



Cryoscopic studies in the citric acid - water system.

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Freezing-point depressions of aqueous solutions of citric acid in the concentration range from 0.00066 mol·kg⁻¹ to 4.5 mol·kg⁻¹ were determined. Osmotic coefficients, activity coefficients and the relative partial molar enthalpies of solution at freezing temperatures were derived from these results.

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1. INTRODUCTION

Citric acid which plays an important role in biochemical reactions (e.g. in the Krebs tricarboxylic acid cycle) is produced on industrial scale serving as an additive to food products and carbonated beverages [1]. As one of most versatile and widely used organic acids its thermodynamic and transport properties were systematically investigated, especially during the last two decades. The survey of available in the literature data associated with aqueous solutions of citric acid was recently prepared by Apelblat [2]. This compilation includes results of thermochemical, volumetric, colligative, solubility, dissociation constants, electrical conductance, viscosity and diffusion constant determinations. The colligative properties which depend mainly on the number and not the nature of molecules present in solution (freezing-point depressions, boiling-point elevations and vapour pressure lowerings) are rather limited in the case of citric acid. Only few freezing temperatures are reported in the International Critical Tables (1926) [3].

In this investigation, systematic cryoscopic measurements in the citric acid - water system were performed and osmotic and activity coefficients at freezing-point temperatures were evaluated by the integration of the Gibbs - Duhem equation.

2. EXPERIMENTAL

Citric acid, $\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2$, (99.5 - 100.5 mass per cent) was supplied by Riedel-de Haen and used in experiments without further purification.

Cryoscopic measurements [4-11] were performed in a jacketed vessel cooled or heated by running alcohol from a Julabo refrigerating bath. Precisely weighed amounts of citric acid and double distilled water were introduced into the vessel. Homogeneity of temperature of the solution+ice mixture was ensured by mixing with a mechanical stirrer (85 - 120 rpm). Temperature as a function of time was measured with a Hart Scientific Model 1502 thermometer equipped with a printer. The thermometer of sensitivity ± 0.001 K was calibrated with a double distilled water and the error in the *freezing-point depression* of solution of molality m , $\theta(m) = T_f(\text{H}_2\text{O}) - T_f(m)$, is estimated to be ± 0.002 K. The freezing temperatures $T_f(m)$ were determined from the temperature vs time curves using the Moulin method [8]. In this method $T_f(m)$ are derived from an interception of the hyperbola and straight lines which were determined from cooling curves using a computer program prepared by us.

3. RESULTS AND DISCUSSION

Determined freezing-point lowerings of citric acid solutions are presented in Table 1 and compared with the literature values [3] in Figure 1. As can be observed, there is a very satisfactory agreement between these two sets of results. The freezing-point depressions can be correlated by

$$\theta(m) = 2.504m - 4.224m^2, \quad m \leq 0.1 \text{ mol} \cdot \text{kg}^{-1} \quad (1)$$

$$\theta(m) = 0.01827 + 1.88994m + 0.09178m^2, \quad m \geq 0.1 \text{ mol} \cdot \text{kg}^{-1}$$

Using these values it is possible to evaluate the *activities of water* a_1 [12]

$$-\ln a_1 = 9.687 \cdot 10^{-3}\theta + 4.8 \cdot 10^{-6}\theta^2 \quad (2)$$

An alternative method is to calculate a_1 from the ratio of vapour pressures of ice and supercooled water

$$a_1 = p_{\text{ice}}(T_f) / p_{\text{water}}(T_f) \quad (4)$$

where $p_{\text{ice}}(T_f)$ can be taken from the tabulation in Handbook of Chemistry and Physics [13] and $p_{\text{water}}(T_f)$ calculated from the Saul and Wagner equation [14] (see also [15]). Both methods gave practically the same results.

The activity of water a_1 leads to the *osmotic coefficient* ϕ . Levien [16] who determined various properties of aqueous citric acid solutions called ϕ the *apparent osmotic coefficient* in order to distinguish it from the osmotic coefficient of molecular citric acid and the osmotic coefficient associated with formation of hydrogen and citrate ions. Considering that at infinite dilution [12,17-18]

$$\lim_{m \rightarrow 0} \left(\frac{\theta}{\lambda m} \right) = \nu \quad (5)$$

where $\lambda = 1.86 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{K}$ is the *cryoscopic constant of water* and v is the total number of ions formed from an electrolyte entity. At finite concentrations, values of $\theta/\lambda m$ represent the apparent number of ions and undissociated molecules in the solution. As can be seen in Figure 2, at low molalities of citric acid the effect of dissociation is evident (a large scattering of $\theta/\lambda m$ values is due to inadequate precision of θ in this region, Table 1). For more concentrated solutions, as can be expected from small values of dissociation constants of the acid [19-20], citric acid behaves as nearly undissociated molecule.

Table 1
Experimental freezing-point depressions θ of citric acid solutions.

m/mol·kg ⁻¹	θ/K	m/mol·kg ⁻¹	θ/K	m/mol·kg ⁻¹	θ/K
0.00066	0.0077	0.5994	1.204	2.000	4.10
0.00256	0.0163	0.7399	1.499	2.170	4.60
0.00356	0.0164	0.7947	1.635	2.519	5.00
0.00514	0.0180	0.9002	1.831	2.520	5.00
0.00522	0.0143	0.9994	1.997	3.03	6.74
0.01057	0.0250	1.0000	2.052	3.20	7.21
0.01998	0.0617	1.0948	2.285	3.43	7.74
0.03033	0.0692	1.3010	2.734	3.71	8.16
0.04050	0.0943	1.4001	2.912	3.96	8.64
0.05000	0.121	1.5006	3.37	4.20	9.44
0.1006	0.216	1.600	3.38	4.50	10.75
0.2920	0.581	1.697	3.54		
0.3996	0.807	1.800	3.99		

Since in the investigated range of concentrations the degree of dissociation associated with the secondary step of dissociation α_2 is very small (e.g. for the lowest concentration, $m = 0.00066 \text{ mol}\cdot\text{kg}^{-1}$, α_2 is only about 0.02), citric acid can essentially be treated as the monobasic, weak acid.

$$K_1 = \frac{m\alpha^2\gamma_{H^+}\gamma_{H_2Cit^-}}{(1-\alpha)\gamma_{H_3Cit}} \quad (6)$$

where $\alpha = \alpha_1$ is the degree of dissociation related to the primary dissociation step of the acid. The activity coefficients of individual ions are available from the Debye-Hückel expression

$$\ln \gamma_j = -\frac{A\sqrt{m\alpha}}{1+a_jB\sqrt{m\alpha}}, \quad j = H^+, H_2Cit^- \quad (7)$$

where $a(\text{H}^+) = 9 \text{ \AA}$ and $a(\text{H}_2\text{Cit}^-) = 3.5 \text{ \AA}$ [21] ; $A = 1.1324 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2}$ and $B = 3.248 \cdot 10^7 \text{ mol}^{-1/2} \cdot \text{dm}^{3/2} \cdot \text{cm}^{-1}$ [12] (distinction between molarity and molality is neglected here).

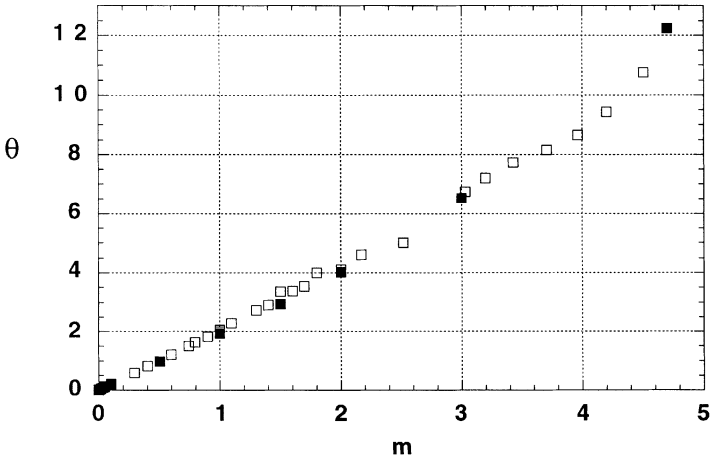


Figure 1. Experimental freezing point lowerings of aqueous solutions of citric acid, θ in K, as a function of concentration m in $\text{mol} \cdot \text{kg}^{-1}$. ■ - [3] ; □ - this work.

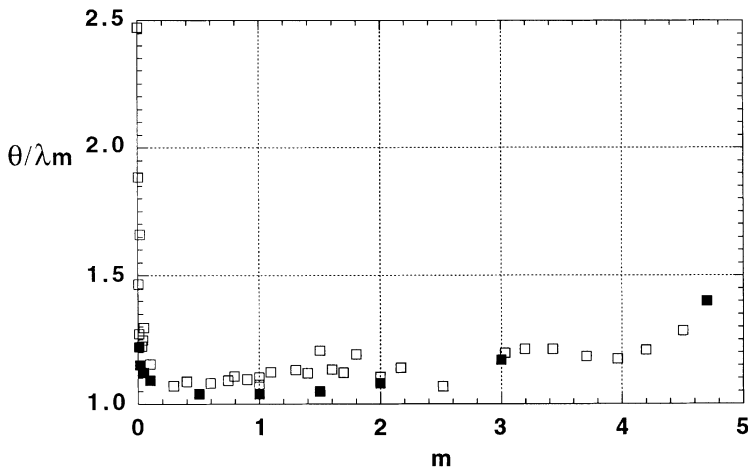


Figure 2. The apparent number of particles in solution, $\theta/\lambda m$, as a function of concentration of citric acid m in $\text{mol} \cdot \text{kg}^{-1}$. ■ - [3] ; □ - this work.

The activity coefficient of undissociated citric acid γ_{H_3Cit} is assumed to be unity in the mass-action equation (6).

The osmotic coefficient of citric acid ϕ is directly related to the activity of water

$$\phi = -55.508 \frac{\ln a_1}{\sum_i \nu_i m_i} \quad (8)$$

where the sum in (8) expresses the total number of particles in the solution, ν_i are stoichiometric coefficients and m_i are the molalities of corresponding species

$$\sum_i \nu_i m_i = \nu_{H^+} m_{H^+} + \nu_{H_2Cit^-} m_{H_2Cit^-} + \nu_{H_3Cit} m_{H_3Cit} \quad (9)$$

In the case under consideration: $\nu_{H^+} = \nu_{H_2Cit^-} = \nu_{H_3Cit} = 1$, $m_{H^+} = m_{H_2Cit^-} = m\alpha$ and $m_{H_3Cit} = m(1-\alpha)$ and therefore ϕ takes the form

$$\phi = -55.508 \frac{\ln a_1}{m(1+\alpha)} \quad (10)$$

Thus, the osmotic coefficient depends not only on the activity of water a_1 but also on α and the coefficient $1+\alpha = i$, is known as the *van't Hoff factor*. Degrees of dissociation as a function of concentration can be calculated from equations (6) and (7) if the equilibrium constants K_1 at freezing temperatures are known. The equilibrium constants for the primary step of dissociation of citric acid in a wide temperature range are available from electromotive force measurements of Bates and Pinching [12,19] and from electrical conductance determinations of Apelblat and Barthel [20]. However, they cover temperatures higher than 278.15 K [20]

$$\ln K_1 = -16.862 + \frac{6138.1}{T} - \frac{9.7725 \cdot 10^5}{T^2} \quad (11)$$

An extrapolation of (11) to $T = 273.15$ K gives $K_1 = 5.6 \cdot 10^{-4}$ which is close to $K_1 = 6.0 \cdot 10^{-4}$ the value based on Bates and Pinching results. Osmotic coefficients at round concentrations evaluated from (6), (7) and (10) are presented in Table 2 (the iterative procedure for solving (6) and (7) is described in [20]).

In determination of osmotic coefficients of citric acid from isopiestic measurements at $T = 298.15$ K Levien [16] applied a quite different approach. The apparent osmotic coefficients ϕ_{app} were evaluated by disregarding the dissociation process, the sum in (8) was replaced with m , i.e. citric acid was treated as nonelectrolyte and

$$\phi_{app} = \alpha[\phi_{H^+} + \phi_{H_2Cit^-}] + (1-\alpha)\phi_{H_3Cit}, \quad \phi_{H^+} = \phi_{H_2Cit^-} \quad (12)$$

The osmotic coefficients of the ions were assumed to be similar to those of any other 1:1 salt of the same ionic concentration (e.g. NaCl). Thus, the main assumption in this procedure is that the logarithms of the water activities due to the undissociated molecule and to the ions are additive. However, such assumption is inconsistent with the definition of osmotic coefficients as given in (8). Evidently, with increasing concentration, when α is less and less important, both approaches become practically identical and $\phi_{app} \approx \phi$. This fact permitted to apply the Levien procedure to the vapour-pressure lowerings of citric acid because experimental results

started with rather concentrated solutions, $m > 0.5 \text{ mol}\cdot\text{kg}^{-1}$ [22]. It is worthwhile to note that comparison between osmotic coefficients determined from the cryoscopic, isopiestic and isoteniscopic measurements (Figure 3) shows a similar functional form of $\phi = f(m)$ at $T = 298.15 \text{ K}$ and at freezing temperatures T_f . Curves are shifted, but unusually, at low molalities ϕ increases as m decreases when the expected behaviour is $\phi \rightarrow 1$ as $m \rightarrow 0$.

Table 2

Calculated freezing-point depressions θ , osmotic coefficients ϕ and activity coefficients γ of citric acid at freezing-point temperatures.

$m/\text{mol}\cdot\text{kg}^{-1}$	θ/K	ϕ	γ	$m/\text{mol}\cdot\text{kg}^{-1}$	θ/K	ϕ	γ
0.01	0.025	1.086	1.037	1.20	2.418	1.059	1.333
0.02	0.048	1.119	1.112	1.40	2.844	1.069	1.360
0.03	0.071	1.126	1.179	1.60	3.28	1.080	1.388
0.04	0.093	1.122	1.218	1.80	3.72	1.090	1.417
0.05	0.115	1.113	1.239	2.00	4.17	1.101	1.446
0.06	0.135	1.102	1.247	2.20	4.63	1.111	1.476
0.07	0.159	1.088	1.248	2.40	5.08	1.121	1.506
0.08	0.173	1.072	1.254	2.60	5.55	1.131	1.537
0.09	0.190	1.056	1.237	2.80	6.03	1.142	1.570
0.10	0.208	1.038	1.219	3.00	6.51	1.153	1.603
0.20	0.400	1.018	1.216	3.20	7.01	1.164	1.637
0.30	0.593	1.016	1.223	3.40	7.51	1.174	1.670
0.40	0.789	1.019	1.232	3.60	8.01	1.184	1.705
0.50	0.986	1.023	1.244	3.80	8.53	1.194	1.740
0.60	1.185	1.028	1.256	4.00	9.05	1.205	1.776
0.70	1.386	1.033	1.268	4.20	9.58	1.215	1.813
0.80	1.589	1.038	1.280	4.40	10.11	1.225	1.851
0.90	1.793	1.043	1.293	4.50	10.38	1.231	1.870
1.00	2.000	1.048	1.306	4.70	10.93	1.241	1.909

The activity coefficient of citric acid γ , can be evaluated from the Gibbs-Duhem equation in the form [12]

$$-\ln \gamma = j + \int_0^m j d \ln m - 0.00054 \lambda \int_0^\theta (1-j) d\theta$$

$$j = 1 - \frac{\theta}{\lambda m(1 + \alpha)}$$
(13)

In Figure 4 are plotted j values and those uncorrected for the dissociation effect, i.e. with $\alpha = 0$. As can be seen, both sets of the j values differ considerably for low concentrations of citric acid, but as expected the difference rapidly diminishes for more concentrated solutions.

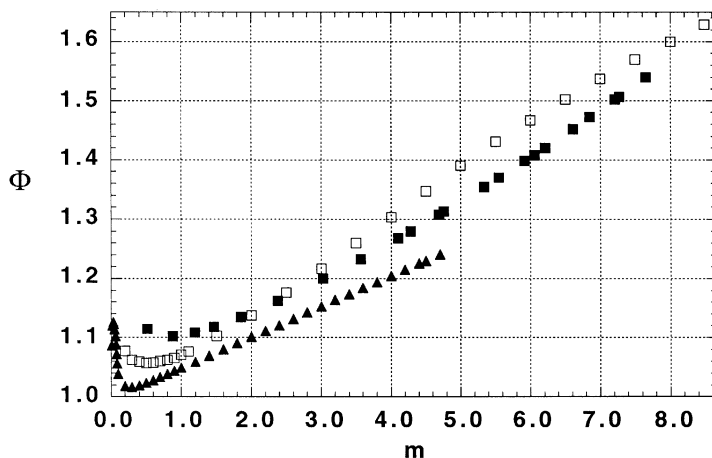


Figure 3. The osmotic coefficient ϕ as a function of concentration of citric acid m in $\text{mol}\cdot\text{kg}^{-1}$, At 298.15 K, \square - [16]; \blacksquare - [22]; \blacktriangle - at freezing-point temperatures, this work.

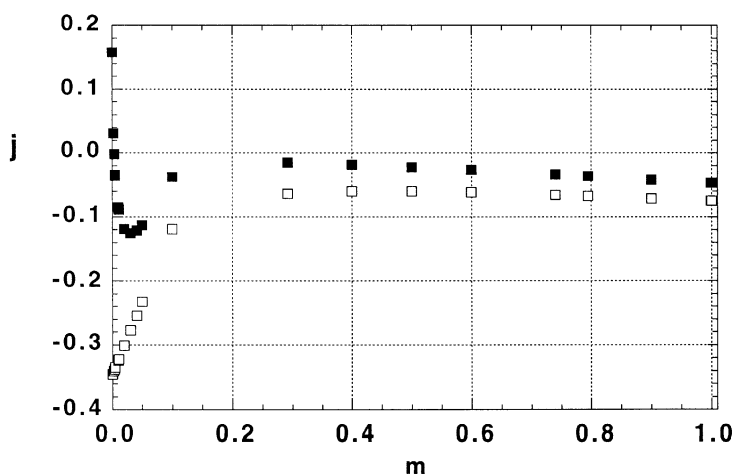


Figure 4. Functions: $j = 1 - \theta/\lambda m(1 + \alpha)$, \blacksquare ; and $j = 1 - \theta/\lambda m$, \square ; correlated with m (see text).

Since at infinite dilution, $m \rightarrow 0$, the limit of j is uncertain (Figure 4), it was decided to use the Gibbs-Duhem equation in the Bjerrum form

$$\ln\left(\frac{\gamma}{\gamma^*}\right) = \phi - \phi^* + \int_{m^*}^m (\phi - 1) d \ln m \tag{14}$$

where the numerical integration was performed from the arbitrary value of $m^* = 0.01 \text{ mol}\cdot\text{kg}^{-1}$ with $\phi^* = 1.086$. In table 2, are presented at round concentrations calculated values of the freezing-point depressions θ , the osmotic coefficients ϕ and the activity coefficients γ at freezing temperatures (γ^* is assumed to be close to unity).

The relative partial molar enthalpy of solution $\bar{L}_2 = (\bar{H}_2 - \bar{H}_2^\infty)$ is defined by [18,23]

$$\left(\frac{\partial \ln a_2}{\partial T}\right)_{P,m} = -\frac{(\bar{H}_2 - \bar{H}_2^\infty)}{RT^2} = -\frac{\bar{L}_2}{RT^2} \tag{15}$$

Since activity coefficients of citric acid at $T_r = 298.15 \text{ K}$ are known [22], it is possible to estimate $\bar{L}_2(T_f, m)$ from

$$\bar{L}_2(T_f, m) \approx RT_f^2 \frac{\ln[\gamma(T_f)/\gamma(T_r)]}{T_r - T_f} \tag{16}$$

Calculated from (16) values of $\bar{L}_2(T_f, m \geq 0.2 \text{ mol}\cdot\text{kg}^{-1})$ are plotted in Figure 5 as a function of m and they can be correlated by

$$\bar{L}_2(T_f, m) = 4422.8 - 1219.6m + 57.157m^2 - 57.483m^3 \tag{17}$$

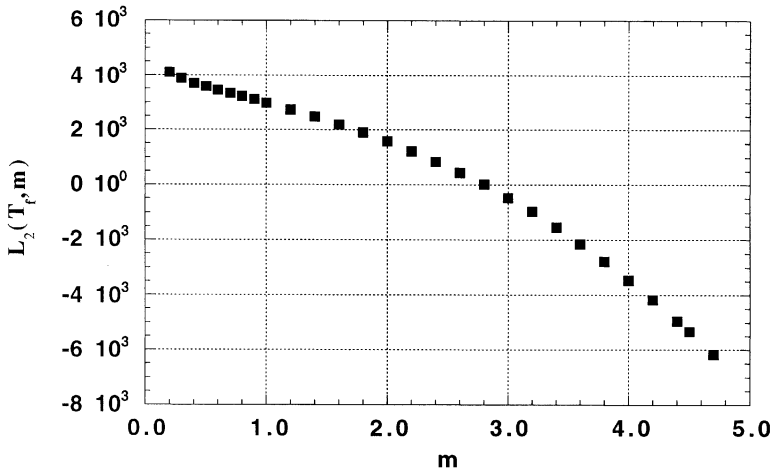


Figure 4. The relative partial molar enthalpy of solution $\bar{L}_2(T_f, m)$ in $\text{J}\cdot\text{mol}^{-1}$ as a function of concentration of citric acid m in $\text{mol}\cdot\text{kg}^{-1}$,

As can be seen, $\bar{L}_2(T_f, m)$ is positive for $m \leq 2.9 \text{ mol}\cdot\text{kg}^{-1}$, which means that heat is taken up on mixing of components, but for more concentrated solutions of citric acid $\bar{L}_2(T_f, m)$ is negative and heat is evolved on the mixing.

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