Electrolytic conductivity for Tetra Aqua 1,10-Phenanthroline Nickel (II) Chloride in Mixtures of Methanol and Water at Different Temperatures

Yasir O.Hameed* **Omar A.Shareef** **Shyma'a H.Abdul Rahman**
Chemistry Department, College of Science, *Mosul University*

Abstract

Electrolytic conductivities of mixed ligand complex of Ni(II) in binary mixtures of methanol and water have been measured at 288.15-308.15 K. The limiting molar conductances (Λ_o) and the ion association constants (K_A) of the electrolytes have been evaluated by analysis of the conductance data using the Lee and Wheaton conductivity equation. Thermodynamics of the association processes have also been studied and the coulombic forces are found to play a major role in the association processes. Walden product ($\Lambda_o\eta_o$) have also been calculated for each solvent composition. A linear relationship was found to exist between the logarithm of the association constant (log K_A) and the reciproced of the dielectric constant (1/D) of the medium which indicate the tendency of the association of ions.

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

Introduction

To obtain more information about electrolytic solution and ion-solvent interactions and their implication on ionic association and to determined the specific influence of solvent properties and ion size on the association process we have studied the association of the complex above in a series of methanol-water mixtures. The association behaviour of some examples of the available data are shown as follow:

Preise measurements of electrical conductances of solutions of potassium picrate, potassium tetraphenyl borate at temperatures 288.15-308.15 K have been reported. The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation. Thermodynamics of the association processes have also been studied(1). Electrolytic conductivities of dilute solutions of Ni(II), Cd(II), Mg(II) and Cu(II) sulfate in binary mixtures of methanol and water have been measured at 293.15 K. The (Λ_o) and (K_A) have been evaluated by using Lee-Wheaton equation(2). The conductivity of several alkali metal thiocyanates in water-methanol mixtures was measured at 25 °C. The data were analyzed using the Lee-Wheaton theory for symmetrical electrolytes to obtain ion association constant (K_A) limiting molar conductivity (Λ_o) and limiting ionic conductivity in all the solvent systems(3). Measurements of the electrical conductivity of the compounds 2-(2,4-dichlorophenoxy methyl-5-(3-chlorophenyl)-1,3,4-oxadiazole and 2,5-di(2,4-dichlorophenoxy methyl)-1,3,4-oxadiazole in mixture of methanol water as a solvent at different percentages were analyzed by using Lee-Wheaton equation the values of Λ_o, K_A and R are calculated(4,5).

Experimental

Tetra aqua (1,10-phenanathroline) nickel (II) chloride was prepared by mixing 2 mM of 1,10-phenanthroline in 10 cm^3 of ethanol and 2mM of $NiCl_2.6H_2O$ 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 °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.

Methanol was purified and dried by the methanol described by Perrin(6) 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(7), 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. 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 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 (14) additions have been made.

Results and discussion

We have measured the conductivity of tetra aqua (1,10-phenanthroline) nickel (II) chloride in a mixture of methanol water at different percentages and temperatures and analyze the data by using Lee-Wheaton equation for unsymmetrical electrolytes which 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(8). The measured equivalent conductivities for different molalities of the complex solution are shown in Table 1. The electrical conductivity of the desired complex have been studied in methanol-water mixture at different temperatures to investigate the dependence of the ion association behaviors on the properties of the complex ion. The data were treated using L-W method 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(9).

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

$$M^{2-} + X^- \overset{K_A^{(1)}}{\rightleftharpoons} MX_2 \quad ....(1.11)$$

$$MX^- + X^- \overset{K_A^{(2)}}{\rightleftharpoons} MX^+ \quad ....(1.12)$$

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 ion pair MX^+ is a conducting species.

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

This equation is derived as follows:

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

$$\sigma_i = i\lambda_i / 1000 = |Z_i|\, m_i \lambda_i / 1000$$

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

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

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

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, thus for 2:1 associated salts

$$\Lambda_{MX2} = f\,(\lambda^o_{M^{2+}} , \lambda^o_{MX^+} , \lambda^o_{X^-} , K_A^{(1)} , K_A^{(2)} , R)$$

where R is the average center to center distance for the ion pairs, a multi parameter “least square” curve-fitting procedure is used to give the lowest value of curve fitting parameter $\sigma(\Lambda)$ between the experimental and calculated points. An iterative numerical method which was found to be very successful has been used to find the minimum $\sigma\Lambda$(7).

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

A computer program is used to analysis the concentration conductivity measurements in which the input data are (T, D, η) where T is the temperature in Kelvin, D and η are the dielectric constant and viscosity (poise) of the solvent at that temperature.

The conductivity-concentration data for the studied complex in different percentage at different temperatures are shown in Table (1 A-E). The plot of equivalent conductance (Λ_o) against the square root of the molar concentration ($C^{1/2}$) are shown in Figures (1A-E). From Table and Figure (1) it can be seen clearly that the equivalent conductivity(10) decrease with increasing water percent suggesting an increasing tendency of the ions for association into ion pairs, and increasing hydrogen bonding and viscosity of the mixed solvent, except for 90% methanol, were the equivalent conductance increase due to the polarity of methanol and gradually increase of dielectric constant for each percentage.

The values of K_A (Table 2) decrease with increasing temperature, this may be attributed to the short range interaction and the hydrogen bonding formed at low temperature. And this will lead to increasing λM^{2+} for each percentage , also the value of K_A increase as water percentage increase due to H-bonding formation and increasing viscosity till 50% when the nutralanity between H-bonding and dielectric constant accurse The results of the distances parameter R show that the complex electrolytes form solvent separated ion pairs and the results show that R values are almost more than (30 A°) which means that the cation is separated by solvent molecules from the anion.

Plot of K_A values against the composition of the solvent mixture at 25 °C as an example are shown in Fig. (2). The variation of the association constant with the dielectric constant (D) of the solvent mixtures is presented as a plot of pK_A values against log D in Fig. (3). pK_A values are shown to decrease with increasing values of the dielectric constant suggesting an increasing tendency of the ions for association into ion-pairs. It is assumed that atrue chemical reaction occurs The standard enthalpy of the ion association reaction (ΔH^o) are evaluated by the following:

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

The plot of $\ln K_A$ against 1/T is shown a linear relation (Fig. 4).

The standard entropy of ion-pair formation is a linear combination of two variables:

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

Gibbs energy had to be estimated from the relationship:

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

Results 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(11). The negative entropy provides a good indication of ionic association which has an ordering effect on the solution. The solvation effect i.e interaction of the ions with the solvent molecules may exert on the solution structure in the same manner leading relatively to a negligible decrease in the entropy as temperature increase and increase with increasing water percentage(12).

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), $\Delta H°$ decrease with increasing water percentage due to the broken of ion-ion bond in solution as a result of increasing dielectric constant of the solvent(13). Finally the values of ΔG are negative which indicate the reaction is spontaneous.

If Stoke's law were obeyed in a system the value of the Walden product ($\Lambda_o\eta_o$) 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 unit will undoubtedly vary to some extent and exact constancy of the conductance-viscosity product is not to be expected(14). This is the case in the behaviour of the present system as indicated in Fig. (5) where the cations are expected to suffer various degrees of salvation with increasing amount of methanol in the methanol-water mixtures. Hemes(14) suggested that the major deviation in the Walden product is due to the variation of the electrochemical equibilirium between ions and the solvent molecules with the composition of the mixed polar solven.

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

Conc. x 10^5M	T=288 K	T=293 K	T=298 K	T=303 K	T=308 K
1.960	٢٠٣,٤١٢	١٩٧,٠٦٤	١٩٥,٧٤٥	١٨٠,٤٣٨	١٨٨,٥٣٩
3.846	٢٠٣,٣٦٢	١٩٦,٨٤١	١٩٤,٤٤١	١٨٠,٢٣٤	١٨٨,٢٩٢
5.660	٢٠٣,١٨٤	١٩٦,٥٧١	١٩٤,٠٣٨	١٧٩,٩٢٨	١٨٨,٢٨٥
7.407	٢٠٣,٠٦٣	١٩٦,٤٢٣	١٩٢,٢٨٢	١٧٩,٦٩٦	١٨٨,٢٢٩
9.909	٢٠٢,٦٦٤	١٩٥,٩٦٧	١٨٦,٥٥٤	١٧٩,٣٢٤	١٨٨,٢٠٢
10.714	٢٠٢,٣٦٨	١٩٥,٩١٩	١٨٥,٦١٤	١٧٨,٦٥٣	١٨٨,١٣٩
12.228	٢٠٢,٣٨٠	١٩٥,٨٤٠	١٨٥,٤٣٦	١٧٨,٤٤٥	١٨٨,٠٧٤
13.793	٢٠١,٩٣٧	١٩٤,٩٢٢	١٨٥,٥٢٨	١٧٨,١٢٦	١٨٧,٦٨٠
15.254	٢٠١,٩٢١	١٩٤,٣٨٦	١٨٥,٥٠٤	١٧٨,١٢١	١٨٧,٥٨٩
16.666	٢٠٠,٩٩٨	١٩٤,٣٥٣	١٨٥,٢١٧	١٧٧,١٣٥	١٨٧,٥٧٦
18.032	٢٠٠,٨٧٢	١٩٣,٢٥٦	١٨٤,٦٨٨	١٧٦,١٥٤	١٨٦,١١٦
19.354	١٩٩,٧١٦	١٩١,٨٦٢	١٨٢,٨٨٦	١٧٣,٥٠٢	١٨٤,٥٦٠
20.634	١٩٥,٥٣٤	١٨٨,٦٤٩	١٨١,٧٦٤	١٦٧,٥٨٦	١٨٢,٠٠٢
21.875	١٨٣,٨٠٤	١٨٠,٢٠٠	١٧٢,٩٤٢	١٦٠,٢٧٥	١٧١,٩٤٥
23.076	١٦٧,٠٧٦	١٧٦,٢٣٤	١٥٦,٤٦٨	١٥١,١٦٤	١٦٨,٤٠٢

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

Conc. x 10^5M	T=288 K	T=293 K	T=298 K	T=303 K	T=308 K
1.960	٢٢٩,٠٠١	٢٢٤,٤٢٤	٢١٤,٩٦٤	٢١٤,١٨٩	٢١٣,٩٦٣
3.846	٢٢٨,٢٦٦	٢٢٣,٦٦٨	٢١٤,٨٩٦	٢١٣,٤٠٨	٢١٣,٤٠٨
5.660	٢٢٨,٢٢٨	٢٢٢,٧٠٥	٢١٤,٣٩٦	٢١٣,٢٥٠	٢١٣,٢٥٠
7.407	٢٢٧,٦١٤	٢٢١,٥٠٢	٢١٤,٣٥٥	٢١٣,٠٢٣	٢١٣,١٤٧
9.909	٢٢٧,٣٥٤	٢٢٠,٠٠٣	٢١٤,١٨٩	٢١٢,٦٢٩	٢١٢,٠٤٠
10.714	٢٢٦,٤٠٤	٢١٨,٦٥٢	٢١٣,٦٧٧	٢١١,٧٨٠	٢١١,٧٨٠
12.228	٢٢٧,٣٢١	٢١٥,٦٨٨	٢١٣,٤٠٨	٢١٠,٦٧٢	٢١١,٣٥٦
13.793	٢٢٥,٦٩٤	٢١٠,٨٤٣	٢١٣,٣٧٣	٢١٠,٠٠٠	٢١٠,٧٤٨
15.254	٢٢٤,٨٠٨	٢٠٧,٣٤١	٢١٢,٩٩٦	٢٠٨,٢٧٨	٢٠٨,٢٧٨
16.666	٢٢٣,٧١٦	٢٠٢,٥٦٤	٢١١,٦٤٩	٢٠٦,٠٧٩	٢٠٥,١٥١
18.032	٢٢٢,٣٧٦	٢٠٠,٠٣٠	٢١٠,٦٧٢	٢٠٤,٢٨٨	٢٠٣,٢٢٤
19.354	٢١٨,١٩٦	١٩٧,٨٤٣	٢٠٩,٤١٨	١٩٩,٣٨٦	٢٠٠,٦٤٠
20.634	٢١٠,٨٤٣	١٩٥,٥٦٤	٢٠٧,٧٦٥	١٩٣,٩١٤	١٩٦,٩٩٢
21.875	٢٠١,٤٠٠	١٩٣,٧٤٦	٢٠١,٤٠٠	١٨٣,٢٧٤	١٨٨,٣١٦
23.076	١٨٠,٨٠٤	١٩٢,٣٣٧	١٨٩,٦٩٦	١٨٠,٠٥٦	١٧١,٩١٢

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

Conc. x 10^5M	T=288 K	T=293 K	T=298 K	T=303 K	T=308 K
1.960	١٦٤,٤٥٣	١٦١,٨٤٠	١٦٣,١٥٧	١٥٥,٢٧٣	١٤٩,٨٣٨
3.846	١٦١,٧٧٢	١٦١,٥٦٨	١٦٢,٧٩٢	١٥٥,١٤٢	١٤٩,٦٧٧
5.660	١٦١,٢٦٢	١٦١,١٣٠	١٦٢,٦٩٦	١٥٤,٩٣٨	١٤٩,٢٠٨
7.407	١٦٠,٩٣٦	١٦١,١٠٩	١٦٢,٤٨٥	١٥٤,٧١٨	١٤٩,١٤١
9.909	١٦٠,٤٢٥	١٦٠,٤٧١	١٦٢,٣٣٧	١٥٤,٨٣٦	١٤٨,٧٦٢
10.714	١٥٩,٨٣٦	١٦٠,٣٧٨	١٦١,٩٦١	١٥٤,٤١٨	١٤٨,٧١٦
12.228	١٥٨,٢٥٣	١٥٩,١٤٢	١٦٠,٨٤٠	١٥٤,٤٦٢	١٤٧,٧٧٥
13.793	١٥٧,٨٠٦	١٥٩,١٢٠	١٦١,٥٦٨	١٥٣,٦٥٥	١٤٧,١٦٠
15.254	١٥٧,٣٢٥	١٥٩,١٢٠	١٦١,٢٦٢	١٥٣,٨١٦	١٤٦,١٨٠
16.666	١٥٧,٢٨٤	١٥٨,٣٧٨	١٦٠,٦٥٠	١٥٢,٣٢٠	١٤٤,٧٠٤
18.032	١٥٧,٢٤٦	١٥٨,١٠٠	١٦٠,٣٧٨	١٥١,٤٧٠	١٤٣,٦١٦
19.354	١٥٧,٢٠٠	١٥٧,٧٩٤	١٥٩,٩٣٦	١٥٠,٠٩٣	١٤٠,٤٥٥
20.634	١٥٧,١٨٩	١٥٧,٦٨٤	١٥٩,٩٣٦	١٤٥,٩٦٢	١٣٤,٢٤٩
21.875	١٥٧,١٣٨	١٥٧,٦٠٤	١٥٩,٦٦٢	١٣٧,٩٠٤	١١٩,٣٤٠
23.076	١٥٦,٠٦٠	١٥٦,٠٦٠	١٥٦,٤٦٨	١٠٩,٢٤٢	١٠٠,٥٦٧

Table(1-D) : The equivalent conductivities ($\Omega^{-1}.cm^{2}.equiv^{-1}$) with molar concentration for $[Ni(phen)(H_2O)_4]Cl_2$ in 70% 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	105.638	112.561	١١٧,٥٠٤	118.902	١٢٤,٠٣٢
3.846	١٠٣,٩٨١	١١٢,٣٧٤	١١٧,١٣٠	١١٨,٨٩٨	١٢٣,٧١٨
5.660	١٠١,٨٧٧	١١١,٩٩٦	١١٦,٩٦٨	١١٧,٨١٠	١٢٣,٣٠٠
7.407	١٠٠,١٣٠	١١١,٩١٩	١١٦,٦٥٦	١١٧,١٥٠	١٢٣,١٧٧
9.909	٩٧,٣٠٨	١١١,٨٢٦	١١٥,٤١٣	١١٧,٠١٦	١٢٣,٠٣٤
10.714	٩٥,٠٢٦	١١١,٧٢٤	١١٤,٨٢٤	١١٦,٢٨٠	١٢٣,٠٠٢
12.228	٩٤,٩٥٦	١١١,٧١٣	١١٤,٤٤٤	١١٦,١٠١	١٢٢,٠٢٨
13.793	٩٤,٦٥٦	١١٠,٩٩٨	١١٤,٣٤٢	١١٥,٩٤٠	١٢٢,٢٩٨
15.254	٩٢,١٩٣	١١٠,١٨٥	١١٣,٨٨٣	١١٤,٦١٨	١٢٢,١٧٧
16.666	٨٧,٥٨٤	١٠٧,٩٧٤	١١٢,١٢٧	١١٣,٢٨٨	١٢١,٧٨٨
18.032	٧٨,٥٤٠	١٠٥,٤٦٨	١٠٨,٥٢٦	١١١,٠٧٨	١٢١,١٠٥
19.354	٧١,٦٠٤	١٠٠,٥٢١	١٠٦,٥٩٠	١٠٤,٦٥٢	١٢٠,١٥٦
20.634	٥٥,٨٦٢	٩١,٩٠٢	١٠١,٨٩٨	١٠٠,٩١٢	118.422
21.875	٤١,٦١٦	٧٦,٩٠٨	٩٣,٧٠٤	٨٤,٨٦٤	١١٧,١٣٠
23.076	٢٩,١٧٢	٧٠,١٢٠	٧٦,٩٠٨	٥٢,٠٢٠	١١١,٣٨٤

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

Conc. x 10^5 M	T=288 K	T=293K	T=298 K	T=303 K	T=308 K
1.960	٩٦,٨٨٤	٩٨,٨٦١	٩٩,٣١٨	١٠٦,٥٥٤	١١٠,٥٠٩
3.846	٩٦,١٥٨	٩٨,٨٥٢	٩٨,٣٦٧	١٠٤,٧٩٣	١٠٩,٧٣٦
5.660	٩٥,٥٨٨	٩٨,٠٢٢	٩٨,٠٢٢	١٠٤,٦٨١	١٠٩,٦١٦
7.407	٩٤,٣٣٠	٩٧,٢٨٩	٩٧,٢٨٩	١٠٤,٣٥٩	١٠٨,٣٢٤
9.909	٩٢,٤٦٠	٩٦,٢٨٨	٩٥,٦٧٦	١٠٤,٢٠٣	١٠٦,٩٠٥
10.714	٩٠,٤٦١	٩٥,٦٧٦	٩٤,٩٥٠	١٠٢,٣٠٦	١٠٦,١١٨
12.228	٨٣,٨٤٤	٩٥,٣٩٥	٩٤,٦٦٨	١٠٢,٢٠٤	١٠٤,٦٥٢
13.793	٨٣,٥٨٣	٩٥,١٠٠	٩٣,٩١٦	١٠٠,٤٩٩	١٠٤,٥٢٠
15.254	٨٣,٥٨٣	٩٤,٢٤٨	٩٢,١٩٣	٩٩,٨٩٦	١٠٣,٩٢٥
16.666	٨٢,٢٢٦	٩٣,٨٢٧	٨٩,٤٨٨	٩٩,٢٩٧	١٠٢,٨١٦
18.032	٧٩,٠١٦	٩٣,٦٣٦	٨٢,٦٢٠	٩٩,٦٩٥	٩٩,٨٥٨
19.354	٧٤,٦١٣	٩٢,٨٦٢	٨٠,٤٣٠	٩٧,٦١٤	٩٥,٠١٣
20.634	٧٣,٨٨٢	٩٢,٢٥٩	٧٨,٥٢٠	٩٠,٨٨٢	٩٠,٤٩٦
21.875	٧٢,٩٨١	٨٢,٨٩٢	٧٦,٩٣٠	٨٨,٦٣٠	٨٦,٤٩٦
23.076	٧٠,٥٣٠	٧٦,٩٠٨	٧٥,٣٢٠	٨٥,٥٣٠	٨٥,٦٠٤

Table (2) : Values of λM^{+2} ,K_A , R , dielectric constant and viscosity of the complex at different percentages and temperatures.

Temp. K	K_A	RA^o	λM^{+2}	D	η
100 % Methanol					
288.15	780	70	146	40.0	0.00623
293.15	760	70	155	36.31	0.00597
298.15	750	70	160	32.62	0.00544
303.15	700	70	170	29.81	0.00516
308.15	650	70	180	27.0	0.00483
90 % Methanol					
288.15	465	38	240	44.19	0.00673
293.15	368	38	245	40.88	0.00638
298.15	290	34	250	37.22	0.00581
303.15	254	38	271	34.48	0.00513
308.15	205	34	275	31.78	0.00500
80 % Methanol					
288.15	900	70	110	48.39	0.00725
293.15	800	70	120	45.07	0.00679
298.15	700	70	160	41.82	0.00582
303.15	680	70	135	39.16	0.00565

308.15	660	70	140	36.56	0.00529
70 % Methanol					
288.15	1320	50	120	52.58	0.00772
293.15	1280	50	130	49.45	0.00721
298.15	1250	50	135	46.42	0.00640
303.15	1220	50	140	43.83	0.00598
308.15	1200	50	150	41.34	0.00553
50 % Methanol					
288.15	1000	70	50	60.97	0.00880
293.15	950	70	55	58.21	0.00805
298.15	920	70	59	55.40	0.00710
303.15	900	70	64	53.87	0.00657
308.15	880	70	70	50.19	0.00600

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

Temp K	**ΔG^o KJmole^{-1}**	**ΔS^o K cal.mole^{-1}**	**ΔH^o K cal.mole^{-1}**
	100 % Methanol		
288.15	-3.799	-84.088	-28.029
293.15	-3.849	-82.483	
298.15	-3.908	-80.902	
303.15	-3.932	-79.488	
308.15	-3.951	-78.137	
	90 % Methanol		
288.15	-3.504	-12.101	-6.991
293.15	-3.428	-12.154	
298.15	-3.358	-12.185	
303.15	-3.322	-12.102	
308.15	-3.247	-12.149	
	80 % Methanol		
288.15	-3.881	2.172	-3.255
293.15	-3.880	2.132	
298.15	-3.867	2.052	
303.15	-3.914	2.173	
308.15	-3.961	2.291	
	70 % Methanol		
288.15	-4.099	11.313	-0.893
293.15	-4.154	11.123	
298.15	-4.209	11.121	
303.15	-4.265	11.119	
308.15	-4.325	11.137	
	50 % Methanol		
288.15	-3.941	10.432	-0.935
293.15	-3.979	10.383	
298.15	-4.027	10.370	
303.15	-4.083	10.384	
308.15	-4.136	10.387	

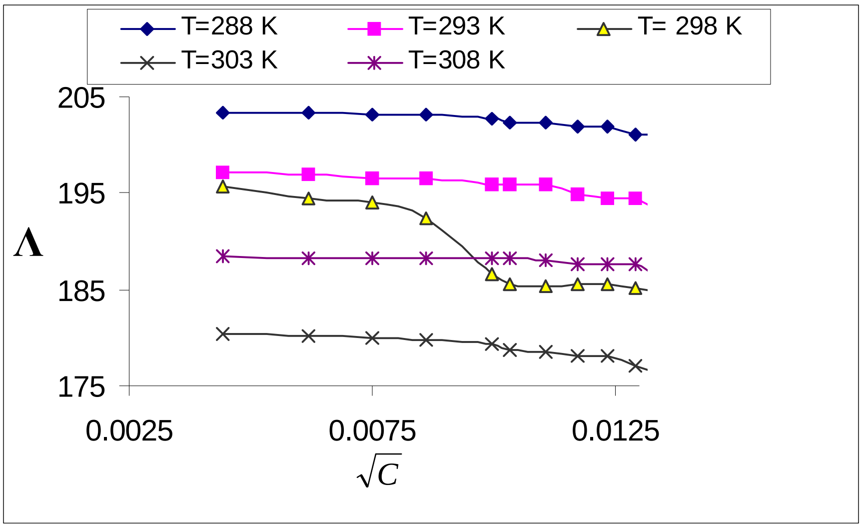

Fig (1-A) : plot of equivalent conductivities against Square root of concentration for [Ni(phen)$(H_2O)_4$]Cl_2 in 100% methanol at different temperatures

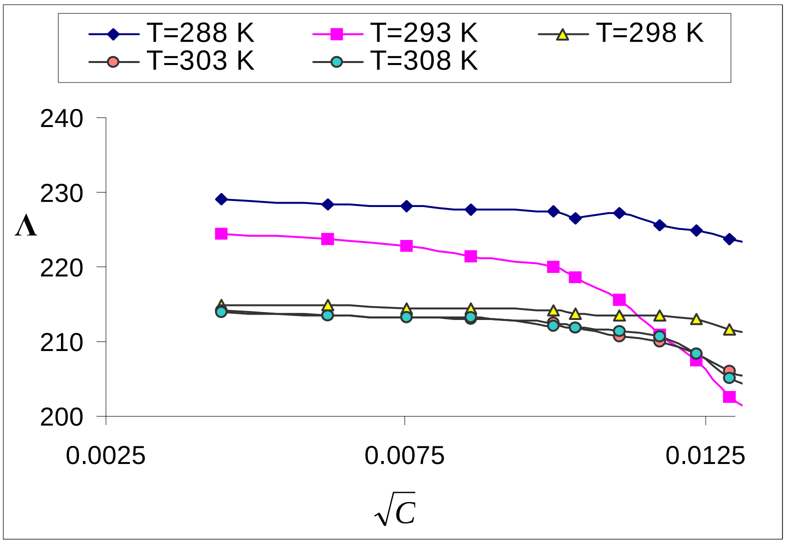

Fig (1-B) : plot of equivalent conductivities against Square root of concentration for [Ni(phen)$(H_2O)_4$]Cl_2 in 90% methanol-water mixture at different temperatures

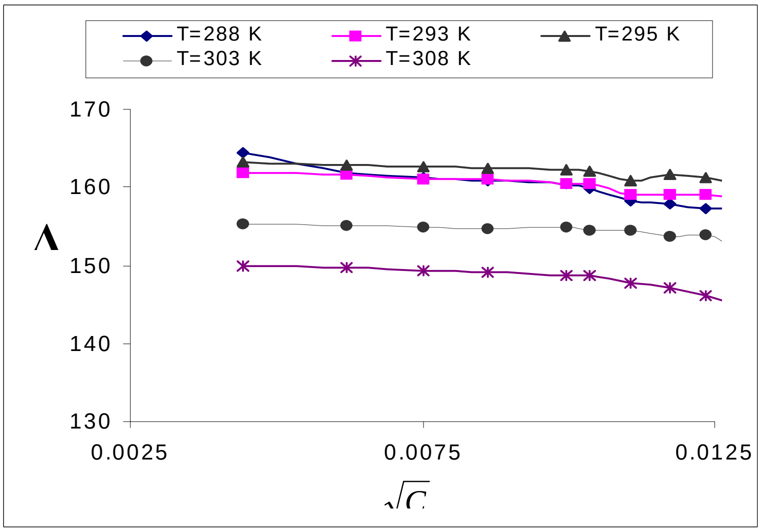

Fig (1-C) : plot of equivalent conductivities against Square root of concentration for [Ni(phen)$(H_2O)_4$]Cl_2 in 80% methanol-water mixture at different temperatures

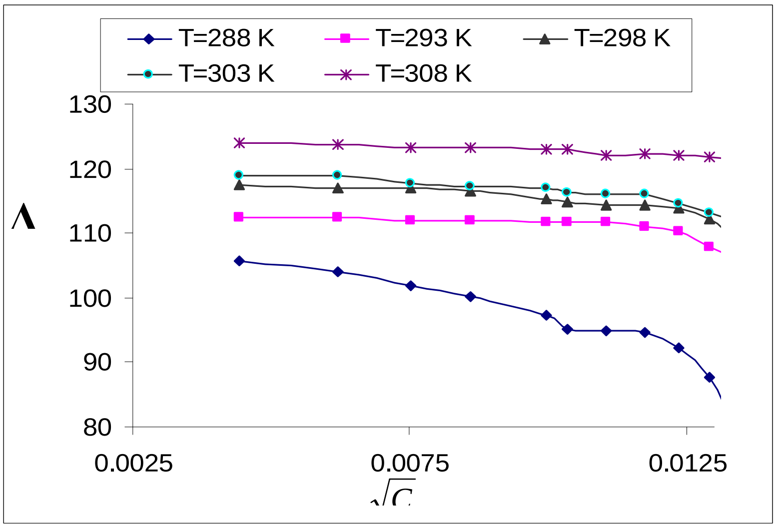

Fig (1-D) : plot of equivalent conductivities against Square root of concentration for [Ni(phen)(H_2O)$_4$]Cl_2 in 70% methanol-water mixture at different temperatures

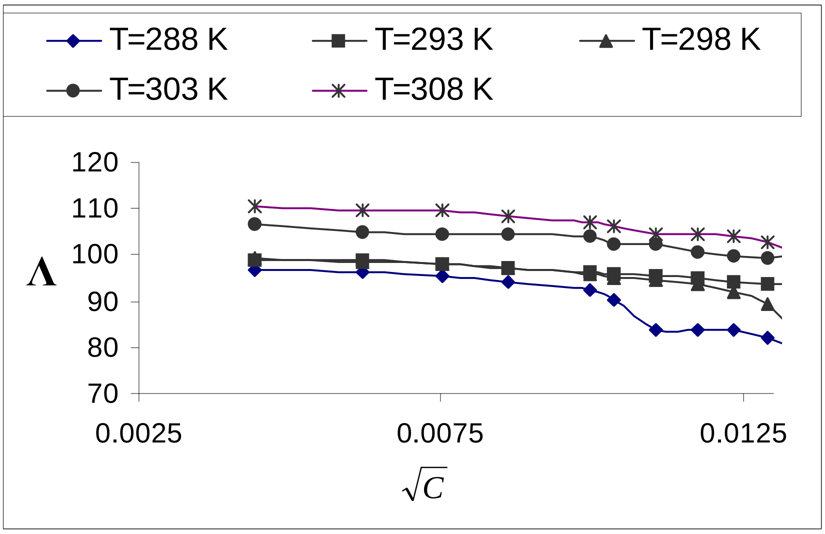

Fig (1-E) : plot of equivalent conductivities against Square root of concentration for [Ni(phen)(H_2O)$_4$]Cl_2 in 50% methanol-water mixture at different temperatures

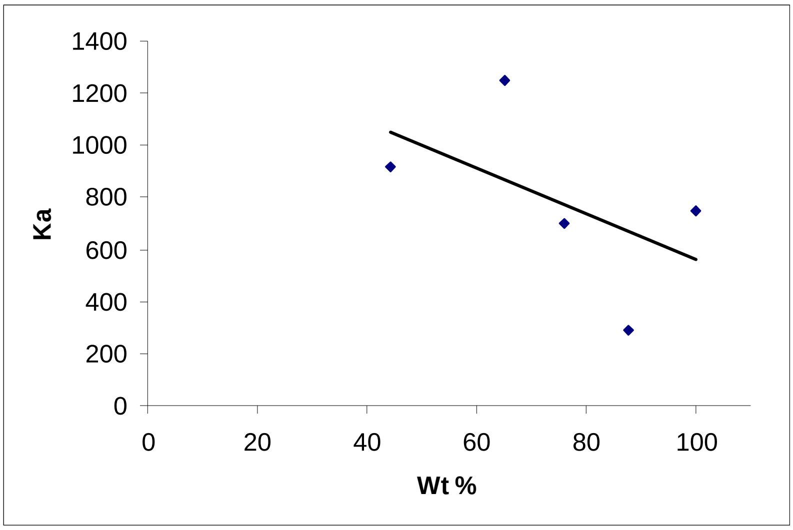

Fig (2) : Plot of K_A versus the composition of solvent mixtures at 298 K

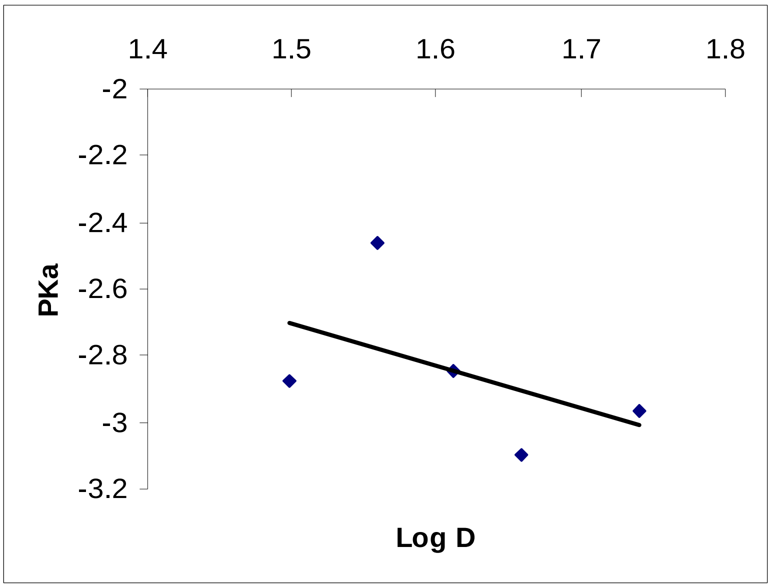

Fig (3) : Variation of PK_A values of the complex in methanol-Water Mixtures at 298 k with dielectric constant of the mixtures (Log D

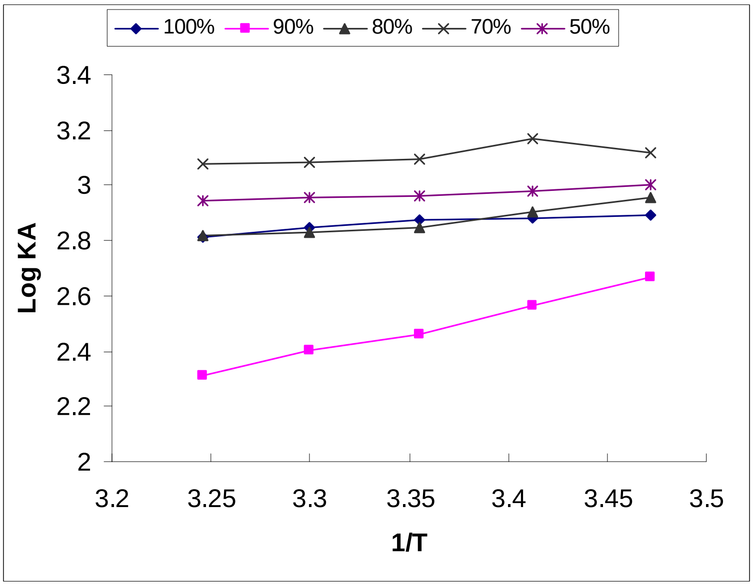

Fig (4): plot of Log K_A against 1/T for the Complex at different solvent composition

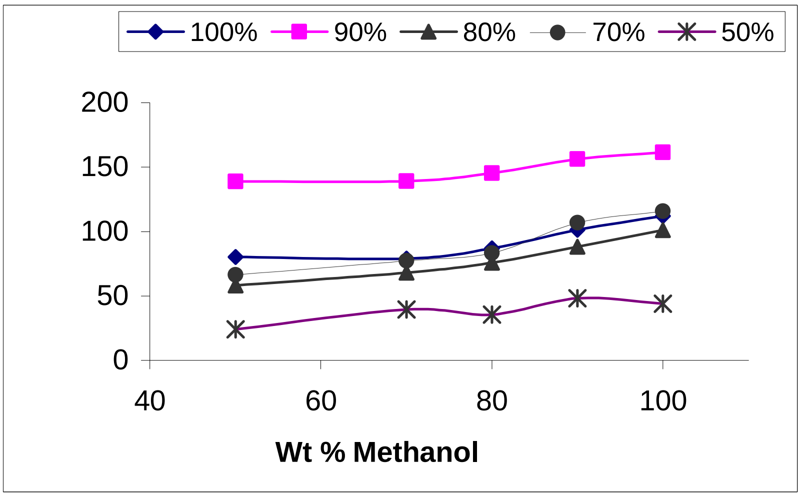

Fig (5) : Walden products (Λ_o η_o) for the complex in methanol-water mixture plotted versus the composition of the mixture at different temperatures

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التوصيل الكهربائي للمركب $[Ni(phen)(H_2O)_4]Cl_2$ في مزيج من الميثانول والماء بدرجات حرارية مختلفة

ياسر عمر العلاف و عمر عادل شريف و شيماء هاشم عبد الرحمن

قسم الكيمياء ، كلية العلوم ، جامعة الموصل، العراق، جمهورية العراق

الملخص

تم قياس التوصيلية الالكتروليتية لمعقد النيكل (II) الحاوي على مزيج من الليكند في مذيب مزدوج مكون من الميثانول والماء بنسب مختلفة تتراوح بين (٥٠-١٠٠) ميثانول في درجات حرارية بين(٢٨٨,١٥-٣٠٣,١٥) مطلقة . حيث تم قياس التوصيلية المولارية المكافئة عند التخفيف اللانهائي (Λ_o) ، وثابت التجمع الايوني (K_A) والمسافة بين الايونات في المحلول(R) وتم تحليل النتائج التوصيلية باستخدام معادلة لي-ويتون وحسبت كذلك الدوال الثرموداينيمكية لعملية التجمع ألايوني ووجد ان القوى الكولومية هي التي تلعب دوراً هاماً في عملية التجمع الايوني وكذلك حسب ناتج فالدن($\Lambda_o\ \eta_o$) لكل مكون من المذيب حيث اعطى علاقة خطية بين لوغارتيم ثابت التجمع الايوني ($\mathrm{Log}\ K_A$) ضد مقلوب ثابت العزل (1/D) للوسط والذي يبين ميل الايونات الى التجمع في المحلول والتذاوب الكاتيوني والى التفاعلات ذات المديات القصيرة للتداخل والتي تحصل بين الايونات وجزيئات المذيب .