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Enthalpies of solution of citric acid in water at 298.15 K. The effect of association processes on thermochemical properties of electrolyte solutions

A. Bald [a,*] and J. Barczyńska [b]

[a] *Department of Chemistry Didactics, University of Łódź, Lindleya 3, 90-136 Łódź (Poland)*
[b] *Department of Physical Chemistry, University of Łódź, Pomorska 18, 90-313 Łódź (Poland)*

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Abstract

Enthalpies of solution ΔH_s of citric acid in water were measured within the molality range 0.004–0.09 mol kg^{-1} at 298.15 K. The effect of an incomplete dissociation of electrolyte on the ΔH_s values was determined and a method for the determination of standard enthalpy of solution of weak asymmetric electrolytes was proposed.

INTRODUCTION

In order to examine to a greater degree and to elucidate the nature of the interactions taking place in electrolyte solutions, intensive studies on many properties of these solutions using various experimental procedures are indispensable.

In studies on electrolyte solution properties carried out in our laboratory over many years, much attention has been paid to taking into account the incomplete dissociation of electrolytes in the determination of properties such as the standard enthalpies of solution [1–6], the standard electromotive forces of cells [4–6] and the coefficient *B* of the Jones–Dole equation [7, 8]. These data are very important for the interpretation of electrolyte–solvent interactions.

Our publications [1–8], however, have dealt mainly with solutions of symmetric electrolytes of the 1:1 type. Recently, we proposed and used a method for including the incomplete dissociation of asymmetric electrolytes in the determination of the coefficient *B* of the Jones–Dole equation [9–11].

The present paper proposes a method of accounting for the incomplete dissociation of asymmetric electrolytes in the analysis of the enthalpy of

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* Corresponding author.

solution (and also the enthalpy of dilution) of these electrolytes, and is mainly aimed at the development of a method for the determination of the standard enthalpy of solution of asymmetric, incompletely dissociated electrolytes.

It is our opinion that the lack of methods for including the incomplete dissociation of weak asymmetric electrolytes is the main drawback in investigations of this important, large group of electrolytes. The literature contains a few studies on the enthalpy of solution or of dilution of asymmetric electrolytes in which the following two approaches are used.

1) One of the ionic equilibria is ignored because of the low values of its constant; therefore, such an electrolyte can be considered symmetric, see, for example, refs. 12 and 13.

2) If none of the equilibria in solution can be ignored, the effect of these equilibria on the enthalpy values is not usually interpreted; thus, either only values for the enthalpy of solution are reported (often as an arithmetic average of concentrations within a narrow range, e.g. ref. 14) or the extrapolation of these values to infinite dilution is attempted, e.g. ref. 15.

Solutions of citric acid in water were chosen as the object of study because citric acid is a weak asymmetric electrolyte in water, characterized by as many as three dissociation steps; thus the proposed method of accounting for ionic equilibria must be of a more general character and should be applicable to electrolytes with a lower degree of asymmetry, i.e. of the type 2:1 or 1:2, and also to symmetric electrolytes. Moreover, citric acid is an electrolyte whose ionic equilibria in water [16] and enthalpies of dilution [17] have been examined fairly extensively. The results of the cited papers are useful [17] or indispensable [16] for the analysis of data from measurements of heats of solution.

EXPERIMENTAL

Anhydrous citric acid (Fluka, puriss p.a.) was used without any further purification. Redistilled water with a conductivity lower than 10^{-6} S cm^{-1} was used in the experiment.

Enthalpies of solution for 41 concentrations of citric acid within the molality range 0.004–0.09 mol kg^{-1} were measured with an isoperibol-type calorimeter. Further details concerning the experimental method are given in ref. 18.

THEORY

To analyse the values of the enthalpy of dilution of symmetric electrolytes, Barthel et al. [19] and Wachter and Riederer [20] have used the assumption, made by Larson [21], and earlier by Hopkins and Wulff [12, 13], that the apparent molal enthalpy of an electrolyte ϕ_H can be treated as a sum of two contributions, i.e. for free ions $\phi_{H,i}$ and undissociated electrolyte $\phi_{H,u}$. This leads to the relationship

$$\phi_H = \alpha\phi_{H,i} + (1-\alpha)\phi_{H,u} \tag{1}$$

where α is the degree of dissociation and $\lim_{m\to 0} \phi_H = \phi^{\ominus}_{H,i}$. The relative apparent molal enthalpy of an electrolyte ϕ_L is the difference between values of ϕ_H at the given concentration and at infinite dilution

$$\phi_L = \phi_H - \phi^{\ominus}_H = \alpha\phi_{H,i} + (1-\alpha)\phi_{H,u} - \phi^{\ominus}_{H,i} \tag{2}$$

Ignoring the concentration relationship $\phi_{H,u}$, one can assume that

$$\phi_{H,u} = \phi^{\ominus}_{H,u} \tag{3}$$

Introducing the enthalpy of ion association

$$\Delta H^{\ominus}_A = \phi^{\ominus}_{H,u} - \phi^{\ominus}_{H,i} \tag{4}$$

the following relationship is obtained

$$\phi_L = \alpha\phi_{L,i} + (1-\alpha)\Delta H^{\ominus}_A \tag{5}$$

ϕ_L is related to the enthalpy of infinite dilution $\Delta H^{\ominus}_{dil}$

$$\phi_L = -\Delta H^{\ominus}_{dil} = \Delta H_s - \Delta H^{\ominus}_s \tag{6}$$

where ΔH_s is the enthalpy of solution and $\Delta H^{\ominus}_s$ the standard enthalpy of solution.

Therefore, for the incompletely dissociated symmetric electrolytes, the enthalpy of solution can be described as

$$\Delta H_s = \Delta H^{\ominus}_s + \alpha\phi_{L,i} + (1-\alpha)\Delta H^{\ominus}_A \tag{7}$$

Values of $\phi_{L,i}$ can be calculated from equations given in refs. 19 and 20. To calculate these values, one has to know the permittivity and density of the solvent, and the temperature coefficients of these parameters.

In the case of an asymmetric electrolyte such as citric acid (H_3Cit) in water, the following equilibria should be taken into account

$$H_2Cit^- + H^+ \underset{K_{D1}}{\overset{K_{A1}}{\rightleftharpoons}} H_3Cit \tag{8a}$$

$$HCit^{2-} + H^+ \underset{K_{D2}}{\overset{K_{A2}}{\rightleftharpoons}} H_2Cit^- \tag{8b}$$

$$Cit^{3-} + H^+ \underset{K_{D3}}{\overset{K_{A3}}{\rightleftharpoons}} HCit^{2-} \tag{8c}$$

The association constants can be described respectively

$$K_{A1} = \frac{[H_3Cit]\,y_{H_3Cit}}{[H_2Cit^-][H^+]\,y_{H_2Cit^-}\,y_{H^+}} \tag{9a}$$

$$K_{A2} = \frac{[H_2Cit^-]\,y_{H_2Cit^-}}{[HCit^{2-}][H^+]\,y_{HCit^{2-}}\,y_{H^+}} \tag{9b}$$

$$K_{A3} = \frac{[HCit^{2-}]\,y_{HCit^{2-}}}{[Cit^{3-}][H^+]\,y_{Cit^{3-}}\,y_{H^+}} \tag{9c}$$

The concentrations $[H_3Cit]$, $[H_2Cit^-]$, $[HCit^{2-}]$, $[Cit^{3-}]$ and $[H^+]$ in the solution with concentration c, can be described using the equations

$$[H_3Cit] = (1 - \alpha_1)c = (1 - \beta_1 - \beta_2 - \beta_3)c \tag{10a}$$

$$[H_2Cit^-] = \alpha_1(1 - \alpha_2)c = \beta_1 c \tag{10b}$$

$$[HCit^{2-}] = \alpha_1\alpha_2(1 - \alpha_3)c = \beta_2 c \tag{10c}$$

$$[Cit^{3-}] = \alpha_1\alpha_2\alpha_3 c = \beta_3 c \tag{10d}$$

$$[H^+] = (\alpha_1 + \alpha_1\alpha_2 + \alpha_1\alpha_2\alpha_3)c = (\beta_1 + 2\beta_2 + 3\beta_3)c \tag{10e}$$

where α_1, α_2 and α_3 are dissociation degrees related to the particular dissociation steps, and β_1, β_2 and β_3 are degrees of dissociation (fractions) describing what part of the total concentration c is represented by the ion concentrations H_2Cit^-, $HCit^{2-}$ and Cit^{3-}, respectively.

The activity coefficients of ions within the investigated electrolyte concentration range can be described approximately by the Debye–Hückel equation

$$\ln y_i = \frac{A z_i^2 \sqrt{I}}{1 + R_i B \sqrt{I}} \tag{11}$$

where R_i is the average cation–anion distance and I is the ionic strength described by the equation

$$I = c(\alpha_1 + 2\alpha_1\alpha_2 + 3\alpha_1\alpha_2\alpha_3) = c(\beta_1 + 2\beta_2 + 3\beta_3) \tag{12}$$

The coefficients A and B for water are 1.1727 $\mathrm{mol^{-1/2}\,dm^{3/2}}$ and 0.3286×10^8 $\mathrm{mol^{-1/2}\,cm^{-1}\,dm^{3/2}}$, respectively.

Equations (9a), (9b) and (9c) can then be given as

$$K_{A1} = \frac{(1 - \alpha_1)y_{H_3Cit}}{\alpha_1^2(1 - \alpha_2)(1 + \alpha_2 + \alpha_2\alpha_3)c y_{H_2Cit^-} y_{H^+}} = \frac{(1 - \beta_1 - \beta_2 - \beta_3)y_{H_3Cit}}{\beta_1(\beta_1 + 2\beta_2 + 3\beta_3)c y_{H_2Cit^-} y_{H^+}} \tag{13a}$$

$$K_{A2} = \frac{(1 - \alpha_2)y_{H_2Cit^-}}{\alpha_1\alpha_2(1 - \alpha_3)(1 + \alpha_2 + \alpha_2\alpha_3)c y_{H_2Cit^{2-}} y_{H^+}} = \frac{\beta_1 y_{H_2Cit^-}}{\beta_2(\beta_1 + 2\beta_2 + 3\beta_3)c y_{HCit^{2-}} y_{H^+}} \tag{13b}$$

$$K_{A3} = \frac{(1 - \alpha_3)y_{HCit^{2-}}}{\alpha_1\alpha_2(1 + \alpha_2 + \alpha_2\alpha_3)c y_{Cit^{3-}} y_{H^+}} = \frac{\beta_2 y_{HCit^{2-}}}{\beta_3(\beta_1 + 2\beta_2 + 3\beta_3)c y_{Cit^{3-}} y_{H^+}} \tag{13c}$$

Knowing the values of the association constants K_{A1}, K_{A2} and K_{A3} which can be determined independently by potentiometric [22, 23] or conductometric methods [16], one can determine the values of α_1, α_2, α_3 or β_1, β_2, β_3 by numerical methods of successive approximation, using eqns. (11)–(13). The system of eqns. (11)–(13) can be solved more easily when the values of β_1, β_2 and β_3 are known. However, the values of α_1, α_2 and α_3 can be calculated using the relationships

$$\alpha_1 = \beta_1 + \beta_2 + \beta_3 \tag{14a}$$

$$\alpha_2 = (\beta_2 + \beta_3)/(\beta_1 + \beta_2 + \beta_3) \tag{14b}$$

$$\alpha_3 = \beta_3/(\beta_2 + \beta_3) \tag{14c}$$

The citric acid solution can be treated as being composed of three parts

$H_3Cit_{(u)}$	undissociated electrolyte
$H_3Cit_{(i1)}$	completely dissociated according to the scheme: $H_3Cit \rightarrow H_2Cit^- + H^+$
$H_3Cit_{(i2)}$	completely dissociated according to the scheme: $H_3Cit \rightarrow HCit^{2-} + 2H^+$
$H_3Cit(_{i3})$	completely dissociated according to the scheme: $H_3Cit \rightarrow Cit^{3-} + 3H^+$

In the case of solutions of concentration *c*, the concentrations $[H_3Cit]$, $[H_2Cit^-]$, $[HCit^{2-}]$ and $[Cit^{3-}]$ are respectively equal to the concentrations of electrolyte in the forms: $H_3Cit_{(u)}$, $H_3Cit_{(i1)}$, $H_3Cit_{(i2)}$ and $H_3Cit_{(i3)}$.

As in eqn. (1), the apparent molal enthalpy of citric acid can be expressed

$$\phi_H = \alpha_1\alpha_2\alpha_3\phi_{H,i3} + \alpha_1\alpha_2(1-\alpha_3)\phi_{H,i2} + \alpha_1(1-\alpha_2)\phi_{H,i1} + (1-\alpha_1)\phi_{H,u} \tag{15}$$

Because $\lim\limits_{m\to 0} \phi_H = \phi_H^\ominus = \phi_{H,i3}^\ominus$, therefore

$$\begin{aligned}\phi_L &= \phi_H - \phi_H^\ominus = \phi_H - \phi_{H,i3}^\ominus \\ &= \alpha_1\alpha_2\alpha_3\phi_{H,i3} + \alpha_1\alpha_2(1-\alpha_3)\phi_{H,i2} + \alpha_1(1-\alpha_2)\phi_{H,i1} \\ &\quad + (1-\alpha_1)\phi_{H,u} - \phi_{H,i3}^\ominus \end{aligned} \tag{16}$$

Equation (16), after several transformations, can assume the form

$$\begin{aligned}\phi_L &= \alpha_1\alpha_2\alpha_3\phi_{L,i3} + \alpha_1\alpha_2(1-\alpha_3)\phi_{L,i2} + \alpha_1(1-\alpha_2)\phi_{L,i1} \\ &\quad + \Delta H_{A3}^\ominus(1-\alpha_1\alpha_2\alpha_3) + \Delta H_{A2}^\ominus(1-\alpha_1\alpha_2) + \Delta H_{A1}^\ominus(1-\alpha_1)\end{aligned} \tag{17}$$

where $\phi_{L,i3} = \phi_{H,i3} - \phi_{H,i3}^\ominus$; $\phi_{L,i2} = \phi_{H,i2} - \phi_{H,i2}^\ominus$; $\phi_{L,i1} = \phi_{H,i1} - \phi_{H,i1}^\ominus$; $\Delta H_{A1}^\ominus = \phi_{H,u}^\ominus - \phi_{H,i1}^\ominus$; $\Delta H_{A2}^\ominus = \phi_{H,i1}^\ominus - \phi_{H,i2}^\ominus$; $\Delta H_{A3}^\ominus = \phi_{H,i2}^\ominus - \phi_{H,i3}^\ominus$; and ΔH_{A1}, ΔH_{A2} and ΔH_{A3} are enthalpies of the association processes described respectively by eqns. (8a), (8b) and (8c).

Equation (17) can also assume another form if relationship (14) is taken into account:

$$\phi_L = \beta_3\phi_{L,i3} + \beta_2\phi_{L,i2} + \beta_1\phi_{L,i1} + (1-\beta_3)\Delta H^{\ominus}_{A3} + (1-\beta_2-\beta_3)\Delta H^{\ominus}_{A2} + (1-\beta_1-\beta_2-\beta_3)\Delta H^{\ominus}_{A1} \quad (18)$$

Equation (18) is used later in the study.

For electrolytes of the type 2:1, e.g. dicarboxylic acids of the general formula H_2A, there are two equilibria, described by

$$HA^- + H^+ \underset{K_{D1}}{\overset{K_{A1}}{\rightleftharpoons}} H_2A$$

$$A^{2-} + H^+ \underset{K_{D2}}{\overset{K_{A2}}{\rightleftharpoons}} HA^-$$

and the equivalent of eqn. (18) assumes the form

$$\phi_L = \beta_2\phi_{L,i2} + \beta_1\phi_{L,i1} + (1-\beta_2)\Delta H^{\ominus}_{A2} + (1-\beta_1-\beta_2)\Delta H^{\ominus}_{A1} \quad (19)$$

For symmetric electrolytes, e.g. monocarboxylic acids of the type HA, there is an equilibrium described by

$$A^- + H^+ \underset{K_{D1}}{\overset{K_{A1}}{\rightleftharpoons}} HA$$

and the equivalent of eqn. (18) assumes the form

$$\phi_L = \beta_1\phi_{L,i1} + (1-\beta_1)\Delta H^{\ominus}_{A1} \quad (20)$$

which is the same as the equation used by Barthel et al. [19] and Wachter and Riederer [20].

Taking into account eqns. (6) and (18), the enthalpy of solution of citric acid can be described as

$$\Delta H_s = \Delta H^{\ominus}_s + \beta_3\phi_{L,i3} + \beta_2\phi_{L,i2} + \beta_1\phi_{L,i1} + (1-\beta_3)\Delta H^{\ominus}_{A3} + (1-\beta_2-\beta_3)\Delta H^{\ominus}_{A2} + (1-\beta_1-\beta_2-\beta_3)\Delta H^{\ominus}_{A1} \quad (21)$$

RESULTS AND DISCUSSION

The enthalpy of solution values ΔH_s of citric acid in water determined for various molalities m are given in Table 1. The concentrations values c corresponding to the molalities used m are also given. The relationship $\Delta H_s = f(m)$ is illustrated in Fig. 1. From the equilibrium constants of the processes described in eqns. (8a), (8b) and (8c) determined by Apelblat and Barthel [16] ($K_{A1} = 1/K_{D1}$; $K_{D1} = 6.98 \times 10^{-4}$; $K_{A2} = 1/K_{D2}$; $K_{D2} = 1.40 \times 10^{-5}$) and those of Bates and Pinching [23] ($K_{A3} = 1/K_{D3}$; $K_{D3} = 4.05 \times 10^{-7}$), the dissociation degrees β_1, β_2 and β_3 were calculated by solving the system of equations, eqns. (11)–(13), by the method of successive approximation.

TABLE 1

Heats of solution and degrees of dissociation of citric acid in water at 298.15 K

No.	$m/(\mathrm{mol\,kg^{-1}})$	$c/(\mathrm{mol\,dm^{-3}})$	$H_s/(\mathrm{J\,mol^{-1}})$	β_1	β_2
1	0.004897	0.004877	19024	0.32203	0.00335
2	0.004903	0.004884	19233	0.32187	0.00335
3	0.004955	0.004935	19024	0.32056	0.00331
4	0.004990	0.004703	19125	0.31969	0.00329
5	0.005887	0.005862	18894	0.29968	0.00281
6	0.005918	0.005894	18899	0.29905	0.00280
7	0.007766	0.007731	18940	0.26818	0.00216
8	0.008218	0.008180	18786	0.26206	0.00204
9	0.008414	0.008375	18853	0.25955	0.00200
10	0.008776	0.008737	18723	0.25508	0.00192
11	0.009016	0.008975	18786	0.25226	0.00187
12	0.01064	0.01056	18622	0.23554	0.00160
13	0.01067	0.01062	18660	0.23526	0.00159
14	0.01099	0.01093	18769	0.23237	0.00155
15	0.01149	0.01143	18618	0.22808	0.00249
16	0.01242	0.12353	18660	0.22073	0.00138
17	0.01270	0.01263	18564	0.21869	0.00135
18	0.01536	0.01526	18552	0.20167	0.00113
19	0.01635	0.01624	18379	0.19634	0.00107
20	0.01899	0.01886	18359	0.18407	0.00093
21	0.01923	0.01910	18296	0.18307	0.00091
22	0.01929	0.19161	18410	0.18283	0.00091
23	0.02079	0.02064	18451	0.17698	0.00085
24	0.02247	0.02231	18204	0.17110	0.00079
25	0.02375	0.02357	18095	0.16701	0.00075
26	0.02427	0.02408	18242	0.16544	0.00074
27	0.02748	0.02725	18309	0.15668	0.00065
28	0.02965	0.02939	18200	0.15153	0.00061
29	0.03152	0.03126	18334	0.14750	0.00057
30	0.03255	0.03225	18112	0.14543	0.00056
31	0.03542	0.03508	18313	0.14010	0.00052
32	0.03576	0.03541	18166	0.13950	0.00052
33	0.03765	0.03727	18225	0.13636	0.00049
34	0.04029	0.03986	18129	0.13232	0.00047
35	0.04356	0.04307	18033	0.12782	0.00043
36	0.04890	0.04830	18058	0.12142	0.00039
37	0.05657	0.05579	18062	0.11379	0.00034
38	0.05766	0.05686	18137	0.11283	0.00034
39	0.06038	0.05950	18217	0.11054	0.00032
40	0.06784	0.06676	18108	0.10495	0.00029
41	0.08710	0.08541	18150	0.09389	0.00024

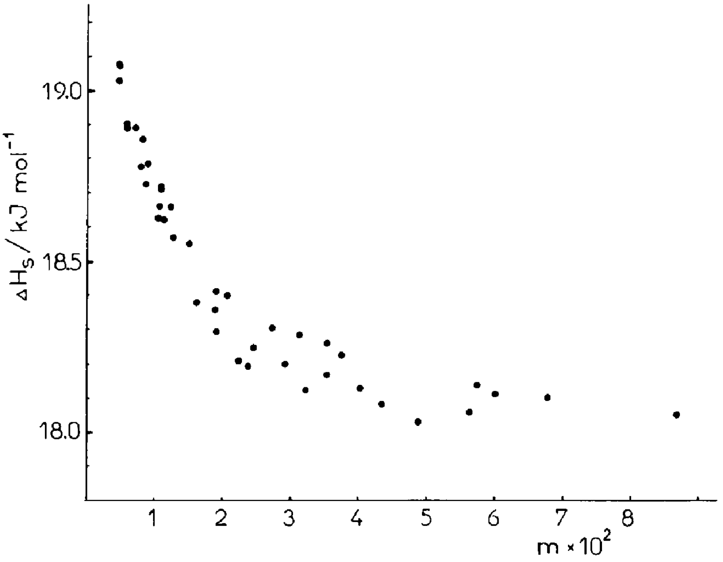

Fig. 1. Plot of the enthalpy of solution of citric acid in water at 298.15 K versus molality *m*.

Values of β_1 and β_2 for particular concentrations *c* of the electrolyte are also given in Table 1. Values of β_3 are not included because they were very small (lower than 5×10^{-6}) and negligible for further calculations.

From eqn. (21), the standard enthalpy of solution can be calculated from the relationship

$$\Delta H_s^{\ominus} = \Delta H_s - \beta_3 \phi_{L,i3} - \beta_2 \phi_{L,i2} - (1 - \beta_3)\Delta H_{A3}^{\ominus} - (1 - \beta_2 - \beta_3)\Delta H_{A2}^{\ominus} - (1 - \beta_1 - \beta_2 - \beta_3)\Delta H_{A1}^{\ominus} \tag{22}$$

If the method of including the incomplete dissociation of electrolyte as proposed in this study is correct, the calculated values of the standard enthalpy of solution $\Delta H_s^{\ominus}$ should be approximately the same for all the concentrations of H_3Cit used. In order to determine the values of the standard enthalpy of solution $\Delta H_s^{\ominus}$ from eqn. (22), in addition to the values of β_1, β_2 and β_3 and $\phi_{L,i1}$, $\phi_{L,i2}$, $\phi_{L,i3}$ (which, as mentioned above, can be calculated), the values of $\Delta H_{A1}^{\ominus}$, $\Delta H_{A2}^{\ominus}$ and $\Delta H_{A3}^{\ominus}$ must also be known. The values $\Delta H_{A1} = -\Delta H_{D1} = -3470$ J mol^{-1} and $\Delta H_{A2} = -\Delta H_{D2} = -1880$ J mol^{-1} were taken from ref. 16.

Because of the very low dissociation that takes place according to $HCit^{2-} \rightarrow H^+ + Cit^{3-}$, as mentioned above, it was assumed that $\beta_3 = 0$. Then, eqn. (22) can be written

$$\Delta H_s^{\ominus} = \Delta H_s - \beta_2 \phi_{L,i2} - \beta_1 \phi_{L,i1} - \Delta H_{A3}^{\ominus} - (1 - \beta_2)\Delta H_{A2}^{\ominus} - (1 - \beta_1 - \beta_2)\Delta H_{\alpha 1}^{\ominus} \tag{23}$$

Because the value of $\Delta H_{A3}^{\ominus}$ was not given in ref. 16, eqn. (23) was modified to

$$\Delta H_s^\ominus + \Delta H_{A3}^\ominus = \Delta H_s - \beta_2\phi_{L,i2} - \beta_1\phi_{L,i1} - (1-\beta_2)\Delta H_{A2}^\ominus \\ - (1-\beta_1-\beta_2)\Delta H_{A1}^\ominus \qquad (24)$$

and for each concentration, the sum of $\Delta H_s^\ominus + \Delta H_{A3}^\ominus = \delta$ was calculated; the results are given in Table 2. As can be seen, the values are much the same: the average value of δ is 23105 ± 105 J mol^{-1}. The independence of $\delta = \Delta H_s^\ominus + \Delta H_{A3}^\ominus$ on the concentration of H_3Cit also confirms the validity of the proposed method of including the incomplete dissociation of electrolyte. In order to verify this method further, the values of the enthalpy of dilution of citric acid determined by Dobrogowska et al. [17] were used. Based on these data [17], values of the relative apparent molal enthalpy of H_3Cit for the electrolyte concentrations used in this study, were calculated by the method of interpolation. The results in the form of ϕ_L^A are given in Table 2. Because the values of $\Delta H_{A3}^\ominus$ are unknown, one cannot calculate the values of ϕ_L directly from eqn. (18) and compare them with those of ϕ_L^A.

However, for each citric acid concentration, one can calculate the value of the difference $\theta = \phi_L - (1-\beta_3)\Delta H_{A3}^\ominus$, which assuming that $\beta_3 = 0$, can be described as

$$\theta = \phi_L - \Delta H_{A3}^\ominus = \beta_2\phi_{L,i2} + \beta_1\phi_{L,i1} + (1-\beta_2)\Delta H_{A2}^\ominus + (1+\beta_1-\beta_2)\Delta H_{A1}^\ominus \qquad (25)$$

The values of θ are also given in Table 2.

If eqn. (18) describes correctly the values of ϕ_L^A obtained experimentally, the difference $\phi_L^A - \theta = \Delta H_{A3}^\ominus$ should, of course, be the same for each concentration and equal to the enthalpy value of the process $Cit^{3-} + H^+ \rightarrow HCit^{2-}$, which was not determined in ref. 16. The differences $\phi_L^A - \theta = \Delta H_{A3}^\ominus$ are collected in Table 2. As can be seen, the real values of the $\phi_L^A - \theta$ differences for the particular concentrations differ slightly, and their average is $\Delta H_{A3}^\ominus = 3890 \pm 40$ J mol^{-1}.

Using the values of the equilibrium constants K_{D3} determined by Bates and Pinching [23], the value of ΔH_{A3} was estimated for several temperatures to be about 3300 J mol^{-1}. Considering that the method of determination of the enthalpy from temperature relationships of equilibrium constants is of low accuracy, and that both values of $\Delta H_{A3}^\ominus$, i.e. 3890 and 3300 J mol^{-1}, were obtained by various experimental methods, their conformity can be accepted as satisfactory.

From the determined values of the sum $\Delta H_s^\ominus + \Delta H_{A3}^\ominus$ and from ΔH_{A3} (3890 J mol^{-1}), the standard enthalpy of solution of citric acid in water is 19215 ± 150 J mol^{-1}.

Approximation of the relationship $\Delta H_s = f(m)$ with a fourth-degree multinomial and calculation of the value of the function for $m = 0$ yield an estimated standard enthalpy of solution of H_3Cit of about 19400 J mol^{-1}.

TABLE 2

Values of $\delta = \Delta H_s^\ominus + \Delta H_{A3}^\ominus$, ϕ_L^A, $\theta = \phi_L - \Delta H_{A3}^\ominus$ and $\Delta H_{A3}^\ominus = \phi_L^A - \theta$

No.	$(\Delta H_s + \Delta H_{A3}^\ominus)$/ (J mol^{-1})	ϕ_L^A/ (J mol^{-1})	$(\phi_L - \Delta H_{A3}^\ominus)$/ (J mol^{-1})	$(\phi_L^A - \theta)$/ (J mol^{-1})
1	23214	−371	−4189	3817
2	23274	−372	−4190	3817
3	23219	−374	−4195	3821
4	23273	−376	−4198	3822
5	23166	−413	−4270	3856
6	23172	−415	−4273	3858
7	23275	−484	−4385	3899
8	23192	−499	−4407	3906
9	23269	−507	−4416	3908
10	23154	−518	−4432	3912
11	23228	−526	−4442	3914
12	23124	−575	−4502	3926
13	23163	−576	−4503	3926
14	23233	−585	−4513	3928
15	23147	−598	−4529	3930
16	23216	−623	−4555	3932
17	23127	−630	−4562	3932
18	23175	−691	−4623	3932
19	23022	−712	−4642	3930
20	23046	−761	−4686	3925
21	22986	−765	−4690	3924
22	23101	−767	−4691	3923
23	23113	−791	−4711	3920
24	22937	−817	−4733	3915
25	22943	−835	−4747	3912
26	22995	−842	−4753	3910
27	23093	−881	−4784	3902
28	23003	−905	−4802	3897
29	23101	−923	−4817	3893
30	22937	−933	−4824	3891
31	23107	−957	−4843	3886
32	23012	−959	−4845	3886
33	23082	−973	−4856	3882
34	23000	−991	−4871	3879
35	22970	−1011	−4887	3875
36	22989	−1039	−4910	3870
37	22999	−1072	−4937	3864
38	23078	−1077	−4940	3863
39	23065	−1087	−4949	3861
40	23076	−1116	−4968	3852
41	23058	−1205	−5008	3801

This value is also in a good agreement with that of 19215 ± 150 J mol^{-1} determined by the method proposed here.

It is our opinion that the method developed for including the incomplete dissociation of asymmetric electrolytes in the analysis of the values of enthalpy of solution or dilution yields results that are consistent with the experimental data. Thus, this method may be suitable for the determination of the standard enthalpy of solution. Results of further studies on the use of this method will be reported soon.

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