Conductometric Study of Association Phenomena of Tetra Aqua 1,10-Phenanthroline Manganese (II) Chloride in Mixtures of Methanol - Water at Different Temperatures

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Abstract:

The association phenomena of tetra-aqua 1,10 Phenanthroline manganese (II) Chloride in binary mixtures of methanol and water have been studied at 288 - 308 K. The parameters λ_o, K_A and R means limiting molar conductances, ion association constants and the mean distance between ions in solution have been evaluated using Lee -Wheaton conductivity equation. The association constant obtained at different temperatures were used in determining the Thermodynamic quantities of the association reaction of M^{+2} ions and Cl^- ions (where M is the coordination complex)The results are discussed on the basis of the solvent effect on the conductivity parameters of these complexes.

Key word : Conductivity , 1,10 Phenanthroline complex , Lee-Wheaton equation

Introduction:

Mixed ligand complexes of 1,10 Phenanthroline with transition metal are now finding extensive in volcanization of rubber , forth floatation process for concentration of sulphide ores, as antioxidants,lubricans and have been found to possess fungicidal and insecticidal activity [1].

The conductivity measurements are usefel 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 ligand have been elucidated by the study of the electronic spectra [2]. racemization [3] . optical resolution [4], Viscosity and molar volume [5] and conductivity [6]. Very few work, have been done of 1,10 Phenanthroline and water as mixed Ligand with any metal ion [7] had studied the kinetics and conductivity of tris(3,4,7,8-tetramethyl-1,10 Phenanthroline –Fe(II) complex in acetonitrile at 25 ^{0}C and the conductivity data were analyzed by the Lee-Wheaton equation. The analytical applications of the complexes of Mn , Ni , Co and Cu with 1,10 Phenanthroline as aligand 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 [8].

Novel chiral complexes of tin have been synthesized using amino acid as chiral auxiliary and 1,10 Phenanthroline, 3,7- Phenanthroline or 1,7-Phenanthroline as asecondary Ligand, it has been found that the complexes are non-electrolytic and are octahedral in shape with a coordination number six around the tin atom.

Also 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 the conductivity of [Mn(1,10 Phenanthroline) $(H_2O)]Cl_2$ in methanol-Water mixture at different temperatures (288 - 308 K). Lee-Wheaton equation is used to elucidate the conductivity parameters λ_o ,K_A and R in the different percentages and temperatures of the two solvents.

Experimental:

Preparation of complex:

Tetra aqua (1,10-phenanathroline) manganese (II) chloride was prepared by mixing 2 mM of 1,10-phenanthroline in 10 cm^3 of ethanol and 2mM of $MnCl_2.6H_2O$ 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 ^{o}C followed by addition of excess absolute ethanol. The product was dried under vacuum over anhydrous calcium chloride. Magnetic electronic spectral, (UV), infrared measurements used for analysis of the complex and also gas chromatography was used to determine water content and other organic impurities.

Purification of solvents:

Methanol was purified and dried by the method described by Perrin[9] 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[10], 0.01 M 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[11]. The cell constant was checked regularly and found to be 1.14 cm^{-1}.

General procedure:

A general method has been used for measuring the conductance of the electrolyte. 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. Another known amount of the solution was added and the measurement was repeated as before. Generally(11) additions have been made.

Results And Discussion:

Lee and Wheaton obtained an equation for unsymmetrical electrolytes of the form :

$$\lambda i = \lambda i^{o} \left[1+Z_j \sum_{j=2}^{s} X_j^{p} \sum_{\nu=1}^{s} n X_\nu^{p} \left[A^{P}_{\nu}(t)(\beta k)+B^{P}_{\nu}(t)(\beta k)^2+C^{P}_{\nu}(t)(\beta k)^3\right]\right] -$$

$$\frac{Z_j(Kt)}{2(I+t)} \quad I+V_j^{(1)}(t)(\beta k)+V_j^{(2)}(t)(\beta k)^2+\Pi_j^{(5)}\; t/6 \qquad \text{-----(1)}$$

with $\Lambda_{equiv.} = \sum_{j=1}^{S} |Z_i|\, m_i\lambda_i / C$ where S is the number of charged species , Z_j , t_j are the charges and transference number of species j , $\beta=e^2/DKT$, $K=(4\Pi/DKT \sum_{j=1}^{S} n_y e_j^2$ and is proportional to the ionic strength , t = KR and t = Fe/6Πη , n_j is the molar free ion concentration of species , C is the equivalent stoichometric concentration of the electrolyte The plasma coefficients A_V^P , B_V^P ----etc. are functions of KR and q_P while the terms X_j^P and q_P are functions of the limiting mobilities , the concentration and charge on all ions present in solution.

All other terms are define in the original paper (Lee and Wheaton 1978).

This equation has been tested extensively in both aqueous and non-aqueous system and provide a satisfactory explanation of the conductivity behaviour of a variety of system.

For an unsymmetrical electrolyte MX_2 ionizing into M^{2+} and X^-, The possible association equilibria are :

$$M^{2+} + X^- \underset{}{\overset{K_A^{(1)}}{\rightleftharpoons}} MX^+ \quad ......(2)$$

$$MX^+ + X^- \underset{}{\overset{K_A^{(2)}}{\rightleftharpoons}} MX_2 \quad ......(3)$$

This, three ionic species are present in the solution which are M^{2+}, MX^- and X^-.

Thus for 2:1 associated salts

$$\Lambda MX_2 = f(\lambda^o_{M^{2+}}, \lambda^o_{MX^-}, \lambda^o_{X^-}, K_A^{(1)}, K_A^{(2)}, R) \quad \text{-------(4)}$$

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

The input data to the computer program are solvent data (Temp.T , Dielectric constant D and Viscosity η), the charge Zi and ionic mobility λ_i^o for each ionic species , $K_A^{(1)}$, $K_A^{(2)}$, $\lambda^o_{MX^-}$, $\lambda^o_{M^{2+}}$, and R all in the form $K_A^{(1)\,(min)}$, $K_A^{(2)\,(max)}$, $\Delta K_A^{(1)}$ -----etc, then the experimental data (molecular concentration and equivalent conductance) . This program is used to determine values of $K_A^{(1)}$, $K_A^{(2)}$, $\lambda^o_{MX^-}$, $\lambda^o_{M^{2+}}$, R where R is the average center to center distance for the ion pairs, a multi parameter "Least square" curve-fitting procedure is used to give the lowest value of curve fitting parameter. σ(Λ) between the experimental and calculated points. An iterative numerical method which was found to be very successful has been used to find the minimum σ(Λ)

$$\sigma\Lambda = \left\{ \sum_{n=1}^{NP} \left(\Lambda_{calc.} - \Lambda_{exp.}\right)^2 / NP \right\}^{1/2}$$

Table (1 A-D) Shows the molar concentration and equivalent conductance of $[Mn(phen)(H_2O)_4]Cl_2$ in different percentages and temperature of methanol-water and figure (1,A-D) illustrates the relation between them.

Table (1-A) : The equivalent conductivities ($\Omega^{-1}.cm^2.equiv^{-1}$) with molar concentration for $[Mn(phen)(H_2O)_4]Cl_2$ in 100% methanol at different temperatures

Conc. x 10^{-5}M	**T=288 K**	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**
1.960	٢٢٣,٤٤٨	١٥٥,٩٥٨	١٥٨,٥٧٦	١٥٨,٥٧٦	١٥٠,٣٩٣
3.846	٢٠٧,٩٢٧	١٥٥,٦٠١	١٥٦,٩٧٨	١٥٨,٣٥٥	١٥٠,٠٤٨
5.660	١٩٩,٧١٦	١٥٥,١٧٦	١٥٥,١٧٦	١٥٥,٩٥٨	١٤٩,٥٦٦
7.407	١٩٨,٩٦٨	١٥٤,٤٨٦	١٥٣,٦٣١	١٥٣,٨١٦	١٤٨,٥١٢
9.909	١٨٧,٧٠٩	١٥٣,١٧٦	١٥٢,٣٦٤	١٥٣,٢٧٢	١٤٧,٨٤١
10.714	١٨٣,٣٩٦	١٥١,١٦٤	١٥٢,٠٣١	١٥١,١٦٤	١٤٤,٩٤٢
12.228	١٧٨,٥٣٤	١٤٩,٩٤٠	١٥١,١٦٤	١٤٩,٣٧٩	١٤٤,٤٣٢
13.793	١٧٦,٨٦٨	١٤٩,٣٧٩	١٥١,١١٨	١٤٨,٤٤٤	١٤٣,٢٠٨
15.254	١٧٤,٢١٦	١٤٩,٣٢٨	١٥٠,٥٥٢	١٤٦,٨٨	١٤١,٩٧٤
16.666	١٧٢,٣٢٩	١٤٨,٦١٤	١٤٨,٧٦٢	١٤٥,٣٦٨	١٤٠,٧٠٩
18.032	١٧٠,٠٣٦	١٤٧,٣٠٣	١٤٧,٠٣٣	١٤٣,٨٧١	١٤٠,٥٥٦
19.354	١٧٠,٥٢٤	١٤٦,٨٨٠	١٤٥,٣٢٦	١٤٢,٣٦٠	١٣٩,٣٩٤
20.634	١٦٨,٣٢٩	١٤٥,٨٦٠	١٤٤,٥٤٨	١٤٠,٨١٨	١٣٨,٤٨٦
21.875	١٦٧,٠٧٦	١٤٥,٥٧٩	١٤٣,٦٥٠	١٣٩,٦٧٢	١٣٧,٥٨٥
23.076	١٥٣,٨١٦	١٤٤,٢٣٠	١٤٢,٦٣٤	١٣٨,٨٤٧	١٣٦,١٢١

Table (1-B) : The equivalent conductivities ($\Omega^{-1}.cm^2.equiv^{-1}$) with molar concentration for $[Mn(phen)(H_2O)_4]Cl_2$ in 90% methanol water mixtures at different temperatures

Conc. x 10^{-5}M	**T=288 K**	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**
1.960	١٩٧,٦٧٦	١٦٥,٩٨٤	١٦٩,٠٥٣	١٦٨,٤٥٤	١٦٨,٧٠١
3.846	١٨٩,٦٩٦	١٦٥,٤٦٢	١٦٧,٩٦٦	١٦٨,٠٦٨	١٦٨,٠٦٦
5.660	١٨٧,٣٠٢	١٦٥,١٨٦	١٦٧,٢٨٦	١٦٧,٦٧٢	١٦٧,٨٤٤
7.407	١٨٤,٦٨٠	١٦٤,٩٩٩	١٦٥,٥٠٩	١٦٦,٩٧٤	١٦٧,٧٧٦
9.909	١٨٣,٦٨٤	١٦٤,٩٢	١٦٤,٣٦٧	١٦٥,٣٩٢	١٦٧,١١٩
10.714	١٨١,٩٤٤	١٦٤,٤١٣	١٦٢,٧٩٢	١٦٥,١٨٦	١٦٦,٩٨١
12.228	١٨١,٠١٥	١٦٤,١٦٠	١٦١,٤٢٤	١٦٤,٠٣٩	١٦٦,٥٣٩
13.793	١٨١,٠٠٣	١٦٣,٦٤٧	١٦٠,٣٤١	١٦٢,٤٠٧	١٦٦,٢١٢
15.254	١٨٠,٨٥٤	١٦٢,٤٥٠	١٥٨,٧٣٦	١٦١,٠٥٧	١٦٤,٧٧٦
16.666	١٨٠,٨٣٢	١٦٠,٥١٢	١٥٥,٣٤٤	١٥٨,٠٠٤	١٦٢,٢٦٠
18.032	١٨٠,٨٠٤	١٥٨,٥١٧	١٥١,٧٣٤	١٥٧,٣٧٧	١٥٦,١٢٣
19.354	١٨٠,٢٣٤	١٥٣,٠٦٤	١٤٦,٢٠٥	١٥٣,١٣٦	١٥٦,٢٠٨
20.634	١٨٠,١٠٢	١٤٢,٢٧٢	١٣٦,٩٥٢	١٤٤,٠٠١	١٤٧,٠٢٢
21.875	١٧٩,٢٧٣	١٤٠,٥٦٧	١٢٥,٥٩٢	١٤٠,٠٠٦	١٢٥,٩٧٦
23.076	١٧٨,٣٣٤	١٣٨,٢١	١٢٠,٠٠٥	١٣٦,٦٧٥	١٢٠,٨٠٦

Table(1-C) : The equivalent conductivities ($\Omega^{-1}.cm^2.equiv^{-1}$) with molar concentration for $[Mn(phen)(H_2O)_4]Cl_2$ in 80% methanol water mixtures at different temperatures

Conc. x 10^{-5}M	**T=288 K**	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**
1.960	١٠٤,٧٦٦	١٠٦,٧٧٦	١١٣,١٨١	١٠٨,٦٠٢	١١٢,٢٠٠
3.846	١٠٤,٧٥٤	١٠٦,٣١٣	١١٢,٧١٠	١٠٨,٥٦٢	١١١,٣٨٤
5.660	١٠٣,٥١٥	١٠٥,٩٢٧	١١١,٩٠٨	١٠٨,٣٢٤	١١١,٢٩٦
7.407	١٠٣,٣١٠	١٠٥,٦٣٨	١١١,٧١٣	١٠٧,٧٥٩	١١٠,١٨٥
9.909	١٠٣,٢٩٢	١٠٥,٦٠٨	١١١,٤٣٦	١٠٧,٧١٢	١٠٩,٦٦١
10.714	١٠٣,٢٢٨	١٠٥,٢٠٨	١١١,١٩٧	١٠٦,٩٦٤	١٠٩,٥٤٨
12.228	١٠٢,٨١٦	١٠٤,٦٥٢	١١٠,٧٧٢	١٠٦,٨٧٦	١٠٩,٣٩٥
13.793	١٠٠,٩٦٨	١٠٣,٧٩٠	١١٠,٣٣٠	١٠٦,٣١٨	١٠٩,١٧٤
15.254	١٠٠,٥٢٧	١٠٢,٦٤٣	١٠٩,٦٣٥	١٠٥,٧٤٨	١٠٩,١٦٧
16.666	٩٩,٦٦٨	١٠٢,١٦٦	١٠٩,٤٤٦	١٠٥,٤٨٢	١٠٩,١١٠
18.032	٩٨,٠٥٦	١٠٠,٩١٢	١٠٨,٥٢٦	١٠٣,٢٧٥	١٠٨,٧٨٣
19.354	٩٥,٩٣١	٩٩,٨٥٨	١٠٦,٥٩٠	١٠٣,٢٢٤	١٠٨,٥٦٢
20.634	٩٢,٢٥٩	٩٧,٧٦٧	١٠٤,٦٥٢	١٠٢,٨١٦	١٠٧,٧٥٩
21.875	٩٠,٦٩٤	٩٥,٩٠٢	١٠٢,٧١٤	١٠٢,٧١٤	١٠٥,٥٨٣
23.076	٨٨,٢٥٦	٩٤,٢١٢	١٠٠,٧٧٦	١٠٠,٧٧٩	١٠٣,٩٤١

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

Conc. x 10^{-5}M	T=288 K	T=293 K	T=298 K	T=303 K	T=308 K
1.960	٨٦,٧٢٩	٨٧,٦٦١	١٠٣,٧٨٦	١٠٩,٦١٦	١٢١,٧٠٠
3.846	٨٦,٦٩٣	٨٧,٤٨٢	١٠٣,٢٧٥	١٠٩,٢٤٢	١١٧,٦٥٢
5.660	٨٦,٥٢٣	٨٧,٣٩٠	١٠٣,٢٢٤	١٠٩,١٦٧	١١٧,٠١٦
7.407	٨٦,٥٠٣	٨٦,٩٢٦	١٠٢,٩٩٠	١٠٨,٨٠٤	١١٦,٨٩٢
9.909	٨٦,٢٩٢	٨٦,٩٠٤	١٠٢,٧٩٠	١٠٨,٧٠٦	١١٦,٨٤١
10.714	٨٥,٩٧٦	٨٦,٥٢١	١٠١,٦٣٧	١٠٨,٦٠٣	١١٦,١٦٢
12.228	٨٥,١٣٣	٨٥,٥٤٨	١٠٠,٦٨٣	١٠٨,٤٣٠	١١٥,٩٤٠
13.793	٨٤,٢٥٢	٨٤,٢٥٢	١٠٠,٣٦٨	١٠٧,٧١٢	١١٥,٧٠٦
15.254	٨٤,١٥٠	٨٣,٧٢٩	٩٩,٨٥٠	١٠٦,٠٢٩	١١٥,٥٦٦
16.666	٨٢,٤٦٧	٨٣,٦١٦	٩٩,٦٠٣	١٠٥,٦٠٨	١١٥,٤٤٩
18.032	٨٢,٤١٠	٨٣,٠٢٨	٩٩,١١٠	١٠٥,٣٢٣	١١٥,٣٧٤
19.354	٨٢,٢٤٦	٧٩,٨٦٦	٩٦,٩٨٧	١٠٥,٢١٠	١١٥,١٩٢
20.634	٨١,٢٤٣	٧٠,٢٧٨	٩٥,٤٧٢	١٠٤,٣٥٠	١١٤,٢٩١
21.875	٧٧,٤٦٦	٦٥,٥٢٠	٩٤,٢٦٩	١٠٣,٧١٤	١١٣,٥٢٦
23.076	٦٨,٩٥٢	٦٣,٤٢١	٩٤,٢٤٨	١٠٢,١٠١	١١٢,١٢١

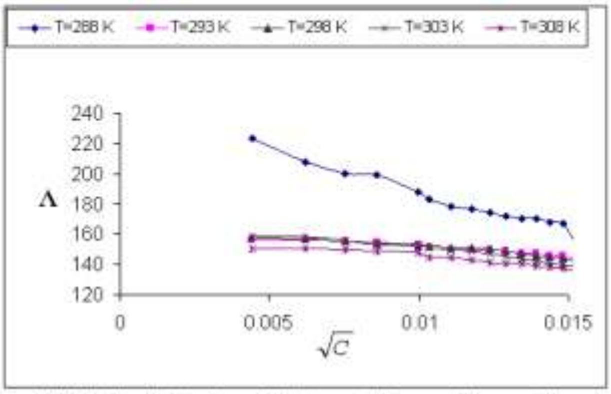


Fig (1-A) The plot of molar conductivities against Square root of concentration for $[Mn(phen)(H_2O)_4]Cl_2$ in 100% methanol at different temperatures

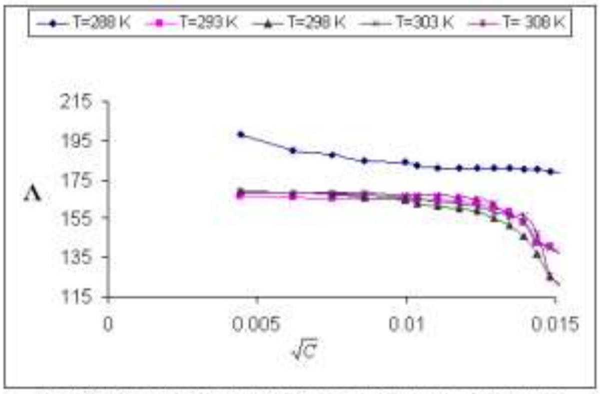


Fig (1-B) :The plot of molar conductivities against Square root of concentration for $[Mn(phen)(H_2O)_4]Cl_2$ in 90% methanol-water mixtures at different temperatures

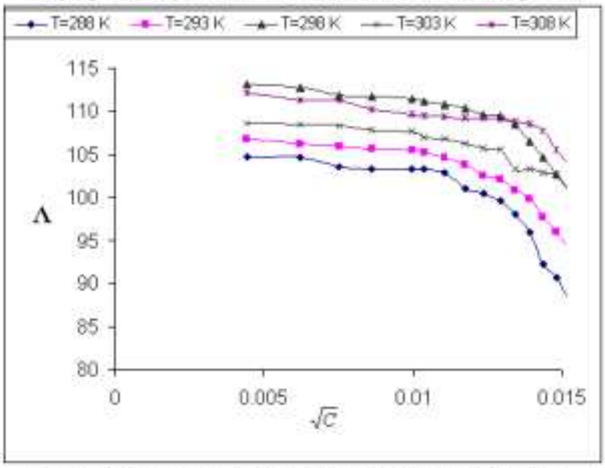


Fig (1-C) :The plot of molar conductivities against Square root of concentration for $[Mn(phen)(H_2O)_4]Cl_2$ in 80% methanol-water mixtures at different temperatures

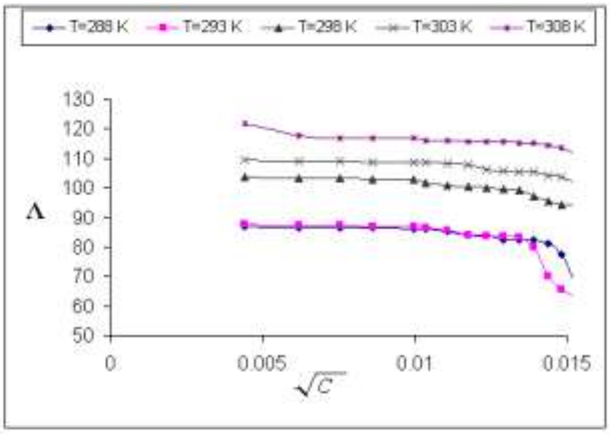


Fig (1-D) :The plot of molar conductivities against Square root of concentration for $[Mn(phen)(H_2O)_4]Cl_2$ in 50% methanol-water mixtures at different temperatures

From tables 1A and 1B the equivalent conductance in general is high than that of tables 1C and 1D because of low values of viscosity and decrease in 100 % and 90 % methanol with temperature due to the decrease in dielectric constant with increasing temperature . While in tables 1C and 1D the equivalent conductance generally is lower than tables 1A and 1B because of viscosity effect of the mixed solvent.

Table (2) show the results of analysis of conductance data by using Lee-Wheaton equation

Table (2): The results of analysis of conductance of $[Mn(phen)(H_2O)_4]Cl_2$ in different percentage and temperatures of methanol water using L –W equation

Temp.	K_A	λ_M^{+2}	λ_{MX}^{+}	R (A^o)	σ
100 % Methanol					
288.15	1100	170	1.0	70	0.039
293.15	1050	150	1.0	70	0.062
298.15	1030	140	1.0	70	0.055
303.15	1000	130	1.0	70	0.046
308.15	950	120	1.0	70	0.049
90 % Methanol					
288.15	450	150	1.0	69	0.023
293.15	500	130	1.0	69	0.057
298.15	510	120	1.0	69	0.087
303.15	550	115	1.0	69	0.049
308.15	560	110	1.0	69	0.093
80 % Methanol					
288.15	970	80	1.0	69	0.052
293.15	960	70	1.0	69	0.040
298.15	950	60	1.0	69	0.047
303.15	920	55	1.0	69	0.034
308.15	900	50	1.0	69	0.047
50 % Methanol					
288.15	1200	50	1.0	70	0.018
293.15	1110	45	1.0	70	0.054
298.15	1100	39	1.0	70	0.044
303.15	1070	35	1.0	70	0.059
308.15	1050	30	1.0	70	0.066

The results show that this complex is associated to form.

$$M^{+2} + X^{-} \rightleftharpoons MX^{+}$$

or

$$[Mn(phen)(H_2O)_4]^{2+} + Cl^{-} \rightleftharpoons [Mn(phen)(H_2O)_4Cl]^{+} \text{------}(5)$$

From table (2) the values of $\lambda^o_M{}^{+2}$ is the highest in pure methanol and decrease with decreasing methanol percentages this can be attributed to the effect of the viscosity which play an important role. Similar observation have also been noted for some electrolytes in other mixed solvents [12] and this may be attributed to the selective solvation of ions besides the solvodynamic viscous force[13].

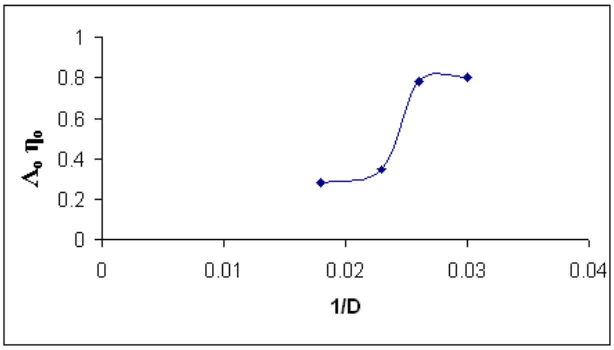
λ_{MX}^{+} is almost constant and Low value because of formation of Large ion and more stable than the other ions(M^{2+}, X^{-}) .

Table(2) shows the results of analysis of conductance data by using L-W equation.

The values of K_A decrease with increasing temperatures because of the short range interaction and the hydrogen bond formed at Low temperature further more K_A values increasing as methanol percentage decrease which means increasing formation of hydrogen bonds and increasing association except for 100 % there is an increase of K_A value which may be due to the polarity of the H-bonding of the solvent.

The result of distance parameter R are high because of the isolated cation which tend to surrounded by extensive solvent shell which gives rise to repulsive force between the ions when they come in to close proximately and because of ion-dipole-ion forces will be significant to form solvent separated ion pair [14]. The small values of $\sigma(\Lambda)$ give an indication of good best fit value (less than 0.1).

In order to analysis the structural changes of the solution when varying the solvent composition figure (2) ., the Walden product ($\Lambda_o \eta_o$) for the media represented as a function of the reciprocal dielectric constant 1/D at 298.15 K as an example.



Fig(2) : Walden product ((Λ_o η_o) for the complex in methanol – water mixture versus 1/D at 298.15.

From this figure it is clear that the Walden product is not constant , the variation is due to the electrochemical equilibrium between ions and the solvent molecules with the composition of the mixed polar solvent [15].

The standard enthalpy of the ion association reaction (ΔH) are evaluated by the following

$\ln K = -\Delta H / RT + C$,

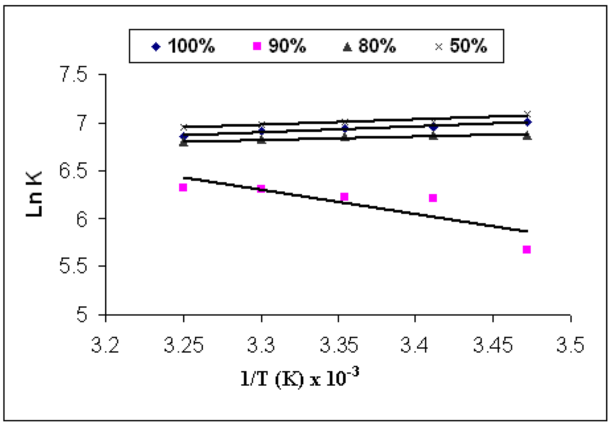
Fig(3) show the plot of Ln K versus 1/T which is a linear relation .

The entropy of ion pair formation is a linear combination of two variable

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

Gibbs energy estimated from the relation

$\Delta G^o = -RT\ln K$



Fig(3) : The plot between Ln K against (1/T) for the complex at different solvent composition

Result of the calculation are gathered in table (3). It is well known that addition of an electrolyte to a solvent causes some structural changes due to the rupture of the bonds between solvent molecules from one side and to the interaction of ions with each other and with solvent molecules from the other side [16]. The negative entropy provides a good indication of ionic association which has an ordering effect on the solution. The solvation effect may exert on the solution structural in the same manner leading relatively to decease in the entropy as temperature increase and decrease with increasing water percentage [17].

Table(3) : Thermodynamic parameters (ΔH, ΔG, ΔS) of the complex in different solvent composition.

% Methanol	ΔG^o (K cal/ mol)	ΔS^o (K cal/ mol)	ΔH^o (K cal/ mol)
100 % Methanol	3.995	982	-7.011
	4.037	1024	
	5.864	2851	
	4.145	1132	
	4.183	1117	
90 % Methanol	3.485	1505	4.606
	3.606	1626	
	3.680	1700	
	3.786	1806	
	3.860	1880	
80 % Methanol	3.923	-1522	-12.666
	3.985	-1460	
	4.047	-1398	
	4.096	-1349	
	4.150	-1295	
50 % Methanol	4.045	-3379	-17.183
	4.070	-3354	
	4.134	-3290	
	4.186	-3283	
	4.244	-3180	

The enthalpy of activation according to the activated complex theory is a result of the energies being expended for the destruction of solvent-solvent bonds and the formation of solvent ion bonds. As can be noticed from table (3) , ΔH decreases with increasing water percentage due to the broken of ion-ion bond in solution as a result of increasing dielectric constant of the solvent [18]. Finally the values of ΔG are negative which indicate the reaction is spontaneous.

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دراسة توصيليه ظاهرة التجمع الايوني للمركب $[Mn(phen)(H_2O)_4]Cl_2$ في مزيج الكحول المثيلي– الماء بدرجات حرارية مختلفة

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الملخص:

درست ظاهرة التجمع الايوني للمعقد $[Mn(phen)(H_2O)_4]Cl_2$ في مزيج من الكحول المثيلي– الماء في درجات حرارة (٢٨٨,١٥ – ٣٠٨,١٥) مطلقة وحسبت الحدود λ_o ، K_A ، R أي التوصيلية المولارية وثابت التجمع الايوني ومعدل المسافة بين الايونات في المحلول باستخدام معادلة لي– ويتون ومن حساب ثابت التجمع الايوني للمعقد في درجات حرارية مختلفة ثم حساب الدوال الثرموداينيمكية لتفاعل التجمع بين ايونات M^{2+} وايون الكلوريد Cl^- والنتائج كذلك نوقشت من جهة تأثير المذيب على معطيات التوصيلية لهذا المعقد.

الكلمات الدالة : التوصيلية ، الثوابث الثرموداينيميكية ، لي– ويتون.