

## Research Article

# The Audio Frequency Conductance Study of Some Metal Succinate Salts in Aqueous Medium at Different Temperatures (Part I: Magnesium, Manganese (II), Barium and Copper Succinates)

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The audio electrical conductances of aqueous solutions of magnesium, manganese II, barium, and copper succinates have been measured at various temperatures in the range of 298.15 K to 313.15 K, using an audio frequency conductance bridge. The evaluation of conductance data was carried out by minimisation technique using the theoretical equations of the complete and modified forms of Pitts (P) and Fuoss-Hsia (F-H), each a three-parameter equation, association constant ( $K_A$ ), molar conductance ( $\Lambda_m$ ), and distance parameter ( $a$ ). Quantitative results showed that these salts do not behave as “strong” electrolytes, and that their dissociations are far from complete. The abnormally low conductances of these electrolytes are not due to the presence of electrically neutral molecules but to the ion-pair formation. The Walden product values, as well as the standard thermodynamics functions ( $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$ ) for the association reaction at the four temperatures studied, have been evaluated.

## 1. Introduction

The conductance of any electrolyte at infinite dilution is generally recognised to be dependent upon temperature, viscosity, and dielectric constant. Also, it is well established that the extent of association of a series of electrolytes in different solvents is specific for any ion-solvent combination, rather than being dielectric constant dependent. Information on ion-ion and ion-solvent and interactions can be obtained from conductivity measurement [1–4]. In a series of conductance studies, there have been numerous investigations of association behavior of 1 : 1 electrolytes in aqueous and binary mixed solvents.

On the other hand, the conductance behavior of 2 : 2 electrolytes (specially salts of dicarboxylic acids) has received relatively little attention. This is largely due to the difficulty encountered in analysing such data since the usual methods require an arbitrary choice for some of the parameters needed in the analysis. However, there were no available cited

recent studies in the literature concerning the association of the bivalent cations with bivalent organic ligands. In part I of this paper, we report conductance measurement of magnesium, manganese II, barium, and copper succinates in aqueous medium at various temperatures in the range 298.15–313.15 K. Metal succinates play an important role in biological and industrial processes [5–8]. Four currently used conductance equations, the complete and expanded forms of both Fuoss-Hsia and Pitts equations, have been used to analyse conductance data for these succinate salts. Also, the thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  were evaluated by investigating the process over a certain temperature range. In addition, Walden product was derived and discussed.

## 2. Experimental

Measurements were made at a range of temperatures between 298.15 and 313.15 K with Oakton-con510 audio frequency

TABLE 1: Experimental conductance data for Ba succinate.

298.15 K		303.15 K		308.15 K		313.15 K	
Conc. *10 <sup>3</sup>	$\Lambda$						
0.56411	199.190	0.50910	209.414	0.70798	202.902	0.62824	208.904
0.74531	193.356	0.62278	204.192	0.75117	201.282	0.66546	207.388
0.79218	192.096	0.67767	202.628	0.79106	200.014	0.70088	206.188
0.83645	191.262	0.77676	199.560	0.82796	199.898	0.73761	204.738
0.87756	190.604	0.82113	197.964	0.86275	197.870	0.77281	203.830
0.91808	190.128	0.86265	195.676	0.89685	196.440	0.80525	202.728
0.95837	189.466	0.90303	195.570	0.93330	195.458	0.83474	202.112
1.03271	187.164	0.97511	193.654	0.96168	194.830	0.86236	201.070
1.09135	186.406	1.00758	192.836	0.98779	193.896	0.88292	200.514
1.10711	186.808	1.03740	190.804	1.01067	193.368	0.90937	199.260
		1.06599	190.326				

$\Lambda$  (ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>); Conc.: concentration (mol·dm<sup>-3</sup>).

TABLE 2: Experimental conductance data for Cu succinate.

298.15 K		303.15 K		308.15 K		313.15 K	
Conc. *10 <sup>3</sup>	$\Lambda$						
0.11875	104.322	0.22592	88.190	0.26685	83.448	0.40075	76.194
0.17218	92.200	0.34929	73.130	0.32137	77.388	0.45082	72.174
0.40553	66.350	0.40233	69.116	0.37259	72.824	0.50755	68.362
0.51577	60.392	0.45097	66.048	0.41829	69.286	0.55875	65.358
0.57000	57.934	0.55605	60.490	0.47100	66.172	0.60713	63.150
0.62195	56.106	0.60216	58.582	0.51965	63.582	0.65040	61.270
0.67296	54.482	0.69118	55.478	0.56405	61.622	0.69433	59.530
0.72053	53.198	0.72973	54.188	0.60434	59.882	0.73652	58.098
0.76804	52.312	0.76627	53.302	0.64214	58.666	0.80993	55.852
0.80697	51.142	0.79876	52.208	0.67746	57.336	0.87104	54.114
0.84202	50.218	0.83003	51.590	0.71418	56.100	0.89970	53.402
0.87450	49.544	0.88436	50.392	0.78025	54.250	0.92202	52.900
0.90625	48.870	0.90694	49.998	0.80909	53.506	0.94071	52.430
0.93728	48.336	0.923890	49.530				

$\Lambda$  (ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>); Conc.: concentration (mol·dm<sup>-3</sup>).

TABLE 3: Experimental conductance data for Mg succinate.

298.15 K		303.15 K		308.15 K		313.15 K	
Conc. *10 <sup>3</sup>	$\Lambda$						
0.32106	152.146	0.53293	167.682	0.56479	171.312	0.06619	222.736
0.38543	150.700	0.62320	165.106	0.65514	166.354	0.23327	200.850
0.44357	147.958	0.73614	159.570	0.77615	163.214	0.52183	181.330
0.49967	144.364	0.95818	153.276	0.88264	159.736	0.72094	172.758
0.56965	141.704	1.07099	150.494	1.01288	157.180	0.81690	169.664
0.63635	139.118	1.19035	147.426	1.13065	153.924	0.93341	165.490
0.69845	136.062	1.32226	145.708	1.25809	151.156	1.16002	160.302
0.77167	133.942	1.44684	143.592	1.40034	148.436	1.41143	155.162
0.83990	131.736	1.57115	142.498	1.53116	146.800	1.53523	152.818
0.91505	129.448	1.83767	137.972	1.66882	144.824	1.66980	149.540

$\Lambda$  (ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>); Conc.: concentration (mol·dm<sup>-3</sup>).

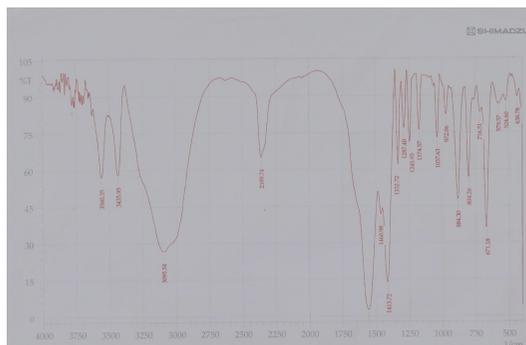


FIGURE 1: FT-IR spectra for Mg succinate.

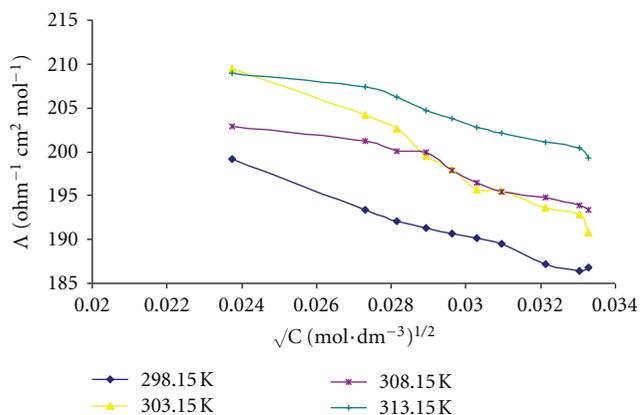


FIGURE 2: Molar conductance versus square root of concentration for Ba-succinate at different temperatures.

bridge of low impedance. It combines speed and simplicity of operation with 0.05% accuracy. The cell used for measuring conductances has been described elsewhere [9]. The cell constant (as determined by standard solutions of potassium chloride) was  $1.04079 \text{ cm}^{-1}$ . The method used for measuring conductances has been described [9].

### 3. Materials

The KCl used in this work was purified and used according to the literature [9]. Magnesium succinate was prepared by addition of clean and dried magnesium ribbon to a solution of succinic acid. The PH of solution was continuously tested until the solution became neutral. Then the mixture was filtered to remove the excess of metal added, after which the solvent was evaporated on a water bath. The product was recrystallized twice from conductivity water and dried by air at room temperature. The final product was a white crystalline powder as the tetrahydrate. The composition of the salt was determined by elemental analysis. The salt was further analysed for magnesium by titration with the disodium salt of ethylenediaminetetraacetic acid (EDTA) using eriochrome black T as indicator [10]. Elemental analysis confirmed the composition with experimental/calculated values (mass percent): C 23.4/22.5, H 6.6/5.7, and Mg 11.38/11.24. FT-IR

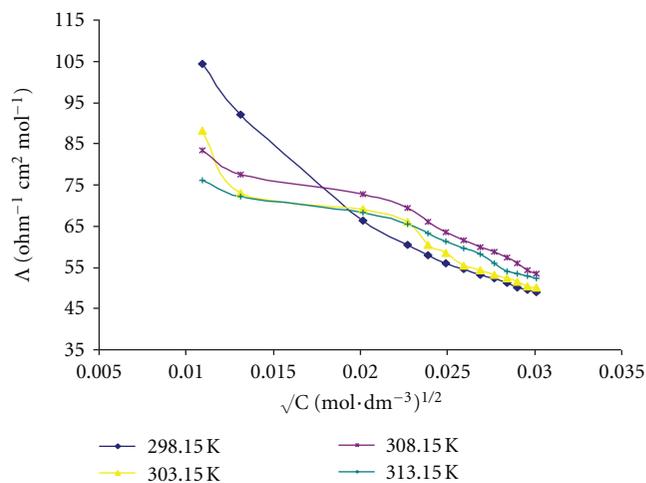


FIGURE 3: Molar conductance versus square root of concentration for Cu-succinate at different temperatures.

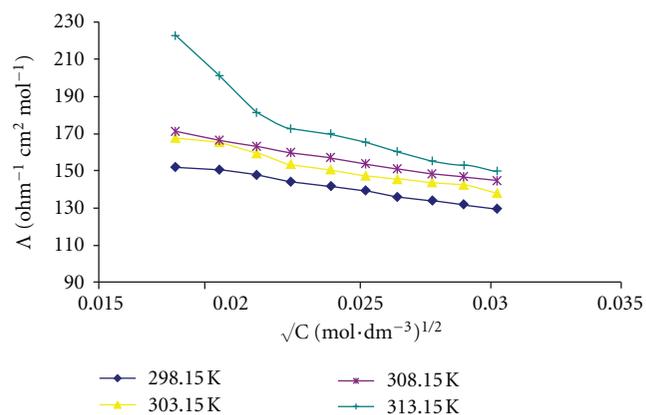


FIGURE 4: Molar conductance versus square root of concentration for Mg-succinate at different temperatures.

exhibits the following absorption bands (KBr pellet,  $\nu/\text{cm}^{-1}$ ): narrow  $\nu(\text{O-H})$  bands at  $3560$  and  $3435 \text{ cm}^{-1}$ ; associated with the existence of hydrogen bonds; stretching frequencies corresponding to the carboxylate ion  $\nu(\text{CO}_2^-)$  and  $\nu(\text{C-O})$  at  $1560$ ,  $1460$ ,  $1413$ ,  $1332$ ,  $1287$ , and  $1245 \text{ cm}^{-1}$ ; the  $1174 \text{ cm}^{-1}$

TABLE 4: Experimental conductance data for Mn-succinate.

298.15 K		303.15 K		308.15 K		313.15 K	
Conc. $\cdot 10^3$	$\Lambda$						
0.43244	162.542	0.19989	182.826	0.10976	197.114	0.34023	176.396
0.51084	158.992	0.31941	171.114	0.14567	191.570	0.39961	169.720
0.60785	153.734	0.37725	167.640	0.33335	170.980	0.47590	167.116
0.69413	149.622	0.46203	162.784	0.39655	167.354	0.53986	163.222
1.01124	139.240	0.54652	159.042	0.47351	160.484	0.61789	159.032
1.12663	135.140	1.08379	138.060	0.54065	159.326	0.69363	155.548
1.24575	132.034	1.20277	134.786	0.69278	148.376	0.77113	151.386
1.37319	129.446	1.32895	131.778	0.77883	146.682	0.85864	147.472
1.49389	127.348	1.56919	125.532	0.87155	141.826	0.93962	146.116
1.59976	125.100	1.69673	124.530	1.25557	131.398	1.02234	143.202

$\Lambda$  ( $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ); Conc.: concentration ( $\text{mol} \cdot \text{dm}^{-3}$ ).

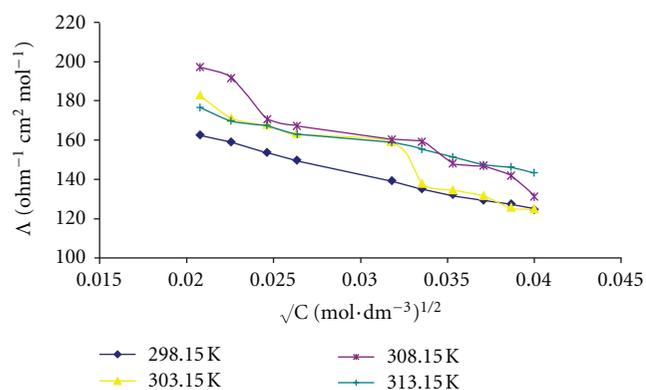


FIGURE 5: Molar conductance versus square root of concentration for Mn-succinate at different temperatures.

absorption band is associated with  $\nu(\text{C}-\text{C})$  and the following absorptions with metal oxygen bonding and with  $\nu(\text{C}-\text{H})$  1037, 972, 884, 804, 716, 671, 579, 524, and 438  $\text{cm}^{-1}$  [11]. The H-NMR was recorded in  $\text{D}_2\text{O}$  solvent  $\delta_H = 2.3$  ppm.

Manganese succinate was prepared by the method described by Vogel [12] with some modification. "Analar" grade manganese chloride solution was added to a solution of sodium succinate. The reaction here was continued until the pH of the mixture became neutral. The mixture was heated on a water bath until a quarter of it was gained. The remaining solution was left for 24 hours. Then light pink crystals formed. The mixture was filtered off. The product was washed with chilled conductivity water until it became free from chloride ions; after that the final product was dried by air at room temperature. Elemental analysis confirmed the composition with experimental/calculated values (mass percent): C 20.3/19.8, H 5.7/5.0. FT-IR spectra exhibit the following absorption bands (KBr pellet,  $\nu/\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  bands at 3505 and 3417  $\text{cm}^{-1}$ ; stretching frequencies corresponding to the carboxylate ion  $\nu(\text{CO}_2^-)$  and  $\nu(\text{CO})$  at 1657, 1552, 1462, 1406,

1329, 1285, and 1244  $\text{cm}^{-1}$ ; the 1172  $\text{cm}^{-1}$  absorption band is associated with  $\nu(\text{C}-\text{C})$  and the following absorptions with metal-oxygen bonding and with  $\nu(\text{C}-\text{H})$  1037, 970, 856, 798, 671, and 525  $\text{cm}^{-1}$ . The H-NMR  $\delta_H = 2.3$  ppm.

The same method [12] was carried out for the preparation of barium succinate. "Analar" grade barium chloride dihydrate solution was added to a solution of sodium succinate, and the rest was that as described before for manganese succinate. The product was a white crystalline powder. Elemental analysis confirmed the composition with experimental/calculated values (mass percent): C 15.8/16.6, H 2.3/2.6. FT-IR spectra exhibit the following absorption bands (KBr pellet,  $\nu/\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3550, 3435  $\text{cm}^{-1}$ ; stretching frequencies corresponding to the carboxylate ion  $\nu(\text{CO}_2^-)$  and  $\nu(\text{CO})$  at 1550, 1397, 1328, 1286, and 1239  $\text{cm}^{-1}$ ; the 1165  $\text{cm}^{-1}$  absorption band is associated with  $\nu(\text{C}-\text{C})$  and the following absorptions with metal-oxygen bonding and with  $\nu(\text{C}-\text{H})$ , 1032, 963, 930, 803, 657, 490, and 464. The H-NMR  $\delta_H = 2.30$  ppm.

The copper succinate was prepared by reaction stoichiometric amounts of both a solution of succinic acid and copper metal. The solution was heated with continuous stirring at 348.15–353.15 K for a period of 3-4 hours. A blue solution appeared which was evaporated on a water bath after filtering and removing the excess metal copper. The product was a blue powder and dried afterwards for 24 hours, as the dihydrate. Elemental analysis confirmed the composition with experimental/calculated values (mass percent): C 22.3/22.3, H 3.2/3.7. The FT-IR spectra exhibit the following absorption bands (KBr pellet,  $\nu/\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  bands at 3579, 3483, and 3380  $\text{cm}^{-1}$  associated with the existence of hydrogen bonds, stretching frequencies corresponding to the carboxylate ion  $\nu(\text{CO}_2^-)$  and  $\nu(\text{C}-\text{O})$  at 1625, 1446, 1329, and 1390  $\text{cm}^{-1}$ ; the 1185  $\text{cm}^{-1}$  absorbance band is associated with  $\nu(\text{C}-\text{C})$  and the following absorptions with metal oxygen bonding and with  $\nu(\text{C}-\text{H})$ , 1001, 973, 886, 730, 694, 618, 581, and 520. The H-NMR was recorded in  $\text{D}_2\text{O}$  solvent  $\delta_H = 2.30$  ppm.

TABLE 5: Best fit results for Ba-succinate.

Temps.	Parameter	F-H complete*	F-H modified*	Pitts complete	Pitts modified
298.15 K	$\Lambda_0$	240.00	238.80	231.40–232.60	236.40
	$K_A$	135.00	114.00	275.00–285.00	78.00
	$a$	0.99	1.01	0.30	0.69
	$D_{\text{salt}} * 10^{-5}$	1.597	1.589	1.544	1.573
	$\sigma$	0.1859	0.2110	0.3086	0.2727
	$\eta\Lambda_0$	2.13816	2.12747	2.06689	2.10609
303.15 K	$\Lambda_0$	261.20	259.20	250.80–251.00	254.20
	$K_A$	182.0	216.0	380.0–382.0	81.0
	$a$	0.70	1.39	0.30	0.70
	$D_{\text{salt}} * 10^{-5}$	1.767	1.754	1.698	1.720
	$\sigma$	0.2410	0.2339	0.2867	0.2267
	$\eta\Lambda_0$	2.08490	2.06893	2.00268	2.02902
308.15 K	$\Lambda_0$	279.80	270.00	261.60–261.80	263.60
	$K_A$	420.0	263.0	430.0	110.0
	$a$	1.41	1.39	0.70	0.30
	$D_{\text{salt}} * 10^{-5}$	1.916	1.857	1.800	1.813
	$\sigma$	0.1866	0.2308	0.2889	0.2190
	$\eta\Lambda_0$	2.02239	1.95156	1.89157	1.90530
313.15 K	$\Lambda_0$	288.80	276.00	275.20	272.00
	$K_A$	455.0	264.7	540.0	150.0
	$a$	1.40	1.39	0.35	0.41
	$D_{\text{salt}} * 10^{-5}$	2.019	1.929	1.924	1.901
	$\sigma$	0.2509	0.3156	0.4114	0.3189
	$\eta\Lambda_0$	1.88875	1.80504	1.79981	1.77888

\* Preferred values.

Units of  $\Lambda_0$ :  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $K_A$ :  $\text{dm}^3\text{mol}^{-1}$ ,  $a$ : nm,  $D_{\text{salt}}$ :  $\text{cm}^2\text{s}^{-1}$ ,  $\sigma$ : unitless, and  $\eta\Lambda_0$ :  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}\text{Cp}$ .

All stock solutions were prepared by weight, and all measurements were done using the weight dilution technique.

Figure 1 illustrates an example of FT-IR run.

#### 4. Result and Discussion

The measured molar conductances  $\Lambda$  and the corresponding concentrations  $C$  in  $\text{mol}\cdot\text{dm}^{-3}$  at four different temperatures are given in Tables 1, 2, 3, and 4. These data were analyzed using the complete and modified forms of both F-H and P equations. For the interpretation of the characteristic parameters of an electrolyte solution from conductance data, a minimisation technique has been used in terms of  $K_A$ ,  $\Lambda_0$ , and  $a$ . For analysis of each set of data,  $C_j$ ,  $\Lambda_j$  ( $j = 1, 2, \dots, N$ ), a Fortran computer program has been written. The results of minimisation technique for the best fit values of the three parameters  $K_A$ ,  $\Lambda_0$ , and  $a$  are listed in Tables 5, 6, 7, and 8 together with diffusion coefficient ( $D_{\text{salt}}$ ).

Walden product and the corresponding values of the standard deviation  $\sigma$  are given by

$$\sigma = \left[ \frac{S^2}{N} \right]^{1/2}, \quad (1)$$

where  $S^2$  is defined by

$$S^2 = \sum_{j=1}^N (\Lambda_{\text{calculated}} - \Lambda_j)^2. \quad (2)$$

Standard thermodynamic quantities for the association reaction are obtained from the temperature dependence of the association constant  $K_A$ . The standard enthalpy change ( $\Delta H^\circ$ ) was determined from the slope of  $\log K_A$  versus  $1/T$  [13] as follows:

$$\log K_A = \left( -\frac{\Delta H}{2.303RT} \right) + \text{constant}, \quad (3)$$

and the standard Gibbs energy ( $\Delta G^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes were calculated using the well-known relations

$$-RT \ln K_A = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (4)$$

Also the diffusion coefficients of the salts ( $D_{\text{salt}}$ ) can be founded from the equation [14]

$$D_{\text{salt}} = \left( \frac{R * T}{F^2} \right) \left( \frac{\Lambda_0}{Z} \right), \quad (5)$$

where  $R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$ ,  $F = 96500 \text{ C}$ , and  $Z = 2$ , while the Walden's product can be calculated as a function of temperature by using

$$\Lambda_0(T) \eta(T) = \text{constant}. \quad (6)$$

TABLE 6: Best fit results for Cu-succinate.

Temps.	Parameter	F-H complete*	F-H modified*	Pitts complete	Pitts modified
298.15 K	$\Lambda_0$	226.20	221.40	214.60–215.00	217.00
	$K_A$	11600.0	10510.0	11100.0–11108.0	10050.0
	$a$	1.01	0.71	0.10	0.31
	$D_{\text{salt}} * 10^{-5}$	1.505	1.473	1.429	1.444
	$\sigma$	0.1723	0.2198	0.2417	0.1998
	$\eta\Lambda_0$	2.01522	1.97245	1.91365	1.93325
303.15 K	$\Lambda_0$	271.40	267.60	267.80 and 268.00	262.20
	$K_A$	16300.0	15020.0	17000.0	14550.0
	$a$	0.69	0.31	1.00	0.30
	$D_{\text{salt}} * 10^{-5}$	1.836	1.811	1.812	1.774
	$\sigma$	0.1800	0.1971	0.2513	0.1869
	$\eta\Lambda_0$	2.16632	2.13598	2.13838	2.09288
308.15 K	$\Lambda_0$	287.80	279.60	277.80–278.10	280.40
	$K_A$	18100.0	15800.0	17950.0–18050.0	16200.0
	$a$	1.01	0.31	0.30	0.31
	$D_{\text{salt}} * 10^{-5}$	1.980	1.923	1.912	1.929
	$\sigma$	0.1130	0.2095	0.2569	0.1770
	$\eta\Lambda_0$	2.08022	2.02095	2.00902	2.02673
313.15 K	$\Lambda_0$	359.20	345.00	331.70–332.30	344.80
	$K_A$	25300.0	22100.0	22700.0–22900.0	22450.0
	$a$	0.29	0.29	1.40	0.29
	$D_{\text{salt}} * 10^{-5}$	2.511	2.411	2.321	2.410
	$\sigma$	0.1083	0.1027	0.2589	0.1071
	$\eta\Lambda_0$	2.34917	2.25630	2.17128	2.25500

\* Preferred values.

Units of  $\Lambda_0$ :  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $K_A$ :  $\text{dm}^3\text{mol}^{-1}$ ,  $a$ : nm,  $D_{\text{salt}}$ :  $\text{cm}^2\text{s}^{-1}$ ,  $\sigma$ : unitless, and  $\eta\Lambda_0$ :  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}\text{Cp}$ .

It was noted that the minimisation  $\Lambda_0$  and  $a$  values for the complete and modified Fuoss-Hsia equations were almost greater than those values obtained using the complete and modified forms of the Pitts. The reason for this has been discussed by Fernandez-Prini and Prue [15, 16] in outline, and by Pitts et al. [17] in detail. The Brownian terms in the velocity of the ion were neglected by Pitts. Also, Pitts equation does not allow for the kinetic (osmotic) terms which contributed to the increase in velocity of the ion.

It was obvious from the minimisation technique that the parameter  $\Lambda_0$  had the greatest effect on the values of  $S^2$  during the variation of the three parameters  $K_A$ ,  $\Lambda_0$ , and  $a$ . This is to be expected, in so far as  $\Lambda_0$  is the leading term in all the conductance equations. However,  $\Lambda_0$  was relatively insensitive to the values of  $K_A$  and  $a$  at the corresponding minima of  $S^2$ .

Form the association constants given in Tables 5–8, at different temperatures, it can therefore be anticipated that these salts do not behave as “strong” electrolytes, and that their dissociations are far from complete. It can also be seen that copper succinate undergoes more ion-pair formation according to the quantitative conductance data. In conclusion, it appears that the copper succinate is capable of showing a marked tendency to autocomplex formation, similar to the same tendency as for copper malonate [18, 19]. The high-association constant for the Cu(II) salt, with the

ready availability of d-levels in the cation, illustrates this tendency. At present, however, it is not possible to make a calculation for such complex formation in our computer programs. So, no further analysis was done for this salt. On the above views, it can be generally predicated, for all studied salts, that the degree of dissociation is highly changed from one to another.

The succinate ion possesses the donor property to a less degree than both oxalate and malonate ions [20, 21], so it can also be emphasized that succinate salts are more highly dissociated than the oxalates [22] and malonates [23, 24].

In Figures 2, 3, 4, and 5, curves of molar conductance versus square root of concentration at four temperatures have been obtained for the four succinate salts. For these electrolytes, the measured conductivity was abnormally small. Abnormally weak salts usually form autocomplexes readily, as are shown by Ives and Riley’s conductivity measurements [25] for copper malonate. In this work, with the exception of copper succinate, however, the experimental conductances give no evidence of this. The same conclusion was found for other systems by other authors [9, 18–24].

Considering the difficulties resulting from the limited solubilities of the succinate salts, the values obtained in this work for  $K_A$ ,  $\Lambda_0$ , and  $a$  are satisfactory, providing a particularly good example for typical incompletely dissociated electrolytes, the thermodynamic association constants of

TABLE 7: Best fit results for Mg-succinate.

Temps.	Parameter	F-H complete*	F-H modified*	Pitts complete	Pitts modified
298.15 K	$\Lambda_0$	225.20	222.60	220.00	223.00
	$K_A$	120.0	170.0	320.0	110.0
	$a$	0.59	1.40	0.70	0.60
	$D_{\text{salt}} * 10^{-5}$	1.499	1.481	1.464	1.484
	$\sigma$	0.5177	0.2390	0.4397	0.3709
	$\eta\Lambda_0$	2.00631	1.98314	1.95998	1.98671
303.15 K	$\Lambda_0$	230.00	229.20	228.00	228.20
	$K_A$	175.0	200.0	460.0	160.0
	$a$	0.65	1.00	0.30	0.60
	$D_{\text{salt}} * 10^{-5}$	1.556	1.551	1.543	1.544
	$\sigma$	0.0975	0.0961	11.4499	0.2885
	$\eta\Lambda_0$	1.83586	1.82947	1.81990	1.82149
308.15 K	$\Lambda_0$	231.80	232.00	231.60	231.40
	$K_A$	370.0	295.0	560.0	280.0
	$a$	1.00	1.00	1.40	0.70
	$D_{\text{salt}} * 10^{-5}$	1.594	1.596	1.593	1.592
	$\sigma$	0.3931	0.9841	1.6379	1.3726
	$\eta\Lambda_0$	1.67545	1.67690	1.67401	1.67256
313.15 K	$\Lambda_0$	260.00	253.20	251.20	253.80
	$K_A$	480.0	329.0	592.0	305.0
	$a$	1.39	1.41	1.00	1.01
	$D_{\text{salt}} * 10^{-5}$	1.817	1.770	1.756	1.774
	$\sigma$	0.8112	0.6646	0.7072	0.6792
	$\eta\Lambda_0$	1.70040	1.65593	1.64285	1.65985

\* Preferred values.

Units of  $\Lambda_0$ :  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $K_A$ :  $\text{dm}^3\text{mol}^{-1}$ ,  $a$ : nm,  $D_{\text{salt}}$ :  $\text{cm}^2\text{s}^{-1}$ ,  $\sigma$ : unitless, and  $\eta\Lambda_0$ :  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}\text{Cp}$ .

which conform to the law of mass action. The abnormally low conductances of these electrolytes are not due to the presence of electrically neutral molecules but to the ion-pair formation. This is to be indicated by further measurements at high different frequencies which will be taken into consideration in the future studies. Such evidence has been shown for both oxalate [22] and malonate salts [9], as well as for Mg and Mn sulphates [26].

It is obvious from Tables (5–8) that some  $a$  values are small, while others are large depending on the type of the four conductance equations used. The explanation for such discrepancies in these results is that the small  $a$  values indicate that the linkage is largely covalent [18, 19, 27] and not merely due to “coulomb” ion association. The large  $a$  values were explained by the fact that the assumption of spherical symmetry and a central charge is far from truth for the succinate ion just like that in barium malonate [18, 19].

Recently, an investigation of Mg, Ca, and Ba complexes in aqueous solution was carried out [28]. The result showed that the conductance of  $\text{Mg}^{+2}$  ion is much lower due to greater interaction between the charge on the ion and the dipoles of the adjacent solvent molecules, which leads to a reduction in mobility. A good agreement between their values of  $\Lambda_0$  for Mg and Ba succinates and our present values was obtained for both salts.

Unfortunately, no recent determinations of  $\Lambda_0$  at 298.15 K for all salts studied have been found. So, in comparison with ionic mobilities at infinite dilution at 298.15 K taken from [14]:  $\lambda_{0\ 1/2}\text{Mg}^{+2} = 53.06$ ,  $\lambda_{0\ 1/2}\text{Mn}^{+2} = 53.10$ ,  $\lambda_{0\ 1/2}\text{Ba}^{+2} = 63.64$ , and  $\lambda_{0\ 1/2}\text{Cu}^{+2} = 53.60$  together with the value of 58.8 [14] or 56.99 [29] of succinate ion, good agreement has been shown in Tables 5–8.

In order to obtain a better understanding of the thermodynamics of the association reactions for the studied salts, it is useful to consider the enthalpic and entropic contributions to these associations. The standard enthalpy, free energy and entropy changes were determined by using (3) and (4), respectively, at different temperatures. Summarizing at this point, give the conductometric association constant  $K_A$ , the standard free energy change for the postulated equilibrium can be determined. This opens the way to a search for correlations between  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  on the one hand and basic properties of solutes and solvents on the other hand. According to the minimisation technique used here, each of the seven systems gave a unique best set of parameters at each temperature. While the best  $K_A$  and  $\Lambda_0$  showed an expected trend with temperature, this trend for  $a$  was quite irregular and covered a broader range of values. Tables 5–8 show clearly the temperature dependence of the  $\Lambda_0$  of particular systems. The increase of  $\Lambda_0$  with an increase of temperature

TABLE 8: Best fit results for Mn-succinate.

Temps.	Parameter	F-H complete*	F-H modified*	Pitts complete	Pitts modified
298.15 K	$\Lambda_0$	224.80	220.00	220.40–220.80	223.40
	$K_A$	353.0	490.0	850.0	550.0
	$a$	0.65	1.10	0.30	0.65
	$D_{\text{salt}} * 10^{-5}$	1.496	1.464	1.468	1.487
	$\sigma$	0.2028	0.1772	0.3644	0.3928
	$\eta\Lambda_0$	2.00274	1.95998	1.96533	1.99027
303.15 K	$\Lambda_0$	226.30	225.80	228.00	226.00
	$K_A$	500.0	525.0	950.0	553.0
	$a$	0.60	1.20	0.30	0.75
	$D_{\text{salt}} * 10^{-5}$	1.531	1.528	1.543	1.530
	$\sigma$	0.4441	0.5212	0.7283	0.8156
	$\eta\Lambda_0$	1.80633	1.80234	1.81990	1.80393
308.15 K	$\Lambda_0$	232.80	229.80	230.60	230.00
	$K_A$	680.0	580.0	990.0	555.0
	$a$	1.00	1.10	0.30	0.80
	$D_{\text{salt}} * 10^{-5}$	1.601	1.581	1.586	1.582
	$\sigma$	0.5795	0.4829	0.7623	0.5641
	$\eta\Lambda_0$	1.68268	1.66099	1.66678	1.66244
313.15 K	$\Lambda_0$	246.00	239.60	240.00	242.60
	$K_A$	820.0	590.0	1010.0	585.0
	$a$	1.40	1.41	0.30	0.71
	$D_{\text{salt}} * 10^{-5}$	1.720	1.675	1.678	1.696
	$\sigma$	0.4200	0.5529	0.5570	0.7734
	$\eta\Lambda_0$	1.60884	1.56698	1.56960	1.58660

\* Preferred values.

Units of  $\Lambda_0$ :  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $K_A$ :  $\text{dm}^3\text{mol}^{-1}$ ,  $a$ : nm,  $D_{\text{salt}}$ :  $\text{cm}^2\text{s}^{-1}$ ,  $\sigma$ : unitless, and  $\eta\Lambda_0$ :  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}\text{Cp}$ .

TABLE 9: Thermodynamic data for Ba-succinate.

	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )				$\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )			
		298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
F-H complete	69.681	-12.159	-13.116	-15.475	-15.934	274.493	273.122	276.346	273.400
F-H modified	42.614	-11.740	-13.548	-14.276	-14.524	182.303	185.260	184.617	182.461
Pitts complete	32.510	-13.968	-14.978	-15.535	-16.380	155.887	156.647	155.913	156.122
Pitts modified	35.069	-10.800	-11.076	-12.042	-13.045	153.846	152.219	152.884	153.646

TABLE 10: Thermodynamic data for Cu-succinate.

	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )				$\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )			
		298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
F-H complete	37.950	-23.199	-24.445	-25.117	-26.396	168.065	168.450	173.372	172.070
F-H modified	35.414	-22.954	-24.239	-24.768	-26.044	158.155	161.510	161.252	159.469
Pitts complete	34.494	-23.090	-24.551	-25.102	-26.125	162.542	163.193	162.353	162.459
Pitts modified	39.125	-22.843	-24.159	-24.832	-26.085	167.448	165.597	166.045	166.597

TABLE 11: Thermodynamic data for Mg-succinate.

	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )				$\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )			
		298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
F-H complete	76.249	-11.867	-13.017	-15.150	-16.074	296.520	294.787	297.659	294.372
F-H modified	36.812	-12.731	-13.354	-14.570	-15.090	162.843	166.122	165.789	163.933
Pitts complete	31.863	-14.299	-15.453	-16.212	-16.620	153.717	154.514	153.814	154.056
Pitts modified	56.333	-11.652	-12.791	-14.436	-14.893	225.165	222.361	221.888	221.548

TABLE 12: Thermodynamic data for Mn-succinate.

	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )				$\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )			
		298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
F-H complete	44.111	-14.542	-15.663	-16.709	-17.468	188.730	188.774	193.366	191.745
F-H modified	10.223	-15.355	-15.786	-16.302	-16.611	73.663	78.412	79.503	79.025
Pitts complete	8.720	-16.720	-17.281	-17.672	-18.010	76.095	78.171	78.710	80.152
Pitts modified	2.906	-15.641	-15.903	-16.189	-16.589	45.969	46.121	48.508	50.936

is due to the decrease of solvent viscosity. Bearing in mind that dielectric constant decreases as temperature increases, an increase in temperature should play important role in stabilizing ion-pairs of reaction. So,  $K_A$  increases as shown in the same mentioned tables. Furthermore, when the dielectric constant of the solvent becomes smaller as temperature increases, the electrostatic contribution dominates. As a consequence, many complexes become significantly stable at high temperatures [30]. The same trend was found by Franchini et al. [31] for a conductometric study of dissociation of picric acid in two different organic solvents at different temperatures, as well as by Sokol et al. [13] in their study for the thermodynamics of the association reaction conductance measurements.

Standard thermodynamic quantities for the association reaction of metal ion ( $M^{+2}$ ) and succinate ions are obtained from the temperature dependence of  $K_A$ , (3), as given in Tables 9, 10, 11, and 12.

The positive entropy values of the associations indicate a change from more order states towards a less order states. This might reflect the role of solvent in the association process.

The above-mentioned results show that the  $\Delta H^\circ$  term is the most important factor in determining the stability of the association, and the differences in the magnitude of  $\Delta H^\circ$  values reflected the differences in the attractive forces between opposite charges of the ions of ion-pair.

Many difficulties and uncertainties are associated with these calculations which are derived from the inevitable experimental errors in  $K_A$  values and partly from the calculator's choice of the function which represents the dependence on the temperature. However, the values of  $\Delta G^\circ$  have proved useful in yielding structural information about solute species and solute-solvent interactions. So, such values indicate a spontaneous association of ions (i.e., the yield of ion-pairs increases) despite of that they differ from one equation to the other depending on their mathematical derivations.

From the dependence of the Walden product  $\eta\Lambda_0$  on the temperature, information can be obtained on ion-solvent interactions. Data from Tables 5–8 show that the Walden product dependence on the temperature is substantially obeyed. For more consistent results, a consideration should be taken for the electrostatic interaction between the fields of the moving ions and those of the solvent dipoles in the surrounding solvent. The gradual decrease of  $\eta\Lambda_0$  with temperature has been attributed to a decrease in dielectric constant, causing a disturbance in the hydrodynamic radii of ions followed by a change in their mobility.

Generally, it is concluded that either Fuoss-Hsia complete or modified is better than those equations of Pitts.

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