

An Analysis of Electrical Conductances of Aqueous Solutions of Polybasic Organic Acids. Benzenhexacarboxylic (Mellitic) Acid and Its Neutral and Acidic Salts

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A general approach is proposed to analyze electrical conductivities in aqueous solutions of polybasic organic acids. Experimental conductivities are examined in the context of dissociation and hydrolysis reactions by applying the Quint–Viallard conductivity equations and the Debye–Hückel equations for activity coefficients. The proposed numerical procedure is illustrated by the case of benzenhexacarboxylic (mellitic) acid and its neutral and acidic salts. From conductivity measurements of mellitic acid and its salts, performed in dilute aqueous solutions in the 278.15–308.15 K temperature range, the limiting conductances of mellitic anions, $\lambda^0(1/j\text{H}_{6-j}\text{Mel}^{-j}, T)$, $j = 1, 2, 3, 4, 5, 6$ are determined.

1. Introduction

The determination of dissociation constants of organic acids in aqueous solutions from measurements of electrical conductivity was initiated in works of Svante Arrhenius (1883) and Wilhelm Ostwald (1888), however, it was limited only to monobasic acids. During the next two decades, by applying the Ostwald dilution law, the apparent dissociation constants and the limited ionic conductances were evaluated for about four hundred organic acids. Evidently, the majority of them were monobasic, but some were dibasic and tribasic acids. These also were considered as monobasic acids.^{1–5} This is justified in many cases when the equilibrium constants of successive steps of dissociation differ considerably. Only a few of the organic acids with higher electrical charges were investigated in the literature. Once again, they were regarded as monobasic acids or the determined conductivities were reported without additional treatment. Because of the number of investigated polybasic acids and their neutral, usually sodium salts, is very small, it is worthwhile to mention all of them here. Pyridinetetracarboxylic acid and pyridinepentacarboxylic acid were considered by Ostwald,^{1,2} benzenetetracarboxylic (pyromellitic), benzenepentacarboxylic, and benzenhexacarboxylic (mellitic) acids by Bethmann,³ Noyes, and Lombard,⁶ Noyes and Falk,⁷ and Lorenz and Scheuermann.⁸ Electrical conductivities of dimethylpentanetetracarboxylic acid, diethylpentanetetracarboxylic acid, and hexamethylenetetracarboxylic acid were reported by Walker.⁵

First attempts to propose molecular models for dibasic acids with overlapping dissociation equilibria were those of Wegscheider,^{9–12} McCoy,¹³ and Chandler.¹⁴ However, real progress was only achieved in the late thirties, especially by Davies,¹⁵ who showed that only the simultaneous analysis of the acid conductivities, together with the acidic and neutral salt conductivities, is the correct procedure. His approach was only

partly successful due to the lack of a conductivity equation for unsymmetrical electrolytes and limited computational possibilities at that time (computer programs dealing with the Davies model were introduced only in 1970 by Spiro and Selvaratnam¹⁸). The contributions coming from the second dissociation step continue to be treated as a small correction to the measured conductances,¹⁶ or simple empirical rules were applied to the intermediate ions.^{4,17} Important progress in the analysis of conductances of organic acids was achieved by two new conductivity equations for unsymmetrical electrolytes introduced in the late seventies by Quint and Viallard^{19–22} and Lee and Wheaton.^{24–27} The molecular model, once again, was limited to dibasic acids when Lee and Wheaton, by using the Quint and Viallard equation, were able to reproduce experimental conductivities of oxalic acid.²³ More than a decade later, in the next step, the problem of tribasic acids with overlapping dissociation equilibria was solved by Apelblat and Barthel.^{28,29} Aqueous solutions of citric acid were chosen to represent model systems for weak, unsymmetrical 1:3 electrolytes. Because conductivities of citric acid and neutral citrates were only determined experimentally, the limiting conductance of the intermediate ion, $\lambda^0(1/2\text{HCit}^{2-})$, was evaluated with the help of the Pethybridge empirical rule³⁰ (this limitation was later removed³¹). The model was successfully applied to 1:2 systems, i.e., to dibasic acids and related salts (succinic acid,³² malonic acid,³³ tartaric acid,^{34–36} and oxalic acid³⁷) and to 1:3 systems (phosphoric acid and neutral and acidic phosphates³⁸).

In this work, a further generalization to polybasic acids of the previously applied model is reported. The proposed numerical procedure illustrates the behavior of aqueous solutions of benzenhexacarboxylic acid (mellitic acid). The investigated system represents a weak, unsymmetrical 1:6 electrolyte and, evidently, also all its subsystems starting from the pentabasic to the monobasic organic acid.

Mellitic acid, like other benzenecarboxylic acids, is produced by drastic oxidation of graphite, coal, wood lignin, and similar materials³⁹ and, therefore, plays an important role in geochemical and ecological problems. The literature contains very limited information about physiochemical properties of mellitic acid and its aqueous solutions.⁴⁰ The dissociation constants of the

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acid, K_i , $i = 1, 2, \dots, 6$, so important to our work, were determined several times by potentiometric titration methods.^{41–46} Surely, the attraction of mellitic acid to Maxwell and Partington^{41–43} and in earlier conductivity measurements^{3,6–8} is associated with the structure of this compound where all hydrogen atoms in benzene are substituted by carboxylic groups. Determination of K_i values by Purdie et al.⁴⁴ is linked with the thermodynamics of ionization of polycarboxylic acids. Beutler and Stebler⁴⁵ considered mellitic acid as a model substance to test the chosen titration method for other polyprotic acids. Giammar and Dziombak⁴⁶ needed the dissociation constants when studying the formation of copper complexes with the mellitic acid series. Their research was motivated by the fact that metal–organic ligands in natural waters are of interest in environmental chemistry considering the toxicity of dissolved copper or other metals in aquatic ecosystems. Unfortunately, the available sets of dissociation constants in the literature disagree, even considerably, and therefore, they will be discussed later in the context of molecular models used to represent measured conductivities of mellitic acid and its acidic salts.

2. Experimental Section

2.1. Materials. Mellitic acid (Fluka, purum, $\geq 98\%$) was used without further purification. A stock solution was prepared by weighing pure mellitic acid and demineralized distilled water, and its concentration was determined with an accuracy of 0.2% by pH titration with standard sodium hydroxide solution (1 M NaOH, Merck Titrisol 1.09956).

The neutral sodium salt of mellitic acid was prepared by complete neutralization of the mellitic acid solution, and its acidic sodium salts were obtained by partial neutralization of the acid according to the desired stoichiometry. The solution of potassium salt solution was prepared by neutralization of mellitic acid with standard potassium hydroxide solution (KOH, Kemika Zagreb Titrisol p.a.).

Demineralized water was distilled two times in a quartz bidistillation apparatus (Destamat Bi 18E, Heraeus). The final product with specific conductance $< 6 \times 10^{-7} \Omega^{-1} \cdot \text{cm}^{-1}$ was distilled into a flask, permitting storage and transfer of water into the measuring cell under an atmosphere of nitrogen.

2.2. Conductivity Measurement. Conductivities were determined by stepwise increase of electrolyte concentration in a three-electrode measuring cell, calibrated with potassium chloride solutions.^{57,58} At the beginning of the first measuring cycle, the cell was filled with a weighed amount of water. After measurement of water conductivity at all temperatures of the program, a weighed amount of a stock solution was added using a gastight syringe, and the temperature program was repeated before the next concentration was established by addition of stock solution, etc. The high-precision thermostat used in conductivity experiments has been described previously.⁵⁶ It can be set to each temperature of a temperature program with reproducibility better than 0.003 K. From the weights and the corresponding solution densities d , the molar concentrations c were determined. For dilute solutions, linear change of d with increasing salt content can be assumed, $d = d_0 + b\tilde{m}$, where d_0 is the density of pure water (Table 1) and \tilde{m} is the molonity of the electrolyte (moles of electrolyte per kilogram of solution). Temperature-independent molonities were converted to temperature-dependent molarities by use of the relationship $c(T) = d(T)\tilde{m}$. The density gradients b are reported in corresponding tables and may serve together with densities d_0 (Table 1) for the calculation of concentrations $c(T)$ at temperatures $T \neq 298.15$ K where the tables report only $c(298.15 \text{ K})$ data for the sake of

TABLE 1: Densities, Viscosities, and Dielectric Constants of Pure Water and Limiting Ionic Conductances in Water^a

T	d_0^b	$\eta \cdot 10^{3c}$	D^d	$\lambda^0(\text{Na}^+)^e$	$\lambda^0(\text{K}^+)^e$	$\lambda^0(\text{H}^+)^e$
278.15	0.99997	1.5192	85.897	30.30	46.72	250.02
283.15	0.99970	1.3069	83.945	34.88	53.03	275.55
288.15	0.99910	1.1382	82.039	39.72	59.61	300.74
293.15	0.99821	1.0020	80.176	44.81	66.44	325.52
298.15	0.99705	0.8903	78.358	50.15	73.50	349.85
303.15	0.99565	0.7975	76.581	55.72	80.76	373.66
308.15	0.99404	0.7195	74.846	61.53	88.20	396.90

^a Units: T , K; d_0 , $\text{kg} \cdot \text{dm}^{-3}$; η , Pa·s; λ^0 , $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. ^b Ref 51. ^c Ref 52. ^d Ref 53. ^e Ref 48.

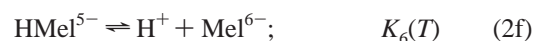
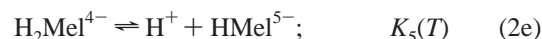
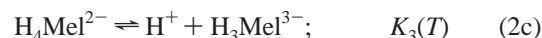
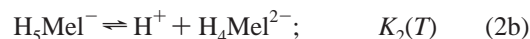
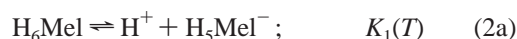
simplicity. As usual b coefficients are considered to be independent of temperature. The densities of the solutions were determined by the method of Kratky et al.⁵⁹ by use of a Paar densimeter (DMA 60 601 HT) at 298.15 K combined with a precision thermostat. The measuring procedure, including corrections and the extrapolation of the sample conductivity to infinite frequency, is described in the literature.⁵⁸ Taking into account the sources of error (calibration, titration, measurements, impurities), the specific conductivities are accurate to within 0.08%.

3. Results and Discussion

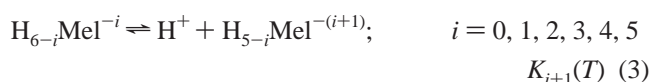
3.1 Dissociation Equilibria, Hydrolysis, and Conductivity Equations. Molar electrolyte conductivity Λ is the sum of ionic contributions given by

$$\Lambda = \frac{\kappa}{c} = \sum_{i=1}^n \frac{|z_i|c_i\lambda_i}{c} \quad (1)$$

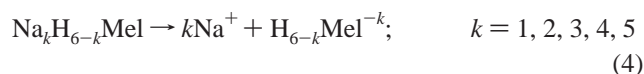
where κ is the measured specific conductance, λ_i are the ionic conductances, c_i and z_i are concentrations and charges of individual ions present in the solution, and c denotes the analytical concentration of electrolyte. As follows from eq 1, the representation of observed conductances must include the solution of the “chemical problem”, i.e., the evaluation of all concentrations of species making up the solution. In the case of dilute aqueous solutions of mellitic acid ($\text{C}_6(\text{COOH})_6 \equiv \text{H}_6\text{-Mel}$, $\text{C}_6(\text{COO})_6 \equiv \text{Mel}$), c_i values can be determined by considering the successive dissociation steps



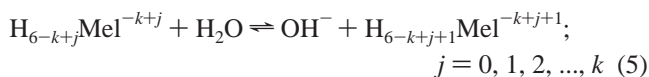
or briefly



Dissolution of the acidic sodium salts of mellitic acid ($\text{Na}_k\text{H}_{6-k}\text{Mel}$, $k = 1, 2, 3, 4$, and 5) in water is represented by



In the hydrolysis reactions, the formed $H_{6-k}Mel^{-k}$ anion reacts with water molecules to produce OH^- and mellitic ions with lower charges up to undissociated acid H_6Mel



These anions and the undissociated mellitic acid molecules undergo the dissociation process as described in eq 3 when the hydroxyl ion can be removed from eq 5 by using



where $K_w(T)$ is the ionization product of water.⁴⁸ This permits treatment of equilibrium relations of mellitic acid and its acidic salts in the same manner by taking into account that they depend on the same dissociation constants. In the general case, with the previously used notation, $k = 0$ in $Na_kH_{6-k}Mel$, means mellitic acid.

Let us express the individual concentrations of species present in the solution c_i in terms of fractions α_i . These fractions describe which part of the total analytical concentration c is represented by ions and undissociated molecules

$$\begin{aligned} [Na^+] &= kc \\ [H^+] &= c\alpha_{H^+} \\ [OH^-] &= c\alpha_{OH^-} \\ [H_6Mel] &= c\alpha_{H_6Mel} \end{aligned} \quad (7)$$

$$[H_{6-j}Mel^{-j}] = c\alpha_j \quad j = 1, 2, 3, 4, 5, 6$$

In the case of hydrogen ion, the term *fraction* becomes correct only after its α value is divided by the number of hydrogen atoms in the acid molecule.

Using eq 7, the dissociation equilibria described by eqs 2 and 6 take the form

$$K_1(T) = \frac{[H^+][H_5Mel^-]}{[H_6Mel]} F_1 = \frac{c\alpha_{H^+}\alpha_1}{(1 - \alpha_1 - \alpha_2 - \alpha_3 - \alpha_4 - \alpha_5 - \alpha_6)} F_1 \quad (8a)$$

$$K_2(T) = \frac{[H^+][H_4Mel^{2-}]}{[H_5Mel^-]} F_2 = \frac{c\alpha_{H^+}\alpha_2}{\alpha_1} F_2 \quad (8b)$$

$$K_3(T) = \frac{[H^+][H_3Mel^{3-}]}{[H_4Mel^{2-}]} F_3 = \frac{c\alpha_{H^+}\alpha_3}{\alpha_2} F_3 \quad (8c)$$

$$K_4(T) = \frac{[H^+][H_2Mel^{4-}]}{[H_3Mel^{3-}]} F_4 = \frac{c\alpha_{H^+}\alpha_4}{\alpha_3} F_4 \quad (8d)$$

$$K_5(T) = \frac{[H^+][HMel^{5-}]}{[H_2Mel^{4-}]} F_5 = \frac{c\alpha_{H^+}\alpha_5}{\alpha_4} F_5 \quad (8e)$$

$$K_6(T) = \frac{[H^+][Mel^{6-}]}{[HMel^{5-}]} F_6 = \frac{c\alpha_{H^+}\alpha_6}{\alpha_5} F_6 \quad (8f)$$

$$K_w(T) = [H^+][OH^-] f_{H^+} f_{OH^-} = c^2 \alpha_{H^+} \alpha_{OH^-} f_{H^+} f_{OH^-} \quad (8g)$$

where F_j , $j = 1, 2, 3, 4, 5$, and 6 denote the quotients of the

activity coefficients

$$F_j = \frac{f_{H^+} f_j}{f_{j-1}} \quad j = 1, 2, 3, 4, 5, 6, \quad f_0 = 1 \quad (9)$$

The activity coefficients of individual ions f_j in dilute solutions can be approximated by the Debye–Hückel equations

$$\begin{aligned} \log[f_j(T)] &= -\frac{z_j^2 A(T) \sqrt{I}}{1 + a_j B(T) \sqrt{I}} \\ A(T) &= \frac{1.8246 \times 10^6}{[D(T)T]^{3/2}}; \quad B(T) = \frac{50.29 \times 10^8}{[D(T)T]^{1/2}} \end{aligned} \quad (10)$$

where $D(T)$ is the dielectric constant of water, a_j is the ion size parameter, and I denotes the ionic strength of the solution, which is

$$I = c(k + \alpha_{H^+} + \alpha_2 + 3\alpha_3 + 6\alpha_4 + 10\alpha_5 + 15\alpha_6) \quad (11)$$

The charge balance in terms of the fractions α_i is given by

$$k + \alpha_{H^+} = \alpha_{OH^-} + \alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4 + 5\alpha_5 + 6\alpha_6 \quad (12)$$

Thus, the chemical problem consists of the simultaneous solution of the nonlinear eqs 8–12 to obtain at given temperature T the complete set of α_i as a function of analytical concentration c .

In this work, the ionic conductances λ_i in eq 1 are represented by the Quint–Viallard conductivity equations^{19–22}

$$\lambda_i = \lambda_i^0 - S_i \sqrt{I} + E_i I \ln I + J_{1i} I - J_{2i} I^{3/2} \quad (13)$$

where λ_i^0 is the limiting conductance of i th ion. The coefficients S_i , E_i , J_{1i} , J_{2i} are rather complex functions of the viscosity η and dielectric constant of pure water and the average cation–anion distances of closest approach (explicit expressions for these coefficients are given also in refs 28, 35, 38, 47). The Quint–Viallard conductivity equation is restricted to dilute solutions. When solutions with highly charged ions are considered, it may occur that, above some concentration c (ionic strength I increases considerably with c), the calculated values of $\Lambda(c)$ increase instead of decrease with c . This situation can be avoided by the use of a truncated eq 13. This limitation of the Quint–Viallard conductivity equation is, however, only important to some extent for the mellitic acid tetrasodium salt and pentasodium salt solutions.

In the case of mellitic acid, the molar conductivity Λ consists of contributions from the six pairs of unequally charged ions (cation + anion). They are: $H^+ + H_5Mel^-$, $H^+ + H_4Mel^{2-}$, $H^+ + H_3Mel^{3-}$, $H^+ + H_2Mel^{4-}$, $H^+ + HMel^{5-}$, and $H^+ + Mel^{6-}$. The contributions coming from each pair of ions, the apparent partial molar conductivities, Λ_j , are defined by

$$\Lambda_j = [\lambda(H^+) + \lambda(1/j H_{6-j}Mel^{-j})]; \quad j = 1, 2, 3, 4, 5, 6 \quad (14)$$

and, therefore,

$$\Lambda = \sum_{j=1}^6 j \alpha_j \Lambda_j \quad (15)$$

The appearance of sodium ions in solutions produces additional contributions from the six pairs of unequally charged ions, Na^+

TABLE 2: Experimental and Calculated Molar Conductivities of Mellitic Acid Solutions at 298.15 K as a Function of Concentration c^a

$10^4 \cdot c^b$	$\Lambda^{(1)}$	$\Lambda^{(2)}$	$\Lambda^{(3)}$	$\Lambda^{(4)}$	$\Lambda^{(5)}$	Λ_{exp}	Λ_{calcd}
0.64	2.67	204.82	829.09	60.84	0.26	1100.75	1097.68
1.27	7.12	301.01	682.21	28.43	0.07	1018.92	1018.84
1.56	9.28	330.04	632.33	22.39	0.05	991.50	994.10
1.98	12.49	363.06	572.15	16.77	0.03	964.08	964.51
2.61	17.27	398.42	502.28	11.87	0.02	929.41	929.86
2.89	19.36	410.38	476.85	10.42	0.01	914.40	917.03
3.24	21.92	422.88	448.94	9.00	0.01	902.53	902.74
3.71	25.26	436.42	416.69	7.54	0.01	885.90	885.92
3.93	26.83	441.88	402.89	6.98	0.01	878.91	878.59
4.63	31.61	455.50	365.53	5.61	0.01	859.15	858.24
5.37	36.44	465.69	333.25	4.58	0.00	841.07	839.96
5.49	37.15	466.94	328.83	4.45	0.00	835.80	837.38
6.23	41.77	473.73	302.53	3.74	0.00	823.11	821.78
7.28	47.89	479.74	272.30	3.01	0.00	804.39	802.95
$\sigma(\Lambda)$							1.57

^a Units: c , mol·dm⁻³; Λ , $\sigma(\Lambda)$, S·cm²·mol⁻¹. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.1802.

TABLE 3: Experimental and Calculated Molar Conductivities of Mellitic Acid Solutions as a Function of Concentration c and Temperature T^a

$10^4 \cdot c^b$	278.15 K		283.15 K		288.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.64	787.50	782.21	868.30	863.69	947.86	943.95
1.27	734.46	732.29	808.53	807.05	880.98	880.11
1.98	697.40	697.17	766.94	767.32	834.64	835.58
2.61	673.86	674.51	740.79	741.75	805.64	806.99
3.24	655.46	656.68	720.02	721.62	782.77	784.55
3.93	639.25	640.66	703.64	703.41	763.13	764.44
4.63	625.77	627.15	686.89	688.38	746.41	747.49
5.37	613.37	614.98	672.98	674.65	731.15	732.23
6.23	601.07	602.89	659.36	661.02	716.06	717.05
7.28	588.11	590.33	645.06	646.88	700.29	701.29
$\sigma(\Lambda)$		2.34		2.06		1.76

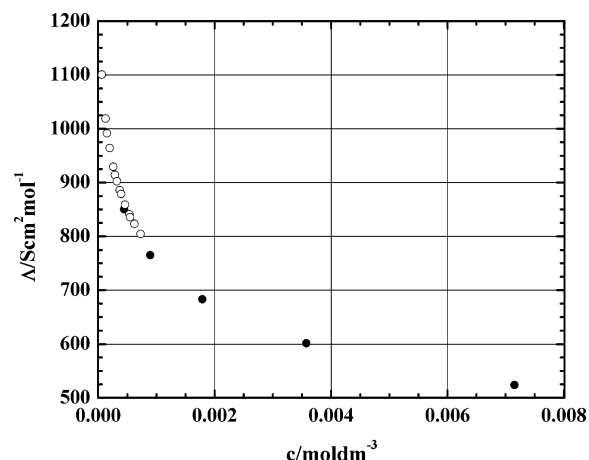
$10^4 \cdot c^b$	293.15 K		303.15 K		308.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.64	1025.58	1022.02	1173.57	1170.63	1243.78	1240.40
1.27	951.57	950.74	1084.13	1083.92	1146.95	1145.76
1.98	900.70	901.40	1024.85	1024.64	1083.21	1081.59
2.61	868.79	869.74	987.65	987.01	1043.18	1041.11
3.24	843.97	844.94	958.48	957.68	1012.06	1009.58
3.93	822.13	822.81	933.25	931.57	985.07	981.60
4.63	804.02	804.13	911.81	909.59	962.10	958.09
5.37	787.30	787.36	892.50	889.84	941.34	937.01
6.23	770.08	770.67	873.14	870.30	920.77	916.09
7.28	753.43	753.35	852.97	849.99	899.19	894.46
$\sigma(\Lambda)$		1.36		2.15		3.61

^a Units: c , mol·dm⁻³; Λ , $\sigma(\Lambda)$, S·cm²·mol⁻¹. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.1802

+ H₃MeI⁻, Na⁺ + H₄MeI²⁻, Na⁺ + H₃MeI³⁻, Na⁺ + H₂MeI⁴⁻, Na⁺ + HMeI⁵⁻, and Na⁺ + MeI⁶⁻ (the contribution from the OH⁻ ion is neglected because its fraction always is extremely small). To yield equations of pairs, the mellitic ions should be “distributed” between the hydrogen and sodium ions, and the corresponding pairs of ions are denoted with the superscripts (1) and (2)

$$\Lambda = x \sum_{j=1}^6 j \alpha_j \Lambda_j^{(1)} + (1-x) \sum_{j=1}^6 j \alpha_j \Lambda_j^{(2)} \quad (16)$$

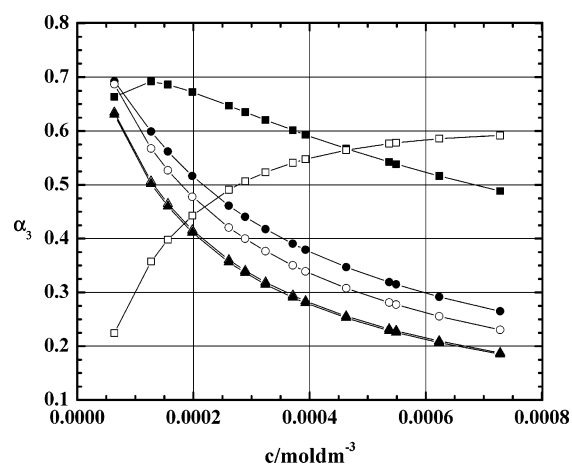
where the partition fraction x results from the charge balance

**Figure 1.** Molar conductivity Λ of mellitic acid at 298.15 K; ●, Bethman, ref 3; ○, this work.**TABLE 4: Dissociation Constants of Mellitic Acid at 298.15 K and Their Temperature Dependence^d**

	ref 43	ref 46	ref 44 ^b	ref 44 ^c	ref 45	this work
K_1	0.04	0.331	0.209	0.062	0.231	0.209
$K_2 10^3$	6.4	17.0	6.17	6.46	21.9	6.17
$K_3 10^4$	4.9	13.8	3.02	2.95	56.2	4.00
$K_4 10^5$	1.65	6.17	0.813	0.813	47.9	0.813
$K_5 10^6$	1.28	5.0	0.479	0.490	8.51	0.479
$K_6 10^8$	11	61.7	3.24	3.55	933	3.24

T/K^d	K_1	$K_2 10^3$	$K_3 10^4$	$K_4 10^5$	$K_5 10^6$	$K_6 10^8$
278.15	0.206	9.73	5.15	0.866	0.452	3.11
283.15	0.211	8.59	4.89	0.863	0.464	3.19
288.15	0.213	7.64	4.61	0.853	0.473	3.24
293.15	0.212	6.84	4.31	0.836	0.478	3.25
298.15	0.209	6.17	4.00	0.813	0.479	3.24
303.15	0.204	5.59	3.69	0.785	0.478	3.20
308.15	0.196	5.10	3.38	0.753	0.474	3.14

^a Units: K , mol·dm⁻³. ^b Titration with the Harned cell. ^c Titration with the glass calomel electrode. ^d Based on the data from ref 44.

**Figure 2.** Fraction of the H₃MeI³⁻ anions in mellitic acid as calculated using different sets of dissociation constants; ●, ref 43; ▲, ref 44; □, ref 45; ○, this work.

of eq 12, i.e.

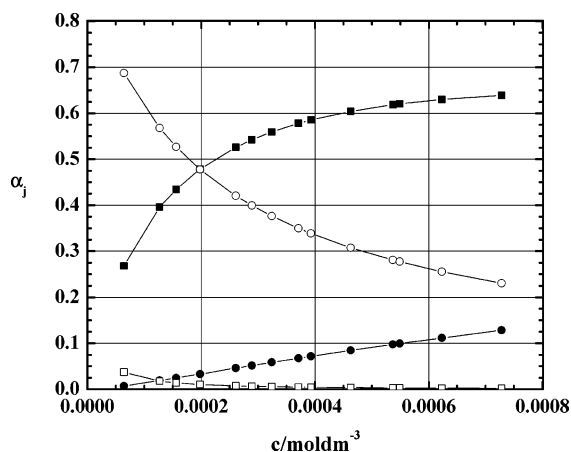
$$x = \frac{\alpha_{H^+}}{\sum_{j=1}^6 j \alpha_j}; \quad 1 - x = \frac{k}{\sum_{j=1}^6 j \alpha_j} \quad (17)$$

and k is the number of sodium atoms in mellitic salts.

TABLE 5: Fractions α_j as a Function of Mellitic Acid Concentration c at 298.15 K^a

$10^4 \cdot c^b$	$\alpha_{H/6}$	α_1	α_2	α_3	α_4
0.64	0.4592	0.0071	0.2683	0.6871	0.0373
1.27	0.4307	0.0189	0.3957	0.5678	0.0175
1.56	0.4217	0.0247	0.4344	0.5271	0.0138
1.98	0.4109	0.0332	0.4785	0.4778	0.0104
2.61	0.3982	0.0460	0.5261	0.4204	0.0074
2.89	0.3934	0.0516	0.5423	0.3995	0.0065
3.24	0.3881	0.0584	0.5593	0.3765	0.0056
3.71	0.3819	0.0674	0.5778	0.3499	0.0047
3.93	0.3792	0.0716	0.5853	0.3385	0.0043
4.63	0.3716	0.0844	0.6041	0.3076	0.0035
5.37	0.3647	0.0974	0.6184	0.2809	0.0029
5.49	0.3637	0.0993	0.6202	0.2772	0.0028
6.23	0.3578	0.1117	0.6299	0.2554	0.0023
7.28	0.3507	0.1282	0.6388	0.2303	0.0019

^a Units: c , mol·dm⁻³. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.1802.

**Figure 3.** Fractions α_1 , α_2 , α_3 , and α_4 in mellitic acid solutions at 298.15 K; ●, α_1 ; ■, α_2 ; ○, α_3 ; □, α_4 .

The partition fraction x is unity when $k = 0$, and as expected, eq 16 reduces to eq 15 for aqueous solutions of mellitic acid. For neutral salts, $k = 6$, and evidently, x becomes zero, but for the investigated cases of hexasodium or hexapotassium salts of mellitic acid, α_6 is practically unity (i.e., these salts are strong 1:6 electrolytes), and therefore, the second sum in eq 16 reduces to one term only, $\Lambda = 6\Lambda_6$. Thus, the neutral salts can be represented by the Onsager conductivity equation.⁴⁸

To sum up: the model for description of the experimental conductivities in aqueous solutions of hexabasic organic acids requires the solution of the chemical problem (evaluation of all α_i) and the use of 12 Quint–Viallard conductivity equations (if conductivities were determined only for the acid) or 24 equations (when conductivities of acidic salts are also measured). In practice, the actual number of contributing conductivity equations is evidently smaller, depending on the values of α_i .

In principle, the determination of the acid and neutral salt conductivities suffices to yield the limiting ionic conductances λ_j^0 and dissociation constants K_j . The measured conductivities of polybasic acids and their acidic salts should be consistent because the acidic salt conductivities can be calculated by using the same values of λ_j^0 and K_j . Thus, the comparison between the calculated and determined conductivities of acidic salts indicates the reliability of the applied model.

3.2. Optimization Procedure in Data Analysis. In the case of mellitic acid and its salts, the model representation of the experimental conductivity–concentration data set (Λ , c) can formally be expressed in the form: $\Lambda = f[c; K_j, \lambda^0(1/j$

TABLE 6: Coefficients of the Quint–Viallard Conductivity Equations for Pairs of Ions with Hydrogen Cation at Different Temperatures T^a

j	Λ_j^0	S_j	E_j	J_{1j}	J_{2j}
278.15 K					
1	267.61	94.58	47.75	628	1539
2	271.05	142.43	111.48	973	1391
3	283.83	185.56	106.92	948	1539
4	287.37	219.18	-54.24	213.0	-2163
5	294.20	252.64	-414.8	-1361	-6683
6	305.09	288.52			
283.15 K					
1	296.00	107.21	53.13	705	1726
2	300.00	161.68	123.07	1088	1553
3	314.85	211.23	112.48	1040	1727
4	318.97	249.93	-82.20	159.0	-2637
5	326.91	288.61	-510.9	-1709	-7963
6	339.13	329.86			
288.15 K					
1	324.22	120.32	58.60	785	1918
2	328.81	181.69	134.69	1206	1719
3	345.87	238.02	116.99	1131	1921
4	350.59	282.09	-114.57	89.0	-3164
5	359.71	326.31	-617.7	-2100	-9368
6	373.61	373.54			
293.15 K					
1	352.19	133.89	64.16	867	2116
2	357.40	202.43	146.35	1327	1887
3	376.78	265.88	120.48	1221	2121
4	382.15	315.60	-151.28	3.0	-3746
5	392.51	365.69	-734.9	-2532	-10899
6	408.08	419.15			
298.15 K					
1	379.87	147.89	69.83	951	2318
2	385.73	223.88	158.05	1450	2058
3	407.54	294.80	122.94	1309	2326
4	413.59	350.43	-192.40	-99.60	-4384
5	425.25	406.70	-862.8	-3009	-12560
6	442.49	466.68			
303.15 K					
1	407.17	162.32	75.60	1037	2525
2	413.72	246.02	169.81	1576	2232
3	438.06	324.73	124.37	1396	2537
4	444.82	386.56	-238.01	-219.0	-5081
5	457.83	449.29	-1001.5	-3530	-14357
6	476.62	515.95			
308.15 K					
1	434.04	177.15	81.46	1125	2736
2	441.30	268.80	181.59	1704	2408
3	468.28	355.65	124.74	1480	2754
4	475.77	423.92	-288.18	-355.0	-5837
5	490.19	493.44	-1151.2	-4097	-16292
6	510.62	567.12			

^a Units: Λ_j^0 , $S_j \cdot c^{1/2}$, $E_j \cdot c$, $J_{1j} \cdot c$, $J_{2j} \cdot c^{3/2}$, S·cm²·mol⁻¹.

$H_{6-j}Mel^{-j}$), $a(H_{6-j}Mel^{-j})$, $j = 1, 2, 3, 4, 5, 6$, $a(H^+)$, $a(Na^+)$, $a(K^+)$], assuming that, at given temperature T , the physical properties of pure water and the limiting ionic conductances $\lambda^0(H^+)$, $\lambda^0(Na^+)$, and $\lambda^0(K^+)$ are known from the literature (Table 1). The distances of closest approach in the Quint–Viallard conductivity equations were taken as the average value of the ion size parameters in the pairs of ions. Because the ion size parameters, especially for organic anions, are usually unknown, they were appropriately chosen in accordance with values suggested by Kielland⁴⁹ and Harris:⁵⁰ $a(H^+) = 9.0$ Å, $a(H^+) = 9.0$ Å, $a(OH^-) = 3.5$ Å, $a(K^+) = 3.5$ Å, $a(H_6Mel) = 6.0$ Å, $a(H_5Mel^-) = 5.8$ Å, $a(H_4Mel^{2-}) = 5.6$ Å, $a(H_3Mel^{3-}) = 5.4$ Å, $a(H_2Mel^{4-}) = 5.2$ Å, $a(HMel^{5-}) = 5.0$ Å, and $a(Mel^{6-}) = 4.8$ Å. All ion size parameters were assumed to be independent of temperature. Fortunately, the Quint–Viallard

TABLE 7: Experimental and Calculated Molar Conductivities of Mellitic Acid Monosodium Salt Solutions at 298.15 K as a Function of Concentration c^a

$10^4 \cdot c^b$	$\Lambda^{(1)}$	$\Lambda^{(2)}$	$\Lambda^{(3)}$	$\Lambda^{(4)}$	$\Lambda^{(5)}$	Λ_{exp}	Λ_{calcd}
0.59	0.83	102.22	676.98	80.11	0.56	873.56	860.69
1.23	2.43	161.46	583.90	38.31	0.16	791.73	786.26
1.79	3.98	194.01	521.61	25.69	0.08	747.99	745.36
2.61	6.21	224.99	455.05	17.05	0.05	704.26	703.34
3.43	8.37	245.48	405.83	12.54	0.03	672.02	672.25
4.25	10.45	259.88	367.40	9.78	0.01	646.73	647.53
5.07	12.38	270.02	337.22	7.99	0.01	626.74	627.63
5.78	14.00	276.70	315.11	6.85	0.01	611.75	612.68
6.98	16.56	284.70	284.70	5.48	0.00	590.36	591.43
8.48	19.49	290.89	255.00	4.34	0.00	568.89	569.72
10.30	22.70	294.91	227.44	3.44	0.00	547.56	548.49
$\sigma(\Lambda)$							4.56

^a Units: c , mol·dm⁻³; Λ , $\sigma(\Lambda)$, S·cm²·mol⁻¹. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.2139.

TABLE 8: Experimental and Calculated Molar Conductivities of Mellitic Acid Monosodium Salt Solutions as a Function of Concentration c and Temperature T^a

$10^4 \cdot c^b$	278.15 K		283.15 K		288.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.59	613.71	601.56	679.99	667.93	745.80	733.55
1.23	561.11	554.35	620.47	614.72	678.80	673.47
1.79	532.45	528.07	588.02	585.13	642.71	640.20
2.61	503.21	500.73	555.22	554.45	606.25	605.82
3.43	481.40	480.30	530.78	531.49	579.17	580.17
4.25	464.24	463.89	511.64	513.12	557.97	559.66
5.07	450.53	450.63	496.32	498.27	541.08	543.10
5.78	440.31	440.63	484.93	487.10	528.47	530.65
6.98	425.58	426.36	468.54	471.13	510.42	512.90
8.48	410.56	411.77	451.85	454.80	492.30	494.76
10.30	396.03	397.38	435.56	438.71	474.13	476.89
$\sigma(\Lambda)$		4.73		4.73		4.66

$10^4 \cdot c^b$	293.15 K		303.15 K		308.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.59	810.41	797.81	934.49	917.31	994.42	982.78
1.23	736.18	730.72	845.67	838.66	897.66	893.38
1.79	696.15	693.65	798.11	795.51	846.44	844.41
2.61	656.01	655.48	750.67	751.13	795.32	794.67
3.43	626.31	627.13	716.02	718.29	758.18	758.12
4.25	603.18	604.51	688.77	692.15	728.99	729.25
5.07	584.70	586.28	667.22	671.12	705.93	706.10
5.78	570.92	572.56	651.04	655.33	688.48	688.73
6.98	551.13	553.04	628.20	632.87	663.84	664.13
8.48	531.35	533.11	605.05	609.97	639.46	639.09
10.30	511.58	513.46	582.14	587.39	615.01	614.48
$\sigma(\Lambda)$		4.62		6.89		3.99

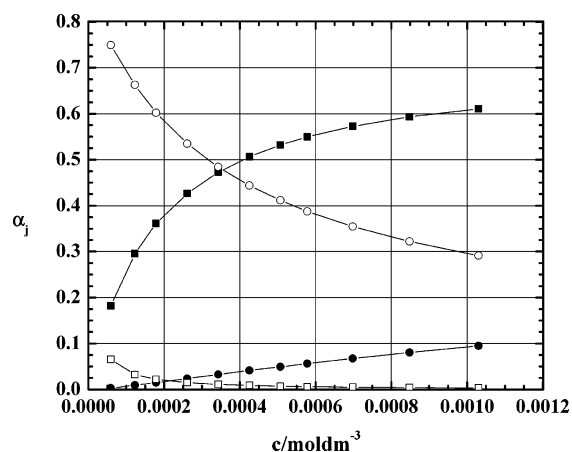
^a Units: c , mol·dm⁻³; Λ , $\sigma(\Lambda)$, S·cm²·mol⁻¹. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.2139.

conductivity equation weakly depends on the distances of closest approach. After preselection of the ion sizes and the knowledge of some of the limiting ion conductances, the number of adjustable parameters in the optimization problem is reduced from 21 to 11, $\Lambda = f[c; K_j, j = 1, 2, 3, 4, 5, 6, \lambda^0(1/j \text{ H}_{6-j}\text{Mel}^-)]$, $j = 1, 2, 3, 4, 5$. This is still too much considering the reasonable number of experimental (Λ , c) points that can be determined in the concentration region covered by the Quint–Viallard conductivity equation. In the case of mellitic acid, we are in a favorable situation because the dissociation constants are known from potentiometric measurements.^{41–46} Thus, five limiting conductances $\lambda^0(1/j \text{ H}_{6-j}\text{Mel}^-)$ remain to be evaluated from six experimental sets of conductivities of mellitic acid and its acidic salts. It is worthwhile to mention that independently derived K_j values, from potentiometric, spectroscopic, or other methods, not only reduce the number of adjustable parameters,

TABLE 9: Fractions α_j and x as a Function of Mellitic Acid Monosodium Salt Concentration c at 298.15 K^a

$10^4 \cdot c^b$	$\alpha_{\text{H}/6}$	α_1	α_2	α_3	α_4	α_5	x
0.59	0.3130	0.0030	0.1822	0.7492	0.0653	0.0004	0.6603
1.23	0.2864	0.0091	0.2956	0.6632	0.0320	0.0001	0.6397
1.79	0.2718	0.0150	0.3610	0.6021	0.0218	0.0001	0.6273
2.61	0.2567	0.0239	0.4265	0.5348	0.0147	0.0000	0.6136
3.43	0.2455	0.0326	0.4723	0.4840	0.0110	0.0000	0.6028
4.25	0.2366	0.0412	0.5064	0.4436	0.0087	0.0000	0.5937
5.07	0.2294	0.0493	0.5319	0.4115	0.0072	0.0000	0.5861
5.78	0.2239	0.0562	0.5497	0.3877	0.0062	0.0000	0.5802
6.98	0.2162	0.0673	0.5728	0.3546	0.0050	0.0000	0.5714
8.48	0.2082	0.0802	0.5934	0.3220	0.0040	0.0000	0.5620
10.30	0.2003	0.0947	0.6103	0.2912	0.0032	0.0000	0.5524

^a Units: c , mol·dm⁻³. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.2139.

**Figure 4.** Fractions α_1 , α_2 , α_3 , and α_4 in mellitic acid monosodium salt solutions at 298.15 K; \bullet , α_1 ; \blacksquare , α_2 ; \circ , α_3 ; \square , α_4 .

but they also support the validity of the dissociation constants determined from conductivity experiments.

In the optimization process, the ionic limiting conductances λ_j^0 were determined to give the “best fit” of the mellitic acid experimental conductivities. However, it was impossible to obtain accurately those values of the ionic limiting conductances that are associated with species having negligible α_j in the mellitic acid solutions. Therefore, the combined optimization procedure was applied. The mellitic acid conductivities and the acidic salt conductivities, which have maximal values of α_j , were analyzed together to yield λ_j^0 values.

In this work, the solution of the “chemical” problem, consisting of the evaluation of all α_j , f_j , and I for each concentration c , was performed by the Newton–Raphson method.⁶⁰ The set of simultaneous nonlinear eqs 8–12 was solved by using the POLYMATH program, which is a user-friendly interactive numerical analysis package developed to solve linear, nonlinear, algebraic, and differential equations in chemical engineering problems. Physically consistent and stable results were easily obtained, and the transfer from one salt to another salt is simple. However, when many experimental points are examined, the program is rather tiresome because it only processes one concentration c at a time. The results obtained by the Newton–Raphson method using the POLYMATH program were compared to those from the much more sophisticated MATLAB program, and the comparison was very satisfactory. The POLYMATH program was preferred because the MATLAB program is less user-friendly and requires separate adaptation for each salt.

Values of α_j and I determined for each concentration c , were introduced into the computer program with 24 Quint–Viallard

TABLE 10: Coefficients of the Quint–Viallard Conductivity Equations for Pairs of Ions with Sodium Cation at Different Temperatures T^a

j	Λ_j^0	S_j	E_j	J_{1j}	J_{2j}
278.15 K					
1	43.66	44.83	−0.57	87.74	125.22
2	47.10	71.22	61.29	−25.68	16.34
3	59.88	103.70	−102.68	−362.69	−776.6
4	63.42	130.94	−342.87	−1226	−2517
5	70.25	161.97	−772.0	−2710	−5497
6	81.14	200.12			
283.15 K					
1	55.33	53.33	0.39	109.86	156.24
2	59.33	84.52	74.25	−15.79	35.22
3	74.18	122.42	−115.50	−408.85	−898.8
4	78.30	154.06	−396.35	−1421.0	−2944
5	86.24	189.90	−900.5	−3168	−6451
6	98.46	233.04			
288.15 K					
1	63.20	61.40	0.45	126.8	180.47
2	67.79	97.35	85.75	−18.7	38.84
3	84.85	141.11	−133.68	−474.4	−1048
4	89.57	177.61	−459.3	−1650	−3429
5	98.69	218.99	−1043.8	−3679	−7510
6	112.59	268.68			
293.15 K					
1	71.48	69.97	0.55	144.95	206.46
2	76.69	110.98	98.05	−21.68	42.46
3	96.07	160.96	−153.06	−544.7	−1209.9
4	101.44	202.65	−526.7	−1896	−3954
5	111.80	249.93	−1197.4	−4229	−8657
6	127.37	306.45			
298.15 K					
1	80.17	79.04	0.67	164.36	234.29
2	86.03	125.40	111.17	−24.63	46.11
3	107.84	181.98	−173.60	−619.6	−1385
4	113.89	229.15	−598.6	−2160	−4520
5	125.55	282.70	−1361.5	−4819	−9893
6	142.79	346.34			
303.15 K					
1	89.23	88.58	0.83	185.01	263.93
2	95.78	140.59	125.12	−27.53	49.71
3	120.12	204.14	−195.30	−699.1	−1572
4	126.88	257.10	−675.0	−2441	−5128
5	139.89	317.25	−1536.2	−5450	−11222
6	158.68	388.14			
303.15 K					
1	98.67	98.60	1.03	206.97	295.46
2	105.93	156.55	139.88	−30.35	53.27
3	132.91	227.44	−218.12	−783.3	−1774
4	140.40	286.47	−755.9	−2741	−5780
5	154.82	353.57	−1721.6	−6122	−12645
6	175.25	432.13			

^a Units: Λ_j^0 , $S_j \cdot c^{1/2}$, $E_j \cdot c$, $J_{1j} \cdot c$, $J_{2j} \cdot c^{3/2}$, $S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$.

conductivity equations. In the optimization process, the organic anion limiting conductances $\lambda^0(1/j\text{H}_{6-j}\text{Mel}^-)$, $j = 1, 2, 3, 4$, and 5, were determined, and the mean value of deviation of the measured and calculated conductivities Λ was evaluated from

$$\sigma(\Lambda) = \sqrt{\frac{\sum_{i=1}^N (\Lambda_{i,\text{exp}} - \Lambda_{i,\text{calcd}})^2}{N-1}} \quad (18)$$

where N is number of experimental points.

3.3. Mellitic Acid Conductivities. The results of conductivity measurements on aqueous solutions of mellitic acid are presented in Table 2 for 298.15 K and in Table 3 for the other

TABLE 11: Experimental and Calculated Molar Conductivities of Mellitic Acid Disodium Salt Solutions at 298.15 K as a Function of Concentration c^a

$10^4 \cdot c^b$	Λ_{calcd}^c	Λ_{calcd}^d	Λ_{exp}
0.56	623.61	612.37	600.04
1.21	559.88	543.51	536.61
1.56	539.13	521.37	508.70
1.84	524.85	506.28	500.63
2.67	493.31	473.34	468.46
2.88	486.80	466.63	459.30
3.65	466.30	445.65	440.61
3.68	465.46	444.85	442.00
4.92	440.45	419.69	414.91
5.43	431.89	411.14	409.60
6.44	417.31	396.72	392.16
8.40	394.82	374.75	370.20
11.40	369.86	350.67	346.29
15.40	345.52	327.45	323.10
19.60	327.12	310.03	306.03

^a Units: c , $\text{mol} \cdot \text{dm}^{-3}$; Λ , $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. ^b c are molalities at 298.15 K; ^b, coefficient in the density equation is 0.2356. ^c Calculated using the Purdie et al. dissociation constants.⁴⁴ ^d Calculated with dissociation constants used in this work (see text).

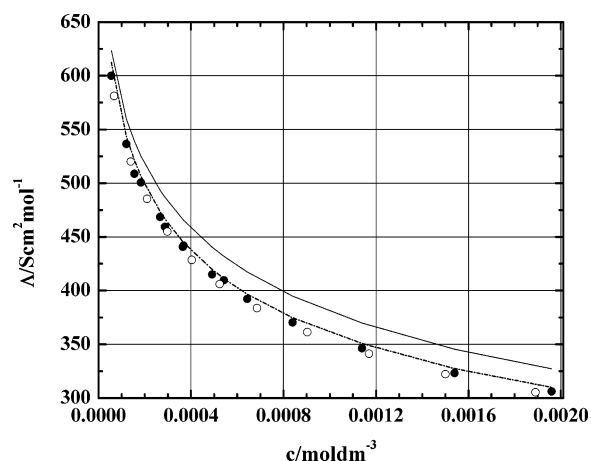


Figure 5. Experimental and calculated conductivities of mellitic acid disodium salt solutions at 298.15 K; ●, first set of data; ○, second set of data; (—) calculated using dissociation constants from ref 44; (---) calculated with dissociation constants used in this work (see text).

temperatures of the program. Mellitic acid conductivities at 298.15 K were already measured in 1890 by Bethmann³ (old values of conductivities should be multiplied by the factor 1.066⁵⁴) and are presented together with our results in Figure 1, showing that Bethmann's historical conductivities covering concentrated solutions are in reasonable agreement with our measurements for very dilute solutions required for reliable data analysis.

A detailed analysis of the data for mellitic acid and its salts is given only at 298.15 K, for other temperatures, only the final results are presented. For the calculation of temperature-dependent concentrations $c(T)$ from $c(298.15 \text{ K})$, see Section 2.2.

There are five different sets of dissociation constants at 298.15 K in the literature,^{43–46} whereas temperature dependence of $K_j(T)$ is given only by Purdie et al.⁴⁴ (Table 4). As can be seen, the values of Maxwell and Partington⁴³ and Purdie et al.⁴⁴ are reasonably close, whereas other sets of K_j , the Giammar and Dziombak⁴⁶ and especially the Beutler and Stebler⁴⁵ values, differ considerably. The dissociation constants derived by data modeling are strongly influenced, not only by actually present species, but also by those with negligible concentrations. Therefore, such large discrepancies are attributed to different

TABLE 12: Experimental Molar Conductivities of Mellitic Acid Disodium Salt Solutions as a Function of Concentration c and Temperature T^a

$10^4 \cdot c^{b,c}$	Λ_{exp}						
	$T = 278.15 \text{ K}$	$T = 283.15 \text{ K}$	$T = 288.15 \text{ K}$	$T = 293.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 303.15 \text{ K}$	$T = 308.15 \text{ K}$
0.56	404.48	453.07	502.07	551.07	600.04	648.52	696.37
1.21	364.04	407.18	450.48	493.61	536.61	578.97	620.62
1.56					508.70		
1.84	341.11	381.16	421.11	461.04	500.63	539.73	578.01
2.67	319.98	357.24	394.54	431.53	468.46	504.61	539.36
2.88					459.30		
3.65	301.68	336.62	371.50	406.21	440.61	474.45	507.80
3.68					442.00		
4.92	284.49	317.31	350.11	382.67	414.91	446.70	477.95
5.43					409.60		
6.44	268.92	300.00	330.92	361.69	392.16	422.12	451.67
8.40	254.07	283.19	312.47	341.49	370.20	398.54	426.47
11.40	237.49	264.79	292.14	319.34	346.29	372.89	399.16
15.40	221.33	246.82	272.38	297.87	323.10	348.11	372.83
19.60	209.30	233.52	257.76	281.90	306.03	329.85	353.52

$10^4 \cdot c^{b,d}$	Λ_{exp}						
	$T = 278.15 \text{ K}$	$T = 283.15 \text{ K}$	$T = 288.15 \text{ K}$	$T = 293.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 303.15 \text{ K}$	$T = 308.15 \text{ K}$
0.68	392.09	439.27	486.56	534.04	581.27	627.98	673.47
1.40	352.89	394.80	436.68	478.62	520.15	561.24	601.38
2.10	330.38	369.16	408.10	446.83	485.31	523.21	560.32
2.98	310.60	346.73	383.00	419.08	454.86	490.17	524.71
4.04	293.08	327.20	361.03	395.07	428.59	461.78	494.28
5.25	277.98	310.12	342.24	374.39	406.07	437.40	468.17
6.86	262.58	292.93	323.31	353.61	383.62	413.08	442.19
9.03	247.26	275.84	304.47	333.01	361.27	389.15	416.65
11.67	231.27	260.39	287.45	314.54	341.21	367.62	393.72
15.05	220.10	245.68	271.26	296.82	322.23	347.38	372.23
18.91	208.18	232.46	256.82	281.11	305.27	329.26	353.02

^a Units: c , $\text{mol} \cdot \text{dm}^{-3}$; Λ , $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. ^b c are molalities at 298.15 K; ^b, coefficient in the density equation is 0.2356. ^{c,d} Different sets of conductivity experiments (see text).

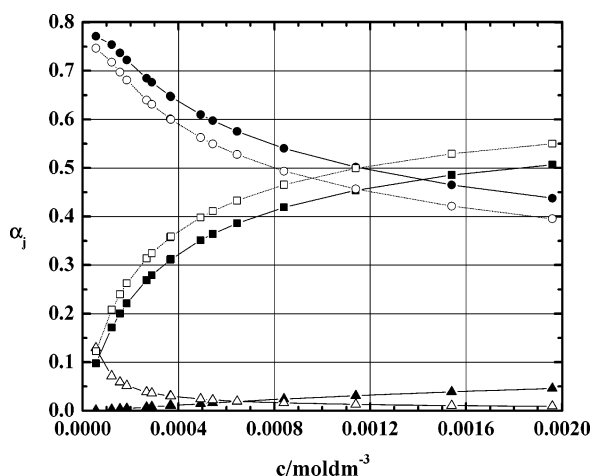


Figure 6. Fractions α_1 , α_2 , α_3 , and α_4 in mellitic acid disodium salt solutions at 298.15 K; \blacktriangle , α_1 ; \blacksquare , α_2 ; \square , α_2 ref 44; \bullet , α_3 ; \circ , ref 44; \triangle , α_4 , (see text).

ionic strengths of solutions during titration experiments (Maxwell and Partington⁴³ $I \sim 0.03 \text{ M}$, Purdie et al.⁴⁴ $I \sim 0.01 \text{ M}$, Giammar and Dziombak⁴⁶ $I \sim 0.1 \text{ M}$, and Beutler and Stebler⁴⁵ $I \sim 3 \text{ M}$). Beutler and Stebler noted that solutions of high ionic strength favor the formation of charged species, and mellitic acid is a considerably stronger acid than concluded by Maxwell and Partington. The effect of different sets of K_j values is illustrated in Figure 2, where α_3 (it represents the largest contribution to the conductivity of mellitic acid) is plotted as a function of c . In the optimization process with various sets of K_j , it was found that the Purdie et al. set is the most suitable one, but it should be slightly adjusted by replacing $K_3 = 3.02$

TABLE 13: Experimental and Calculated Molar Conductivities of Mellitic Acid Trisodium Salt Solutions at 298.15 K as a Function of Concentration c^a

$10^4 \cdot c^{b,c}$	$\Lambda^{(1)}$	$\Lambda^{(2)}$	$\Lambda^{(3)}$	$\Lambda^{(4)}$	$\Lambda^{(5)}$	$\Lambda^{(6)}$	Λ_{exp}	Λ_{calcd}
0.77	0.01	6.66	253.12	161.00	6.21	0.02	430.28	427.03
1.50	0.02	8.95	254.10	122.44	3.66	0.01	391.92	389.18
1.55	0.02	9.06	253.95	120.90	3.58	0.01	393.80	387.52
2.56	0.03	10.75	249.77	100.54	2.57	0.00	367.71	363.66
2.87	0.03	11.12	248.39	96.65	2.39	0.00	364.70	358.58
3.67	0.04	11.90	244.93	89.20	2.09	0.00	345.40	348.15
3.92	0.04	12.10	243.88	87.38	2.02	0.00	341.49	345.42
5.40	0.04	12.90	238.81	78.97	1.75	0.00	339.30	332.47
5.49	0.05	12.94	238.53	78.61	1.73	0.00	329.30	331.86
7.22	0.05	13.58	233.27	72.89	1.56	0.00	319.30	321.34
9.25	0.06	14.06	228.05	68.42	1.43	0.00	310.66	312.03
11.40	0.06	14.42	223.20	64.97	1.35	0.00	303.30	304.01
14.10	0.07	14.71	217.90	61.79	1.28	0.00	296.11	295.75
18.60	0.08	14.98	210.25	57.86	1.19	0.00	287.30	284.36
$\sigma(\Lambda)$								3.90

^a Units: c , $\text{mol} \cdot \text{dm}^{-3}$; Λ , $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. ^b c are molalities at 298.15 K; ^b, coefficient in the density equation is 0.2711.

$\times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ by $K_3 = 4.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. The temperature dependence of dissociation constants is similar to that given by Purdie et al.⁴⁴ (Table 4).

From the solution of the “chemical problem” (Table 5 and Figure 3) it is clear that mellitic acid is actually a *tetrabasic* organic acid, and in the investigated concentration region, the acid is 36–47% ionized (comes from the $\alpha_{\text{H}^+}/6$ values). The limiting anion conductances $\lambda^0(1/4 \text{ H}_2\text{Mel}^{4-})$, $\lambda^0(1/5 \text{ HMel}^{5-})$, and $\lambda^0(1/6 \text{ Mel}^{6-})$ cannot be determined from the mellitic acid conductivities. They should be derived from its salts. Because of a small contribution, $\lambda^0(\text{H}_5\text{Mel}^-)$ values are not particularly accurate. This means that, when conductivity experiments are

TABLE 14: Experimental and Calculated Molar Conductivities of Mellitic Acid Trisodium Salt Solutions as a Function of Concentration c and Temperature T^a

$10^4 \cdot c^b$	278.15 K		283.15 K		288.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.77	268.95	265.21	307.69	305.21	347.57	344.72
1.50	243.09	238.88	278.57	276.71	315.40	313.06
2.56	220.49	221.08	253.05	257.40	286.87	291.63
3.92	209.39	208.47	240.59	243.71	273.11	276.38
5.49	201.25	199.32	231.28	233.75	262.78	265.26
7.22	194.53	192.23	223.80	226.00	254.43	256.60
9.25	188.82	186.01	217.37	219.17	247.26	248.96
11.40	183.91	180.63	211.90	213.24	241.10	242.29
14.10	179.26	175.23	206.56	207.31	235.26	235.58
18.60	173.52	167.91	200.04	199.32	227.88	226.58
$\sigma(\Lambda)$		3.50		2.48		2.67

$10^4 \cdot c^b$	293.15 K		303.15 K		308.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.77	388.49	386.39	471.84	469.02	509.81	511.25
1.50	353.21	351.14	430.76	428.21	470.06	467.75
2.56	321.83	327.56	394.29	400.51	430.93	438.17
3.92	306.29	310.63	376.97	380.76	413.06	417.11
5.49	295.50	298.29	363.84	366.33	398.65	401.69
7.22	286.35	288.70	353.13	354.99	386.55	389.54
9.25	278.43	280.23	343.24	344.90	377.01	378.66
11.40	271.68	272.71	335.90	336.14	369.42	369.19
14.10	265.11	265.23	328.08	327.12	361.04	359.42
18.60	256.95	255.10	318.47	314.65	350.68	346.00
$\sigma(\Lambda)$		3.01		3.26		3.68

^a Units: c , $\text{mol} \cdot \text{dm}^{-3}$; Λ , $\sigma(\Lambda)$, $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. ^b c are molalities at 298.15 K; ^b, coefficient in the density equation is 0.2711.

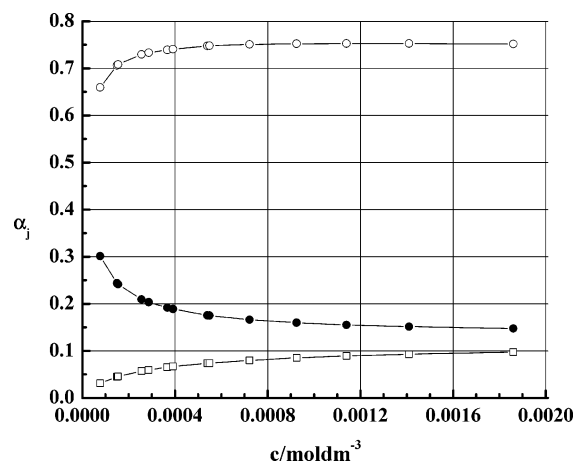
TABLE 15: Fractions α_j and x as a Function of Mellitic Acid Trisodium Salt Concentration c at 298.15 K^a

$10^4 \cdot c^b$	$\alpha_{\text{H}/6}$	α_2	α_3	α_4	α_5	x
0.77	0.0479	0.0309	0.6593	0.3011	0.0085	0.0873
1.50	0.0348	0.0448	0.7062	0.2435	0.0053	0.0651
1.55	0.0343	0.0455	0.7080	0.2411	0.0052	0.0641
2.56	0.0266	0.0569	0.7295	0.2094	0.0039	0.0505
2.87	0.0251	0.0596	0.7332	0.2033	0.0036	0.0477
3.67	0.0220	0.0653	0.7395	0.1916	0.0032	0.0421
3.92	0.0212	0.0669	0.7408	0.1887	0.0031	0.0407
5.40	0.0177	0.0737	0.7476	0.1754	0.0028	0.0342
5.49	0.0176	0.0740	0.7479	0.1749	0.0027	0.0339
7.22	0.0150	0.0798	0.7508	0.1662	0.0025	0.0292
9.25	0.0131	0.0848	0.7523	0.1598	0.0024	0.0254
11.40	0.0115	0.0889	0.7529	0.1552	0.0023	0.0225
14.10	0.0102	0.0927	0.7528	0.1514	0.0022	0.0200
18.60	0.0087	0.0973	0.7520	0.1475	0.0021	0.0172

^a Units: c , $\text{mol} \cdot \text{dm}^{-3}$. ^b c are molalities at 298.15 K; ^b, coefficient in the density equation is 0.2711.

performed with beforehand knowledge of α_j values, they should be extended also to more concentrated solutions of mellitic acid to have larger α_1 values (α_1 increases with c , Table 5).

As can be observed in Tables 2 and 3, the agreement between experimental and calculated conductivities at all temperatures is excellent. At 298.15 K, the limiting anion conductances are: $\lambda^0(\text{H}_5\text{Mel}^-) = 30.02 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, $\lambda^0(1/2\text{H}_4\text{Mel}^{2-}) = 35.88 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, $\lambda^0(1/3\text{H}_3\text{Mel}^{3-}) = 57.69 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, $\lambda^0(1/4\text{H}_2\text{Mel}^{4-}) = 63.74 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, $\lambda^0(1/5\text{HMel}^{5-}) = 75.40 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, and $\lambda^0(1/6\text{Mel}^{6-}) = 92.64 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, at other temperatures they can be calculated from the Walden products $\lambda^0(1/j\text{H}_{6-j}\text{Mel}^{j-}) \cdot T \cdot \eta(T) = \text{const}$. In Table 6 are presented the coefficients of the Quint–Viallard conductivity equations for the pairs of mellitic anions and hydrogen ion, $\Lambda_j(c) = [\lambda(\text{H}^+) + \lambda(1/j\text{H}_{6-j}\text{Mel}^{j-})]$, (eq 14), which were used to calculate contributions coming from different pairs $\Lambda^{(j)} = j\alpha_j\Lambda_j(c)$ (Table

**Figure 7.** Fractions α_2 , α_3 , and α_4 in mellitic acid trisodium salt solutions at 298.15 K; \square , α_2 ; \circ , α_3 ; \bullet , α_4 .**TABLE 16: Experimental and Calculated Molar Conductivities of Mellitic Acid Tetrasodium Salt Solutions at 298.15 K as a Function of Concentration c^a**

$10^4 \cdot c^b$	$\Lambda^{(2)}$	$\Lambda^{(3)}$	$\Lambda^{(4)}$	$\Lambda^{(5)}$	$\Lambda^{(6)}$	Λ_{exp}	Λ_{calcd}
0.76	0.13	52.80	286.09	120.31	2.78	462.11	477.98
1.68	0.15	50.37	287.33	107.15	2.66	447.66	458.96
2.84	0.15	50.76	279.63	105.30	2.60	438.44	442.96
4.00	0.16	50.83	273.48	104.83	2.58	431.87	432.55
5.41	0.16	50.76	267.09	104.10	2.56	424.67	422.29
6.98	0.17	50.59	260.68	103.10	2.55	417.10	413.11
8.83	0.17	50.35	253.69	101.63	2.55	408.38	404.03
10.72	0.18	50.06	246.84	99.31	2.54	398.93	396.04
12.78	0.18	49.74	239.55	97.10	2.54	389.10	388.87
15.92	0.18	49.24	228.66	92.98	2.52	373.58	379.41
$\sigma(\Lambda)^c$							5.07

^a Units: c , $\text{mol} \cdot \text{dm}^{-3}$; Λ , $\sigma(\Lambda)$, $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. ^b c are molalities at 298.15 K; ^b, coefficient in the density equation is 0.3200. ^c In calculation of $\sigma(\Lambda)$, the first point is excluded.

2). As expected, the contributions $\Lambda^{(1)}$ and $\Lambda^{(2)}$ increase with increasing concentration of mellitic acid, whereas the others decrease. In the investigated concentration range from $c = 0.64 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ to $c = 7.28 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ at the low limit, $\Lambda^{(2)}$, $\Lambda^{(3)}$, and $\Lambda^{(4)}$ are important, whereas at the high limit, $\Lambda^{(1)}$, $\Lambda^{(2)}$, and $\Lambda^{(3)}$ are important. The most significant contribution comes from $\Lambda^{(3)}$ when $\Lambda^{(5)}$ and $\Lambda^{(6)}$ are negligible.

3.4. Mellitic Acid Monosodium Salt Conductivities. Experimental and calculated conductivities of NaH_5Mel solutions are presented at 298.15 K in Table 7 and for the other temperatures in Table 8. It is worthwhile to note that, in the calculations for this and for other mellitic acid salts, no new parameters are introduced, with the exception of $\lambda^0(\text{Na}^+, T)$ from Table 1. Thus, the agreement between Λ_{exp} and Λ_{calcd} values gives an indication about the correctness of the chosen molecular model and the applied numerical procedure.

Tables 7 and 8 show a very satisfactory representation of experimental conductivities of mellitic acid monosodium salt solutions. In very dilute solutions, Λ_{exp} values are expected to be less accurate, and this is observed for the lowest concentration $c = 0.56 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, where the difference between Λ_{exp} and Λ_{calcd} is relatively large.

The speciation in mellitic acid monosodium salt aqueous solutions is given in Table 9 and in Figure 4. The general picture is similar to that of mellitic acid, but the average number of hydrogen ions, in the investigated concentration region, is now reduced (from about 42% for mellitic acid to about 25% for monosodium salt). The fractions α_1 and α_2 increase with

TABLE 17: Experimental and Calculated Molar Conductivities of Mellitic Acid Tetrasodium Salt Solutions as a Function of Concentration c and Temperature T^a

$10^4 \cdot c^b$	278.15 K		283.15 K		288.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.76	284.49	273.45	329.44	318.46	376.64	363.79
1.68	272.62	264.37	315.73	308.43	361.15	352.71
2.84	263.02	258.65	304.72	302.05	348.55	345.49
4.00	256.96	254.42	297.59	297.31	340.36	339.98
5.41	250.99	249.84	290.59	292.30	332.32	334.16
6.98	245.54	245.25	284.27	287.17	325.11	328.20
8.83	240.19	240.01	278.18	281.27	318.09	321.42
10.72	235.60	234.77	272.72	275.41	311.91	314.60
12.78	231.14	228.76	267.85	268.72	306.28	306.84
15.92	225.81	219.41	261.39	258.27	298.88	294.76
$\sigma(\Lambda)^c$		3.98		3.32		3.79

$10^4 \cdot c^b$	293.15 K		303.15 K		308.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.76	426.40	413.86	531.56	513.28	586.86	569.05
1.68	409.01	401.35	510.84	498.57	564.06	553.08
2.84	394.76	393.27	494.37	488.76	545.00	542.34
4.00	385.43	387.08	481.49	481.14	532.23	533.87
5.41	376.15	380.57	470.16	473.01	519.19	524.85
6.98	368.13	373.77	459.65	464.55	508.04	515.34
8.83	360.12	365.75	449.51	454.72	495.65	504.36
10.72	353.08	357.92	440.69	443.65	486.61	492.96
12.78	346.67	349.02	432.46	433.21	477.53	480.79
15.92	338.26	335.56	422.02	415.93	466.15	460.74
$\sigma(\Lambda)^b$		4.51		5.66		6.43

^a Units: c , mol·dm⁻³; Λ , $\sigma(\Lambda)$, S·cm²·mol⁻¹. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.3200. ^c In calculation of $\sigma(\Lambda)$, the first point is excluded.

TABLE 18: Fractions α_j and x as a Function of Mellitic Acid Tetrasodium Salt Concentration c at 298.15 K^a

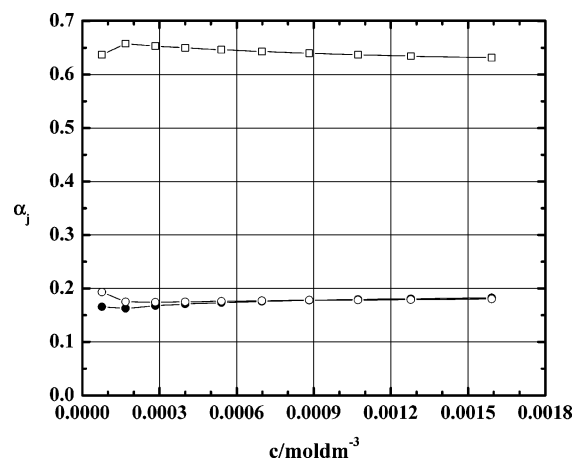
$10^4 \cdot c^b$	$\alpha_{\text{H}/6}$	α_2	α_3	α_4	α_5	α_6	x
0.76	0.0055	0.0007	0.1655	0.6372	0.1930	0.0034	0.0082
1.68	0.0029	0.0009	0.1628	0.6581	0.1750	0.0034	0.0042
2.84	0.0019	0.0010	0.1677	0.6536	0.1740	0.0034	0.0029
4.00	0.0015	0.0010	0.1708	0.6500	0.1750	0.0035	0.0022
5.41	0.0012	0.0011	0.1734	0.6464	0.1760	0.0036	0.0018
6.98	0.0010	0.0011	0.1755	0.6431	0.1770	0.0037	0.0015
8.83	0.0009	0.0011	0.1775	0.6400	0.1780	0.0038	0.0013
10.72	0.0008	0.0012	0.1792	0.6373	0.1780	0.0039	0.0012
12.78	0.0007	0.0012	0.1807	0.6347	0.1790	0.0041	0.0011
15.92	0.0006	0.0013	0.1825	0.6315	0.1800	0.0042	0.0009

^a Units: c , mol·dm⁻³. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.3200.

concentration c when α_3 and α_4 decrease, and contributions of the pairs with hydrogen ions are reduced from 100% to 55–66%.

The measure of distribution between hydrogen ion and sodium pairs of ions x , as defined in eq 17, is evaluated considering that number k of sodium atoms in the salt is stoichiometrically exact. However, the experimental errors associated with sodium hydroxide titrations of mellitic acid to produce the salt, entail a small uncertainty $k \pm \Delta k$. The result is that the Λ_{exp} curve is shifted with regard to the Λ_{calcd} curve by a small, but almost constant quantity. Evidently, this can be “corrected” by multiplying x or $1 - x$ by a very close to unity constant factor f . Its value can be estimated from the accuracy of titration experiments. The expected accuracy of our titration experiments is probably about 1–2%, and therefore, it is expected that $f = 1.00 \pm 0.02$. In the case of mellitic acid monosodium salt solutions, the “best” value of the factor f was 1.012.

For acidic salts, the apparent molar conductivities Λ_j represent two pairs with the same anion, i.e., $\Lambda_j(c) = [\lambda(\text{H}^+) + \lambda(1/j\text{H}_{6-j}\text{Mel}^{-j})]$

**Figure 8.** Fractions α_3 , α_4 , and α_5 in mellitic acid tetrasodium salt solutions at 298.15 K; ●, α_3 ; □, α_4 ; ○, α_5 .**TABLE 19: Experimental and Calculated Molar Conductivities of Mellitic Acid Pentasodium Salt Solutions at 298.15 K as a Function of Concentration c^a**

$10^4 \cdot c^b$	$\Lambda^{(3)}$	$\Lambda^{(4)}$	$\Lambda^{(5)}$	$\Lambda^{(6)}$	Λ_{exp}	Λ_{calcd}
0.86	1.02	92.06	326.27	173.10	618.14	592.45
1.73	0.94	83.54	343.43	152.78	595.58	580.69
2.62	0.96	82.17	340.90	147.16	576.30	571.19
3.65	0.98	81.01	337.09	142.03	558.20	561.12
4.94	1.00	79.96	331.11	136.83	540.48	548.90
6.44	1.04	80.10	319.74	133.59	523.79	534.47
7.89	1.08	79.69	309.76	129.84	510.05	520.37
9.17	1.05	78.14	304.01	124.68	500.49	507.88
10.70	1.07	77.82	292.20	121.26	490.38	492.35
12.50	1.09	77.45	277.59	117.43	479.52	473.56
$\sigma(\Lambda)^c$						6.83

^a Units: c , mol·dm⁻³; Λ , S·cm²·mol⁻¹. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.3606. ^c In calculation of $\sigma(\Lambda)$, the first point is excluded.

$\text{Mel}^{-j}) + [\lambda(\text{Na}^+) + \lambda(1/j\text{H}_{6-j}\text{Mel}^{-j})] = \Lambda_j^{(1)} + \Lambda_j^{(2)}$, and therefore, contributions to Λ_{calcd} are $\Lambda^{(j)} = xj\alpha_j\Lambda_j^{(1)} + (1 - x)j\alpha_j\Lambda_j^{(2)}$ (Table 7). Similarly, as for mellitic acid, with increasing concentration of mellitic acid monosodium salt, the contributions $\Lambda^{(1)}$ and $\Lambda^{(2)}$ increase, whereas the others decrease. In very dilute solutions $\Lambda^{(2)}$, $\Lambda^{(3)}$, and $\Lambda^{(4)}$ are important, whereas at increasing c , $\Lambda^{(1)}$, $\Lambda^{(2)}$, and $\Lambda^{(3)}$ are important. The most significant contribution continues to be $\Lambda^{(3)}$, whereas $\Lambda^{(5)}$ and $\Lambda^{(6)}$ are negligible.

Coefficients of the Quint–Viallard conductivity equations for the pairs of mellitic anions with sodium ion, $\Lambda_j(c) = [\lambda(\text{Na}^+) + \lambda(1/j\text{H}_{6-j}\text{Mel}^{-j})]$, are presented in Table 10.

Thus, when the “chemical problem” is solved, the Quint–Viallard coefficients from Table 6 for hydrogen pairs and those from Table 10 for sodium pairs are sufficient to calculate the conductivity of all mellitic salts.

3.5. Mellitic Acid Disodium Salt Conductivities. Surprisingly, in the case of mellitic acid disodium aqueous solutions, the expected differences between the experimental and calculated conductivities exceed 1–2% and reach about 6–7%. Λ_{calcd} values are systematically greater than Λ_{exp} values (about 23 S·cm²·mol⁻¹ at 298.15 K). The experiments with Na₂H₄Mel were repeated, but despite a systematic shift with regard to the first set of data, the two sets of conductivities do not differ more than 1% (Table 11 and Figure 5). This result supports the reliability of the experiments, but at the same time, it indicates the difficulty to obtain the correct stoichiometric composition by titration. The problem already has been discussed above. If the Λ_{calcd} are larger than expected, then one or more contribu-

TABLE 20: Experimental and Calculated Molar Conductivities of Mellitic Acid Pentasodium Salt Solutions as a Function of Concentration c and Temperature T^a

$10^4 \cdot c^b$	278.15 K		283.15 K		288.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.86	368.19	354.07	426.08	407.95	487.02	466.55
1.73	354.28	346.52	410.00	399.65	468.61	456.98
2.62	343.35	340.28	397.21	392.81	453.93	449.12
3.65	333.04	333.94	385.27	385.75	440.38	440.98
4.94	322.89	326.32	373.50	377.33	426.63	431.28
6.44	313.26	317.69	362.15	367.81	413.71	420.35
7.89	305.45	309.33	353.08	358.56	403.23	409.68
9.17	299.36	301.92	346.39	350.37	395.50	400.15
10.70	293.59	293.05	339.44	340.56	387.54	388.71
12.50	287.27	281.48	332.01	327.78	379.14	374.66
$\sigma(\Lambda)^c$		4.18		5.15		5.86

$10^4 \cdot c^b$	293.15 K		303.15 K		308.15 K	
	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}	Λ_{exp}	Λ_{calcd}
0.86	551.13	528.05	691.27	654.90	764.56	727.76
1.73	530.26	517.17	662.03	641.27	731.35	712.68
2.62	513.90	508.22	640.42	630.18	707.25	700.13
3.65	498.09	498.94	620.28	618.51	684.69	687.20
4.94	482.44	487.99	600.46	604.67	662.54	671.69
6.44	467.65	475.38	581.88	588.81	641.17	653.88
7.89	455.84	463.25	566.09	573.39	624.93	636.55
9.17	447.00	452.33	555.83	559.50	612.90	621.04
10.70	437.98	439.12	544.40	542.41	599.73	602.80
12.50	428.33	423.00	532.38	521.83	586.68	578.29
$\sigma(\Lambda)^c$		6.73		9.35		10.20

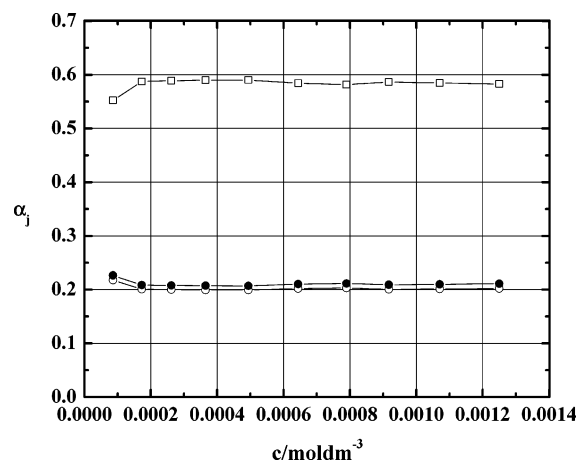
^a Units: c , $\text{mol} \cdot \text{dm}^{-3}$; Λ , $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.3606. ^c In calculation of $\sigma(\Lambda)$, the first point is excluded.

TABLE 21: Fractions α_j as a Function of Mellitic Acid Pentasodium Salt Concentration c at 298.15 K^a

$10^4 \cdot c^b$	$\alpha_{\text{H}/6}$	α_3	α_4	α_5	α_6
0.86	0.0025	0.0034	0.2176	0.5524	0.2266
1.73	0.0014	0.0032	0.2008	0.5875	0.2085
2.62	0.0010	0.0033	0.2000	0.5891	0.2076
3.65	0.0008	0.0035	0.1994	0.5899	0.2072
4.94	0.0007	0.0036	0.1992	0.5902	0.2070
6.44	0.0006	0.0038	0.2019	0.5843	0.2101
7.89	0.0005	0.0040	0.2028	0.5819	0.2113
9.17	0.0005	0.0040	0.2004	0.5869	0.2088
10.70	0.0005	0.0041	0.2012	0.5849	0.2098
12.50	0.0004	0.0043	0.2019	0.5829	0.2109

^a Units: c , $\text{mol} \cdot \text{dm}^{-3}$. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.3606.

tions $\Lambda^{(j)}$ are overestimated. The main contribution to Λ_{calcd} coming from $\Lambda^{(3)}(c) = 3\alpha_3\Lambda_3(c)$ could be reduced if α_3 values were smaller, i.e., by the use of a smaller value of dissociation constant K_3 . By preserving the original value of Purdie et al.⁴⁴ for $K_3 = 3.02 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, the agreement between Λ_{calcd} and Λ_{exp} is considerably improved (Table 11 and Figure 5). However, simultaneously, the agreement for mellitic acid and other acidic salts is worsened. This was the reason to introduce $K_3 = 4.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ into calculations instead of the Purdie et al. K_3 value. Because the emphasis is on mellitic acid conductivities, the chosen K_3 value is also used in the case of $\text{Na}_2\text{H}_4\text{Mel}$ solutions. Only Λ_{calcd} values for both sets of experiments are reported (Table 12). The use of either K_3 entails similar solution of the chemical problem. It is worthwhile to illustrate the behavior of α_j also in the case of mellitic acid disodium salt (Figure 6). The behavior already observed for mellitic acid and monosodium salt is also observed here; the fractions α_1 and α_2 increase with concentration c , whereas α_3 and α_4 decrease, but α_1 becomes less and less important when

**Figure 9.** Fractions α_4 , α_5 , and α_6 in mellitic acid pentasodium salt solutions at 298.15 K; \circ , α_4 ; \bullet , α_5 ; \square , α_6 .

α_4 starts to play a significant role, especially in very dilute solutions. For the key ions, $\text{H}_4\text{Mel}^{2-}$ and $\text{H}_3\text{Mel}^{3-}$, the values α_2 as calculated with the Purdie et al.⁴⁴ dissociation constants are larger than those with our K_j set, whereas for α_3 , the situation is opposite (Figure 6). However, this “compensation” is illusory because $\Lambda^{(3)}$ is considerably larger than $\Lambda^{(2)}$. The average number of hydrogen ions continues to decrease (from about 42% for mellitic acid to about 25% for monosodium salt and to about 12% for disodium salt). Consequently, the contributions of the pairs with hydrogen ions are also reduced from 100% for mellitic acid to 55–66% for monosodium salt and to 17–34% for mellitic acid disodium salt.

3.6. Mellitic Acid Trisodium Salt Conductivities. Experimental and calculated conductivities in aqueous solutions of mellitic acid trisodium salt at 298.15 K are presented in Table 13 and for other temperatures in Table 14. As can be seen, the agreement between Λ_{exp} and Λ_{calcd} values is very satisfactory, again supporting the applied treatment of conductivities. The effect of hydrolysis is small and only noticeable in very dilute solutions (about 1–5%, Table 15). This is expressed by further reduction of contributions coming from the pairs with hydrogen ions (from 17 to 34% for disodium salt to 2–9% for trisodium salt). In more concentrated solutions, only three pairs with sodium ion exist (Figure 7), namely $\text{Na}^+ + \text{H}_4\text{Mel}^{2-}$, $\text{Na}^+ + \text{H}_3\text{Mel}^{3-}$, and $\text{Na}^+ + \text{H}_2\text{Mel}^{4-}$. However, the largest contributions come only from two pairs of ions $\Lambda^{(3)}$ and $\Lambda^{(4)}$, whereas the other pairs of ions are less important (Table 13).

3.7. Mellitic Acid Tetrasodium Salt Conductivities. In Table 16 are reported Λ_{exp} and Λ_{calcd} values of aqueous solutions of mellitic acid tetrasodium salt at 298.15 K and in Table 17 for other temperatures. With the exception of very dilute solutions (two first points), the agreement between experimental and calculated conductivities is very satisfactory. Hydrolysis disappears completely (Table 18). Over the entire concentration range, mellitic acid tetrasodium salt solutions are mixtures of three pairs of ions: $\text{Na}^+ + \text{H}_3\text{Mel}^{3-}$, $\text{Na}^+ + \text{H}_2\text{Mel}^{4-}$, and $\text{Na}^+ + \text{HMel}^{5-}$, which exist in constant ratio 1:3.5:1, expressing the fact that the fractions α_3 , α_4 , and α_5 are almost independent of c (Figure 8). A first small appearance of $\Lambda^{(6)}$ is observed, but the contributions to calculated conductivity result mainly from $\Lambda^{(3)}$, $\Lambda^{(4)}$, and $\Lambda^{(5)}$, $\Lambda^{(3)}$ being the smallest one (Table 16).

3.8. Mellitic Acid Pentasodium Salt Conductivities. The mellitic acid pentasodium salt solutions behave similarly to those of tetrasodium salt. Among the acidic salts, mellitic acid pentasodium salt has the highest electrical charge. In the investigated concentration range, aqueous solutions contain three

TABLE 22: Experimental and Calculated Equivalent Conductivities of Mellitic Acid Hexasodium and Hexapotassium Salt Solutions as a Function of Concentration c and Temperature T^a

Na ₆ Mel								
$10^4 \cdot c^b$	$T = 278.15$ K		$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K	
	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$
0.46	83.08	81.17	96.01	93.85	109.67	107.22	123.90	121.14
0.97	79.27	78.32	91.59	90.52	104.67	103.38	118.17	116.77
1.52	76.24	76.01	88.06	87.82	100.50	100.26	113.50	113.21
2.36	72.69	73.16	83.92	84.53	95.67	96.46	108.05	108.88
3.27	69.73	70.63	80.49	81.54	91.83	93.02	103.50	105.00
4.26	67.21	68.25	77.56	78.77	88.33	89.83	99.69	101.31
5.19	65.24	66.26	75.26	76.45	85.83	87.15	96.70	98.29
6.38	63.18	63.94	72.88	73.74	83.00	84.03	93.62	94.73
7.56	61.47	61.86	70.90	71.32	80.83	81.23	91.06	91.54
9.10	59.61	59.37	68.76	68.42	78.33	77.90	88.27	87.73
11.00	57.68	56.62	66.53	65.20	75.76	74.18	85.39	83.48
$\sigma(\Lambda)$	0.98		1.14		1.33		1.52	

$10^4 \cdot c^b$	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$
0.46	138.75	135.63	154.19	150.65	171.42	166.22
0.97	132.31	130.69	146.97	145.12	162.70	160.07
1.52	127.00	126.68	141.10	140.63	155.45	155.09
2.36	120.84	121.77	133.99	135.13	147.61	148.97
3.27	115.66	117.38	128.28	130.21	141.11	143.49
4.26	111.36	113.26	123.40	125.59	135.72	138.34
5.19	108.01	109.81	119.77	121.74	130.99	134.07
6.38	104.53	105.81	115.76	117.25	127.23	129.08
7.56	101.66	102.20	112.56	113.21	123.72	124.58
9.10	98.53	97.90	109.07	108.40	119.86	119.24
11.00	95.29	93.07	105.49	102.94	115.91	113.10
$\sigma(\Lambda)$	1.74		1.98		2.65	

K ₆ Mel								
$10^4 \cdot c^b$	$T = 278.15$ K		$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K	
	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$
0.54	96.06	92.35	110.19	106.04	125.00	120.67	140.50	135.26
1.07	91.67	89.59	105.17	102.81	119.33	116.96	134.02	131.04
1.61	88.29	87.45	101.29	100.32	114.83	114.08	128.94	127.77
2.15	85.67	85.66	98.24	98.23	111.33	111.68	125.03	125.03
2.78	83.19	83.80	95.35	96.07	108.00	109.18	121.17	122.19
3.47	80.91	82.02	92.73	93.99	105.00	106.78	117.78	119.46
4.24	78.83	80.22	90.31	91.90	102.33	104.37	114.65	116.71
5.26	76.51	78.08	87.62	89.40	99.17	101.49	111.24	113.44
6.48	74.28	75.78	85.06	86.72	96.33	98.40	107.84	109.92
8.53	71.27	72.35	81.61	82.72	92.33	93.78	103.41	104.67
$\sigma(\Lambda)$	1.77		1.99		2.23		2.51	

$10^4 \cdot c^b$	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$	$\Lambda_{e,exp}$	$\Lambda_{e,calcd}$
0.54	156.53	151.51	173.05	166.54	191.16	182.92
1.07	149.20	146.72	165.16	161.20	181.19	176.99
1.61	143.68	143.02	158.68	157.07	174.02	172.37
2.15	138.98	139.92	153.44	153.61	168.20	168.55
2.78	134.77	136.70	148.66	150.02	162.89	164.52
3.47	130.90	133.61	144.40	146.57	158.18	160.72
4.24	127.39	130.50	140.45	143.10	153.79	156.85
5.26	123.55	126.80	136.16	138.97	149.02	152.27
6.48	119.78	122.81	131.95	134.52	144.39	147.29
8.53	114.78	116.86	126.42	127.88	138.28	139.93
$\sigma(\Lambda)$	2.81		3.18		3.58	

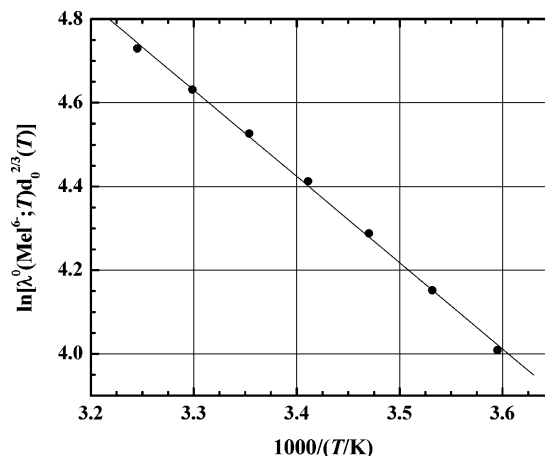
^a Units: c , mol·dm⁻³; Λ , $\sigma(\Lambda)$, S·cm²mol⁻¹. ^b c are molalities at 298.15 K; b , coefficient in the density equation is 0.3948 for mellitic acid hexasodium salt and 0.4255 for mellitic acid hexapotassium salt.

pairs of ions: Na⁺ + H₂Mel⁴⁻, Na⁺ + HMel⁵⁻, and Na⁺ + Mel⁶⁻, existing in the ratio 1:3:1 (Table 21 and Figure 9).

TABLE 23: Limiting Ionic Conductances $\lambda^0(1/6\text{Mel}^{6-})$ and Walden Products as a Function of Temperature T^a

T/K	λ^0 (1/6Mel ⁶⁻) ^b	λ^0 (1/6Mel ⁶⁻) ^c	λ^0 (1/6Mel ⁶⁻) ^d	$\eta\lambda^0$ (1/6Mel ⁶⁻)
278.15	57.18	52.35	55.07 ± 2.99	0.0877
283.15	66.32	60.84	63.88 ± 3.87	0.0835
288.15	75.96	69.77	72.87 ± 4.38	0.0829
293.15	85.99	79.10	82.56 ± 4.87	0.0827
298.15	96.38	88.76	92.62 ± 5.46	0.0825
303.15	107.14	98.77	102.96 ± 5.92	0.0821
308.15	118.27	109.17	113.72 ± 6.43	0.0818
				0.0833 ± 0.002

^a Units: λ^0 , S·cm²mol⁻¹; $\eta\lambda^0$, S·cm²mol⁻¹Pa·s. ^b Derived from conductivities of Na₆Mel solutions. ^c Derived from conductivities of K₆Mel solutions. ^d Average values of $\lambda^0(1/6\text{Mel}^{6-})$ used in calculations.

**Figure 10.** Values of $\ln[\lambda^0(1/6\text{Mel}^{6-}; T)d_0^{2/3}(T)]$ as a function of $1/T$, (eq 21).**TABLE 24: Experimental and Calculated with Different Sets of Dissociation Constants Molar Conductivities of Mellitic Acid Solutions at 298.15 K as a Function of Concentration c^a**

$10^4 \cdot c$	Λ_{calcd}^b	Λ_{calcd}^c	Λ_{calcd}^d	Λ_{calcd}^e	Λ_{calcd}^f	Λ_{calcd}^g	Λ_{exp}
0.64	1628.41	1133.00	1275.63	1072.21	1070.18	1100.75	1097.68
1.27	1501.32	1049.82	1190.18	989.71	987.73	1018.92	1018.84
1.56	1464.30	1023.57	1164.59	964.72	962.83	991.50	991.10
1.98	1421.63	992.58	1134.8	935.38	933.65	964.08	964.51
2.61	1373.20	956.17	1099.93	901.70	900.20	929.41	929.86
2.89	1355.65	942.65	1086.94	889.40	888.00	914.40	917.03
3.24	1336.27	927.47	1072.26	875.77	874.51	902.53	902.74
3.71	1313.63	909.47	1054.79	859.85	858.71	885.90	885.92
3.93	1303.85	901.81	1047.34	852.97	856.37	878.91	878.59
4.63	1276.74	880.05	1025.98	833.91	832.96	859.15	858.24
5.37	1252.49	860.41	1006.57	816.89	816.05	841.07	839.96
5.49	1249.08	857.50	1003.66	814.51	813.69	835.80	837.38
6.23	1228.45	840.78	987.05	800.06	799.43	823.11	821.78
7.28	1203.48	820.29	966.57	782.67	781.92	804.39	802.95

^a Units: c , mol·dm⁻³; Λ , S·cm²mol⁻¹. ^b Ref 45. ^c Ref 43. ^d Ref 46. ^e Ref 44. ^f Ref 44. ^g This work.

Practically, there are only three contributions, $\Lambda^{(4)}$, $\Lambda^{(5)}$, and $\Lambda^{(6)}$, $\Lambda^{(5)}$ being the largest one (Table 19). Without the lowest two first concentration points, the agreement between experimental and calculated conductivities is satisfactory (Table 19 and Table 20).

3.9. Mellitic Acid Hexasodium and Hexapotassium Salt Conductivities. Conductivity measurements on solutions of neutral salts of mellitic acid permits independent determination of the limiting anion conductance, $\lambda^0(1/6\text{Mel}^{6-})$, by taking into account that the salts are strong electrolytes. Thus, in dilute solutions, the Quint–Viallard conductivity equation reduces to

the Onsager equation⁴⁸

$$\Lambda_e = \Lambda_e^0 - \left\{ \frac{2.801 \times 10^6 q |z_+| |z_-| (\lambda_+^0 + \lambda_-^0)}{(DT)^{3/2} (1 + \sqrt{q})} + \frac{41.248 (|z_+| + |z_-|)}{\eta (DT)^{1/2}} \right\} \sqrt{I} \quad (19)$$

$$q = \frac{|z_+| |z_-| (\lambda_+^0 + \lambda_-^0)}{(|z_+| + |z_-|) (|z_+| \lambda_-^0 + |z_-| \lambda_+^0)}$$

where $|z_+| = 1$ and $|z_-| = 6$, the ionic strength is $I = 21c$, and the equivalent conductivity is $\Lambda_e = \Lambda/6$.

Because $\lambda^0(\text{Na}^+)$ and $\lambda^0(\text{K}^+)$ are known (Table 1), $\lambda^0(1/6\text{Mel}^{6-})$ can be determined from the optimization procedure to satisfy eq 19 together with the Kohlrausch law of the independent migration of ions at infinite solution

$$\Lambda_e^0 = \lambda^0(\text{Me}^+) + \lambda^0(1/6\text{Mel}^{6-}); \quad \text{Me}^+ = \text{Na}^+, \text{K}^+ \quad (20)$$

In Table 22 are presented the experimental and calculated equivalent conductivities in aqueous solutions with sodium and potassium cations. The agreement between $\Lambda_{e,\text{exp}}$ and $\Lambda_{e,\text{calc}}$ values is similar to that observed for other salts. Values of $\lambda^0(1/6\text{Mel}^{6-}; T)$ derived from conductivity experiments with Na_6Mel and K_6Mel are close, but they exceed the limits of expected error. The explanation is that, in the preparation of salts (titrations of mellitic acid with NaOH or KOH solutions), the exact value at $k = 6$ is difficult to achieve. Evidently, the excess or deficiency in amount of base will shift the entire $\Lambda(c)$ curve, and consequently, different limiting values are obtained. In our calculations, average values of $\lambda^0(1/6\text{Mel}^{6-}; T)$ were used, which are reported with the limits of error in Table 23.

The observed Walden product varies but rather weakly with temperature, $\lambda^0(1/6\text{Mel}^{6-}; T) \cdot \eta(T) = 0.0833 \pm 0.0020$ (Table 23). An alternative approach to consider temperature dependence of $\lambda^0(1/6\text{Mel}^{6-}; T)$ is given by the Eyring theory of transition state to movement of individual ions⁵⁵

$$\left(\frac{\partial \ln[\lambda^0(T) d_0^{2/3}(T)]}{\partial T} \right)_P = \frac{\Delta H_\lambda^\ddagger}{RT^2} \quad (21)$$

Assuming the partial molar enthalpy of activation associated with the ion movement, $\Delta H_\lambda^\ddagger$ independent of temperature, yields

$$\ln[\lambda^0(T) d_0^{2/3}(T)] = -\frac{\Delta H_\lambda^\ddagger}{RT} + \text{const} \quad (22)$$

In Figure 10, this equation was tested by using densities of pure water d_0 from Table 1 and $\lambda^0(1/6\text{Mel}^{6-}; T)$ values from Table 23 to obtain

$$\ln[\lambda^0(1/6\text{Mel}^{6-}; T) d_0^{2/3}(T)] = 11.432 - \frac{2061.1}{(T/K)}; \quad R^2 = 0.99923 \quad (23)$$

where $\Delta H_\lambda^\ddagger = 17.13 \text{ kJ} \cdot \text{mol}^{-1}$.

4. Conclusions and Remarks

A general, efficient, and consistent numerical procedure is proposed to analyze electrical conductivities of aqueous solu-

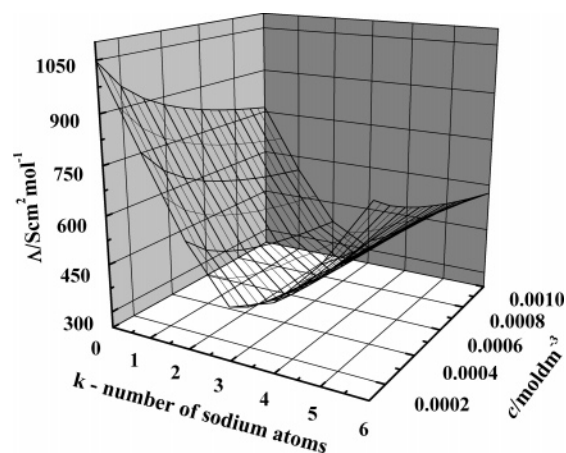


Figure 11. Conductivities of mellitic acid and its salt solutions at 298.15 K as a function of concentration c and the number of sodium atoms in the acid molecule k .

tions of polybasic carboxylic acids, where conductivity of unsymmetrical weak electrolytes overlap successive steps of acid dissociation and hydrolysis of salts take place.

The approach is illustrated for the case of benzenhexacarboxylic acid and its acidic and neutral salts. By using only parameters from the analysis of mellitic acid conductivities, it is possible to reproduce satisfactorily the experimental conductivities of acidic salt solutions. This fact strongly supports the reliability of the results reported here.

The proposed numerical procedure permits the determination of the sets of the limiting ionic conductances as well as the dissociation constants of polybasic acids. The dissociation constants obtained by parallel potentiometric titrations and spectroscopic measurements prove to be of considerable value to ensure the consistency of data analysis. The importance of the accuracy of dissociation constants is illustrated in Table 24, where the experimental conductivities of mellitic acid are compared with those calculated using different sets of K_j from the literature and from this work.

The difficulty in obtaining exact stoichiometric compositions of salts by titration manifests itself by the shifting of the $\Lambda(c)$ curves. Not all values of k are necessary in the data analysis, but it is preferable to have a complete set of experimental conductivities for all acidic salts. The effect of changing k values on conductivities at constant concentrations c ($k = 0$ for mellitic acid and $k = 1, 2, 3, 4, 5$, and 6 for its salts) is illustrated in Figure 11. The minimum with regard to k (for mellitic acid trisodium salt) results from large differences in the conductances of hydrogen and sodium ions (Table 1). The surface in Figure 11 expresses the gradual replacement of hydrogen ions with sodium ions in the acid molecule by two parallel processes, by the partial neutralization, and by the strong reduction of hydrolysis.

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