamma_{\mathrm{L}^{2-}} - \log \gamma_{\mathrm{H}_i\mathrm{L}^{i-2}} + \log\left(1 + {}^{\circ}K^{\mathrm{Na}^+}_{\mathrm{H}_i\mathrm{L}^{i-2}} \frac{\gamma_{\mathrm{H}_i\mathrm{L}^{i-2}}}{\gamma_{\mathrm{Na}^+}\gamma_{\mathrm{L}^{2-}}}\right) - \log\left(1 + {}^{\circ}K^{\mathrm{Na}^+}_{\mathrm{L}^{2-}} \frac{\gamma_{\mathrm{NaL}^-}}{\gamma_{\mathrm{Na}^+}\gamma_{\mathrm{L}^{2-}}}\right) \qquad (20)$$

equation there are a large number of parameters to be calculated (five Bromley interaction parameters and four thermodynamic constants) and only a few data (I, $\log {}^{I}\beta'_i$) are available. Thus it is necessary to fix some of the parameters before correlating the experimental data.

Table 3 Thermodynamic protonation constants and interaction parameters obtained with the different models

Parameter[a]	Model 1[b]	Model 2[c]
$\log {}^{\circ}\beta_1$	4.36 ± 0.02	4.36[d]
$\log {}^{\circ}\beta_2$	7.36 ± 0.02	7.36[d]
$B_{\mathrm{L}^{2-},\mathrm{Na}^+}$	0.0145 ± 0.0001	−0.08 ± 0.07
$B_{\mathrm{HL}^-,\mathrm{Na}^+}$	−0.0012 ± 0.0005	−0.66 ± 0.02
$S_{\mathrm{H_2L},\mathrm{NaClO_4}}$	−0.0125 ± 0.0006	−0.82 ± 0.03
$B_{\mathrm{NaL}^-,\mathrm{Na}^+}$	—	−0.59 ± 0.05
$S_{\mathrm{Na(HL)},\mathrm{NaClO_4}}$	—	−0.62 ± 0.02
$B_{\mathrm{L}^{2-},\mathrm{NEt_4}^+}$	0.4505 ± 0.0003	—
$B_{\mathrm{HL}^-,\mathrm{NEt_4}^+}$	0.8981 ± 0.001	—
$S_{\mathrm{H_2L},\mathrm{NEt_4I}}$	0.7176 ± 0.001	—

[a] B and S in dm^3 mol^{-1}. [b] Only the protonation equilibria have been considered, taking into account the results in this work and those of Daniele *et al.*[21] and De Robertis *et al.*[22] [c] Both protonation equilibria and sodium–tartrate complex formation have been considered, taking into account only the results in this work. [d] Thermodynamic protonation constant from this work.

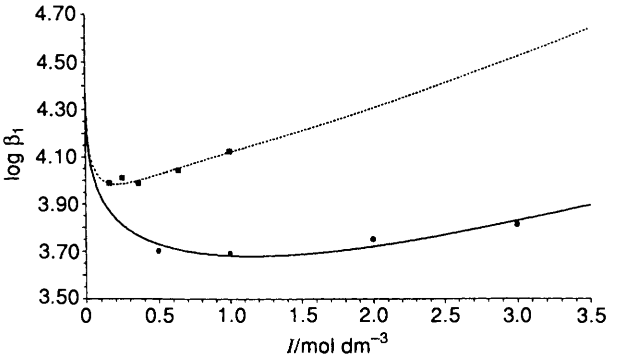

Fig. 2 Variation of log β_1 with ionic strength in different media: (——), theoretical function in $NaClO_4$; (●), experimental values in $NaClO_4$; (- - -), theoretical function in NEt_4I; and (■), experimental values in NEt_4I

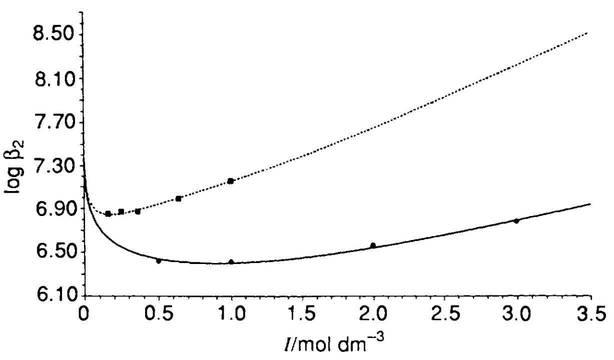

Fig. 3 Variation of log β_2 with ionic strength in different media; details as in Fig. 2

Taking into account the good agreement between the values of the thermodynamic protonation constants (${}^{\circ}\beta_i$) obtained in this work and the literature values,[21,22] the values for each acid–base equilibrium were fixed at those obtained in the previous correlation. The same assumption was made for the thermodynamic formation constants of sodium tartrate and sodium hydrogentartrate complexes (${}^{\circ}K^{\mathrm{Na}^+}_{\mathrm{H}_i\mathrm{L}^{i-2}} = 4.64$ and ${}^{\circ}K^{\mathrm{Na}^+}_{\mathrm{L}^{2-}} = 1.0$). The results of these calculations are also collected in Table 3 and Figs. 4 and 5 compare the values obtained by this model and those determined experimentally. As can be seen, there is a great difference between the values of the conditional protonation constants (${}^{I}\beta'_i$) and the stoichiometric ones (${}^{I}\beta_i$); in some cases the difference is higher than two logarithmic units.

According to the results obtained by both treatments it can be inferred that even if both approaches explain satisfactorily the experimental results, the assumption of mixed species is not strictly necessary. It is concluded that the experimental behaviour can be explained only in terms of the variation of activity coefficients and not in terms of the formation of weak

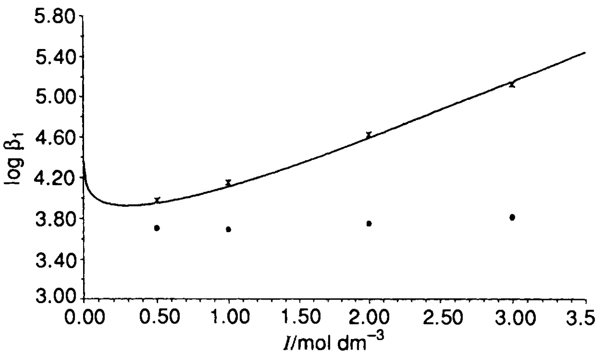

Fig. 4 Variation of log β_1 with ionic strength in $NaClO_4$ considering the formation of weak complexes between sodium and tartrate: (——), theoretical function; (●), experimental values (= conditional stoichiometric constants); (∗), corrected values (= stoichiometric constants)

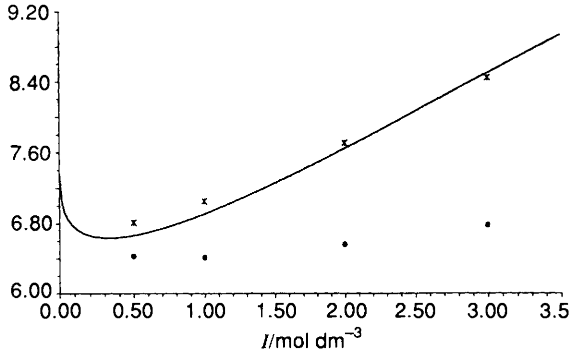

Fig. 5 Variation of log β_2 with ionic strength in $NaClO_4$; details as in Fig. 4

complexes with the cation of the medium. This does not mean that mixed species are not formed or that their consideration is not generally valid. It demonstrates that those species are not needed to build a thermodynamic model.

Finally, it should be mentioned that the interaction parameters and thermodynamic constants given in Table 3 can be used to model the protolytic behaviour of tartrate in different sodium media.

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