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Electrical Behaviour of Association Phenomena of Tetra aqua-1,10-phenanthroline Iron (II) Chloride in Methanol-Water Mixtures at Different Temperatures

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الملخص

تم دراسة الخواص الكهربائية لمعقد الحديد ثنائي الليكند في نسب مختلفة من مذيب ثنائي من الميثانول والماء في درجات حرارية مختلفة والتي تعطي معلومات عن تداخلات ايون-ايون وايون-مذيب في المحلول. وتم حساب كل من الدوال الفيزياوية التالية ($\Lambda_{M^{2+}}$ و K_A و R) أي التوصيل المكافئ لايون المعقد وثابت التجمع الايوني للمعقد والمسافة بين الايونات في المحلول كنتيجة لهذا التداخل. وكذلك تم حساب الدوال الثرموديناميكية (ΔH و ΔG و ΔS) لعملية التجمع الايوني والقوى الكولومبية والتي تلعب دور هام في عملية التجمع الايوني. فضلا عن حساب قيم والدن ($\Lambda_o\eta$) مع تركيب المذيب (أي نسبة المذيب) والتي تعطي معلومات عن كيفية التجمع الايوني في النسب المختلفة.

ABSTRACT

The electrical behaviour of mixed ligand complex of Fe(II) in different percentage of binary mixture of methanol and water at different temperatures can give information about ion-ion and ion-solvent interaction in solution so the limiting molar conductance $\lambda^{o}_{Fe^{2+}}$, K_A the association constant and (R) the main distance between ions in solution as a results of those interaction can be calculated. Thermodynamics parameters (ΔH, ΔG, ΔS) of the association processes and the coulombic forces which play an important role in the association process also have been studied, Walden product also calculated for solvent composition which indicate the tendency of the association of the ions in different percentages.

INTRODUCTION

The conductivity measurements are useful as an effective means to understand the nature of solute-solvent interaction since the degree of ionic mobility is exceedingly sensitive to interactions. The characteristics of metal chelate electrolytes is of their solute-solvent interaction concerning charge, size and chemical properties of liquid have been elucidated by the study of the electronic spectra(1) racemization(2), optical resolution(3), viscosity, molar volume(4) and conductivity(5). Very few work have been done on 1,10-phenanthroline and water as mixed ligand with any metal ion(6) had studied. The analytical applications of complexes of metal ions as Mn(II), Ni(II), Co(II) and Cu(II) with 1,10-phenanthroline as ligand which have vary wide applications in industry and have a biological effects were studied by Lee-Wheaton equation to investigate their behaviour of interaction by conductivity(7). Electrolytic conductivities of dilute solutions of Ni(II), Cd(II), Mg(II) and Cu(II) sulfate in binary mixture of methanol and water have been evaluated by using Lee-Wheaton equation(8). The complexes have been screened against a number of fungi and bacteria to assess their growth inhibiting potential. In this work we have measured the electrical conductivities of [Fe(1,10-phenanthroline (H_2O)]Cl_2 in methanol water mixture at different temperatures (288.15-308.15 K) to investigate the thermodynamic behaviours by application of Lee-Wheaton equation and to elucidate the conductivity parameters of assymetrical electrolytes 2:1 (λ_o, K_A, R) in mixed solvents.

EXPERIMENTAL

Tetra aquo (1,10-phenanathroline) Iron (II) chloride was prepared by mixing 2 mM of 1,10-phenanthroline in 10 cm^3 of ethanol and 2mM of $FeCl_3.4H_2O$ in 30 cm^3 of deionized water and refluxed for about 45 min on a water bath. On cooling and adding excess of absolute ethanol the complex was precipitated, filtered then washed with ice cold 50% ethanol and then recrystallized by slow cooling to 0 °C followed by addition of excess absolute ethanol(9). The product was dried under vacuum over anhydrous calcium chloride. Electronic spectrum and infrared measurements are used for analysis of the complexes and also gas chromatography was used to determine water content and other organic impurities.

Methanol was purified and dried by the methanol described by Perrin(10). Conductivity water was prepared by distilling twice distilled water with specific conductance of 2×10^{-6} μS. Conductivity measurements were made using Jenway PCM3 conductivity meter with frequency range of 50 Hz-1KHz and accuracy of 0.01 μS. The cell constant for the conductivity cell was measured using the method of

Jones and Bradshaw(11), 0.01M KCl solution was prepared from potassium chloride (BDH reagent) recrystallized three times from conductivity water and then dried at (760) Torr and 500 °C for 10 hrs. The cell constant was checked regularly and found to be 1.14 cm^{-1}.

A general method has been used for measuring the conductance of the electrolytes. The conductivity cell was washed, dried and then weighed empty and kept at any temperature (± 0.1 °C) using a water-circulating ultra thermostat type VH5B radiometer. A certain amount of solution was injected into the conductivity cell and the conductivity of the solution was measured. Successive known amount of the solution was added and the measurement was repeated as before. Generally (14) additions have been made for any measurement.

RESULTS AND DISCUSSION

Lee-Wheaton equation is an extended form of the Debye-Hukel equation for the calculation of molar (or equivalent) conductance, association constant and main distance between ion in solution of electrolytes(12). Conductivity data were treated by this equation in which a wide temperature range for electrolyte solution can provide detailed information concerning ion-ion and ion-solvent interaction especially from thermodynamic point of view(13).

For unsymmetrical electrolyte MX_2 ionizing to M^{2+} and X^- the possible equilibria are:

$$M^{2+} + X^- \overset{K_{(1)}}{\rightleftharpoons} MX^+$$

$$MX^+ + X^- \overset{K_{(2)}}{\rightleftharpoons} MX_2$$

Thus, three ionic species are present in the solution which are M^{2+}, MX^+ and X^-. All such solutions are in effect "mixed electrolyte" since the pair MX^+ is conducting species.

$$\Lambda_{equiv.} = \sum_{i=1}^{s} | z_i | m_i \lambda_i / C$$

This equation is derived as follows:

$$\lambda_i = f\,(\lambda_i^o, \varepsilon K, R)$$

$$\sigma_i = C_i \lambda_i / 1000 = |z_i|\, m_i \lambda_i / 1000$$

$$\text{and } \sigma_{solu.} = \sum_{i=1}^{s} | C_i$$

$$\text{or } 1000\, \sigma_{solu.} = \sum_{i=1}^{s} | C_i \lambda_i$$

and $\Lambda_{\text{solu.}} = \sum_{i=1}^{s} | z_i | m_i \lambda_i / \sum C_i$

where (s) is the number of ionic species, σ is specific conductance, C stoichiometric equivalent concentration, λ_i, m_i, C_i and z_i are the equivalent conductance, molar free ion concentration, equivalent concentration and charge of the species respectively. The equation is:

$$\lambda_i = \lambda_i^o \left[1 + z_j \sum_{p=2}^{s} z_i x_j^p \sum_{v=1}^{s} tvx_v^p \left(A^p(t)(\beta k) + B_v^p(t)(\beta k)^2 + C_v^p(t)(\beta k)^3 \right) \right]$$

$$- \left[\frac{z_j(kt)}{2(1+t)} \left\{ I + v_j^{(1)}(t)(\beta k) + v_j^{(2)}(t)(\beta k)^2 + \pi_j^{(5)} t/6 \right\} \right]$$

t is the transference number of species

$\beta = e^2/DKT, k = 4\pi/DKT \sum_{j=1}^{s} nje_j^2$ and is proportional to the strength, t = KR and T = Fe/6$\pi\eta$, m_i is the molar free ion concentration of species I, c is the equivalent stoichiometric concentration of the electrolyte. The plasma coefficients A_v^p, B_v^p . . . etc are functions of KR and q_p (Bjeerum value) while the terms X_j^p and q_p are functions of the limiting mobilities. All other terms are defined in the original paper (Lee and Wheaton, 1978)$^{(12)}$.

Thus for associated salts 2:1 unsymmetrical electrolyte:

$\Lambda\ M^{2+} = f\ (\lambda^o_{M^{2+}}, \lambda^o_{MX^+}, \lambda^o_{X^-}, K_A^{(1)}, K_A^{(2)}, R)$

where R is the average center to center distance for the ion pairs.

The input data to computer program are solvent data (Temp. T, dielectric constant D, viscosity η), the charge and ionic mobility λ^o for each ionic species, $K_A^{(1)}$, $K_A^{(2)}$, $\lambda^o_{MX^+}$, $\lambda^o_{M^{2+}}$ and R all in the form $K_{A(\min)}^{(1)}$, $K_{A(\min)}^{(2)}$, $\Delta K_A^{(1)}$ . . . . etc then the experimental data (molecular concentration and the equivalent conductances). This program is used to determine values of $K_A^{(1)}$, $K_A^{(2)}$, $\lambda^o_{MX^+}$, $\lambda^o_{M^{2+}}$ and R which minimize $\sigma_s(\Lambda)$. Table (1A-D) show the molar concentration and equivalent conductance of [Fe(1,10-Phen)$(H_2O)_4$]Cl_2 in [50%-90%] methanol and water at different temperatures and Figure (1A-D) show the relation between them. It can be seen from Table (1A-D) that the equivalent conductance increase as temperature increase and decrease as methanol percent decrease because of increasing water percent and the formation of hydrogen bonds more and more except for %50 which increase due to the nutralinity between methanol and water and the increasing in dielectric constant of the mixed solvent at this percentage.

The decrease of equivalent conductance with increasing concentration were shown in Figs. (1A-D) which obey Koloraush equation of weak electrolytes.

$\Lambda = \Lambda^{o} - aC^{1/2}$

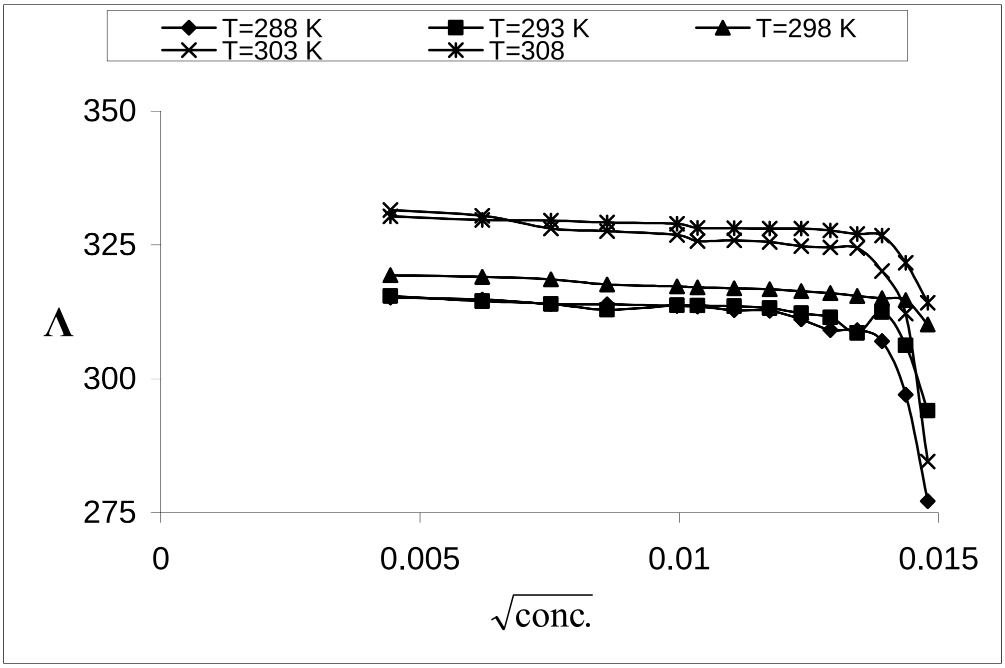

Fig (1-A) :The plot of equivalent conductivities ($\Omega^{-1}.cm^{2}.equiv^{-1}$) against square root of concentration ($mole.L^{-1}$) for $[Fe(phen)(H_2O)_4]Cl_2$ in 90% methanol-water mixtures at different temperatures.

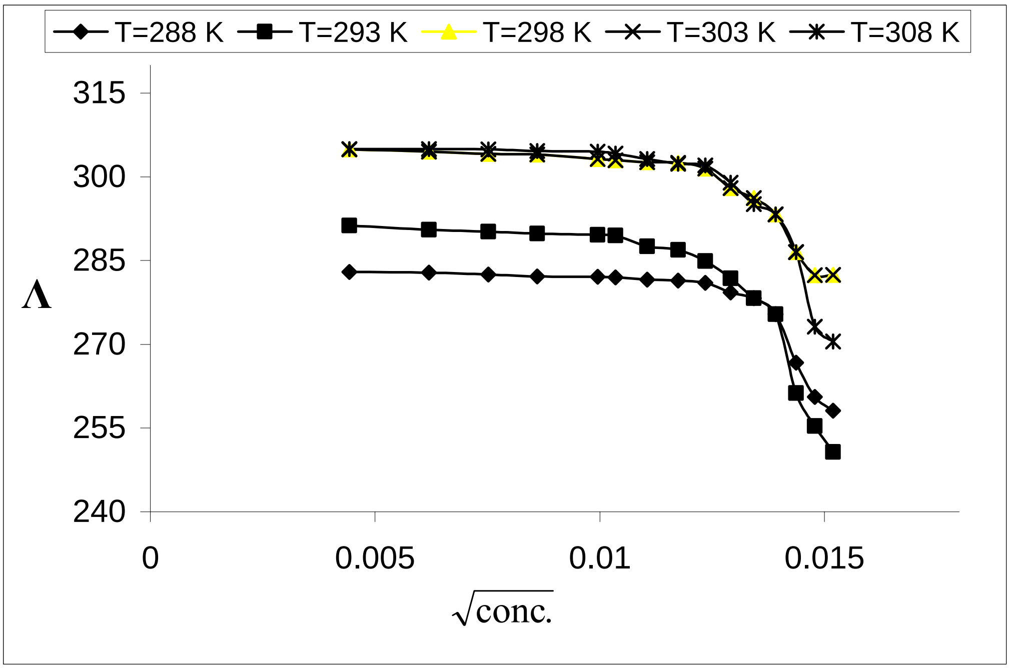

Fig (1-B) :The plot of equivalent conductivities ($\Omega^{-1}.cm^{2}.equiv^{-1}$) against square root of concentration ($mole.L^{-1}$) for $[Fe(phen)(H_2O)_4]Cl_2$ in 80% methanol-water mixtures at different temperatures.

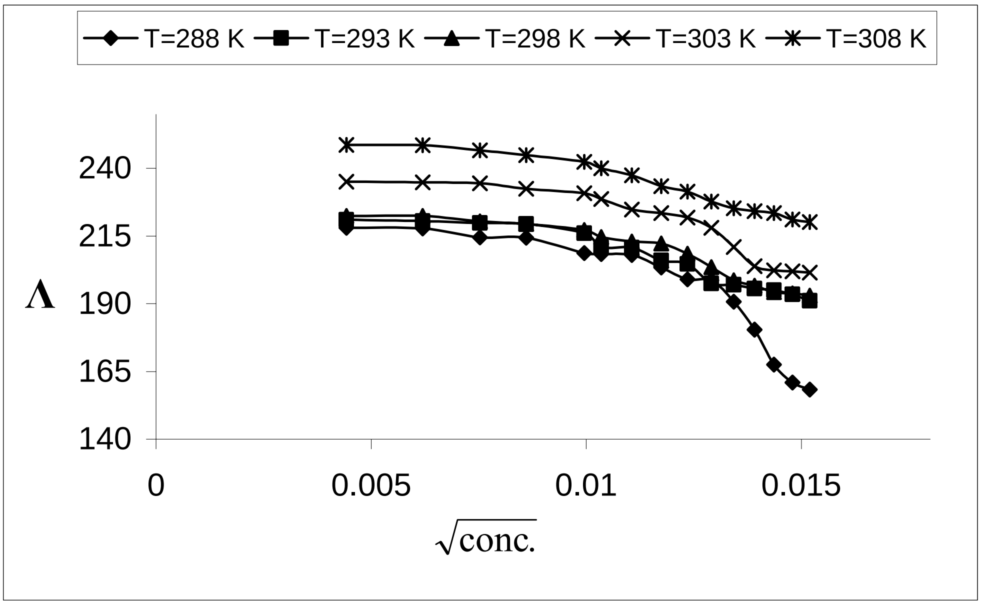

Fig (1-C) :The plot of equivalent conductivities ($\Omega^{-1}.cm^2.equiv^{-1}$) against square root of concentration ($mole.L^{-1}$) for $[Fe(phen)(H_2O)_4]Cl_2$ in 70% methanol-water mixtures at different temperatures.

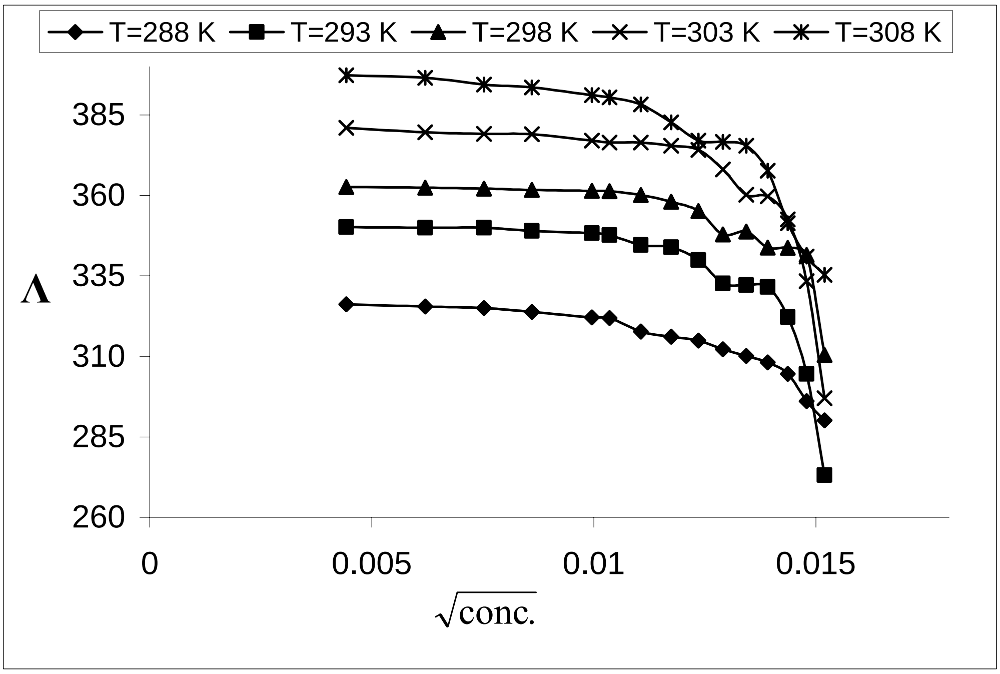

Fig (1-D) :The plot of equivalent conductivities ($\Omega^{-1}.cm^2.equiv^{-1}$) against square root of concentration ($mole.L^{-1}$) for $[Fe(phen)(H_2O)_4]Cl_2$ in 50% methanol-water mixtures at different temperature.

Table (1A): The equivalent conductivities (Ω^{-1}.cm^{2}.equiv^{-1}) with molar concentration for [Fe(1,10-Phen)(H_2O)$_4$]Cl_2 in methanol water mixtures at different temperatures (K) (90%)

conc. × 10^{-5}	T = 288 K	T = 293 K	T = 298 K	T = 303 K	T = 308 K
1.960	315.179	315.455	319.33	331.526	330.35
3.846	314.822	314.526	319.029	330.468	329.688
5.660	313.986	313.955	318.573	328.079	329.541
7.407	313.878	312.88	317.616	327.607	329.175
9.909	313.614	313.728	317.262	326.895	328.947
10.714	313.506	313.656	317.072	325.756	328.162
12.228	312.836	313.562	316.882	325.8283	328.102
13.793	312.702	313.196	316.723	325.5736	328.073
15.254	311.07	312.246	316.333	324.786	328.07
16.666	309.111	311.439	316.008	324.52	327.712
18.032	309.092	308.56	315.455	324.4013	327.028
19.354	307.03	312.484	315.067	320.112	326.756
20.634	297.065	306.261	314.676	312.17	321.651
21.875	277.134	294.044	310.156	284.544	314.184
23.076	194.769	296.742	302.328	215.118	299.754

Table (1B): The equivalent conductivities (Ω^{-1}.cm^{2}.equiv^{-1}) with molar concentration for [Fe(1,10-Phen)(H_2O)$_4$]Cl_2 in methanol water mixtures at different temperatures (K) (80%)

conc. × 10^{-5}	T = 288 K	T = 293 K	T = 298 K	T = 303 K	T = 308 K
1.960	282.941	291.278	304.912	304.980	303.654
3.846	282.846	290.496	304.493	304.950	303.552
5.660	282.472	290.158	304.096	304.912	302.022
7.407	282.132	289.850	304.018	304.606	299.221
9.909	282.102	289.605	303.195	304.493	298.044
10.714	281.996	289.476	302.940	304.164	297.344
12.228	281.563	287.526	302.615	303.195	297.279
13.793	281.404	286.926	302.498	302.328	296.888
15.254	281.016	284.886	301.497	302.049	296.072
16.666	279.256	281.792	297.976	298.928	295.647
18.032	278.256	278.256	296.208	295.088	293.694
19.354	275.406	275.400	293.301	293.301	291.924
20.634	266.696	261.290	286.518	286.518	284.716
21.875	260.563	255.350	282.357	273.156	270.504
23.076	258.140	250.743	282.446	270.500	265.873

Table (1C): The equivalent conductivities ($\Omega^{-1}.cm^{2}.equiv^{-1}$) with molar concentration for [Fe(1,10-Phen)(H_2O)$_4$]Cl_2 in methanol water mixtures at different temperatures (K) (70%)

conc. × 10^{-5}	T = 288 K	T = 293 K	T = 298 K	T = 303 K	T = 308 K
1.960	217.989	221.019	222.438	235.008	248.636
3.846	217.755	220.461	222.418	234.796	248.530
5.660	214.489	219.759	220.386	234.515	246.636
7.407	214.376	219.466	219.466	232.476	244.920
9.909	208.692	216.036	217.260	230.742	242.352
10.714	208.325	210.795	214.640	228.684	240.051
12.228	207.955	210.757	212.899	224.808	237.379
13.793	203.362	205.981	212.236	223.418	233.390
15.254	198.968	204.680	208.437	221.762	231.336
16.666	198.605	197.472	203.473	218.008	227.766
18.032	190.740	196.940	198.594	210.936	225.230
19.354	180.387	195.550	196.641	203.796	224.150
20.634	167.586	194.940	194.320	202.320	223.500
21.875	160.930	193.462	193.750	201.967	221.150
23.076	158.356	191.116	192.911	201.532	220.130

Table (1D): The equivalent conductivities ($\Omega^{-1}.cm^{2}.equiv^{-1}$) with molar concentration for [Fe(1,10-Phen)(H_2O)$_4$]Cl_2 in methanol water mixtures at different temperatures (K) (50%)

conc. × 10^{-5}	T = 288 K	T = 293 K	T = 298 K	T = 303 K	T = 308 K
1.960	326.2	350.18	362.572	381.021	397.358
3.846	325.5	349.969	362.417	379628	396.477
5.660	325	349.928	362.049	379.09	394.434
7.407	323.8	348.997	361.692	378.976	393.516
9.909	322.1	348.228	361.371	376.992	391.17
10.714	321.9	347.706	361.338	376.459	390.458
12.228	317.7	344.607	360.136	376.405	388.215
13.793	316.1	343.856	357.976	375.418	382.704
15.254	314.9	339.864	355.096	374.136	376.992
16.666	312.2	332.66	347.82	368.016	376.571
18.032	310.1	332.112	348.796	360.192	375.43
19.354	308.2	331.551	343.796	359.741	367.659
20.634	304.6	322.218	343.716	352.512	351.39
21.875	296.1	304.538	341.496	333.37	340.986
23.076	290.1	273.156	310.45	297.024	335.282

Table (2) show the results of analysis of the complex [Fe(1,10-Phen)$(H_2O)_4]Cl_2$ in different percentages of methanol-water (90%-50%) at different temperatures by using Lee-Wheaton equation for unsymmetrical electrolytes (2:1) which indicates the values of (K_A, $\lambda_{M^{2+}}$, λ_{MX^+}, R and $\sigma\Lambda$).

Table (2): The results of analysis of [Fe(1,10-Phen)$(H_2O)_4]Cl_2$ in different percentages and temperatures of methanol water by L-W equation

Temp.	K_A	$\lambda_{M^{2+}}$	λ_{MX^+}	RA°	$\sigma\Lambda$
%90 methanol					
288.15	180	277	1.0	50	0.020
293.15	165	280	1.0	48	0.080
298.15	130	284	1.0	45	0.025
303.15	105	287	1.0	43	0.021
306.15	73	292	1.0	40	0.053
%80 methanol					
288.15	590	260	1.0	70	0.083
293.15	575	267	1.0	67	0.083
298.15	563	272	1.0	65	0.098
303.15	557	275	1.0	62	0.090
306.15	540	278	1.0	60	0.080
%70 methanol					
288.15	670	170	1.0	78	0.010
293.15	630	180	1.0	76	0.029
298.15	620	190	1.0	73	0.036
303.15	600	200	1.0	71	0.039
306.15	580	210	1.0	70	0.039
%50 methanol					
288.15	595	300	1.0	71	0.070
293.15	570	320	1.0	69	0.019
298.15	565	335	1.0	68	0.016
303.15	530	342	1.0	66	0.013
306.15	500	350	1.0	65	0.064

From Table (2) the values of K_A (association constant) decrease with increasing temperatures at each percentage because of breaking of H-bonds formed at low temperature and this will lead to increasing of $\lambda_{M^{2+}}$ as shown in Table (2) and K_A is also increase as methanol percentage decrease because of increasing H-bonding due to increasing water percentage and increasing viscosity which play an important role. Similar observations have also been noted for some electrolytes in other mixed solvents(14), and this may be attributed to the selective solvation of ions besides the solvodynamic viscous force(15).

λ_{MX^+} is almost constant and low value due to the formation of larger ion than $\lambda_{M^{2+}}$ and more stable than the other ions (M^{2+},X^-).

The values of R (distance parameter) are high because of the isolated cation which tend to surrounded by extensive solvent shell which gives rise to are pulsive force between the ions which they come into close proximately and because of ion-dipol-ion forces will be significant to form solvent separated ion pair(16). The small values of ($\sigma\Lambda$) give an indication of good best fit value (less than 0.1).

Thermodynamic parameters from the association reaction are evaluated by the following equations:

$\ln K_A = - \Delta H/RT + C$

$\Delta G = - RT \ln K_A$

$\Delta S = (\Delta H - \Delta G) / T$

The enthalpy evaluated from Fig. (2) by plotting lnKa against 1/T from the equation:

$$\ln Ka = -\frac{\Delta H}{RT} + c$$

and (ΔH) of ion association reaction according to the activated complex theory is a result of the energies being expended for the distruction of solvent-solvent bonds, and the formation of solvent ion bonds. As can be noticed from Table (3), ΔH decrease with decreasing methanol percentage due to the broken of ion-ion bond in solution as a result of increasing dielectric constant of the solvent by increasing water percentage(17). The entropy is positive as water percent age increase of the complex and this may be recognized as a structure-maker in these media. Finally, the values of ΔG are negative which indicate the reaction is spontaneous.

The value of Walden product ($\Lambda_o\eta$) would be constant only if the effective radius of the ion remains the same in the different media. Since most ions are solvated in solution to different extent, the dimensions of the moving will undoubtedly vary to some extent and exact constancy of the conductance viscosity product is not to be expected(18). This is the case in the behaviour of the present system as indicate in Fig. (3) where the cations are expected to suffer various degree of solvation with increasing amount of methanol in the methanol-water mixtures. The major deviation in the Walden product is due to the variation of the electrochemical equilibrium between ions and the solvent molecules with the composition of the mixed polar solvent.

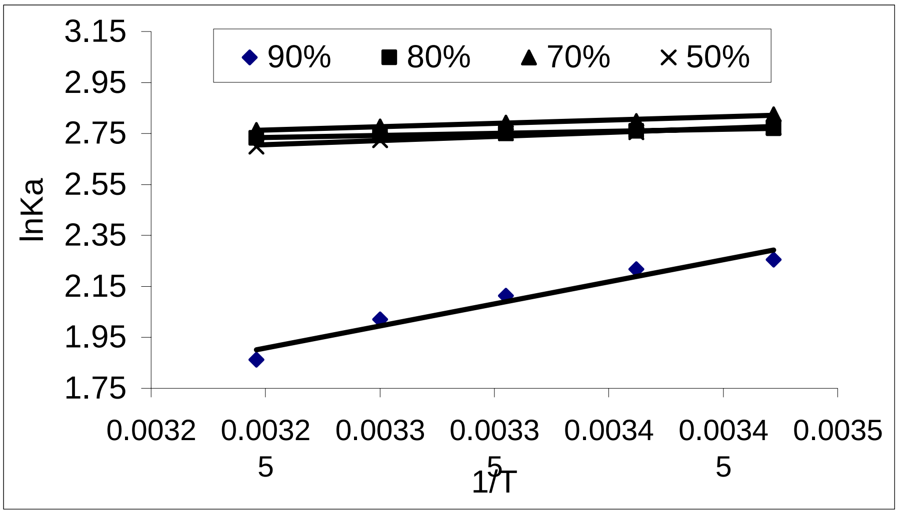

Fig (2): Plot of lnKa against 1/T for the complexes at different solvent composition

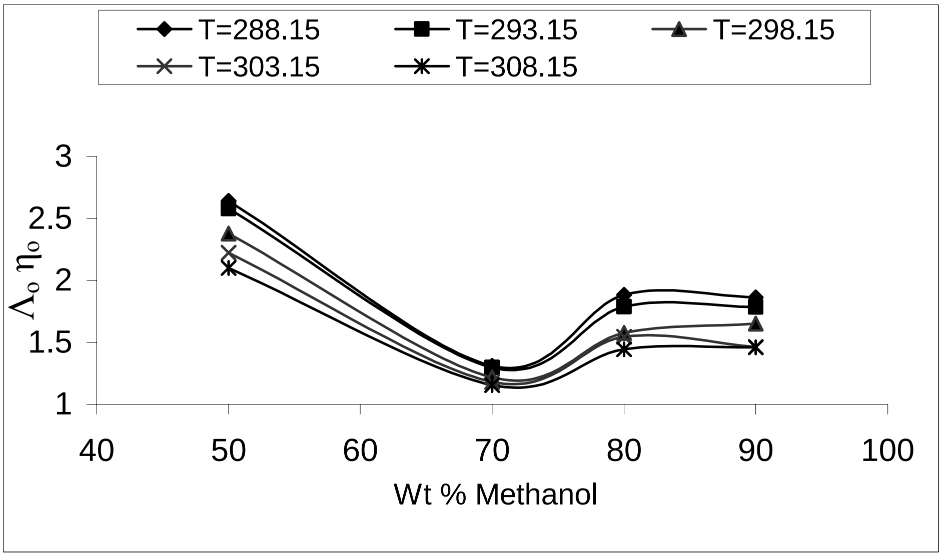

Fig (3) : Walden products (Λ_o η_o) for the complex in methanol-water mixture plotted versus the composition of the mixture at different temperature

Table (3): Thermodynamic parameters (ΔH, ΔG, ΔS) of the complex in different solvent composition from the association constant (K_A)

Temp.	ΔG Kcal/mole	ΔS cal/deg.mole	ΔH Kcal/mole
%90 methanol			
288.15	- 2.963	- 17.877	- 7.884
293.15	- 2.964	- 16.783	
298.15	- 2.873	- 16.856	
303.15	- 2.793	- 16.793	
306.15	- 2.575	- 17.228	
%80 methanol			
288.15	- 3.640	7.083	- 0.729
293.15	- 3.688	6.924	
298.15	- 3.739	6.778	
303.15	- 3.795	6.540	
306.15	- 3.839	6.500	
%70 methanol			
288.15	- 3.713	5.694	- 1.185
293.15	- 3.741	5.505	
298.15	- 3.796	5.389	
303.15	- 3.840	5.254	
306.15	- 3.882	5.120	
%50 methanol			
288.15	- 3.645	4.532	- 1.468
293.15	- 3.683	4.390	
298.15	- 3.741	4.306	
303.15	- 3.765	4.143	
306.15	- 3.730	3.991	

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