Conductance Studies of Aqueous Succinic Acid

Alexander Apelblat
Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel

Josef Barthel
Institut für Physikalische und Theoretische Chemie, Universität Regensburg

Z. Naturforsch. 47a, 493–498 (1992); received November 2, 1991

Conductance measurements of aqueous solutions of succinic acid and of di-sodium succinate were performed from 278.15 to 308.15 K and the limiting conductances \( \lambda_0 \) are reported. The Walden product is independent of temperature: \( \lambda_0 (1/2 \text{Succ}^2^-) \cdot \eta (T) = 0.503 \pm 0.001 \). The salt conductances closely obey the Onsager limiting law. The evaluation of the equilibrium constants for the primary and secondary steps of dissociation, \( K_1 \) and \( K_2 \), and the limiting conductances of the hydrosuccinate ion, \( \lambda_0 (\text{HSucc}^2^-) \), are discussed using the Quint and Viallard conductance equation.

1. Introduction

This work is a continuation of our studies on aqueous solutions of polybasic organic acids [1], where it is difficult to obtain a simple interpretation of conductance measurements due to the overlapping dissociation equilibria. From many reported conductances of organic acids only in few cases the results for dibasic acids are analysed [2–4], and even then the contribution coming from the second dissociation step is usually considered as a small correction to the measured conductance. Succinic acid, a weak unsymmetrical 1:2 electrolyte is considered here in a similar way as citric acid [1] by using the Quint and Viallard conductance equation.

The conductances of aqueous succinic acid solutions have already been measured in 1912 by Jones [5]. Neutral and acidic succinates were considered by Jeffery and Vogel [6], Davies [2] and Topp and Davies [7]. Dissociation constants of succinic acid at room temperature were determined many times, mainly by potentiometric methods [8, 9]. Pinching and Bates [10, 11] performed a systematic evaluation of the dissociation constants from 273.15 to 323.15 K.

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

\[
\begin{align*}
\text{H}_2\text{Succ} & \rightarrow \text{H}^+ + \text{HSucc}^-; \quad K_1, \quad (1a) \\
\text{HSucc}^- & \rightarrow \text{H}^+ + \text{Succ}^{2-}; \quad K_2. \quad (1b)
\end{align*}
\]

The equilibrium constants of these reactions are

\[
\begin{align*}
K_1 &= \frac{[\text{H}^+] \cdot [\text{HSucc}^-]}{[\text{H}_2\text{Succ}]}, \quad (2a) \\
K_2 &= \frac{[\text{H}^+] \cdot [\text{Succ}^{2-}]}{[\text{HSucc}^-]}. \quad (2b)
\end{align*}
\]

2. Experimental

The Fluka puriss. p.a. reagents anhydrous succinic acid (> 99.5%), and di-sodium succinate (> 98%), were used without further purification.

The solutions were prepared by weight, and conversion from molalities to molarities was performed with the help of the density of pure water at given temperature for dilute solutions (c < 1.1 \( \cdot \) 10\(^{-3}\) mol dm\(^{-3}\)) of succinic acid and di-sodium succinate. 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.

A detailed description of the measuring system and applied procedures is given in [1, 12, 13].

3. Data Analysis

Reprint requests to Prof. Dr. J. Barthel, Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Postfach 10 42, W-8400 Regensburg, FRG.

0932-0784 / 92 / 0300-0493 $ 01.30/0. – Please order a reprint rather than making your own copy.
where \( F_j \) denotes corresponding quotients of the activity coefficients:

\[
F_1 = \frac{f_{H^+} f_{HSucc^-}}{f_{HSucc}}, \quad F_2 = \frac{f_{H^+} f_{SuC2^-}}{f_{SuC2^-}}.
\]

In terms of the total degree of dissociation \( \alpha \) and the degrees associated with the primary and secondary steps of dissociation, \( \alpha_1 \) and \( \alpha_2 \), the concentrations of species present in the solution are

\[
[H^+] = c(\alpha_1 + 2\alpha_2), \quad [H_2SuC] = c(1 - \alpha), \quad [HSucc^-] = c\alpha_1, \quad [SuC2^-] = c\alpha_2,
\]

where \( c \) is the total (analytical) concentration of succinic acid and

\[
\alpha = \alpha_1 + \alpha_2.
\]

Use of (2) and (4) yields

\[
K_1 = \frac{c(\alpha_1 + 2\alpha_2) \alpha_1}{1 - \alpha} F_1, \quad K_2 = \frac{c(\alpha_1 + 2\alpha_2) \alpha_2}{\alpha_1} F_2.
\]

For given values of the equilibrium constants and activity coefficients it follows at concentration \( c \), that the degrees of dissociation \( \alpha_1 \) and \( \alpha_2 \) can successively be evaluated by an iterative solution of two quadratic equations:

\[
\alpha_1 = \frac{1}{2} \left[ -\left( \frac{K_1}{c F_1} + 2\alpha_2 \right) \right.
\left. + \sqrt{\left( \frac{K_1}{c F_1} + 2\alpha_2 \right)^2 + \frac{4 K_1 (1 - \alpha_2)}{c F_1}} \right], \quad \alpha_2 = \frac{1}{4} \left[ -\alpha_1 + \sqrt{\alpha_1^2 + \frac{8 K_2 \alpha_1}{c F_2}} \right].
\]

In very dilute solutions, as considered in this study, the activity coefficients \( f_j \) of the different ions can be approximated by the Debye-Hückel expression (\( j = H^+, HSucc^- \) and \( SuC2^- \))

\[
\log f_j = -\frac{A z_j^2 \sqrt{I}}{1 + a_j B \sqrt{I}},
\]

where \( z_j \) is the average cation-anion distance (distance closest approach) and the ionic strength is \( I = c(x_1 + 3\alpha_2) \). At 298.15 K the constants are \( A = 0.5115 \text{ mol}^{-1/2} \text{ dm}^{3/2} \) and \( B = 0.3291 \cdot 10^8 \text{ mol}^{-1/2} \cdot \text{ dm}^{3/2} \cdot \text{cm}^{-1} \). The activity coefficient of undissociated succinic acid is assumed to be unity.

Molecular conductances \( A \) are the sum of the ionic contributions:

\[
A = \frac{1000 L}{c} = \sum_{j=1}^{n} \frac{|z_j| c_j \lambda_j}{c},
\]

where \( L \) is the measured specific conductance and \( \lambda_j, c_j \) and \( z_j \) are the individual conductances, concentrations and valences of the ions.

In the case under consideration we have

\[
A = \alpha_1 \left[ \lambda(H^+) + \lambda(HSucc^-) \right] + 2\alpha_2 \left[ \lambda(H^+) + \lambda(Suc2^-) \right].
\]

The equation for \( \lambda_j \) exact up to the linear term in the ionic strength \( I \), has the form

\[
\lambda_j = \lambda_j^0 - S_j \sqrt{I} + E_j I \ln I + J_{1j} I.
\]

For unsymmetrical electrolytes, the coefficients \( S_j, E_j, J_{1j} \) are available from the Quint-Viallard theory \([15, 16]\), and with \( E_j = 0 \) and \( J_{1j} = 0 \) (11) reduces to the Onsager limiting equation \([17]\). At given temperature these coefficients depend on the limiting conductances of the corresponding ions, on the viscosity and the dielectric constant of water; the linear term in (11) depends also on the distance of closest approach \( a_j \). The complete expressions for the coefficients are presented in \([1, 15, 16]\).

When expressed in terms of the two step dissociation model, the experimental \( (A, c) \) data require an adjustment or preselection of six parameters. These are the equilibrium constants \( K_1 \) and \( K_2 \), the limiting conductances of the anions, \( \lambda^0(HSucc^-) \) and \( \lambda^0(Suc2^-) \), and the distances of closest approach \( a_1 \) and \( a_2 \). The values of \( a_j \) are equal for the activity coefficient and conductance equations, (8) and (11).

4. Results and Discussion

The equivalent conductances of di-sodium succinate and the molecular conductances of succinic acid are presented in Table 1 and in Figs. 1 and 2. The conductances are plotted as functions of the square root of the ionic strength \( I \), which for a completely dissociated
A. Apelblat and J. Barthel • Conductance Studies of Aqueous Succinic Acid

Fig. 1. Equivalent conductances of di-sodium succinate as functions of the square root of ionic strength $I$. 1: 278.15 K; 2: 283.15 K; 3: 288.15 K; 4: 293.15 K; 5: 298.15 K; 6: 303.15 K; 7: 313.15 K.

Fig. 2. Molar conductances of succinic acid as a function of the square root of ionic strength at 298.15 K. •: Jones [5], o: this work.

1:2 electrolyte is $I = 3c$. As can be seen, di-sodium succinate is a completely dissociated electrolyte and succinic acid is a partially dissociated weak electrolyte. In Fig. 2 the results of Jones [5] are also presented, which cover more concentrated solutions of succinic acid. As many old conductances, they are systematically lower than those determined in modern experiments; the differences are significant especially in dilute solutions. Taking this into account, both sets of data are in reasonable agreement (Figure 2). The units of the equivalent and molar conductances are $S \text{ cm}^2 \text{ equiv}^{-1}$ and $S \text{ cm}^2 \text{ mol}^{-1}$; they will be omitted hereafter.

The equivalent conductance of completely dissociated electrolytes of the type 1:2, in the Onsager approximation [17] is given by

$$A_e = A^0 - S\sqrt{I},$$

$$A^0 = \lambda^0(Na^+) + \lambda^0(Succ^2-),$$

$$S = \alpha A^0 + \beta,$$

where

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

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

$$q = \frac{2}{3} \left( \lambda^0(Na^+) + \lambda^0(Succ^2-) + \lambda^0\left(Succ^2-\right) \right),$$

and $D$ and $\eta$ denote the dielectric constant and viscosity of water.

At a given temperature $T$, the measured equivalent conductances $A_e$ can be approximated by a straight line (Fig. 1) and the slopes of these lines are very close to the Onsager slopes (Table 2). The Onsager slopes are based on $\lambda^0(Na^+), D(T), \eta(T)$ values from [14, 17]. The intercepts of the straight lines serve as the limiting equivalent conductances of di-sodium succinate.

Table 1. Experimental equivalent conductances of di-sodium succinate and molar conductances of succinic acid in the investigated temperature range.

<table>
<thead>
<tr>
<th>$m \cdot 10^4$</th>
<th>$T / K$</th>
<th>$\lambda^0(Na_2Succ)$</th>
<th>$\lambda^0(H_2SUCC)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>287.15</td>
<td>0.06</td>
<td>0.9619</td>
<td>0.9171</td>
</tr>
<tr>
<td>283.15</td>
<td>0.25</td>
<td>62.18</td>
<td>144.90</td>
</tr>
<tr>
<td>288.15</td>
<td>0.35</td>
<td>71.88</td>
<td>162.25</td>
</tr>
<tr>
<td>293.15</td>
<td>0.45</td>
<td>82.20</td>
<td>179.68</td>
</tr>
<tr>
<td>298.15</td>
<td>0.55</td>
<td>93.02</td>
<td>196.73</td>
</tr>
<tr>
<td>303.15</td>
<td>0.65</td>
<td>104.38</td>
<td>213.60</td>
</tr>
<tr>
<td>308.15</td>
<td>0.75</td>
<td>116.01</td>
<td>230.00</td>
</tr>
</tbody>
</table>
Table 2. Limiting equivalent conductances of succinate and sodium ions, the Walden products and the ratios of the observed to the Onsager slopes.

<table>
<thead>
<tr>
<th>T/K</th>
<th>(\lambda^0(\text{Succ}^2^-))</th>
<th>(\lambda^0(\text{Na}^+})</th>
<th>(\lambda^0\eta)</th>
<th>(S_{\text{obs}}/S_{\text{Onsager}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>278.15</td>
<td>30.30</td>
<td>0.501</td>
<td>1.007</td>
<td></td>
</tr>
<tr>
<td>283.15</td>
<td>33.81</td>
<td>0.502</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>288.15</td>
<td>39.72</td>
<td>0.503</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>293.15</td>
<td>44.81</td>
<td>0.504</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>50.15</td>
<td>0.503</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>303.15</td>
<td>56.72</td>
<td>0.503</td>
<td>1.018</td>
<td></td>
</tr>
<tr>
<td>308.15</td>
<td>61.53</td>
<td>0.503</td>
<td>1.001</td>
<td></td>
</tr>
</tbody>
</table>

From the Kohlrausch law the limiting conductances were calculated (Table 2), and at 298.15 K we have \(\lambda^0(\text{Succ}^2^-) = 56.2\). This result is in agreement with the Davies value [2], \(\lambda^0(\text{Succ}^2^-) = 57.4\); the Waiden products of succinate and sodium ions, the Waiden products and the ratios of the observed to the Onsager slopes were calculated (Table 2), and at 298.15 K we have \(\lambda^0(\text{Na}^+) = 56.2\). This result is in a fair agreement with the Davies value [2].

The ratio of limiting conductances varies from system to system and is usually not constant; its value must be properly assigned. From an analysis of the ammonium hydrogen succinate and sodium hydrogen succinate conductances, the values of \(\lambda^0(\text{HSucc}^-) = 31.9\) and \(\lambda^0(\text{HSucc}^-) = 35.8\) were adopted by Davies [2] and Topp and Davies [7]. The ratio of limiting conductances varies from system to system and is usually found between 0.5 and 1.2 [18]. Recently, Pethybridge [19] suggested to fix the ratio at 0.80. Evidently, with increasing succinic acid concentration, the contribution due to the second dissociation step is less and less important and the problem can be reduced to the case of a weak, monobasic acid. In the MacInnes and Shedlovsky procedure [20], the degree of dissociation of the primary step is given by

\[
x_1 = A/A^*,
\]

where \(A^*\) is the conductance of the hypothetically completely dissociated acid (to the primary dissociation step only) at the same concentration \(c\) as for the measured conductance \(A\). Values of \(A^*\) can be calculated from

\[
A^* = A(\text{HCl}) - A(\text{NaCl}) + A_e(\text{Na}_2\text{Succ}).
\]

At 298.15 K, the following expressions for the conductances of HCl and NaCl were used [21]:

\[
A(\text{HCl}) = 426.04 - 156.70 \sqrt{c} + 165.5c(1 - 0.2274 \sqrt{c}),
\]

\[
A(\text{NaCl}) = 126.42 - 88.53 \sqrt{c} + 89.5c(1 - 0.2274 \sqrt{c})
\]

and from this investigation

\[
A_e(\text{Na}_2\text{Succ}) = 106.35 - 195.65 \sqrt{c}.
\]

From (14), (15), (16), and (17), for the highest concentration in this work, \(c = 1.0675 \times 10^{-3}\) mol dm\(^{-3}\), we have \(A^*(\text{Na}_2\text{Succ}) = 397.40\), and \(x_1 = 0.2068\), and from

\[
K_{11} = \frac{c x^2_1 F_1}{1 - x_1}
\]

the estimated value of the equilibrium constant is \(K_{11} = 5.6 \times 10^{-5}\). This value may be compared with dissociation constants of succinic acid reported in the literature, which vary from \(K_1 = 6.03\) to \(7.24 \times 10^{-5}\) and from \(K_2 = 1.90\) to \(2.47 \times 10^{-6}\) [8, 9]. The Pinching and Bates constants are \(K_1 = 6.21 \times 10^{-5}\) and \(K_2 = 2.31 \times 10^{-6}\) [10, 11]. The activity coefficient quotient \(F_1\) was determined from the individual activity coefficients (8). Using \(x_1 = 0.2068\), \(A = 82.18\), and \(\lambda^0(\text{H}^+) = 349.85\), the Quint-Viallard equations (11) for \(A^* = A_1 = \lambda(\text{H}^+) + \lambda(\text{HSucc}^-)\) were solved simultaneously with (14) to yield the limiting conductance of \(\lambda^0(\text{HSucc}^-) = 49.75\), \(\lambda^0(\text{HSucc}^-)/\lambda^0(\text{Succ}^2^-) = 0.89\). Evidently, this result is much higher than that adopted by Davies [2] and Topp and Davies [7].

It follows from (10) that the measured conductance of succinic acid \(A\) as a function of concentration \(c\) is

\[
A = x_1 A_1 + 2 x_2 A_2,
\]

\[
A_1 = x_1 [\lambda(\text{H}^+) + \lambda(\text{HSucc}^-)],
\]

\[
A_2 = 2 x_2 [\lambda(\text{H}^+) + \lambda(\frac{1}{2}\text{Succ}^2^-)],
\]

where \(x_1\) and \(x_2\) are given by (7) and the individual conductances are calculated from the Quint-Viallard equations (11). The value of \(a(\text{Succ}^2^-) = 8.0\) Å was selected, but the final results are not sensitive to the choice of the distances of closest approach. Considering (19), it is assumed that the contributions coming from the binary electrolyte constituents are additive. Formally, in the limit at infinite dilution (\(x_1\) tends to zero and \(x_2\) approaches unity) we have \(A = 2 A_2\), and this is the molecular conductance of a fully dissociated electrolyte of the type 1:2.
set of \((A, c)\) values the dissociation constants can be approximated with the help of an appropriate iteration procedure. If the equilibrium constants \(K_1\) and \(K_2\) are known at a given concentration \(c\), then \(x_1, x_2, F_1\) and \(F_2\) can consecutively be evaluated from (7), starting with initial values \(x_2 = 0\) and \(x_1\) calculated from (18) with \(F_1 = 1\). The calculations are continued until repetition does not change the \(x_2\) and \(f_j\) values. Few runs were sufficient in most cases to complete the calculations. \(x_1\) and \(x_2\) determined in this way permit the evaluation of the ionic strength \(I\) and finally of \(A_1\) and \(A_2\). The search for the best agreement between the measured and calculated (19) values of \(A\) will therefore produce a set of the selfconsistent equilibrium constants. The limiting conductance at 298.15 K can be used for the evaluation of \(\lambda^0(\text{HSucc}^-)\) at other temperatures from the Walden rule:

\[
\lambda^0(\text{HSucc}^-, T) = \lambda^0(\text{HSucc}^-, 298.15 \text{ K}) \frac{\eta(298.15 \text{ K})}{\eta(T)}. \tag{20}
\]

The temperature dependence of \(\lambda^0(\text{H}^+)\) and the constants \(A\) and \(B\) (8) are known \([14,17]\) and the distances of closest approach, \(a_j\), can be assumed to be independent of temperature.

At 298.15 K, the determined "best" set of parameters is: \(\lambda^0(\text{HSucc}^-) = 47.0, \lambda^0(\text{HSucc}^-)/\lambda^0(\text{Succ}^2^-) = 0.84, K_1 = 5.69 \cdot 10^{-5}\) and \(K_2 = 5 \cdot 10^{-8}\), and the average standard deviation is \(\sigma = 0.23 \text{ S cm}^2 \text{ mol}^{-1}\). Since the equilibrium constants, especially \(K_2\), are significantly lower than those reported in the literature, three additional data sets were considered. If the Davies value, \(\lambda^0(\text{HSucc}^-) = 31.9, \lambda^0(\text{HSucc}^-)/\lambda^0(\text{Succ}^2^-) = 0.57\), is selected, then we have from (19): \(K_1 = 6.17 \cdot 10^{-5}\) and \(K_2 = 0.69 \cdot 10^{-6}\) with \(\sigma = 0.28 \text{ S cm}^2 \text{ mol}^{-1}\). The choice of the Topp and Davies value, \(\lambda^0(\text{HSucc}^-) = 35.8, \lambda^0(\text{HSucc}^-)/\lambda^0(\text{Succ}^2^-) = 0.64\), gives \(K_1 = 6.05 \cdot 10^{-5}\) and \(K_2 = 0.49 \cdot 10^{-6}\) with \(\sigma = 0.26 \text{ S cm}^2 \text{ mol}^{-1}\). Finally, if the Pinching and Bates dissociation constants are introduced we have: \(\lambda^0(\text{HSucc}^-) = 22.9, \lambda^0(\text{HSucc}^-)/\lambda^0(\text{Succ}^2^-) = 0.41\), with \(\sigma = 1.38 \text{ S cm}^2 \text{ mol}^{-1}\). The measured and calculated values of \(A\) for these four sets of parameters are presented in Table 3. As can be seen, in the framework of the Quint and Viallard theory there is no satisfactory description of the observed conductances with regard to a proper choice of \(\lambda^0(\text{HSucc}^-)\). Preselection of the dissociation constants gives results which are clearly inconsistent with the accuracy of our experiments. The "best" set of parameters is practically equivalent to the case of a monobasic weak acid with a very small correction due to the second dissociation step. This disagrees with the accepted values of \(K_1\) and \(K_2\) for succinic acid \([8,9]\). Considering \(K_2\), the selection of the Davies limiting conductance is somewhat better than that chosen by Topp and Davies. However, there is no clear distinction between these two cases, because the calculations are rather insensitive to changes in \(\lambda^0(\text{HSucc}^-)\). The same picture is observed at other temperatures. At this stage of investigation, without knowledge of transference numbers, it is difficult to assign properly the limiting conductance of the ion \(\text{HSucc}^-\); only accurate \(\lambda^0(\text{HSucc}^2^-)\) values as a function of temperature are available.

\begin{table}
\caption{Experimental and calculated (19) molar conductances of succinic acid at 298.15 K.}
\label{table:3}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\(c \cdot 10^4\) & \(A_{\text{exp}}\) & \(A_{\text{calc}}^a\) & \(A_{\text{calc}}^b\) & \(A_{\text{calc}}^c\) & \(A_{\text{calc}}^d\) \\
\hline
0.9144 & 213.60 & 213.83 & 213.97 & 213.88 & 216.76 \\
1.7040 & 173.50 & 173.26 & 173.21 & 173.33 & 173.64 \\
2.3596 & 153.84 & 153.65 & 153.59 & 156.63 & 153.36 \\
3.0523 & 139.52 & 139.14 & 139.09 & 139.13 & 138.52 \\
4.0212 & 124.64 & 124.66 & 124.63 & 124.67 & 123.82 \\
5.1647 & 112.67 & 112.50 & 112.48 & 112.53 & 111.55 \\
6.3427 & 103.04 & 103.21 & 103.21 & 103.26 & 102.22 \\
7.8627 & 93.89 & 94.17 & 94.19 & 94.23 & 93.17 \\
10.7563 & 82.18 & 82.17 & 82.20 & 82.23 & 81.19 \\
\hline
\end{tabular}
\end{table}

\begin{itemize}
\item \(\lambda^0(\text{HSucc}^-) = 47.0, K_1 = 5.69 \cdot 10^{-5}\) and \(K_2 = 5 \cdot 10^{-8}\)
\item \(\lambda^0(\text{HSucc}^-) = 31.9 [2], K_1 = 6.17 \cdot 10^{-5}\) and \(K_2 = 0.69 \cdot 10^{-6}\)
\item \(\lambda^0(\text{HSucc}^-) = 35.8 [7], K_1 = 6.05 \cdot 10^{-5}\) and \(K_2 = 0.49 \cdot 10^{-6}\)
\item \(\lambda^0(\text{HSucc}^-) = 22.9, K_1 = 6.21 \cdot 10^{-5}\) and \(K_2 = 2.31 \cdot 10^{-6}\)
\end{itemize}

\cite{10,11}.

Acknowledgement

The authors are indebted to H. Hilbinger for his kind interest and assistance throughout the course of this investigation. One of us (A.A.) is grateful to the staff of the Chemistry Department for the warm hospitality offered during his stay at the University of Regensburg.


