Conductivity Study of Tetra aqua-1,10-Phenanthroline Cobalt (II) Chloride $[Co(1,10\text{-}Phen)(H_2O)_4]Cl_2$ in Methanol-Water Mixture at Different Temperatures

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Abstract

The hydrodynamic behaviour of tetra aquo-1,10-phenanthroline cobalt (II) chloride in methanol-water mixture have been investigated by precise conductance measurements at 288.15-308.15 K. The limiting molar conductances (Λ_o), ion association constant K_A of the electrolyte and the main distance between ion in solution (R) have been evaluated by Lee-Wheaton conductivity equation. Coulombic forces are found to play a major role in the association processes from thermodynamic point of view. Walden products ($\Lambda_o\eta_o$) have also been calculated for each solvent composition.

الخلاصة

تمت دراسة سلوك الديناميي المائي للمعقد $[Co(1,10\text{-}Phen)(H_2O)_4]Cl_2$ في مزيج من المـاء والميثـانول كمذيب بواسطة قياسات التوصيلية في درجات حرارية مختلفة (288.15-308.15 K) وتم حساب التوصيلية المولارية المحددة (Λ_o) وثابت التجمع الايوني (K_A) للالكتروليت ومعدل المسافة بين الايونات (R) باستخدام معادلة لي-ويتون. ووجد ان القوة الكولومية تلعب دور هام في عملية التجمع الايوني من وجهة نظر الثرموديناميكية وتم حساب ناتج والدن ($\Lambda_o\eta_o$) لكل تركيب من المذيب.

Introduction

Following our investigations of the association reaction of electrolytes in mixed alcohol-water solvents with higher alcohol content, we examined the association of $[Co(1,10\text{-}Phen)(H_2O)_4]^{2+}$ and Cl^- ions in methanol + water mixtures. The investigations were based on the measurement of solution conductivity. To obtain more information about electrolytic solution and ion-solvent interactions and their implication on ionic association and to determine 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: The ion association of $[Fe(Phen)_3]^{2+}$ with o- and m-benzenedisulfonate 2,6-and 2,6-naphthalene disulfonate ions, determined by conductivity measurements at 0-50 °C, were considerably large than the electrostatic prediction, the significant enthalpy contribution was found to the hydropholic ion association(1). The association constants K_A for Mg, Ca, Sr and

Ba salts of acetate, propronate and butyrate have been determined at 25, 35, 45 and 55 °C in aqueous solutions using the conductometric technique, the data were treated by the Lee and Wheaton method(2). The conductivity of several metal thiocyantes in water-methanol mixtures was measured at 25 °C. The data were analyzed using the above theory for symmetrical electrolytes to obtain ion association constant (K_A), limiting molar conductivity (λ_o)(3). Conductance measurements of $[Ni(Phen)_3]Cl_2$ in water, methanol and ethanol at (280.15-318.15 K) are reported. Limiting equivalent conductance (Λ_o) association constant (K_A) and distance of closest approach of ions (R) are calculated by means of Lee-Wheaton equation(4).

Molar conductivity of HBr in 2-propanol + water mixtures, with alcohol mass fraction of 70, 80, 90 and 95% were determined at five temperatures in the region from 288.15 to 308.15 K. Data were processed by the Lee-Wheaton conductivity equation, the thermodynamic quantities for the ion-association reaction were obtained(5).

Experimental

Preparation of the complex

Tetra aquo (1,10-phenanathroline) cobalt (II) chloride was prepared by mixing 2 mmole of 1,10-phenanthroline in 10 cm^3 of ethanol and 2mmole of $CoCl_2.4H_2O$ 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 ^oC followed by addition of excess absolute ethanol. The product was dried under vacuum over anhydrous calcium chloride. The 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(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}.

Method of measurement

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

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 behaviour on the properties of the complex ion. The data were treated 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) in which a wide temperature range can provide detailed information concerning ion-ion and ion-solvent interaction especially from thermodynamic point of view(9). Table (1) shows the electrical conductivity of the desired complex studied in methanol-water mixture at different temperature.

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

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

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

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 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:

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

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

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

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

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

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

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

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

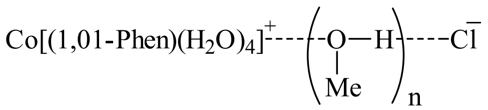
The conductivity-concentration data for the studied complex in different percentage at different temperatures are shown in Table (1A-E). The plot of equivalent conductance (Λ_o) against the square root of the molar concentration ($C^{1/2}$) are shown in Figures (1A-E).

From Table and Figure (1) it can be seen clearly that the equivalent conductivity decrease with increasing water percent suggesting an increasing tendency of the ions to associate into ion pairs, because of increasing hydrogen bonding and viscosity of the mixed solvent, except for 50% methanol, were the equivalent conductance increase due to the increasing dielectric constant of the mixed solvent and formation of triple ions (M^{2+}, X^-, MX^+).

The values of K_A (Table 2) decrease with increasing temperature, because of the short range interaction and the hydrogen bond formed at low temperature. Furthermore, K_A values increase from 90% to 70% of methanol which means increasing of water percentage forming more hydrogen bonding and increasing association except 100% and 50% methanol which the first due to the polarity of solvent and the second due to the increasing in dielectric constant, which means neutralization between H-bonding and dielectric constant.

The results of the distance parameter R are large because of these two effects. Firstly isolated ions (in particular the cation) will tend to be surrounded by extensive solvent shells. The existence of these dielectrically saturated regions gives rise to a repulsive force between the ions when they come into close approximately. The second effect is ion-dipole-ion forces will be significant and solvent separated ion paris will have same stability(8).

In methanol δ values are more irregular however the species:



$$\mathrm{Co}[(1{,}01\text{-Phen})(\mathrm{H_2O})_4]^{+}\text{---}\left(\text{-}\underset{\mathrm{Me}}{\mathrm{O}}\text{—H}\right)_{n}\text{----}\mathrm{Cl}^{-}$$

would appear to exist in all cases, so the addition of 10% water affect the values of R while the addition of other percentages (20-50%) does not affect largely the values of R, this is may be due to the influence of H-bonding between water molecules in the higher percentage.

$\lambda^{o}_{M^{2+}}$ show an increase in each percent due to increasing temperature and increasing dielectric constant of the mixed solvent $\lambda^{o}_{M^{2+}}$ at 90% methanol higher than the other percent because of the increasing dielectric constant after addition of water to methanol then it decreases because of formation of H-bonding in the other percents. $\lambda_{MX^{+}}$ is almost constant and low value because of formation of large ion and more stable than the other ions (M^{2+}, X^{-}). The small values of $\sigma(\Lambda)$ give an indication of the good best fit value (less than 0.1).

A plot of Ka values against the composition of solvent mixture at 298.15 K as an example are shown in Figure (2). The variation of the association constant with the dielectric constant (D) of solvent mixtures is presented as a plot of pK_A values against log D in Figure (3). pK_A values shown a decrease with increasing values of the dielectric constant suggesting an increasing tendency of the ions for association into ion pairs(9).

The 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), 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 shown 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(10.

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 structure in the same manner leading relatively to a decrease in the entropy as temperature increase and decrease with increasing water percentage(11).

The enthalpy decrease with increasing water percentage due to the broken at ion-ion bond in solution as a result of increasing dielectric constant of the mixed solvent(12) and the increase due to the formation of H-bonding. Finally the values of ΔG are negative which indicate the reaction is spontaneous.

Fig. (5) show the variation of Walden product ($\Lambda_o\eta_o$) against solvent composition, where the cationes are expected to suffer various degree of solvation with increasing the amount of water in the methanol-water mixtures.

The major deviation in Walden product is due to the variation of the electrochemical equilibrium between ions and the solvent molecules with the composition of the mixed polar solvents(13).

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

Conc. x 10^{-5}	T=15°	T=20°	T=25°	T=30°	T=35°
1.960	161.334	163.2	164.598	171.593	179.053
3.846	161.144	163.121	164.357	171.277	178.445
5.660	160.208	162.843	163.897	171.275	178.126
7.407	160.075	162.337	163.468	170.256	177.609
9.909	159.426	161.568	162.792	169.524	177.48
10.714	158.622	160.48	162.486	169.345	177.196
12.228	157.808	159.732	161.211	169.171	176.001
13.793	156.802	158.639	160.3	168.606	174.42
15.254	154.836	157.086	158.032	166.6	173.264
16.666	154.589	156.78	157.584	164.934	171.253
18.032	153.994	155.677	156.939	164.016	170.544
19.354	151.47	152.592	155.958	163.251	170.403
20.634	145.962	148.716	152.847	161.109	167.994
21.875	135.252	142.258	145.962	154.972	148.512
23.076	130.002	140.020	143.244	153.021	145.254

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

Conc. x 10^{-5}	T=15°	T=20°	T=25°	T=30°	T=35°
1.960	160.726	161.147	162.830	165.144	173.554
3.846	158.678	161.33	162.656	163.761	172.259
5.660	157.189	159.469	161.801	162.500	172.150
7.407	157.138	159.167	161.144	161.885	172.019
9.909	156.519	159.154	160.208	160.971	170.484
10.714	156.115	157.246	158.509	160.423	169.408
12.228	155.448	157.284	158.093	157.471	169.218
13.793	153.124	155.799	156.488	154.925	167.835
15.254	152.337	153.446	155.295	152.409	165.278
16.666	149.502	150.333	150.337	149.940	164.868
18.032	149.464	147.560	148.512	143.616	161.364
19.354	143.618	143.616	144.738	134.946	158.763
20.634	139.077	134.946	136.323	119.833	154.912
21.875	127.942	123.437	126.146	88.842	143.259
23.076	106.080	98.124	98.124	60.419	131.274

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

Conc. x 10^{-5}	T=15°	T=20°	T=25°	T=30°	T=35°
1.960	157.604	157.812	156.205	160.868	163.121
3.846	157.189	157.604	155.706	160.155	162.180
5.660	156.519	157.573	155.550	159.944	162.966
7.407	156.468	157.284	155.465	159.509	161.789
9.909	156.115	157.189	154.224	159.126	161.772
10.714	156.060	156.468	153.793	158.474	161.148
12.228	155.295	155.295	153.816	157.513	160.471
13.793	154.486	154.488	151.994	156.147	159.469
15.254	151.368	153.272	151.368	155.176	158.032
16.666	150.348	152.031	149.226	154.836	155.256
18.032	149.576	149.787	148.524	151.470	154.836
19.354	144.585	148.027	145.962	145.962	151.470
20.634	138.754	144.160	138.754	140.600	145.962
21.875	121.992	129.949	130.696	138.636	140.252
23.076	116.380	125.350	128.351	135.530	135.838

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

Conc. x 10^{-5}	T=15°	T=20°	T=25°	T=30°	T=35°
1.960	166.458	183.260	271.258	261.193	363.520
3.846	165.165	182.988	270.864	259.934	330.155
5.660	165.240	182.700	270.712	259.578	315.212
7.407	165.065	182.546	270.573	259.084	308.461
9.909	164.951	181.895	270.393	258.875	302.871
10.714	164.908	181.764	270.351	258.828	302.829
12.228	164.604	181.551	270.258	258.402	301.245
13.793	164.453	181.177	268.274	258.276	299.673
15.254	164.424	179.753	268.199	258.115	296.400
16.666	164.092	179.010	267.545	257.705	293.719
18.032	163.803	177.977	265.848	257.599	293.060
19.354	162.690	178.398	264.936	256.443	293.008
20.634	161.840	176.542	264.708	256.243	292.949
21.875	161.279	169.728	263.532	250.743	291.819
23.076	157.794	165.330	261.301	244.530	291.668

Table(1-E) : The equivalent conductivities ($\Omega^{-1}.cm^{2}.equiv^{-1}$) with molar concentration for $[Co(1,10\text{-}Phen)(H_2O)_4]Cl_2$ in methanol water mixtures at different temperatures Co 100%

Conc. x 10^{-5}	T=15°	T=20°	T=25°	T=30°	T=35°
1.960	187.895	199.155	191.031	181.152	182.784
3.846	187.709	198.997	189.681	181.024	182.725
5.660	187.225	198.492	189.057	180.918	181.815
7.407	187.093	196.337	188.972	180.609	181.764
9.909	186.660	196.253	188.898	180.438	181.177
10.714	186.558	196.222	188.190	179.871	181.003
12.228	185.859	193.730	188.074	179.698	179.894
13.793	185.640	193.145	186.601	179.572	179.520
15.254	185.640	191.791	186.294	179.452	179.520
16.666	185.130	191.828	185.814	179.010	179.010
18.032	185.115	191.651	185.419	178.572	178.398
19.354	183.141	191.250	185.130	177.977	178.215
20.634	174.794	191.177	185.021	176.944	172.992
21.875	161.772	188.309	181.101	172.992	168.532
23.076	114.444	176.358	165.750	160.875	160.446

Table (2): The results of analysis of the conductance data for $[Co(Phen)(H_2O)_4]Cl_2$ in methanol-water mixtures at different temperature

T	K_A	$\lambda^o_{M^{2+}}$	$\lambda^o_{MX^+}$	RA°	σΛ
100% methanol					
288.15	680	150	0.001	70	0.066
293.15	660	160	0.001	70	0.059
298.15	640	165	0.001	70	0.063
303.15	620	170	0.001	70	0.074
308.15	600	180	0.001	70	0.076
90% methanol					
288.15	570	140	0.001	30.5	0.071
293.15	550	160	0.001	30	0.06
298.15	530	250	0.003	29	0.05
303.15	515	263	0.001	30	0.076
308.15	505	280	0.001	30	0.09
80% methanol					
288.15	700	120	0.001	69.9	0.071
293.15	680	122	0.002	69.9	0.055
298.15	650	125	0.002	69.9	0.048
303.15	670	127	0.001	69.9	0.041
308.15	610	136	0.001	69.9	0.049
70% methanol					
288.15	1190	100	0.001	70	0.083
293.15	1180	113	0.001	70	0.099
298.15	1150	115	0.001	70	0.099
303.15	1130	116	0.001	70	0.09
308.15	1110	118	0.001	70	0.076
50% methanol					
288.15	685	120	0.002	69.9	0.05
293.15	670	130	0.001	69.9	0.046
298.15	650	135	0.001	69.9	0.042
303.15	625	140	0.001	69.9	0.051
308.15	615	145	0.001	69.9	0.056

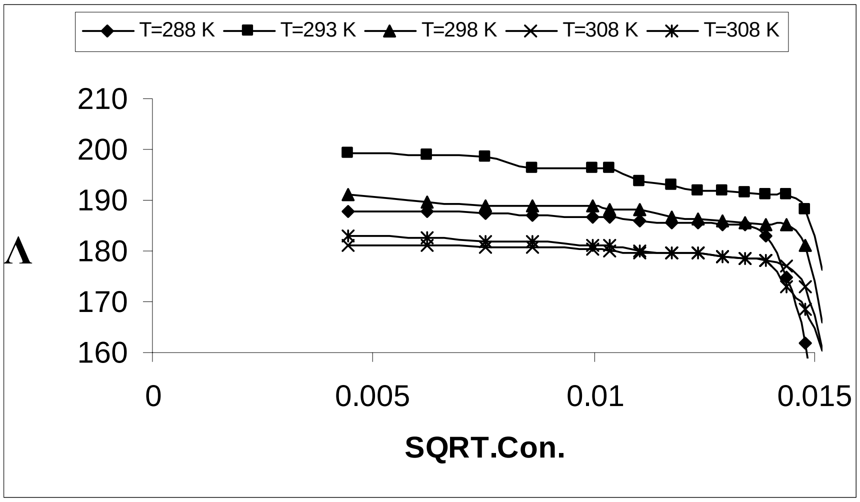


Fig (1-A) :The plot of equivalent conductivities against Square root of concentration for $[Co(phen)(H_2O)_4]Cl_2$ in 100% methanol at different temperatures

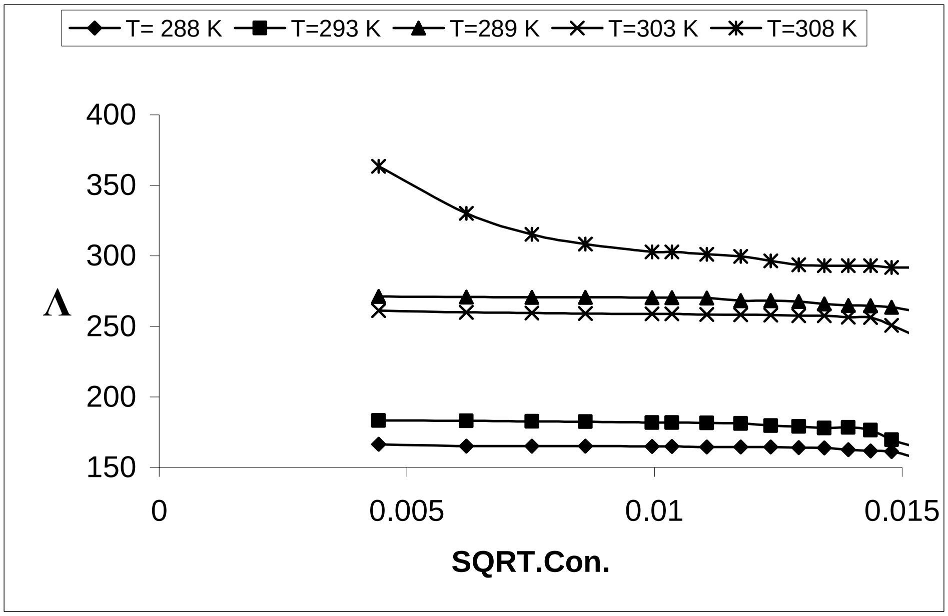


Fig (1-B) :The plot of equivalent conductivities against Square root of concentration for $[Co(phen)(H_2O)_4]Cl_2$ in 90% methanol-water mixtures at different temperatures

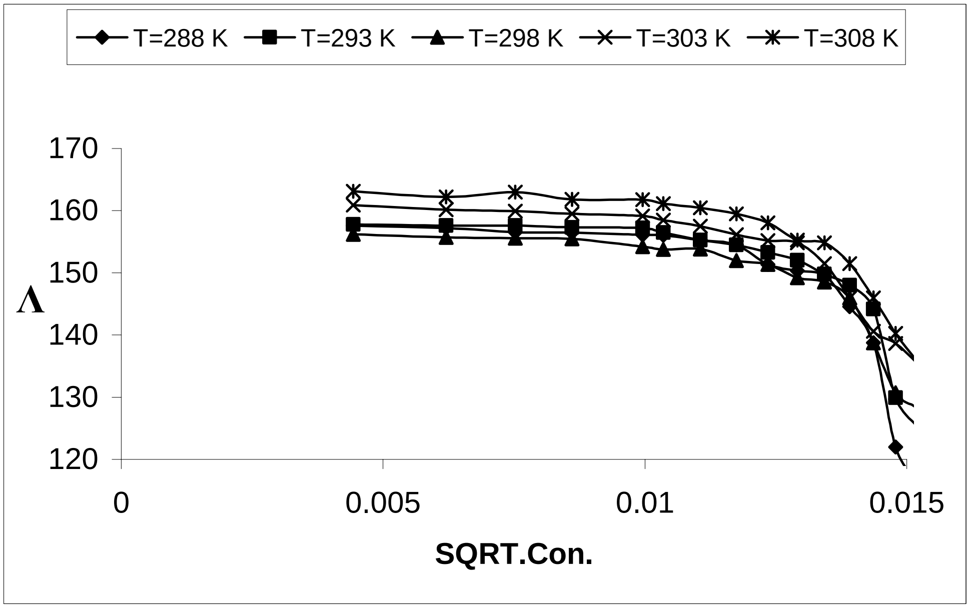


Fig (1-C) :The plot of equivalent conductivities against Square root of concentration for $[Co(phen)(H_2O)_4]Cl_2$ in 80% methanol-water mixtures at different temperatures

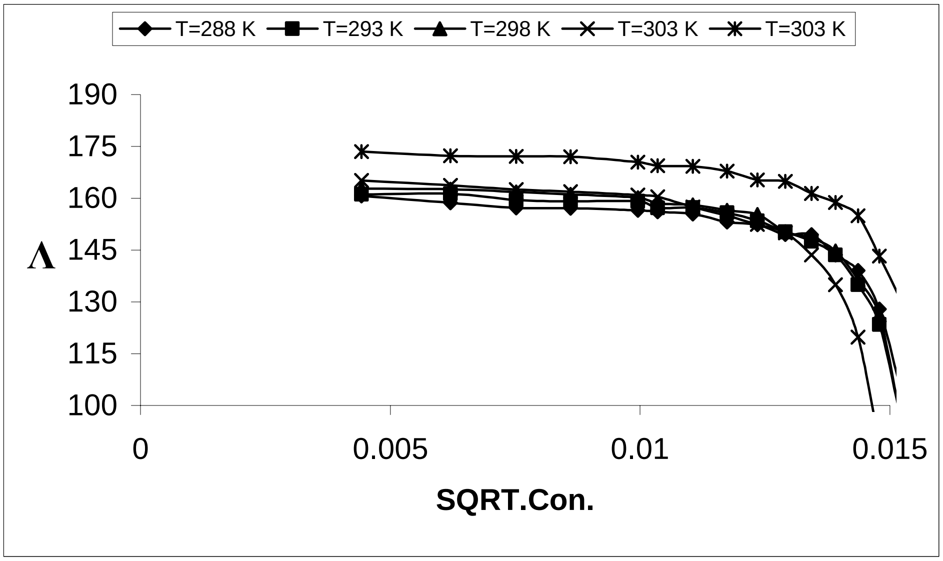


Fig (1-D) :The plot of equivalent conductivities against Square root of concentration for [Co(phen)$(H_2O)_4$]Cl_2 in 70% methanol-water mixtures at different temperatures

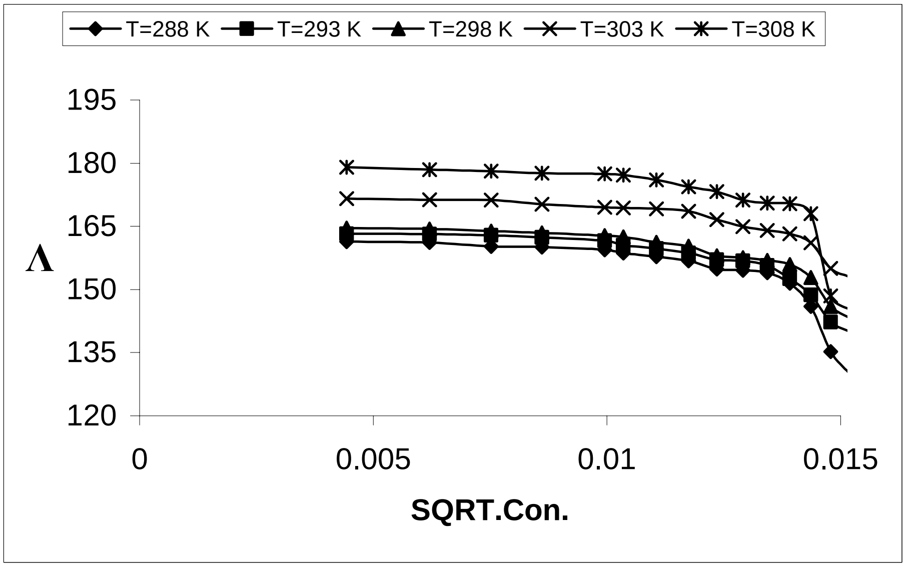


Fig (1-E) :The plot of equivalent conductivities against Square root of concentration for [Co(phen)$(H_2O)_4$]Cl_2 in 50% methanol-water mixtures at different temperatures

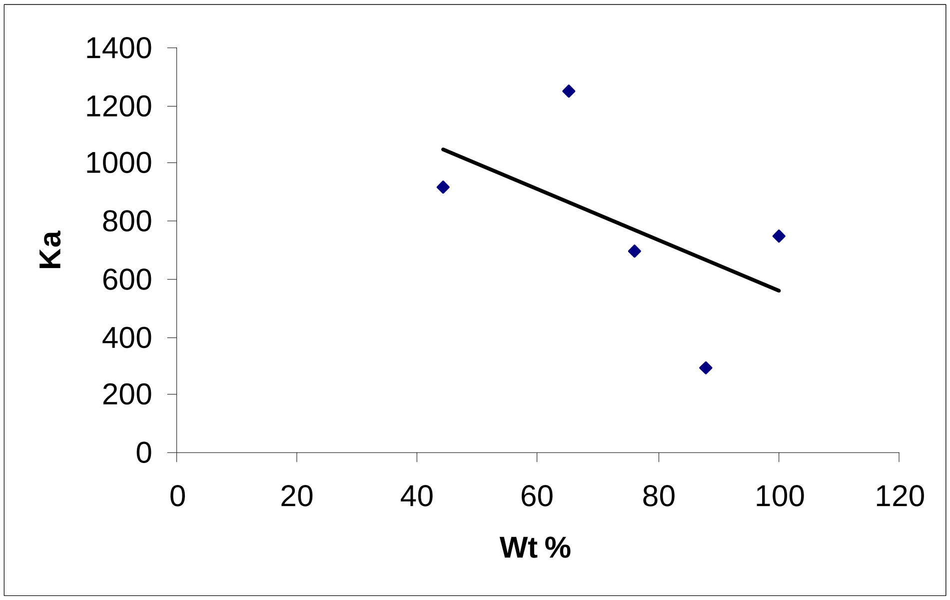


Fig (2) : Plot of K_A versus the composition of solvent mixtures at 298 K

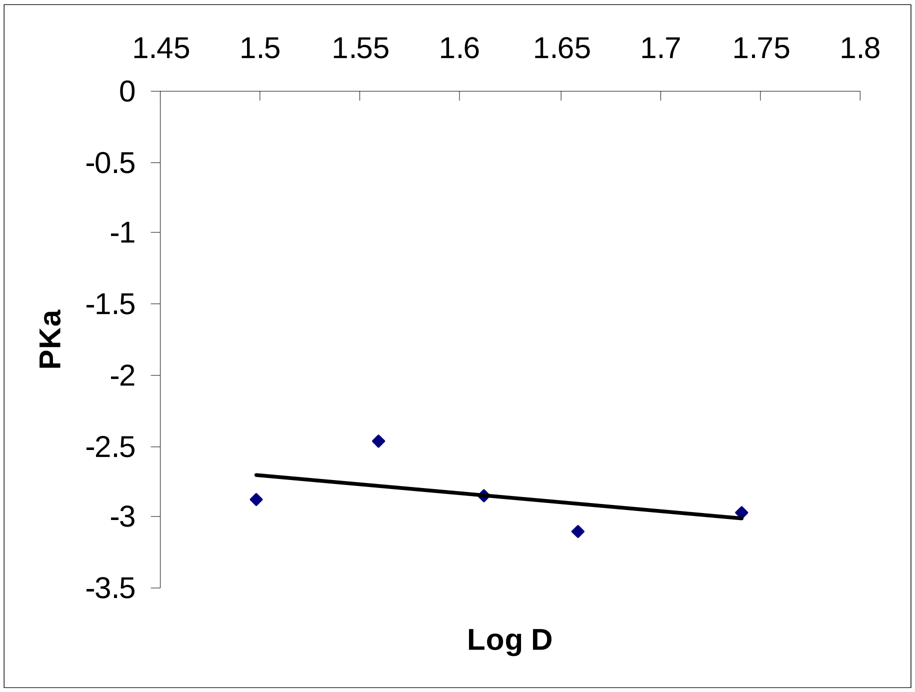


Fig (3) : Variation of PK_A values of the complex in methanol-Water Mixture at 298 k with dielectric constant of the mixtures (Log D)

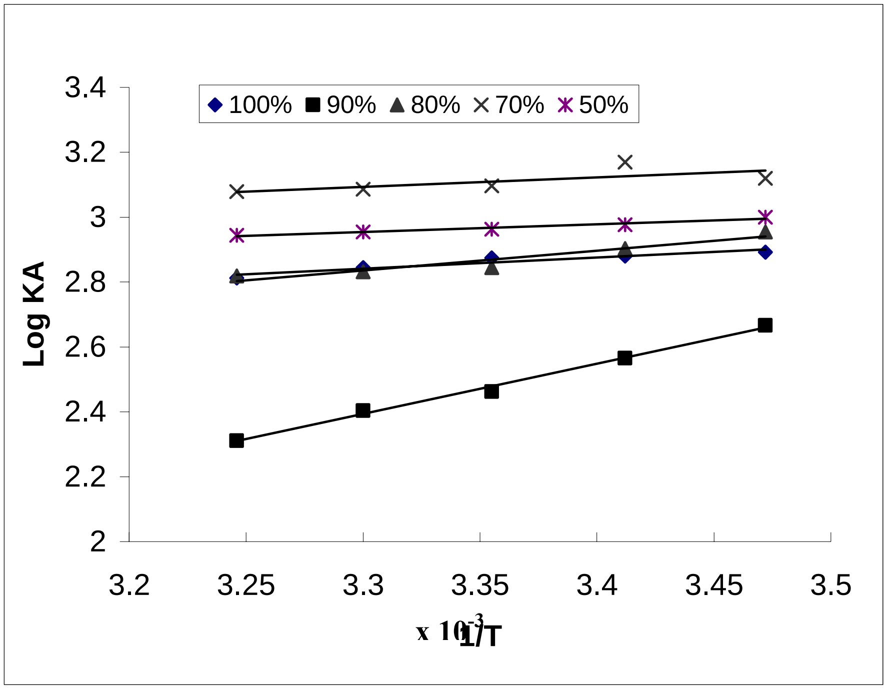


Fig (4): The plot of Log K_A against 1/T for the Complex at different solvent composition

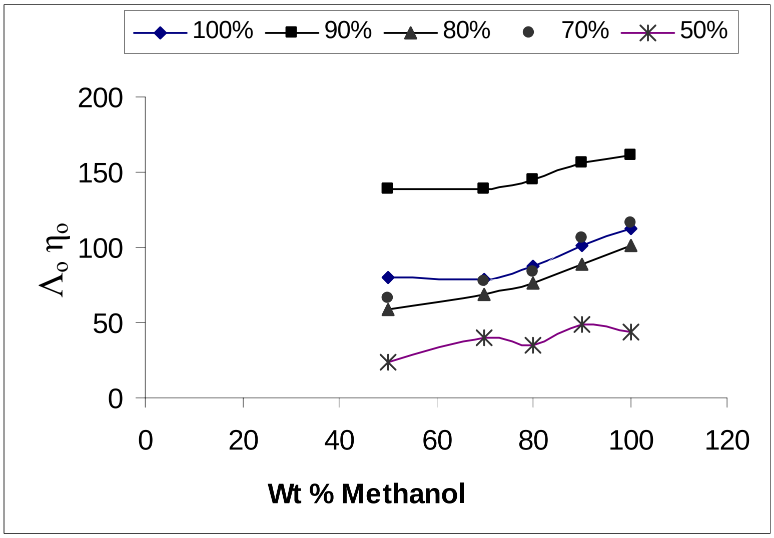


Fig (5) : Walden products (Λ_o η_o) for the complex in methanol-water mixture plotted versus the composition of the mixture at different temperature

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

temp. K	ΔG $KJ.mol^{-1}$	ΔS $KJ.mol^{-1}$	ΔH $KJ.mol^{-1}$
100% methanol			
288.15	-3.721	-16.564	-1.052
293.15	-3.768	-16.442	
298.15	-3.814	-16.320	
303.15	-3.858	-16.716	
308.15	-3.902	-16.235	
90% methanol			
288.15	-3.620	-16.595	-1.162
293.15	-3.661	-16.452	
298.15	-3.702	-16.313	
303.15	-3.753	-16.213	
308.15	-3.766	-15.992	
80% methanol			
288.15	-3.737	-15.009	-0.588
293.15	-3.785	-14.917	
298.15	-3.823	-14.794	
303.15	-3.868	-14.698	
308.15	-3.912	-14.603	
70% methanol			
288.15	-4.039	-16.095	-0.594
293.15	-4.105	-16.046	
298.15	-4.160	-15.961	
303.15	-4.214	-15.893	
308.15	-4.278	-15.820	
50% methanol			
288.15	-3.725	16.220	-0.949
293.15	-3.776	16.118	
298.15	-3.823	16.005	
303.15	-3.863	15.873	
308.15	-3.917	15.791	

References

1. H. Yokoyoma, Y. Koyama, Y. Masuda, ***Chemistry Letters***, 1988, pp. 1453-1456.
2. Shehata H.A., ***J. Chem. Soc.***, 1994, Faraday Transactions, **90(22):** 3401.
3. Kubota E. and Horimoto S., 1999. "Conductivity measurements of alkali metal thiocyanate in water-methanol mixtures". Nippon Kagaku Kaishi, 3: 203-206.
4. Yaser O.H., 2002. "Conductivity measurements of some transition metal complexes in different solvents at different temperatures". Ph.D. Thesis.
5. Tominic I., Tomas R., Visic M. and Soko I.V., ***CROATICA CHEMICA ACTA CCACAA,*** 2004, **77(3)**, 537.
6. Perrin D.D., Armarego W.L.F. and and Perrin D.R., 1966. "Purification of Laboratory Chemicals". 1st ed., Pergamon Press Oxford, p. 199.
7. Jones G. and Bradshow B.C., 1933. "The measurement of conductance of standard potassium chloride solution in absolute units". 55, 1760.
8. Lee W.H. and Wheaton R.J., ***J. Chem. Soc. Faraday Trans. II,*** 1978, **74**, 740.
9. Naema A.H., 2002. "Conductance investigation of ion-pair formation by sodium acetate in methanol water mixture". Vol. **28**, No. 1.
10. Atkines P.W., 1986. "Physical Chemistry". 3rd ed., Oxford University Press.
11. Abdul-Majeed M., Banan A.A. and Yaser O.H., ***Mutah Lil-Buhooth Wa-Al-Dirasat***, 1996, **11(5)**, 119.
12. Laidler K.J., 1965. "Chemical Kinetics". 2nd ed., McGraw-Hill Inc., New York.
13. Hemmes P. ***J. Phy. Chem.***, 1974, **78(9)**, 907.