Conductance Studies on Aqueous Citric Acid

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Dedicated to Dr. K. Heinzinger on the occasion of his 60th birthday

Conductance measurements of citric acid and neutral citrates (tri-lithium citrate, tri-sodium citrate and tri-potassium citrate) were performed in water at 278.15 to 308.15 K. The equilibrium constants for the primary and secondary steps of dissociation, K_1 and K_2, and the limiting conductances, $\lambda^0(H_2Cit^-)$, $\lambda^0(1/2\ HCit^{2-})$, and $\lambda^0(1/3\ Cit^{3-})$ are reported as a function of temperature. They are obtained by application of the Quint and Viallard conductance equation. The enthalpies of dissociation are estimated.

1. Introduction

The determination of dissociation constants from conductance measurements is a well established procedure for monobasic acids [1–6]. The overlapping of successive steps of dissociation and an unsatisfactory state of the theory of unsymmetrical electrolytes makes the interpretation of results in the case of polybasic acids rather difficult [5, 7–10]. Therefore only few dibasic acids were investigated [11–13], and even then the contribution from the second dissociation step is usually considered to be a small correction to the measured conductance. Among the tribasic acids, phosphoric acid was treated as a dibasic acid [14–16] and citric acid as a monobasic acid [17]. There is also a number of conductance and other investigations which are indirectly related to the present study [18–22].

In this investigation the choice of citric acid with its three COOH-groups is not incidental. The acid plays an important role in biological and industrial processes; an accurate knowledge of its thermodynamic and transport properties is of considerable interest. Aqueous solutions of citric acid can be considered as model systems for weak, unsymmetrical 1:3 electrolytes which are characterized by overlapping dissociation equilibria. The actual knowledge about the

dissociation constants comes mainly from potentiometric methods [23–27]. The electric conductance of citric acid was measured by Levien [17] in not especially dilute solutions. The intermediate limiting conductances of the three citrate anions were not determined in Levien's paper and the acid was treated as a weak, monobasic acid. In the present investigation, the electric conductanes of dilute solutions of citric acid and its neutral lithium, sodium and potassium salts were measured and a consistent set, based on the Quint and Viallard theory [28, 29] of the dissociation constants and limiting conductances of the organic anions was determined.

2. Experimental

The Fluka puriss. p.a. reagents anhydrous citric acid ($>99.5\%$), tri-potassium citrate dihydrate ($>99\%$), $K_3C_6H_5O_7 \cdot 2\,H_2O$, tri-sodium citrate dihydrate ($>99\%$), $Na_3C_6H_5O_7 \cdot 2\,H_2O$, and tri-lithium citrate tetrahydrate ($>99\%$), $Li_3C_6H_5O_7 \cdot 4\,H_2O$ were used without further purification.

The solutions were prepared by weight. The conversion from molalities to molarities was performed with the help the density of pure water at given temperature for the dilute solutions ($c < 7 \cdot 10^{-3}$ mol dm^{-3} for citric acid and $c < 2 \cdot 10^{-3}$ mol dm^{-3} for citrates).

Water with a specific conductance of less than $2 \cdot 10^{-7}$ S cm^{-1} was used for the solvent corrections of the specific conductances. The resistances were
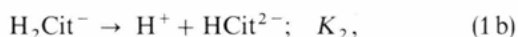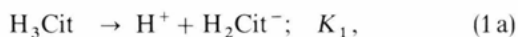
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determined at various frequencies f below 10kHz in a conductance cell with a cell constant of about $4.7\,\text{cm}^{-1}$ and extrapolated to $f^{-1} \to 0$, as usual. A detailed description of the measuring system and applied procedures is given elsewhere [30, 31].

3. Data Analysis

The properties of dilute aqueous solutions of citric acid are usually interpreted in terms of the successive dissociation steps

$$H_3Cit \;\to\; H^+ + H_2Cit^-; \quad K_1, \tag{1a}$$

$$H_2Cit^- \;\to\; H^+ + HCit^{2-}; \quad K_2, \tag{1b}$$

$$HCit^{2-} \;\to\; H^+ + Cit^{3-}; \quad K_3. \tag{1c}$$

The equilibrium constants of these reactions are

$$K_1 = \frac{[H^+][H_2Cit^-]\,f_1}{[H_3Cit]}, \tag{2a}$$

$$K_2 = \frac{[H^+][HCit^{2-}]\,f_2}{[H_2Cit^-]}, \tag{2b}$$

$$K_3 = \frac{[H^+][Cit^{3-}]\,f_3}{[HCit^{2-}]}, \tag{2c}$$

where the f_i denote the corresponding quotients of the activity coefficients

$$f_1 = \frac{f_{H^+}\, f_{H_2Cit^-}}{f_{H_3Cit}}, \tag{3a}$$

$$f_2 = \frac{f_{H^+}\, f_{HCit^{2-}}}{f_{H_2Cit^-}}, \tag{3b}$$

$$f_3 = \frac{f_{H^+}\, f_{Cit^{3-}}}{f_{HCit^{2-}}}. \tag{3c}$$

In terms of the total degree of dissociation α and the degrees associated with the primary, secondary and tertiary steps of dissociation, α_1 to α_3, the concentrations of the species present in the solution are

$$[H^+] \quad = c(\alpha_1 + 2\alpha_2 + 3\alpha_3), \tag{4a}$$

$$[H_3Cit] \;= c(1-\alpha), \tag{4b}$$

$$[H_2Cit^-] = c\,\alpha_1, \tag{4c}$$

$$[HCit^{2-}] = c\,\alpha_2, \tag{4d}$$

$$[Cit^{3-}] \;= c\,\alpha_3, \tag{4e}$$

where c is the total (analytical) concentration of citric acid and α is given by the relation

$$\alpha = \alpha_1 + \alpha_2 + \alpha_3. \tag{5}$$

Use of (2) and (4) yields

$$K_1 = \frac{c(\alpha_1 + 2\alpha_2 + 3\alpha_3)\,\alpha_1}{1-\alpha}\, f_1, \tag{6a}$$

$$K_2 = \frac{c(\alpha_1 + 2\alpha_2 + 3\alpha_3)\,\alpha_2}{\alpha_1}\, f_2, \tag{6b}$$

$$K_3 = \frac{c(\alpha_1 + 2\alpha_2 + 3\alpha_3)\,\alpha_3}{\alpha_2}\, f_3. \tag{6c}$$

From (6) it follows at concentration c, for given values of the equilibrium constants and activity coefficients, that the degrees of dissociation can be evaluated by iterative solution of the set of quadratic equations

$$\alpha_1 = \frac{1}{2}\left[-\left(\frac{K_1}{c f_1} + 2\alpha_2 + 3\alpha_3\right)\right.$$
$$\left. + \sqrt{\left(\frac{K_1}{c f_1} + 2\alpha_2 + 3\alpha_3\right)^2 + \frac{4 K_1}{c f_1}(1 - \alpha_2 - \alpha_3)}\,\right],$$

$$\alpha_2 = \frac{1}{4}\left[-(\alpha_1 + 3\alpha_3) + \sqrt{(\alpha_1 + 3\alpha_3)^2 + \frac{8 K_2 \alpha_1}{c f_2}}\,\right], \tag{7}$$

$$\alpha_3 = \frac{1}{6}\left[-(\alpha_1 + 2\alpha_2) + \sqrt{(\alpha_1 + 2\alpha_2)^2 + \frac{12 K_3 \alpha_2}{c f_3}}\,\right].$$

At the investigated low concentrations, the activity coefficients f_j of the different ions can be approximated by the Debye-Hückel expression ($j = H^+$, H_2Cit^-, $HCit^{2-}$, Cit^{3-})

$$\log f_j = -\frac{A z_j^2 \sqrt{I}}{1 + a_j B \sqrt{I}}, \tag{8}$$

where a_j is the average cation-anion distance of closest approach and $I = c(\alpha_1 + 3\alpha_2 + 6\alpha_3)$ is the ionic strength. At 298.15 K, the constants are [38]

$$A = 0.5115\ \text{mol}^{-1/2}\ \text{dm}^{3/2} \quad \text{and}$$

$$B = 0.3291 \cdot 10^8\ \text{mol}^{-1/2}\ \text{dm}^{3/2}\ \text{cm}^{-1}.$$

The activity coefficient of undissociated citric acid is assumed to be unity.

Molar conductances Λ are the sum of the ionic contributions:

$$\Lambda = \frac{1000\,L}{c} = \sum_{j=1}^{n} \frac{|z_j|\, c_j\, \lambda_j}{c}, \tag{9}$$

Table 1. Experimental conductances of citric acid neutral citrates at 298.15 K.

$c \cdot 10^4$	$\Lambda(H_3Cit)$	$c \cdot 10^4$	$\Lambda_e(Li_3Cit)$	$c \cdot 10^4$	$\Lambda_e(Na_3Cit)$	$c \cdot 10^4$	$\Lambda_e(K_3Cit)$
1.1647	378.52	1.1301	107.06	0.8830	118.78	1.9155	138.36
3.1430	306.38	1.2862	106.42	2.1306	115.83	5.4834	134.36
5.6324	263.30	2.8846	103.84	5.4680	112.06	9.8752	130.81
8.7398	231.79	3.7838	102.84	9.8390	108.40	17.0490	126.59
16.854	186.94	5.2612	100.97	16.0800	104.74		
30.752	150.11	7.1689	99.16				
67.864	109.53	9.5163	97.23				

Table 2. Experimental molar conductances of citric acid in the investigated temperature range.

$m \cdot 10^4$ mol kg^{-1}	T/K						
	278.15	283.15	288.15	293.15	298.15	303.15	308.15
				$\Lambda(H_3Cit)$			
1.168	259.09	289.18	320.84	349.04	378.52	407.51	435.88
3.152	208.09	232.80	257.56	282.09	306.38	330.15	353.04
5.649	176.81	199.16	220.56	242.13	263.30	284.05	304.34
8.766	155.57	174.72	193.90	212.94	231.79	250.25	268.32
19.90	124.57	140.20	155.91	171.49	186.94	202.08	216.87
30.84	99.49	112.15	124.89	137.55	150.11	162.40	174.44
68.06	72.17	81.50	90.91	100.25	109.53	118.61	127.51

where L is the measured specific conductance and λ_j, c_j and z_j are the individual conductances, concentrations and valencies of the ions. In the case under consideration we have

$$\Lambda = \alpha_1 [\lambda(H^+) + \lambda(H_2Cit^-)]$$
$$+ 2\alpha_2 [\lambda(H^+) + \lambda(\tfrac{1}{2} HCit^{2-})]$$
$$+ 3\alpha_3 [\lambda(H^+) + \lambda(\tfrac{1}{3} Cit^{3-})] . \quad (10)$$

The equation for λ_j, exact up to the linear term in the ionic strength I, has the form

$$\lambda_j = \lambda_j^0 - S_j \sqrt{I} + E_j I \ln I + J_{1j} I . \quad (11)$$

For unsymmetrical electrolytes the coefficients S_j, E_j and J_{1j} are available from the Quint-Viallard theory [28, 29]. Evidently, with $E_j = 0$ and $J_{1j} = 0$, (11) reduces to the Onsager limiting equation [3]. At given temperature the coefficients S_j, E_j and J_{1j} depend on the limiting conductances λ_j^0 of the corresponding ions and on the solvent properties (viscosity and dielectric constant); the linear term in (11) depends also on the distance of closest approach a_j. The complete expression for the coefficients are presented in the Appendix. An alternative treatment, based on the Lee-Wheaton theory [32, 33], is not considered in this paper.

The experimental (Λ, c)-data, when expressed in terms of the three step dissociation model, require an adjustment or preselection of nine parameters. These are the equilibrium constants K_1, K_2 and K_3, the limiting conductances of the anions, $\lambda^0(H_2Cit^-)$, $\lambda^0(1/2\, HCit^{2-})$ and $\lambda^0(1/3\, Cit^{3-})$ and the distances of closest approach a_1, a_2, and a_3. The values of a_j are equal for activity coefficient and conductance equations (8) and (11).

4. Results and Discussion

The molecular conductance of citric acid and the equivalent conductances of the neutral citrates of lithium, sodium and potassium are presented in Tables 1 to 3 and in Figs. 1 and 2. The conductances are plotted as functions of the square root of the ionic strength, which for 1:3 electrolytes is $I = 6c$. As can be seen, the citrates behave like strong, completely dissociated electrolytes and citric acid as a partially dissociated, weak electrolyte. Levien's results [17], included in Fig. 2, cover the more concentrated solutions of citric acid $(c > 0.018$ mol dm$^{-3})$; both data sets yield a common curve.

A reliable approximation for the intermediate conductances $\lambda^0(H_2Cit^-)$ and $\lambda^0(1/2\, HCit^{2-})$ is difficult to obtain from the limiting conductances of the anions, $\lambda^0(H_2Cit^-)$, $\lambda^0(1/2\, HCit^{2-})$, and $\lambda^0(1/3\, Cit^{3-})$.

$m \cdot 10^4$ mol kg^{-1}	T/K						
	278.15	283.15	288.15	293.15	298.15	303.15	308.15
			Λ_e(Li$_3$Cit)				
1.1334	63.09	73.29	83.96	95.27	107.06	119.58	132.46
1.2900	62.59	72.64	83.38	94.65	106.42	118.70	131.49
2.8931	61.22	71.03	81.40	92.34	103.84	115.81	128.26
3.7949	60.61	70.33	80.64	91.48	102.84	114.69	126.97
5.2767	59.60	69.12	79.22	89.82	100.97	112.55	124.56
7.1900	58.56	67.90	77.85	88.25	99.16	110.50	122.27
9.5443	57.48	66.64	76.33	86.55	97.23	108.32	119.81
			Λ_e(Na$_3$Cit)				
0.8857	70.63	81.69	93.43	105.83	118.78	132.25	146.31
2.1369	68.90	79.72	91.09	103.19	115.83	129.03	142.74
5.4841	66.67	77.14	88.15	99.86	112.06	124.75	138.04
9.8680	64.58	74.72	85.35	96.67	108.40	120.68	133.41
16.1087	62.40	72.16	82.44	93.36	104.74	116.52	128.75
			Λ_e(K$_3$Cit)				
1.9189	84.74	97.27	110.36	124.06	138.36	153.12	168.40
5.4882	82.34	94.48	107.22	120.50	134.36	148.65	163.40
9.8838	80.31	92.07	104.47	117.38	130.81	144.67	158.99
17.0642	77.78	89.20	101.18	113.64	126.59	139.95	153.71

Table 3. Experimental equivalent conductances of tri-lithium citrate, tri-sodium citrate and tri-potassium citrate in the investigated temperature range.
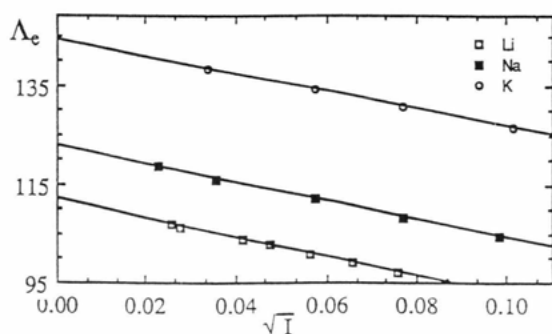

Fig. 1. Equivalent conductances of neutral citrates of lithium, sodium and potassium at 298.15 K as functions of the square root of ionic strength I.
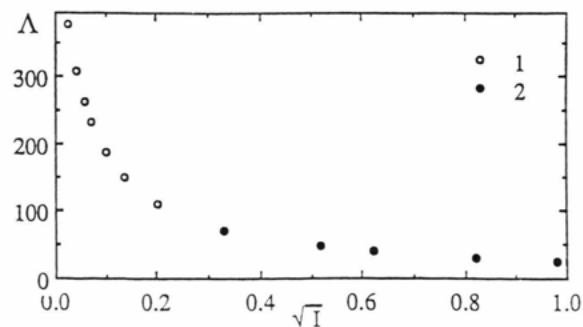

Fig. 2. Molar conductance of citric acid as a function of the square root of the ionic strength I. 1: this work; 2: taken from Levien [17].

The equivalent conductance of completely dissociated electrolytes of the type 1 : 3 in the Onsager approximation [3] is given by

$$\Lambda_e = \Lambda^0 - S \sqrt{I},$$
$$\Lambda^0 = \lambda^0(\text{Me}^+) + \lambda^0(\tfrac{1}{3}\text{Cit}^{3-}), \qquad (12)$$
$$S = \alpha \Lambda^0 + \beta,$$

where Me$^+$ denotes Li$^+$, Na$^+$, and K$^+$, and

$$\alpha = \frac{4.8047 \cdot 10^6}{(DT)^{3/2}} \frac{q}{1+\sqrt{q}},$$

$$\beta = \frac{164.954}{\eta(DT)^{1/2}}, \qquad (13)$$

$$q = \frac{3}{4} \frac{[\lambda^0(\text{Me}^+) + \lambda^0(\tfrac{1}{3}\text{Cit}^{3-})]}{[3\lambda^0(\text{Me}^+) + \lambda^0(\tfrac{1}{3}\text{Cit}^{3-})]}.$$

Since the measured equivalent conductances Λ_e can be approximated by a straight line (Fig. 1), and the observed Onsager slopes are similar ($S/S_{obs} = 0.982$ for Li$_3$Cit; $S/S_{obs} = 1.077$ for Na$_3$Cit and $S/S_{obs} = 1.129$ for K$_3$Cit at 298.15 K), the values of Λ^0(Me$_3$Cit) were determined by the least squares method as intercept of the straight lines. The Onsager slopes were calculated using at 298.15 K the following data [3]: $D = 78.54$, $\eta = 0.008949$ P, $\lambda^0(\text{Li}^+) = 38.64$, $\lambda^0(\text{Na}^+) = 50.15$, and $\lambda^0(\text{K}^+) = 73.50$. The units of the equivalent and molar

Table 4. Limiting conductances of Cit^{3-} ion and of citric acid as functions of temperature.

T/K	$\lambda^0(1/3\ Cit^{3-})$			$\lambda^0(1/3\ Cit^{3-})$	$\Lambda^0(H_3Cit)$
	Li_3Cit	Na_3Cit	K_3Cit		
278.15	42.90	42.33	41.54	42.59 ± 0.55*	293
283.15	49.91	49.19	48.32	49.14 ± 0.80	325
288.15	57.36	56.44	55.41	56.40 ± 0.98	357
293.15	65.14	64.05	62.92	64.04 ± 1.11	390
298.15	73.24	72.07	70.85	72.05 ± 1.20	422
303.15	81.70	80.51	79.07	80.43 ± 1.32	454
308.15	90.51	89.29	87.68	89.16 ± 1.42	486

* Calculated as $\left[\sum_i (\lambda^0_{av.} - \lambda^0_i)^2/(3-1) \right]^{1/2}$, $i = Li_3Cit$, Na_3Cit, and K_3Cit.

conductance are $S\ cm^2\ equiv^{-1}$ and $S\ cm^2\ mol^{-1}$ and are not written.

From the Kohlrausch law, the following limiting conductances of the trivalent citrate anion Cit^{3-} were determined: $\lambda^0(1/3\ Cit^{3-}) = 73.24$, $\lambda^0(1/3\ Cit^{3-}) = 72.07$, and $\lambda^0(1/3\ Cit^{3-}) = 70.85$, based on tri-lithium citrate, tri-sodium citrate and tri-potassium citrate conductance data, respectively. The average value at 298.15 K is $\lambda^0(1/3\ Cit^{3-}) = 72.05 \pm 1.20$; using $\lambda^0(H^+) = 349.85$, the limiting molar conductance of citric acid is $\Lambda^0(H_3Cit) = 422 \pm 1.2$. Our limiting conductance of the trivalent citrate anion is in agreement with the value of $\lambda^0(1/3\ Cit^{3-}) = 71.5$ quoted by Milazzo [34]; unfortunately, it is not clear how his result was obtained. For other investigated temperatures, the values of $\lambda^0(1/3\ Cit^{3-})$ and $\Lambda^0(H_3Cit)$ are presented in Table 4. The Walden product, $\lambda^0(1/3\ Cit^{3-})\,\eta(T) = 64.14 \pm 1.08$, is almost independent of temperature (65.18 ± 0.08 for tri-lithium citrate; 64.20 ± 0.03 for tri-sodium citrate and 63.06 ± 0.04 for tri-potassium citrate); $\lambda^0(Li^+)$, $\lambda^0(Na^+)$, and $\lambda^0(K^+)$ were taken from [3]; the temperature dependence of the limiting conductance of the anion is $\lambda^0(1/3\ Cit^{3-}) = 11.3593 - 2113.32/T$.

With increasing citric acid concentration the contributions to Λ from the secondary and tertiary step of dissociation become less important and the problem reduces to the case of a weak, monobasic acid. In the MacInnes and Shedlovsky treatment [1], the degree of dissociation of the primary step is given by

$$\alpha_1 = \Lambda/\Lambda^*, \qquad (14)$$

where Λ^* is the conductance of the completely dissociation acid (to the primary dissociation step only) at

equal concentration c to that for the measured conductance Λ. Values of Λ^* can be calculated from

$$\Lambda^* = \Lambda(HCl) - \Lambda(MeCl) + \Lambda_e(Me_3Cit). \qquad (15)$$

At 298.15 K, the following expressions for the conductances of HCl and MeCl were used [35]:

$\Lambda(HCl)$
$$= 426.04 - 156.70\sqrt{c} + 165.5\,c(1 - 0.2274\sqrt{c}), \quad (16a)$$

$\Lambda(LiCl)$
$$= 115.00 - 85.94\sqrt{c} + 89.1\ c(1 - 02274\sqrt{c}), \quad (16b)$$

$\Lambda(NaCl)$
$$= 126.42 - 88.53\sqrt{c} + 89.5\ c(1 - 0.2274\sqrt{c}), \quad (16c)$$

$\Lambda(KCl)$
$$= 149.82 - 93.86\sqrt{c} + 94.9\ c(1 - 0.2274\sqrt{c}), \quad (16d)$$

and from this investigation

$$\Lambda_e(Li_3Cit) = 118.88 - 474.10\sqrt{c}, \qquad (17a)$$

$$\Lambda_e(Na_3Cit) = 122.22 - 437.32\sqrt{c}, \qquad (17b)$$

$$\Lambda_e(K_3Cit) = 144.35 - 430.46\sqrt{c}. \qquad (17c)$$

From (14), (15), (16), and (17), $\Lambda^*(Me_3Cit)$ and $\alpha_1(Me_3Cit)$ can be calculated; they are presented in Table 5. Again there is a satisfactory agreement between the calculated Λ^* and α_1 values based on the data from three different citrates. Since $\alpha_1 \leqq \alpha$, and their difference decreases at increasing c, the highest concentration in this work, $c = 6.7864 \cdot 10^{-3}\ mol\ dm^{-3}$, may be used to estimate the equilibrium constant

$$K_{11} = \frac{c\,\alpha_1^2\,f_1}{1 - \alpha_1}. \qquad (18)$$

In (18) the activity coefficient quotient f_1 can be determined from the individual activity coefficients (8) using the data of [36]. The values of K_{11} calculated from (18) are presented in Table 6; they are comparable to the value of $K_1 = 7.44 \cdot 10^{-4}\ mol\ dm^{-3}$ which was determined by Bates and Pinching [25] from electromotive force measurements. However, we will expect a lower value of K_1 from our experiments because $\alpha_1 \leqq \alpha$ and therefore also $K_1 \leqq K_{11}$.

Using $\alpha_1 = 0.2877$, $\Lambda = 109.53$ and $a_1 = 6.25$ Å ($a_1 = 1/2\,(a(H^+) + a(H_2Cit^-))$), the Quint-Viallard equations (11) for $\Lambda^* = \Lambda_1 = \lambda(H^+) + \lambda(H_2Cit^-)$, were solved simultaneously with (14) to yield the limiting conductance of the intermediate anion $\lambda^0(H_2Cit^-)$

$c \cdot 10^4$	$\Lambda(\text{Li}_3\text{Cit})$	$\Lambda(\text{Na}_3\text{Cit})$	$\Lambda(\text{K}_3\text{Cit})$	$\alpha_1(\text{Li}_3\text{Cit})$	$\alpha_1(\text{Na}_3\text{Cit})$	$\alpha_1(\text{K}_3\text{Cit})$
1.1647	417.06	416.40	415.25	0.9076	0.9090	0.9115
3.1430	413.29	412.90	411.84	0.7413	0.7420	0.7424
5.6324	410.03	409.88	408.89	0.6421	0.6442	0.6430
8.7398	406.88	406.96	406.04	0.5697	0.5696	0.5708
16.854	400.68	401.22	400.23	0.4666	0.4659	0.4671
30.752	392.97	394.31	393.43	0.3820	0.3807	0.3815
67.864	378.55	380.70	380.40	0.2893	0.2877	0.2879

Table 5. Conductances of completely dissociated citric acid $\Lambda^* = \Lambda(\text{Me}_3\text{Cit})$ and degrees of the primary dissociation step α_1 at 298.15 K.

Table 6. Approximate equilibrium constants K_{11} at 298.15 K.

	$K_{11} \cdot 10^4$ mol dm^{-3}
$\alpha_1(\text{Li}_3\text{Cit}) = 0.2893$	7.29 *
$\alpha_1(\text{Na}_3\text{Cit}) = 0.2877$	7.17 *
$\alpha_1(\text{K}_3\text{Cit}) = 0.2879$	7.18 *

* Eq. (18), $c = 6.7864 \cdot 10^{-3}$ mol dm^{-3}.

and the conductances

$$\lambda(\text{H}^+) = 349.85 - 110.22\sqrt{I} + 67.77\,I\ln I + 687.8\,I, \tag{19a}$$

$$\lambda(\text{H}_2\text{Cit}^-) = 36.7 - 38.52\sqrt{I} + 3.16\,I\ln I + 116.13\,I. \tag{19b}$$

The contribution due to the primary dissociation step is

$$\Lambda_1 = 386.55 - 148.74\sqrt{I} + 70.93\,I\ln I + 803.9\,I. \tag{20}$$

The value of $\lambda^0(\text{H}_2\text{Cit}^-) = 36.70$ resulting from this procedure is much higher than that estimated by Levien [17], $\lambda^0(\text{H}_2\text{Cit}^-) = 30.39$ (the limiting value of $\Lambda_1 = 380.2$ is also lower than our result $\Lambda_1 = 386.55$), who assumed that it is equal to that of the picrate ion. The Levien calculations [17], based on the conductance data from a significantly higher concentration region, $c > 0.018$ mol dm^{-3}, were performed to be consistent with the Bates-Pinching result [25] for K_1. For the evaluation of the activity coefficients, Levien used $a(\text{H}_2\text{Cit}^-) = 5$ Å, whereas our value is 6.25 Å; however, the final results are not sensitive to the choice of this parameter.

There is no experimental base for the evaluation of the limiting conductance $\lambda^0(1/2\ \text{HCit}^{2-})$ of the intermediate anion. This value must be properly assigned. It is known that the ratio of the limiting conductances of anions with charge ratios $z:(z-1)$ and $(z-1):(z-2)$ varies from system to system and is usually found between 0.5 and 1.2 [5, 11–13, 19, 20, 37]. Pethybridge [37] pointed out that "for most systems we fix the ratio at 0.80, not for any theoretical reason, but rather because this seems intuitively reasonable and some of the

highest precision data give a best-fit in the region of this value". In our case one has $\lambda^0(\text{H}_2\text{Cit}^-)/\lambda^0(1/2\ \text{HCit}^{2-}) = r$; $\lambda^0(1/2\ \text{HCit}^{2-})/\lambda^0(1/3\ \text{Cit}^{3-}) = r^2$ and therefore $\lambda^0(\text{H}_2\text{Cit}^-)/\lambda^0(1/3\ \text{Cit}^{3-}) = r^3$, which finally gives $r = (36.70/72.05)^{1/3} = 0.7886$ in complete agreement with Pethybridge's choice. The values of $\lambda^0(1/2\ \text{HCit}^{2-}) = 46.00$ and $a_2 = 6.75$ Å, selected in this way, were introduced into the Quint-Viallard equations (11) for H^+ and HCit^{2-} ions:

$$\tag{21a}$$

$$\lambda(\text{H}^+) = 349.85 - 151.49\sqrt{I} + 221.82\,I\ln I + 1394\,I,$$

$$\lambda(1/2\ \text{HCit}^{2-})$$

$$= 46.00 - 76.19\sqrt{I} - 55.46\,I\ln I + 219.69\,I. \tag{21b}$$

The contribution due to the secondary dissociation step is

$$\Lambda_2 = \lambda(\text{H}^+) + \lambda(1/2\ \text{HCit}^{2-}), \tag{22a}$$

$$\Lambda_2 = 395.85 - 227.68\sqrt{I} + 166.36\,I\ln I + 1613.7\,I. \tag{22b}$$

For the tertiary dissociation step, using $\lambda^0(1/3\ \text{Cit}^{3-}) = 72.05$ and $a_3 = 7.0$ Å, follows

$$\tag{23a}$$

$$\lambda(\text{H}^+) = 349.85 - 181.29\sqrt{I} + 410.19\,I\ln I + 2156\,I,$$

$$\lambda(1/3\ \text{Cit}^{3-})$$

$$= 72.05 - 121.48\sqrt{I} - 216.51\,I\ln I + 459.7\,I \tag{23b}$$

and

$$\Lambda_3 = \lambda(\text{H}^+) + \lambda(1/3\ \text{Cit}^{3-}), \tag{24a}$$

$$\Lambda_3 = 421.9 - 302.77\sqrt{I} + 148.68\,I\ln I + 2615.9\,I. \tag{24b}$$

From (10), the measured conductance of citric acid as a function of concentration is

$$\Lambda = \alpha_1\Lambda_1 + 2\alpha_2\Lambda_2 + 3\alpha_3\Lambda_3, \tag{25}$$

where α_1, α_2, and α_3 are given by (7). Considering this equation, it is assumed that the contributions coming from the binary electrolyte constituents are additive. Formally, in the limit of infinite dilution (α_1 and α_2 tend to zero and α_3 tends to unity) we have $\Lambda = 3\Lambda_3$,

Table 7. Experimental and calculated, (25), conductances of citric acid and degrees of dissociation at 298.15 K.

$c \cdot 10^3$	α_1	α_2	α_3	Λ	Λ_{calc} [a]	Λ_{calc} [b]
0.11647	0.7758	0.10043	0.003860	378.55	378.10 [a]	388.18 [b]
0.31430	0.7112	0.04281	0.000077	306.38	306.90	314.22
0.56324	0.6370	0.02522	0.000070	263.30	264.18	270.51
0.87398	0.5718	0.01681	0.000030	231.79	232.29	238.04
1.6854	0.4704	0.00910	0.000015	186.94	187.04	191.94
3.0752	0.3823	0.00517	0.000005	150.11	149.98	154.12
6.7864	0.2831	0.00246	0.000002	109.53	109.30	112.99
17.99 *	0.1877	0.00099	0.000001	72.16	72.06	74.15
44.93 *	0.1255	0.00042		47.57	47.80	49.24
64.20 *	0.1069	0.00030		40.12	40.62	41.85
112.2 *	0.0829	0.00018		30.58	31.42	32.39
160.3 *	0.0704	0.00013		25.46	26.64	27.47
280.3 *	0.0545	0.00008		18.85	20.57	21.22

* Levien results [17].
[a] $K_1 = 6.98 \cdot 10^{-4}$ mol dm^{-3}, $K_2 = 1.40 \cdot 10^{-5}$ mol dm^{-3} and $K_3 = 4.05 \cdot 10^{-7}$ mol dm^{-3}; this work.
[b] $K_1 = 7.44 \cdot 10^{-4}$ mol dm^{-3}, $K_2 = 1.73 \cdot 10^{-5}$ mol dm^{-3} and $K_3 = 4.0 \cdot 10^{-7}$ mol dm^{-3}; the Bates and Pinching [25] equilibrium constants.

and this is the molar conductance of the completely dissociated electrolyte of the type 1:3. Thus (10) and (11) tend to the Onsager approximation (12).

Since Λ_1, Λ_2, Λ_3, α_1, α_2, α_3, f_1, f_2, f_3, and $I = c(\alpha_1 + 3\alpha_2 + 6\alpha_3)$ depend on the equilibrium constants K_1, K_2, and K_3, it follows from (25) that $\Lambda = \Lambda(c; K_1, K_2, K_3)$; for a known set of (Λ, c) the dissociation constants can be approximated with the help of an appropriate iteration procedure. If the equilibrium constants K_1, K_2, and K_3 are known at a given concentration c, then α_1, α_2, α_3, f_1, f_2, and f_3 can be evaluated consecutively from (7) starting with initial values $\alpha_2 = 0$, $\alpha_3 = 0$ and α_1, calculated from (18) with $f_1 = 1$. The calculations are continued until repetition does not change α_j and f_j. Few runs were sufficient in most cases, and the number of successive approximations could be fixed to ten in this work. α_1, α_2 and α_3 determined in this way permit the evaluation of the ionic strength I and finally of Λ_1, Λ_2, and Λ_3 from (20), (22) and (24). The search for the best agreement between the measured and calculated values of Λ, (25), will therefore produce a set of the self-consistent equilibrium constants. In our calculations, the dissociation constants of Bates and Pinching [25], $K_1 = 7.44 \cdot 10^{-4}$ mol dm^{-3}, $K_2 = 1.73 \cdot 10^{-5}$ mol dm^{-3}, and $K_3 = 4.0 \cdot 10^{-7}$ mol dm^{-3} at 298.15 K served as the initial values. It is evident that the contribution coming from the tertiary dissociation step is negligible; therefore K_3 is of minor importance and the value of Bates and Pinching can be used throughout the calculations. Table 7 presents the observed and calculated values of Λ and the degrees of dissociation α_1, α_2, and α_3. The chosen model covers very well our and Levien's data [17] when the expressions for activitiy coefficients, (8), are used. At 298.15 K, a satisfactory agreement between the experimental and calculated

Table 8. Dissociation constants of citric acid at 298.15 K.

Method	$K_1 \cdot 10^4$	$K_2 \cdot 10^5$	$K_3 \cdot 10^7$
E.M.F. with liquid junction [a]	8.32	1.82	5.5
E.M.F. with liquid junction [b]	8.77	1.74	4.0
E.M.F. with liquid junction [c]	8.31	2.18	4.17
E.M.F. with liquid junction [d]	7.47	1.66	3.75
E.M.F. without liquid junction [e]	7.44	1.73	4.05
Electrical conductance [f]	6.98	1.40	4.05 [e]

[a] Simms [23]; [b] Bjerrum and Unmack [24]; [c] Heinz [26]; [d] Litchinsky et al. [27]; [e] Bates and Pinching [25]; [f] this work.

conductances of citric acid was established for $K_1 = 6.98 \cdot 10^{-4}$ mol dm^{-3}, $K_2 = 1.40 \cdot 10^{-5}$ mol dm^{-3}, and $K_3 = 4.05 \cdot 10^{-7}$ mol dm^{-3}. It is obvious that for the applied set of parameters the Bates and Pinching [25] equilibrium constants give an unsatisfactory fit to our and Levien's [17] conductances. Our equilibrium constants are compared in Table 8 with the literature; they are somewhat lower than those derived from electromotive force measurements.

The equilibrium constants for other temperatures can be caculated in the same way as shown for 298.15 K. Instead of the commonly used MacInnes and Shedlovsky method [1] (introduction of the temperature dependences of (11) and (14)–(17)), we applied at each temperature the Walden rule

$$\lambda_j^0(T) = \lambda_j^0(298.15 \text{ K}) \frac{\eta(298.15 \text{ K})}{\eta(T)}, \qquad (26)$$

$$j = H_2Cit^-, HCit^{2-}, Cit^{3-}.$$

The temperature dependence of $\lambda^0(H^+)$ is known [3]. The calculation of the activity coefficients according to (8) uses the constants $A(T)$ and $B(T)$ of Robinson and Stokes [38]; the distances of closest approach, a_i, were assumed to be independent of temperature. The

Table 9. Limiting conductances, dissociation constants of citric acid and the standard changes of thermodynamic functions in the investigated temperature range.

	T/K						
	278.15	283.15	288.15	293.15	298.15	303.15	308.15
$\lambda^0(H_2Cit^-)$	21.62	25.08	28.69	32.56	36.70	41.03	45.56
$\lambda^0(1/2\ Cit^{2-})$	27.10	31.43	35.96	40.81	46.00	51.43	57.11
$\lambda^0(1/3\ Cit^{3-})$	42.45	49.23	56.33	63.92	72.05	80.56	89.45
$K_1 \cdot 10^4$	5.96	6.27	6.56	6.79	6.98	7.10	7.22
$K_2 \cdot 10^5$	1.29	1.33	1.36	1.38	1.40	1.42	1.43
$K_3 \cdot 10^7$ *	4.11	4.14	4.13	4.09	4.05	3.93	3.78
Δ_1H^0 kJ mol^{-1}	7.39	6.36	5.36	4.40	3.47	2.57	1.70
Δ_2H^0 kJ mol^{-1}	3.79	3.29	2.80	2.33	1.88	1.44	1.02
Δ_1S^0 J mol^{-1} K^{-1}	-35.2	-38.9	-42.3	-45.6	-48.8	-51.8	-54.6
Δ_2S^0 J mol^{-1} K^{-1}	-80.0	-81.7	-83.4	-85.1	-86.6	-88.0	-89.5

* Bates and Pinching [25].

results are summarized in Table 9. The coefficients of the conductance equation (19)–(24) are omitted; they can easily be evaluated with the help of the Appendix.

The agreement of measured and calulated conductances Λ is satisfactory at all temperatures of the program. The average standard deviation in the temperature range is 0.5 S cm^2 mol^{-1}; the highest deviation is 0.8 S cm^2 mol^{-1} at 288.15 K and the lowest deviation is 0.3 S cm^2 mol^{-1} at 283.15 K.

The temperature dependence of the dissociation constants can be reproduced with the help of the relations

$$\ln K_1 = -16.862 + \frac{6138.1}{T} - \frac{9.7725 \cdot 10^5}{T^2}, \qquad (27a)$$

$$\ln K_2 = -15.722 + \frac{2967.7}{T} - \frac{4.7613 \cdot 10^5}{T^2}. \qquad (27b)$$

Differentiation with regard to temperature T yields the molar enthalpies Δ_1H^0 and Δ_2H^0 and the molar entropies Δ_1S^0 and Δ_2S^0 of dissociation given in Table 9.

The Eqs. (27a) and (27b) predict maxima of the equilibrium constants outside of the studied temperature range $K_{1\,max} = 7.29 \cdot 10^{-4}$ at 318.42 K and $K_{2\,max} = 1.44 \cdot 10^{-5}$ at 320.87 K. Such maxima are commonly found for organic acids; Bates and Pinching [25] report 327.97 K and 310.90 K, respectively. At 298.15 K, it is possible to compare enthalpies and entropies not only with those of Bates and Pinching [25] but also with the results of Bjerrum and Unmack [24]:

$$\Delta_1H^0 = 3.93 \text{ kJ mol}^{-1}\ [24],$$
$$4.17 \text{ kJ mol}^{-1}\ [25] \quad \text{and}$$
$$3.47 \text{ kJ mol}^{-1}\ (\text{this work}),$$

$$\Delta_1S^0 = -46.0 \text{ J mol}^{-1} \text{ K}^{-1}\ [24],$$
$$-46.0 \text{ J mol}^{-1} \text{ K}^{-1}\ [25] \quad \text{and}$$
$$-48.8 \text{ J mol}^{-1} \text{ K}^{-1}\ (\text{this work}),$$

and for the secondary dissociation step:

$$\Delta_2H^0 = 1.71 \text{ kJ mol}^{-1}\ [24],$$
$$2.44 \text{ kJ mol}^{-1}\ [25] \quad \text{and}$$
$$1.88 \text{ kJ mol}^{-1}\ (\text{this work}),$$

$$\Delta_2S^0 = -83.7 \text{ J mol}^{-1} \text{ K}^{-1}\ [24],$$
$$-82.8 \text{ J mol}^{-1} \text{ K}^{-1}\ [25] \quad \text{and}$$
$$-86.6 \text{ J mol}^{-1} \text{ K}^{-1}\ (\text{this work}).$$

Obviously the results are in reasonable agreement when taking into account that the differentiation of experimental data is always associated with a loss of precision.

Appendix

For convenience, the individual conductances λ_j of the Quint-Valliard theory [28] are presented here

without terms in $I^{3/2}$. They are taken from the Quint thesis [29]. The symbols have their usual meaning.

$$\lambda_j = \lambda_j^0 - S_j \sqrt{I} + E_j I \ln I + J_{1j} I,$$

where the coefficients are

$$S_j = \alpha_j \lambda_j^0 + \beta_j,$$
$$E_j = E_{1j} \lambda_j^0 - E_{2j},$$
$$J_{1j} = \sigma_{1j} \lambda_j^0 + \sigma_{2j}, \quad j = 1, 2.$$

$$R_1 = \frac{(1-q)^3 \ln(1+\sqrt{q}) + q(q^2 - q + 2) \ln(2+\sqrt{q}) + 2q(1-2q)\ln(1+2\sqrt{q})}{2q(1-q)},$$

$$R_2 = \frac{6 + 15\sqrt{q} + 30q + 23q^{3/2} - 6q^2}{12\sqrt{q}(1+\sqrt{q})^2},$$

$$R_3 = \frac{2z_1^2 z_2^2 b^2 + 2|z_1| \cdot |z_2| b - 1}{|z_1|^3 |z_2|^3 b^3},$$

$$b = \frac{1.6671 \cdot 10^{-3}}{aDT}.$$

The indices $j = 1, 2$ denote the three pairs of ions: H^+ and H_2Cit^-, H^+ and $HCit^{2-}$, and H^+ and Cit^{3-}, respectively and

$$\alpha_j = \frac{2.8012 \cdot 10^6}{(DT)^{3/2}} |z_1| \cdot |z_2| \frac{q}{1 + \sqrt{q}},$$

$$\beta_j = \frac{41.243}{\eta(DT)^{1/2}} |z_j|,$$

$$q = \frac{|z_1| \cdot |z_2|}{(|z_1| + |z_2|)} \frac{(\lambda_1^0 + \lambda_2^0)}{(|z_2| \lambda_1^0 + |z_1| \lambda_2^0)},$$

where η is the viscosity and D the dielectric constant at temperature T.

$$E_{1j} = \frac{5.8851 \cdot 10^{12}}{(DT)^3} z_1^2 z_2^2 q,$$

$$E_{2j} = \frac{4.3324 \cdot 10^7}{\eta(DT)^2} |z_1| \cdot |z_2| Q_1,$$

$$Q_1 = \left\{ \frac{(|z_1| + |z_2|) q \lambda_j^0}{\lambda_1^0 + \lambda_2^0} + q|z_j| - \frac{2z_j |z_j|(z_1 + z_2)}{z_1 z_2} \right\}.$$

The coefficients σ_{1j} are given by

$$\sigma_{1j} = \frac{1.17702 \cdot 10^{13}}{(DT)^3} z_1^2 z_2^2 Q_2,$$

where

$$Q_2 = \gamma + \ln \xi + R_1 - R_2 + R_3,$$

$$\gamma = 0.5772156649 \ldots,$$

$$\xi = \frac{5.0291 \cdot 10^9 a}{(DT)^{1/2}}.$$

a is the distance of closest approach and

The coefficients σ_{2j} are given by the relations

$$\sigma_{2j} = \frac{8.6648 \cdot 10^7}{\eta(DT)^2} |z_1| \cdot |z_2| q Q_3,$$

$$Q_3 = \left\{ -\frac{(|z_1| + |z_2|) \lambda_j^0 Q_4}{\lambda_1^0 + \lambda_2^0} \right.$$
$$\left. - \left(|z_j| + \frac{2z_j |z_j|(z_1 + z_2)}{q|z_1| \cdot |z_2|} \right) Q_5 + |z_j| Q_6 \right\},$$

where

$$Q_4 = \gamma + \ln \xi + \frac{2}{3|z_1| \cdot |z_2| b} + R_4 - R_5,$$

$$Q_5 = \gamma + \ln 2 + \ln \xi,$$

$$Q_6 = -\ln 2 + \frac{3}{2} + \frac{1}{z_1^2 z_2^2 b^2} + \frac{8 - 3q}{2qb|z_1| \cdot |z_2|} + R_6$$

and

$$R_4 = \frac{(1-q)^2 \ln(1+\sqrt{q}) - q(q-4)\ln(2+\sqrt{q})}{2q},$$

$$R_5 = \frac{6 + 13\sqrt{q} - 6q}{12\sqrt{q}},$$

$$R_6 = \frac{(1+q)\ln(1+\sqrt{q}) - 2q\ln 2 - \sqrt{q}(1-\sqrt{q})}{(1-q)}.$$

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