

The Audio Frequency Conductance and thermodynamic studies of Some Metal Glutarate salts in Aqueous Medium at Different Temperatures

(Part I: Magnesium, Manganese (II), Barium and Copper glutarates)

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Abstract—The audio frequency conductances of aqueous solutions of magnesium, manganese (II), barium, and copper glutarates have been measured at various temperatures in the range 298.15 to 313.15 K, using an audio frequency conductance bridge. These salts were prepared by two methods electrochemical method and, for the first time and chemical method. The evaluation of conductance data was carried out by minimization technique using the theoretical conductance 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 (Λ_0) 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 attributed to the presence of electrically neutral molecules but to the ion-pair formation.

The standard thermodynamic functions [i.e the change in enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°)] for the association reaction as well as the Walden product values at the four temperatures have been evaluated.

Index Terms— Synthesis of Glutarate salts, Audio frequency conductance measurement, thermodynamic parameters, minimization technique.

1. INTRODUCTION

The substances, which in the pure state, already exist as ionic crystals, are known "ionophores", e.g. the alkali metal halides. These substances contain no neutral molecules which can dissociate but are completely dissociated.

On the other hand, substances such as acetic acid which do exist as neutral molecules in pure form are known as "ionogens", and can produce ions by a dissociation process to give conducting solutions in certain solvents. The primary act here is that one of the neutral molecules with the solvent, forming a molecular complex which rearranges to an ion-pair. The ion-pair finally dissociates into free ions.

All electrolytes are partially dissociated or weak, in low dielectric constant, and classification of electrolytes into strong and weak electrolytes becomes somewhat arbitrary. So, it is more convenient to deal with the classification of Fuoss[1] for the properties of electrolytes.

For incompletely dissociated electrolyte, the ion-ion and ion-solvent interactions should be combined with the interionic effect in order to account for the observed conductance values[2]. 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 glutarates in aqueous medium at various temperatures in the range 298.15 - 313.15 K. Metal glutarates play an important role in biological and industrial processes[3-6]. Four currently used conductance equations, the complete and expanded forms of both Fuoss-Hsia[7,8] and Pitts[9,10] equations have been used to analyse conductance data for these glutarate salts. Also, the thermodynamic parameters ΔH° , ΔG° and ΔS° 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 – 313.15 K with OAKTon- con510 audio frequency bridge of low impedance. It combines speed and simplicity of operation with 0.01% accuracy. The cell used for measuring conductances has been described elsewhere[10]. The cell constant (as determined by standard solutions of potassium chloride) was 0.1662295 cm⁻¹. The method used for measuring conductances has been described[10].

2.1. MATERIALS

The KCl used in this work was purified and used according to the literature[11]. As a first time, electrochemical method was applied for the preparation of both magnesium and Copper glutarates. Each metal was fused carefully in a special furnace, followed by pouring them separately into a well designed cavities which were already made before. The electrolysis of glutaric acid was started under a constant voltage of 2V, using the same specified metal as both cathode and anode. The initial resultant current was 3A which afterwards began to decrease gradually until a steady value was reached leaving a neutral solution. This solution was evaporated and a pure salt was obtained.

The suggested mechanism is:

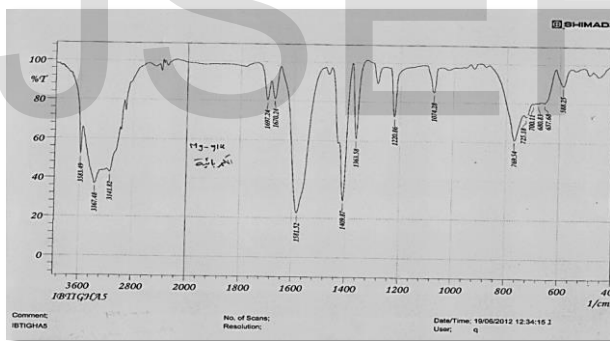
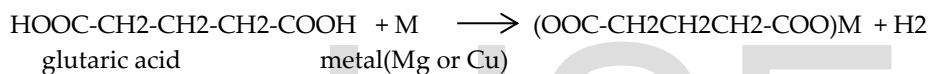
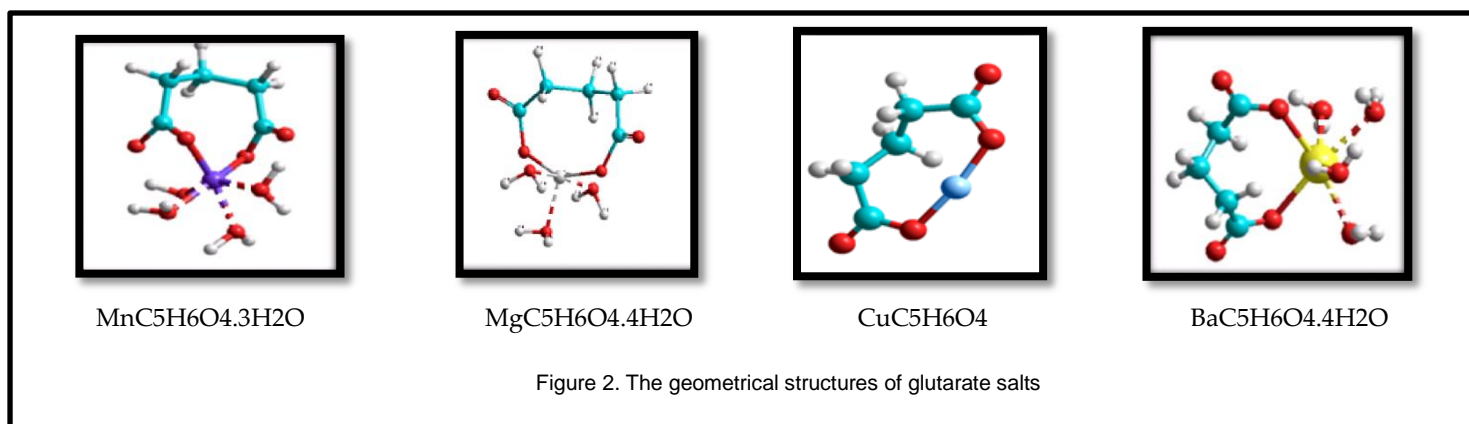


Figure 1. FT-IR spectra for Mg- glutarate

All four salts were prepared chemically. Magnesium glutarate was prepared by addition of clean and dried magnesium ribbon to a solution of glutaric 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 recrystallised 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 prepared salt electrochemically was determined by elemental analysis. Elemental analysis confirmed the composition with experimental / calculated values (mass percent): C 27.604/26.518, H 6.248/6.231. FT-IR exhibits the following absorption bands(KBr pellet,ν/cm-1): (narrow ν(O-H) bands at 3583 and 3367 cm-1; associated with the existence of hydrogen bonds; stretching frequencies corresponding to the carboxylate ion ν(CO₂) and ν(C-O) at 1581, 1440, 1409, 1363, 1270 and 1220 cm-1; the 1074 cm-1 absorption band is associated with ν(C-C) and the following absorptions with metal oxygen bonding and with ν(C-H) 910, 725, 680, 588 and 445 cm⁻¹ [12].



Manganese glutarate was prepared by the method described by Vogel[13]with some modification. "Analar" grade manganese chloride solution was added to a solution of sodium glutarate. 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 a 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 24.882 / 25.119, H 6.004 / 5.059. FT-IR exhibits the following absorption bands(KBr pellet, ν /cm⁻¹ :(narrow ν (O-H) bands at 3556 and 3311 cm⁻¹ associated with the existence of hydrogen bonds; stretching frequencies corresponding to the carboxylate ion ν (CO⁻²) and ν (C-O) 1658,1557, 1409, 1359, 1284 and 1220 cm⁻¹ ; the 1074 cm⁻¹ absorption band is associated with ν (C-C) and the following absorptions with metal oxygen bonding and with ν (C-H) 910, 763, 727, 645and 580 cm⁻¹.

Barium glutarate was prepared by addition of clean and dried barium metal to a solution of succinic acid. The mixture was heated on a water bath until a quarter of it was gained. The PH of solution was continuously tested until the solution became neutral. The remaining solution was left for 24 hours, when a white crystals formed. The mixture was then filtered to remove the excess of metal added, after which the final product was dried by air at room temperature. Elemental analysis confirmed the composition with experimental / calculated values (mass percent): C 17.775/ 17.689, H 4.451 / 4.157. FT-IR exhibits the following absorption bands(KBr pellet, ν /cm⁻¹:(narrow ν (O-H) bands at 3419 and 3340 cm⁻¹; associated with the existence of hydrogen bonds; stretching frequencies corresponding to the carboxylate ion ν (CO⁻²) and ν (C-O) at 1548, 1402, 1305,1271 and 1220 cm⁻¹ ; the 1149 cm⁻¹ absorption band is associated with ν (C-C) and the following absorptions with metal oxygen bonding and with ν (C-H)1060, 914, 869, 709, 645 and 462 cm⁻¹.

The copper glutarate was prepared by a reaction of stoichiometric amounts of both, solution of glutaric acid and copper metal. The solution was heated with continuous stirring at 348.15-353.15K for a period of 3-4 hours. A blue solution was 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 of the prepared salt electrochemically confirmed the composition with experimental /calculated values (mass percent):

C 31.139 / 31.013, H 3.211 / 3.123. The FT-IR spectra exhibits the following absorption bands (KBr pellet, ν /cm⁻¹) stretching frequencies corresponding to the carboxylate ion ν (CO⁻²) and ν (C-O) 1591, 1577, 1407, 1342 and 1276 cm⁻¹ ; the 1195, 1157 cm⁻¹ absorption band is associated with ν (C-C) and the following absorptions with metal oxygen bonding and with ν (C-H) 1068, 880, 729, 682, 601, 561and 520 cm⁻¹.

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.

The geometrical structures of all studied glutarate salts were confirmed by using the computer program Hyperchem 8, with the aid of using PM3 method. This method is mainly concerned with the computation of the dimensions of the chemical bonds as well as their energies. The recommended structures shown in Figure (2) were approved according to their maximum stabilities (lass energies) upon which CHN analysis were detected and taken into consideration.

1 RESULTS AND DISCUSSION

The measured molar conductances Λ and the corresponding concentrations C in mol.dm^{-3} at four different temperatures are given in tables 1–4. 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 , Λ_o and \underline{a} . For analysis of each set of data, C_j , Λ_j ($j=1,2,\dots,N$), an Fortran computer program has been written. The results of minimisation technique for the best fit values of the three parameters K_A , Λ_o and \underline{a} are listed in tables (5-8) together with diffusion coefficient (D_{salt}).

Walden product and the corresponding values of the standard deviation σ , given by

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

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 (ΔH°) was determined from the slope of $\log K_A$ versus $1/T$ [14], as follows :

$$\log K_A = (-\Delta H / 2.303 RT) + \text{constant} \quad (3)$$

and the standard Gibbs energy (ΔG°) and entropy (ΔS°) 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_{salt}) can be founded from the equation(15)

$$D_{\text{salt}} = ((RT)/F^2)(\Lambda_o/Z) \quad (5)$$

Where $R=8.314 \text{ JK}^{-1} \text{ mole}^{-1}$, $F=96500C$, $Z=2$.

While the Walden's product can be calculated as a function of temperature by using

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

It was noted that the minimisation Λ_o and \underline{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 – prin and prue[10,16] in outline, and by Pitts et al[17] in detail. The Brownian terms in the velocity of the ion was 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 Λ_o had the greatest effect on the values of S^2 during the variation of the three parameters K_A , Λ_o and \underline{a} . This is to be expected, in so far as Λ_o is the leading term in all the conductance equations. However, Λ_o was relatively insensitive to the values of K_A and \underline{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 glutarate undergoes more ion-pair formation according to the quantitative conductance data.

In conclusion, it appears that the copper glutarate is capable of showing a marked tendency to auto-complex formation, similar to the same tendency as for both copper Malonate and copper succinate[18-20]. 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 glutarate ion possesses the donor property to a less degree than oxalate, malonate and succinate ions^[21,22], so it can also be emphasized that succinate salts are more highly dissociated than the oxalates[21],Malonate[22] and succinate[20].

TABLE 1. EXPERIMENTAL CONDUCTANCE DATA FOR BA-GLUTARATE

298.15K		303.15K		308.15K		313.15K	
Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ
3.40712	111.287	1.70412	126.370	0.48290	146.814	5.08469	135.901
4.14570	109.906	2.02757	124.658	2.07504	134.022	6.19192	134.419
4.86662	108.537	2.96226	122.361	4.00727	127.890	6.77609	133.870
5.57817	107.608	3.49679	121.720	4.61150	126.993	8.48647	133.333
6.25359	106.618	4.05551	119.707	4.95627	127.550	9.23886	133.270
7.07098	105.126	4.54630	119.582	5.59113	126.743	10.01076	132.127
7.52739	105.138	5.13011	117.962	6.16200	125.792	10.77043	131.296
8.69753	103.146	6.65348	115.435	7.91126	125.293	11.40906	129.775
9.32086	102.742	7.26560	113.720	8.36050	125.520	16.49120	130.406
9.91892	101.994	8.38296	112.443	9.04126	123.423	12.48239	129.935
10.60350	101.192	8.79067	111.955	9.57046	123.546	13.08255	129.692
11.17054	101.135	10.41512	111.252	10.70924	122.050	13.62094	128.837
13.14859	99.382			12.22098	119.194	14.75670	127.370
13.61655	99.018			14.48149	116.085	15.32133	127.016
14.76449	98.075			15.02823	115.73		

Λ (ohm⁻¹ cm² equiv⁻¹); Conc. = concentration (mol.dm⁻³)

TABLE 2. EXPERIMENTAL CONDUCTANCE DATA FOR CU- GLUTARATE

298.15K		303.15K		308.15K		313.15K	
Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ
1.19239	89.989	0.42020	108.789	1.50040	96.055	0.58964	115.867
1.62187	89.220	2.73685	93.536	1.66838	94.354	0.78480	113.571
1.78947	87.831	2.92849	92.807	1.91844	92.887	1.28714	109.258
1.94790	87.514	3.08712	92.077	2.13775	91.522	3.11667	97.391
2.33882	86.035	3.28703	89.764	2.32891	90.077	3.54583	95.448
2.47922	85.856	3.49673	88.659	2.53669	89.580	3.74495	94.146
2.64242	85.272	3.63242	88.551	2.71510	88.285	3.91825	93.800
3.34403	82.542	3.77964	88.400	2.93139	86.739	4.06948	92.561
3.46824	82.222	3.91199	87.573	3.67834	83.243	4.41269	90.824
3.57495	81.860	4.24688	86.503	3.80091	82.964	4.54003	90.474
3.68812	81.602	4.36403	86.085	3.94656	82.343		
3.76091	81.570			4.05633	82.042		
3.85353	80.903			4.15822	81.831		
3.94622	80.899			4.25189	81.006		

Λ (ohm⁻¹ cm² equiv⁻¹); Conc. = concentration (mol.dm⁻³)

Table 3. Experimental conductance data for Mg- glutarate

298.15K		303.15K		308.15K		313.15K	
Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ
4.88375	99.696	1.91032	114.339	2.28466	124.441	5.92416	133.199
5.71497	98.016	3.10992	112.195	2.87749	124.403	6.84846	131.363
6.87027	96.890	4.40851	111.008	3.56327	122.692	7.51972	130.690
7.7679	95.922	5.07941	110.091	4.15314	121.758	8.16505	129.521
9.10606	93.406	6.41612	108.270	4.91910	120.133	8.63865	130.118
9.52163	92.436	7.31558	107.455	5.63926	119.235	9.26579	129.384
9.93720	91.842	7.94820	106.432	7.78041	116.547	10.35460	128.622
11.10081	91.574	8.72202	106.519	9.50602	112.877	11.09992	127.474
13.92671	89.368	9.36712	106.281	10.42666	111.679	11.66201	126.318
14.34229	87.813	9.85126	106.120	11.65423	109.900	12.56167	125.873
15.09032	87.644	10.79007	104.590	12.44838	109.569	13.03903	125.089
		12.36002	103.349	15.32989	106.197	14.00493	124.456
		13.13537	103.409	15.96085	107.947	14.64795	124.177
		14.09362	102.999			16.48142	123.265

Λ ($ohm^{-1} cm^2 equiv^{-1}$); Conc. = concentration ($mol.dm^{-3}$)

TABLE 4. EXPERIMENTAL CONDUCTANCE DATA FOR MN- GLUTARATE

298.15 K		303.15 K		308.15 K		313.15 K	
Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ	Conc.×10 ⁻⁴	Λ
2.83092	97.474	5.59959	97.667	1.03938	127.945	4.91448	116.694
3.61613	94.236	6.31873	96.878	2.06226	124.939	5.69025	115.392
12.03167	81.514	6.96373	95.960	5.24357	116.028	6.62776	114.118
12.53010	81.920	7.70070	94.979	7.03356	113.915	8.70288	110.783
13.42446	81.806	8.34785	94.586	7.93451	113.131	13.72651	103.844
14.22748	80.033	9.06379	93.534	8.77099	111.818	14.71236	103.100
14.85781	79.994	9.56837	92.945	11.35597	109.054	15.62053	102.161
16.84632	78.446	10.08646	92.291	12.11577	107.703	16.30256	101.455
17.58816	77.973	10.65533	91.263	12.82252	106.952	17.74709	100.691
18.23845	77.471	11.89849	90.111	13.57981	106.496	18.43650	100.081
18.95271	77.183	12.39414	89.189	14.34065	105.483		
		12.85998	88.544	14.93580	105.175		

Λ ($ohm^{-1} cm^2 equiv^{-1}$); Conc. = concentration ($mol.dm^{-3}$)

TABLE 5. BEST FIT RESULTS FOR BA-GLUTARATE

Temp.	Parameter*	F-H complete	F-H modified	Pitts complete	Pitts modified
298.15K	Λ_0	127.5	127.0	121.6	125.1
	K_A	80.3	83	214	43
	a	0.77	0.91	0.6	0.61
	$D_{salt} \times 10^{-5}$	1.697	1.690	1.618	1.665
	σ	0.188	0.170	0.261	0.209
	$\Lambda_0 \eta$	1.15897	1.13144	1.08333	1.11452
303.15K	Λ_0	138.4	138.7	133.7	136.4
	K_A	104	106	243	68
	a	1.03	1.13	0.3	1.38
	$D_{salt} \times 10^{-5}$	1.873	1.877	1.809	1.846
	σ	0.416	0.300	0.338	0.336
	$\Lambda_0 \eta$	1.10471	1.10710	1.06719	1.08874
308.15K	Λ_0	147.6	147.8	150	153.6
	K_A	105	94	256	78
	a	1.45	1.41	0.2	0.93
	$D_{salt} \times 10^{-5}$	2.030	2.033	2.063	2.113
	σ	0.378	0.5257	0.4987	0.439
	$\Lambda_0 \eta$	1.06685	1.06830	1.08420	1.11022
313.18K	Λ_0	158	163.8	156.7	156.9
	K_A	109	100	231	50
	a	1.5	1.33	0.1	0.71
	$D_{salt} \times 10^{-5}$	2.209	2.290	2.191	2.193
	σ	0.401	0.435	0.535	0.651
	$\Lambda_0 \eta$	1.03332	1.07125	1.02418	1.02613

* Preferred Value

Units of : Λ_0 ohm-1 cm2 equiv-1 ; K_A dm3 mol-1; a nm; D_{salt} cm2 s-1; σ unitless; $\Lambda_0 \eta$ ohm-1 cm2 equiv -1 p

TABLE 6. BEST FIT RESULTS FOR CU-GLUTARATE

Temp.	Parameter*	F-H complete	F-H modified	Pitts complete	Pitts modified
298.15 K	Λ_0	102.4	102.6	100.8	102
	K_A	259	349	185	324
	a	0.49	1.4	0.3	1.4
	$D_{salt} \times 10^{-5}$	1.315	1.318	1.235	1.131
	σ	0.206	0.207	0.275	0.199
	$\Lambda_0 \eta$	0.91228	0.91406	0.89803	0.90872
303.15 K	Λ_0	116.2	116.8	104.5	113.5
	K_A	344	369	393	372
	a	0.3	0.4	1.4	1
	$D_{salt} \times 10^{-5}$	1.572	1.581	1.411	1.536
	σ	0.572	0.533	0.856	0.697
	$\Lambda_0 \eta$	0.92751	0.93220	0.83412	0.90596
308.15 K	Λ_0	117.2	117.1	108.9	117.3
	K_A	600	617	725	686
	a	0.4	0.66	1.4	0.9
	$D_{salt} \times 10^{-5}$	1.612	1.611	1.498	1.614
	σ	0.162	0.167	0.510	0.166
	$\Lambda_0 \eta$	0.84712	0.84712	0.78713	0.84784
313.18 K	Λ_0	129.3	131.8	123.4	132.1
	K_A	610	629	732	688
	a	0.87	0.9	1.3	1.4
	$D_{salt} \times 10^{-5}$	1.807	1.842	1.725	1.847
	σ	0.469	0.340	0.541	0.305
	$\Lambda_0 \eta$	0.84562	0.86197	0.80703	0.86390

*Preferred Value

Units of : Λ_0 ohm-1 cm2 equiv-1 ; K_A dm3 mol-1; a nm; D_{salt} cm2 s-1; σ unitless; $\Lambda_0 \eta$ ohm-1 cm2 equiv -1 p
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TABLE 7. BEST FIT RESULTS FOR MG-GLUTARATE

Temp.	Parameter*	F-H complete	F-H modified	Pitts complete	Pitts modified
298.15 K	Λ_o	117	116.9	110.8	113.5
	K_A	58	56	190	38
	a	0.65	0.81	1.1	0.96
	$D_{salt} \times 10^{-5}$	1.557	1.556	1.475	1.511
	σ	0.392	0.404	0.348	0.354
	$\Lambda_o \eta$	1.04235	1.04146	0.98712	1.01117
303.15 K	Λ_o	129.5	125.3	120.8	129.9
	K_A	111	64	163	40
	a	1.23	1.58	0.4	0.65
	$D_{salt} \times 10^{-5}$	1.752	1.696	1.635	1.758
	σ	0.358	0.305	0.461	0.350
	$\Lambda_o \eta$	1.03367	1.00014	0.96422	1.03686
308.15 K	Λ_o	141.9	141.9	133.8	140.5
	K_A	97	76	195	60
	a	0.89	0.84	0.9&1.0	0.74
	$D_{salt} \times 10^{-5}$	1.952	1.952	1.841	1.933
	σ	0.584	0.379	0.372	0.293
	$\Lambda_o \eta$	1.02560	1.02565	0.96711	1.01553
313.18 K	Λ_o	157	156.8	150	162.7
	K_A	87	78	201	61
	a	1.13	1.41	0.3	0.67
	$D_{salt} \times 10^{-5}$	2.194	2.157	2.097	2.274
	σ	0.329	0.417	0.397	0.278
	$\Lambda_o \eta$	1.02678	1.02547	0.98100	1.06406

*Preferred Value

Units of : Λ_o ohm-1 cm2 equiv-1; K_A dm3 mol-1; a nm; D_{salt} cm2 s-1; σ unitless; $\Lambda_o \eta$ ohm-1 cm2 equiv-1 p

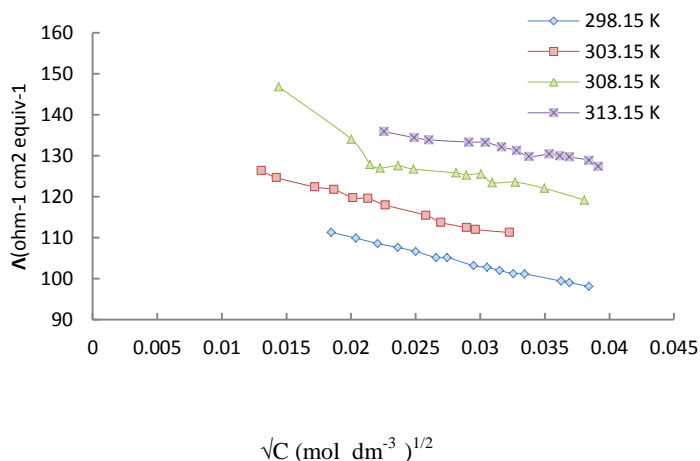


Figure 3. Molar conductance versus square root of concentration for Ba-glutarate at different temperatures

TABLE 8. BEST FIT RESULTS FOR MN-GLUTARATE

Temp.	Parameter*	F-H complete	F-H modified	Pitts complete	Pitts modified
298.15 K	Λ_o	111.5	111.5	106	113.4
	K_A	86	78	189	70
	a	0.48	0.54	1.35	0.45
	$D_{salt} \times 10^{-5}$	1.484	1.148	1.411	1.509
	σ	0.403	0.346	0.944	0.357
	$\Lambda_o \eta$	0.99353	0.99353	0.94435	1.01028
303.15 K	Λ_o	120.5	121.2	114.5	116
	K_A	96	97	263	72
	a	0.61	0.64	1.1	1.01
	$D_{salt} \times 10^{-5}$	1.631	1.640	1.549	1.570
	σ	0.378	0.312	0.310	0.222
	$\Lambda_o \eta$	0.96183	0.96741	0.91394	0.92591
308.15 K	Λ_o	140.9	137.9	135.2	142.6
	K_A	99	114	277	90
	a	0.79	1.41	0.3	0.62
	$D_{salt} \times 10^{-5}$	1.938	1.897	1.860	1.961
	σ	0.416	0.347	0.401	0.436
	$\Lambda_o \eta$	1.01843	0.99674	0.97722	1.03071
313.18 K	Λ_o	144	143.1	135.4	143.6
	K_A	117	119	293	100
	a	0.66	0.85	0.5	0.64
	$D_{salt} \times 10^{-5}$	2.013	2.000	1.893	2.007
	σ	0.367	0.342	0.365	0.619
	$\Lambda_o \eta$	0.94176	0.93587	0.88550	0.93914

*Preferred Value

Units of : Λ_o ohm⁻¹ cm²equiv⁻¹; K_A dm³ mol⁻¹; a nm; D_{salt} cm² s⁻¹; σ unitless; $\Lambda_o \eta$ ohm⁻¹ cm² equiv⁻¹ p

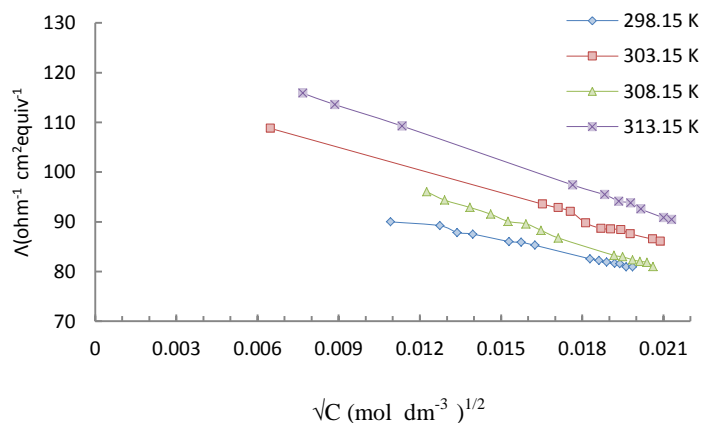


Figure 4. Molar conductance versus square root of concentration for Cu-glutarate at different temperatures

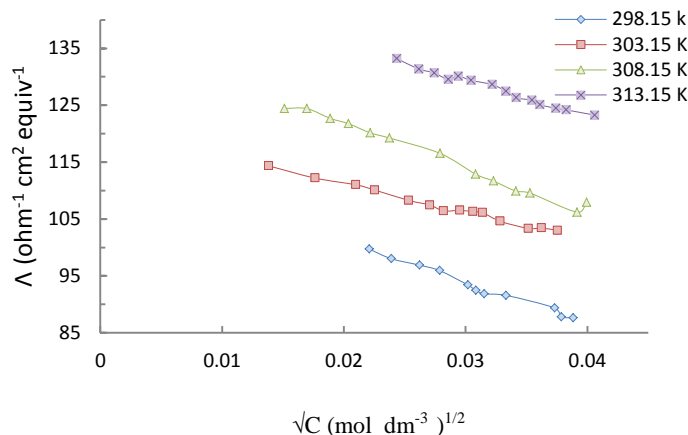


Figure 5. Molar conductance versus square root of concentration for Mg-glutarate at different temperatures

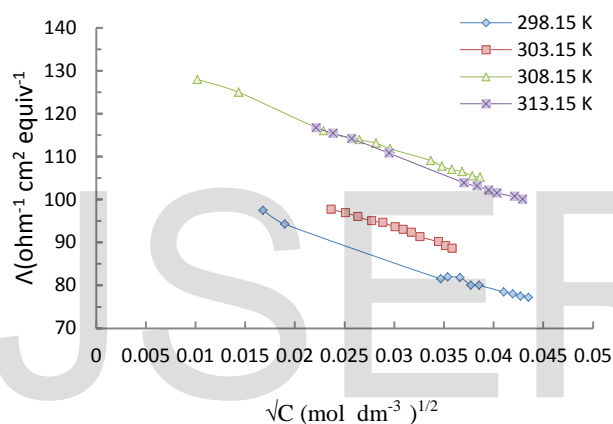


Figure 6. Molar conductance versus square root of concentration for Mn-glutarate at different temperatures

In figures (2 – 5) curves of molar conductance versus square root of concentration at four temperatures have been obtained for the four glutarate salts. For these electrolytes, the measured conductivity was abnormally small. Abnormally weak salts usually form auto-complexes readily, as is shown by Ives and Riley’s conductivity measurements[23] for copper succinate. In this work, with the exception of copper glutarate, however, the experimental conductances give no evidence of this. The same conclusion was found for another systems by other authors[22,24,25].

Considering the difficulties resulting from the limited solubilities of the glutarate salts, the values obtained in this work for K_A , Λ_0 and \underline{a} are satisfactory, providing a particularly good example for typical incompletely dissociated electrolytes the thermodynamic association constants of 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 evidences have been shown for oxalate[21], malonate [22] and succinate salts[20], as well as for Mg and Mn sulphates[26].

It is obvious from tables (5 - 8) that some \underline{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 \underline{a} values indicate that the linkage is largely covalent[24,27] and not merely due to "coulomb" ion association. The large \underline{a} values were explained by the fact that the assumption of spherical symmetry and a central charge is far from truth for the glutarate ion just like that in barium Malonate[24].

An investigation of Mg, Ca and Ba complexes in aqueous solution was carried out[28] . The result showed that the conductance of 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.

Unfortunately, no recent determinations of Λ_o at 298.15K for all salts studied have been found. So, in comparison with ionic mobilities at infinite dilution at 298.15K taken from reference[15]: $\lambda_{o1/2} \text{ Mg}^{+2}=53.0$, $\lambda_{o1/2} \text{ Mn}^{+2}=53.50$, $\lambda_{o1/2} \text{ Ba}^{+2}=63.60$, $\lambda_{o1/2} \text{ Cu}^{+2}=53.60$ together with the value 55.88[29] of glutarate 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 equations (3) and (4) respectively at different temperatures. Summarizing at this point, giving the conductimetric 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 ΔG° , ΔH° and ΔS° on the one hand and basic properties of solutes and solvents on the other. According to the minimisation technique used here, each of the four systems gave a unique best set of parameters at each temperature. While the best K_A and Λ_o showed an expected trend with temperature, this trend for \underline{a} was quite irregular and covered a broader range of values. Tables (5-8) show clearly the temperature dependence of the Λ_o of particular systems. The increase of Λ_o with an increase of temperature 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 conductimetric study of dissociation of picric acid in two different organic solvents at different temperatures, as well as by Sokol et al [14]] in their study for the thermodynamics of the association reaction conductance measurements. Figures (6-9) illustrate such plots for all four investigated glutarate salts .

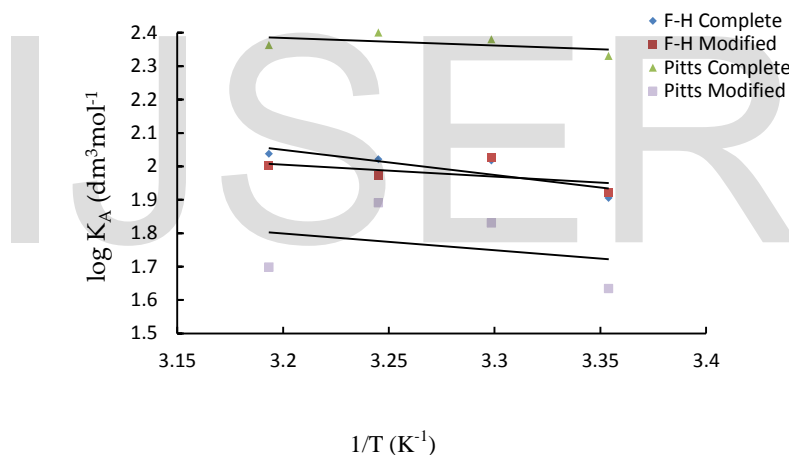


Figure 7. Logarithm of association constant versus inverse temperature for Ba-glutarate

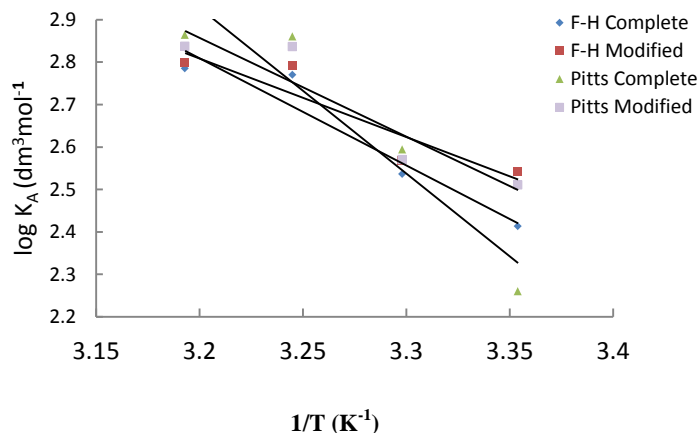


Figure 8. Logarithm of association constant versus inverse temperature for Cu-glutarate

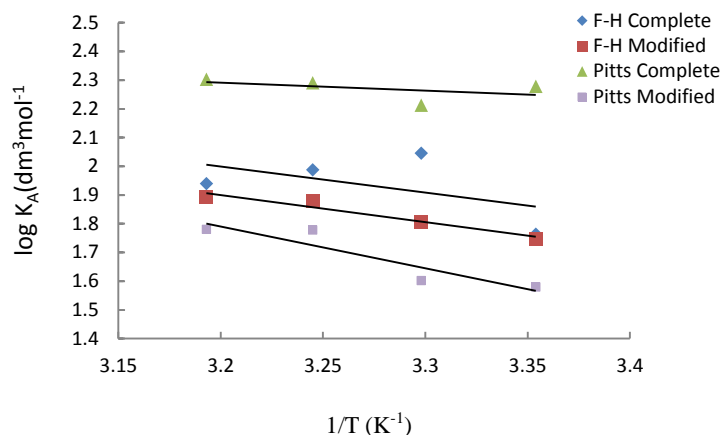


Figure 9. Logarithm of association constant versus inverse temperature for Mg-glutarate

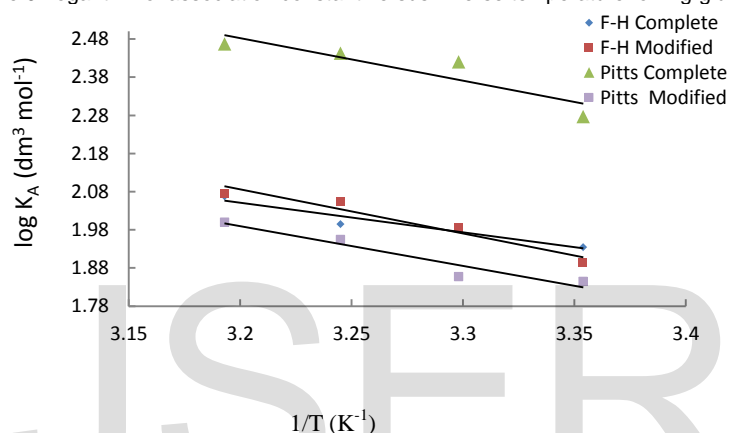


Figure 10. Logarithm of association constant versus inverse temperature for Mn-glutarate

Standard thermodynamic quantities for the association reaction of metal ion (M^{+2}) and glutarate ions are obtained from the temperature dependence of K_A , equation (3), as given in tables (9-12).

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

The above mentioned results show that the ΔH° term is the most important factor in determining the stability of the association, and the differences in the magnitude of ΔH° 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 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 ΔG° 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 $\Lambda_\circ \eta$ 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 $\Lambda_\circ \eta$ 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 Pitts complete or modified is better than those equations of Fuoss-Hsia.

TABLE 9. THERMODYNAMIC DATA FOR BA-GLUTARATE

	T (K)	F-H Complete	F-H Modified	Pitts Complete	Pitts Modified
ΔH° (KJ mol ⁻¹)		14.4447	6.9137	4.31393	9.5363
ΔG° (KJ mol ⁻¹)	298.15	-10.8715	-10.9535	-13.3013	-9.3233
	303.15	-11.7057	-11.7537	-13.8446	-10.6348
	308.15	-11.9233	-11.6397	-14.2065	-11.1617
	313.15	-12.2141	-11.9897	-14.1695	-10.1851
ΔS° (J mol ⁻¹)	298.15	84.9110	59.9270	59.0817	63.2554
	303.15	86.2621	61.5781	59.8997	66.5382
	308.15	85.5686	60.2092	60.1020	67.1685
	313.15	85.1310	60.3654	59.0242	62.9773

TABLE 10. THERMODYNAMIC DATA FOR CU-GLUTARATE

	T (K)	F-H Complete	F-H Modified	Pitts Complete	Pitts Modified
ΔH° (KJmol ⁻¹)		48.3101	35.358	74.6231	44.5485
ΔG° (KJ mol ⁻¹)	298.15	-13.7743	-14.5136	-12.9403	-14.3294
	303.15	-14.7207	-14.8975	-15.0563	-14.9179
	308.15	-16.3886	-16.4602	-16.8735	-16.7318
	313.15	-16.6976	-16.7775	-17.1723	-17.0109
ΔS° (J K ⁻¹ mol ⁻¹)	298.15	208.232	167.2703	293.689	197.477
	303.15	207.9196	165.777	295.825	196.1616
	308.15	209.9588	168.159	296.922	198.865
	313.15	207.593	166.4869	293.1355	196.5812

TABLE 11. THERMODYNAMIC DATA FOR MG-GLUTARATE

	T (K)	F-H Complete	F-H Modified	Pitts Complete	Pitts Modified
ΔH° (KJ mol ⁻¹)		17.2599	18.1317	5.3307	27.8039
ΔG° (KJ mol ⁻¹)	298.15	-10.0651	-9.9781	-13.0064	-9.0169
	303.15	-11.8698	-10.4820	-12.8382	-9.2974
	308.15	-11.7202	-11.0952	-13.5092	-10.4895
	313.15	-11.6271	-11.3428	-13.8073	-10.7027
ΔS° (J mol ⁻¹)	298.15	91.6486	94.2808	61.5031	123.4976
	303.15	96.0903	94.3879	59.9338	122.3859
	308.15	94.0456	94.8462	61.1388	124.2687
	313.15	92.2467	94.1226	61.1146	122.9655

TABLE 12. THERMODYNAMIC DATA FOR MN-GLUTARATE

	T (K)	F-H Complete	F-H Modified	Pitts Complete	Pitts Modified
ΔH° (KJ mol ⁻¹)		14.7997	22.1433	21.3772	20.0037
ΔG° (KJ mol ⁻¹)	298.15	-11.0415	-10.7995	-12.9933	-10.5312
	303.15	-11.5039	-11.5300	-14.0440	-10.7788
	308.15	-11.7725	-12.1339	-14.4085	-11.5283
	313.15	-12.3984	-12.4425	-14.7884	-11.9897
ΔS° (J mol ⁻¹)	298.15	86.6721	110.4908	115.2793	102.4149
	303.15	86.7679	111.0783	116.8438	101.5425
	308.15	86.2316	111.2357	116.1308	102.3271
	313.15	86.8536	110.4452	115.4900	102.1665

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