Temperature dependence of Ion Association of Tetra Aqua (1 , 10 – phenathroline) Nickel (II) Chloride in Ethanol –Water mixture

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Abstract

The ion association constant (K_A) of [Ni(1,10 phenathroline)$(H_2O)_4$] Cl_2 , has been determined by conductivity measurements at 278.15-318.15 K . it is found that the order of magnitude of K_A at any temperature at different percentage of ethanol – water mixture decrease with decreasing ethanol percentage and increasing the temperature .The enthalpy, gibs free energy and entropy increase with increasing ethanol percentage and temperature, this can be attributed to the decrease in the fraction of the contact ion pairs formed by the hydrogen bonding between the polar hydrogen of the complex and solvent atoms . The data were analyzed using Lee – Wheaton equation to calculate: (Λ_o, K_A & R) equivalent conductance Λ_o , association constant K_A and the main distance between ion in solution R .Walden product ($\Lambda_o \eta_o$) have also been calculated for each solvent composition , a relationship was found to exist between the ($\Lambda_o \eta_o$) and 1/D of the medium which indicate the tendency of the association of ions.

Key word: Conductivity , Lee-Wheaton equation ,thermodynamics ,Walden product.

Introduction

The analytical application of complexes of Mn,Ni,Co. ions with 1,10 phenathroline as a ligand which have very wide application in industry and have a biological effects screened against a number of fungi and bacteria to asses their growth inhibiting potential were studied by Lee-Wheaton equation to investigate their behaviour of interaction by conductivity[(1)].

The possible importance of such properties as solubility partition coefficient, surface activity, degree of dissociation , inter atomic distance between functional group , hydrogen bonding , chelation and the spatial configuration of the molecules are worthy of consideration [(2)]

Conductivity measurements over awide temperature range for electrolytesolution can provide detailed information concerning ion – ion and ion –solvent interaction especially from the thermodynamic view point [(3)].

Molar conductivities of NaBr electrolyte in 2-butanol + water mixtures were measured in the temperature range from 5 ^oC to 45 ^oC at 10 ^oC intervals[(5)] , also molar conductivity of HBr in 2-propanol + water mixtures was determined at five temperatures in the region from 288.15 to 308.15 K .Data were processed by the Lee-Wheaton conductivity equation with parameter R and the following quantities were obtained: Limiting molar conductivity (Λ_o), association constant (K_A) and thermodynamic quantities for the ion association reaction [(5)] .

From a conductometric study at temperatures between 278.15 and 318.15 K of [Ni(phen)$(H_2O)_4$]Cl_2, it is clear that the ion association constant (K_A) is smaller at 45 ^oC and increase with decreasing temperature . in the order $K_A > K_A > K_A > K_A > K_A$ 5 ^oC 15 ^oC 25 ^oC 35 ^oC 45 ^oC The remarkable increase in the K_A values with decreasing temperature as well as the relatively small entropy and enthalpy changes were ascribed to the specific short –range interaction, such as hydrogen bonding between the amine hydrogen atoms of the complex and the oxygen atoms of anions in the contact ion pairs. To confirm the validity of the above interpretation and to investigation the dependence of the ion – association behavior on the properties of the complex ions, the association of tetra-aquo (1,10 phenathroline) Nickel (II) chloride in ethanol –water mixture were studied by measuring the conductivities at different percentages and temperatures to know detailed information concerning their thermodynamics and may be used for the understanding of the electrochemical reaction mechanism .

Experimental

Preparation of complex:

In order to prepare the desired complex [(6)], a mixture of 2 mM of 1,10 phenathroline in 10 cm^3 of ethanol and 2 mM of $NiCl_2.6H_2O$ in 30 cm^3 of deionized water was 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 recrystalized by slow cooling to 0 ^oC followed by addition of excess absolute ethanol . the product was dried under vacuum over anhydrous calcium chloride .Ethanolwas purified and dried by the method described by Perrin[(7)] and the procedure repeated twice to ensure that all water was removed. Magnetic electronic spectral, (UV), infrared measurements used for analysis of the complex and also gas chromatography was used to determine the water content and other organic impurities of the purified ethanol as a solvent. Conductivity measurements were made using a (WTW) conductivity meter (Model LBR) with frequency range of 50 Hz -30 KHz and sensitivity between 10^{-1} and 10^{-9} S .

Purification of solvents:

For conductivity measurement in any solvent a especial design is required to ensure complete isolation of the system from outside atmosphere and to maintain the isolation during the addition of solute . Nitrogen gas was passed through lime water, sulphuric acid calcium chloride before interning the cell . The temperature of the cell and its contents was kept constant at certain temperature (± 0.1 ^{o}C) using water circulating ultra thermostat type VHS B radiometer . Purified nitrogen was passed through a known volume of solvent until the conductance of the solvent was constant , addition of solute were then made .

Tools and method:

The design of the conductance cell and the nitrogen line was the same as that previously used by Wheaton [8] . The cell constant for the conductivity cell was measured using the methods of Jones and Bradshow[9] . 0.01 M KCl solution was prepared from KCl (BDH reagent) recrystallized three times from conductivity water and then dried at 760 Torr and 500 ^{o}C for10 hr.The cell constant was checked regularly and found to be 0.0554 cm^{-1}.

A general method has been used for measuring the conductance of electrolytes . The conductivity cell was washed first with conductivity water and then with methanol then dried , weight empty and kept at constant temperature , Purified nitrogen gas was passed for 10-15 min until the conductance of the solvent was constant , whereupon the cell plus the contents were weighed . A certain amount of solution was injected in to the conductivity cell from a plastic syringe (which was weighed before and after each addition) , then nitrogen gas was passed . Small increment of known amount of the complex solution were then added (generally 10 additions) and the conductivity of the solution was measured after each addition . After all additions have been made , the cell was reweighed to find the weight change over the whole run.

It was found that the maximum weight loss in a single run was not more than 0.02 % .

Results and discussion

The electrical conductivity of the desired complex have been studied in ethanol- water mixture at different temperatures to investigate the dependence of the ion association behavior on the properties of the complex ion . The data were treated using LW 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[10].

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

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

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

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

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

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

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

or 1000 $\sigma_{\sigma solu.} = \sum_{i=1}^{S} C_i \lambda_i$

and $\Lambda_{solu.} = \sum_{i=1}^{S} {}_i \; Z_i \; | \; m_i \lambda|_i \,/\, \Sigma\, C_i$

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 ith species respectively . thus for 2:1 associated salts :

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

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[8]

$$\sigma\,\Lambda = \left[\sum_{n=1}^{Np} (\Lambda_{Calc.} - \Lambda_{exper.})^2 / N_p \right]^{1/2}$$

A program (RM_1) 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 [10] .

Table (1) :The equivalent concentration (Ω^{-1} cm^2 $equiv.^{-1}$) and molar conductivity (M) of the complex $[Ni(phen)_2(H_2O)_4]Cl_2$ in ethanol water mixture at 278.15 K .

% 100 EtOH		% 80 EtOH		% 60 EtOH		% 40 EtOH		% 20 EtOH		% 100 H_2O	
M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}
0.8048	22.2933	0.8287	17.7944	0.7940	16.7466	0.8094	21.69404	0.82661	30.9786	0.8241	64.3026
1.6075	21.3036	1.6375	17.6687	1.5763	16.6000	1.6288	20.3245	1.6454	29.9195	1.16345	61.2930
2.3987	20.5858	2.4545	17.6121	2.3496	16.4236	2.4393	19.2736	2.4444	29.8484	2.4487	61.1856
3.1823	19.8877	3.2697	17.2066	3.1138	16.1612	3.2260	18.8856	3.2553	29.8236	3.2519	60.1836
4.5754	19.3044	4.7073	17.1906	4.4658	16.2299	4.6335	18.4324	4.6523	29.7734	4.6606	59.1115
5.9348	18.6332	6.1207	17.1066	5.7903	16.1460	6.0115	18.1407	6.0343	29.7382	6.0334	58.9974
7.2768	18.2552	7.5090	17.1388	7.0887	16.1276	7.3682	18.0475	7.3901	29.4301	7.3866	58.9615
8.5932	17.8544	8.8766	17.0625	8.3614	16.0597	8.6984	18.4860	8.7225	29.2756	8.7166	58.8688
9.8851	17.6879	10.2029	16.7716	9.6110	15.9416	10.0079	18.2631	10.0369	29.0472	16.0240	58.4678
11.1532	17.3980	11.5274	16.4487	10.8467	15.4949	11.2889	17.9159	11.3236	29.0104	11.3045	58.4352

Table (2) : The equivalent conductivity (Ω^{-1} cm^2 $equiv.^{-1}$) and molar concentration (M) of the complex $[Ni(phen)_2(H_2O)_4]Cl_2$ in ethanol water mixture at 288.15 K .

% 100 EtOH		% 80 EtOH		% 60 EtOH		% 40 EtOH		% 20 EtOH		% 100 H_2O	
M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}
0.8059	27.1337	0.8053	24.6257	0.7852	28.8202	0.8261	28.1338	0.8205	43.3562	0.8348	78.3562
1.60276	26.9968	1.6047	24.6308	1.5753	28.7682	1.6574	27.7828	1.6328	43.3182	1.6510	77.9322
2.3879	26.5434	2.4031	24.4537	2.3660	28.1254	2.4735	27.7451	2.4293	42.9159	2.4622	77.2928
3.1625	25.7759	3.1857	24.4684	3.1516	27.6519	3.2951	27.7236	3.2307	42.3146	3.2663	76.2135
4.5492	25.4949	4.5586	24.3334	4.5355	26.9394	4.7277	27.6862	4.6466	42.3369	4.6997	76.3788
5.9117	25.2657	5.9067	24.2500	5.9002	26.8851	6.1456	27.4814	6.0184	42.2948	6.1041	75.9070
7.2878	24.4838	7.2324	24.1788	7.2599	26.7547	7.5211	27.4513	7.3760	42.0995	7.4818	75.7690
8.5623	23.6333	8.5298	23.8736	8.6074	26.7086	8.8725	27.1073	8.7128	41.9945	8.8272	75.7612
9.8515	23.3577	9.8147	23.7852	9.9286	26.2511	10.2032	26.8899	10.0210	41.7692	10.1531	75.5593
11.1115	23.0238	11.0727	24.0988	11.2456	25.5598	11.4994	26.7614	11.3132	40.8526	11.4440	72.1483

Table (3) : The equivalent conductivity (Ω^{-1} cm^2 $equiv.^{-1}$) and molar concentration (M) of the complex $[Ni(phen)_2(H_2O)_4]Cl_2$ in ethanol water mixture at 298.15 K.

% 100 EtOH		% 80 EtOH		% 60 EtOH		% 40 EtOH		% 20 EtOH		% 100 H_2O	
M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}
0.8432	28.7021	0.8609	23.9019	0.8171	26.7510	0.8164	30.4032	0.81157	42.6766	0.8771	69.0102
1.6718	26.1254	1.7135	23.6202	1.6325	26.2898	1.6354	29.4363	1.6206	42.3946	1.6064	68.0010
2.4796	24.9129	2.5876	23.3762	2.4446	26.0585	2.4394	28.6625	2.4051	41.8461	2.3973	67.6279
3.2809	24.5848	3.3953	23.2147	3.2509	25.8755	3.2508	28.1205	3.1915	41.6232	3.1847	67.2756
4.7088	23.4700	4.8886	22.9911	4.6834	25.6931	4.7216	27.4633	4.6152	41.1792	4.6149	67.0398
6.1226	22.8553	6.3484	22.8223	6.0889	25.5752	6.1692	26.9100	6.0135	40.2989	6.0301	66.9998
7.5221	22.6341	7.7821	22.7116	7.4656	25.4754	7.5871	26.6003	7.3912	40.0195	7.4114	66.8462
8.8896	22.2563	9.1906	22.6412	8.8212	25.3916	8.9929	26.4238	8.7406	39.9167	8.7764	66.7571
10.2372	21.0336	10.5709	22.6116	10.1489	25.2774	10.3447	26.2535	10.0671	39.6452	10.1148	66.6676
11.5580	21.0316	11.9272	22.6028	11.4548	25.2325	11.6959	26.1692	11.3794	39.5489	11.4256	66.6089

Table (4) : The equivalent conductivity (Ω^{-1} cm ^{2} equiv.$^{-1}$) and molar concentration (M) of the complex $[Ni(phen)_2(H_2O)_4]Cl_2$ in ethanol water mixture at 308.15 K .

% 100 EtOH		% 80 EtOH		% 60 EtOH		% 40 EtOH		% 20 EtOH		% 100 H_2O	
M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}
0.7161	32.8437	0.8302	28.3157	0.8003	32.3783	.7868	55.5315	0.7927	77.8752	0.8229	95.5362
1.4238	32.6294	1.6416	28.0458	1.5883	30.3785	1.5716	55.7222	1.5724	77.5964	1.6343	95.1075
2.1423	32.2050	2.4524	280761	2.3825	30.1958	2.3420	55.3683	2.3426	77.4087	2.4330	94.5676
2.8512	31.4178	3.2690	27.7004	3.1592	30.1509	3.1029	54.8426	3.1144	75.6603	3.1682	92.9913
4.1176	30.5381	4.7060	27.7547	4.5486	30.0745	4.4693	54.2214	4.4771	75.3004	4.6286	88.6432
5.3626	29.7562	6.1279	27.8067	5.9104	30.0324	5.8157	53.9009	5.8231	74.9852	6.0553	85.0402
6.5982	28.5019	7.5224	26.7940	7.2467	29.9383	7.1399	53.8684	7.1440	74.7961	7.4225	83.0579
7.8086	27.6486	8.8865	26.8760	8.5766	29.7253	8.4464	53.1493	8.4442	73.9956	8.7790	82.5841
8.9951	27.1545	10.2300	26.2289	9.8682	29.2176	9.7272	53.1436	9.7210	72.6261	10.1136	81.8163
10.1665	26.1603	11.5480	25.9818	11.1416	28.8746	10.9842	53.1372	10.9769	72.0784	11.4500	81.5451

Table (5) : The equivalent conductivity (Ω^{-1} cm ^{2} equiv.$^{-1}$) and molar concentration (M) of the complex $[Ni(phen)_2(H_2O)_4]Cl_2$ in ethanol water mixture at 318.15 K .

% 100 EtOH		% 80 EtOH		% 60 EtOH		% 40 EtOH		% 20 EtOH		% 100 H_2O	
M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}	M x 10^4	Λ_{equiv}
0.7928	44.5628	0.8016	51.7579	0.8086	59.5762	0.8441	66.1641	0.7910	94.7032	0.8152	138.3976
1.8810	44.5173	1.6009	51.3524	1.6091	58.9413	1.6757	65.9296	1.5853	93.7528	1.6493	138.1900
2.3592	43.1171	2.3972	51.1873	2.4018	58.6928	2.5022	65.9231	2.3718	92.8848	2.4466	137.6300
3.1164	41.7584	3.1685	50.3779	3.1846	58.3297	3.3044	65.2920	3.1492	92.6208	3.2301	136.8549
4.4836	40.0302	4.5475	49.6139	4.5691	57.6787	4.7429	64.9576	4.5333	91.9176	4.6380	136.1732
5.8308	38.3228	5.9015	49.2632	5.9286	56.8861	6.1553	64.9833	5.8997	90.9275	6.0161	135.7166
7.1429	37.4284	7.0923	49.0512	7.2667	56.8130	7.5424	63.4214	7.2786	90.7999	7.3741	135.0475
8.4307	37.6361	8.4028	48.1062	8.5905	56.6195	8.9008	64.4041	8.5318	90.0813	8.7037	135.0291
9.6969	36.4641	9.6960	47.9303	9.8748	56.3509	10.2342	63.3192	9.8186	89.8096	10.0106	134.6855
10.9339	35.9010	10.9706	47.1798	11.1406	56.2346	11.5444	63.2116	11.0871	88.8083	11.2937	130.9724

Tables (1-5) show the conductivity - concentration data for the studied complex in different percentage at different temperatures . The plots of $\Lambda_{equiv.}$ Against the square root of the molar concentration ($C^{1/2}$) are shown in figures (1 A-B) as an example . From tables and figure. It can be seen generally that the equivalent conductivity increase with increasing the temperature and increasing the percentage of water because of increasing the dielectric constant as water percentage increase except for 80% EtOH were the equivalent conductivity decrease because of formation of ion-solvent bonds between the complex ion and ethanol from one side and between the complex ion water from the other side (hydrogen bonding) , the electrostatic power of attraction between two ions F (r) is equal to $e^2Z^+Z^- / Dr^2$, where Z^+ Z^- are the charges of the ions apart from each other in a distance equal to (r) , e : equal to 1.206 x 10^{-18} coulomb , D is the dielectric constant of the solvent where the value of F(r) is the smallest if D is large [11] .

The ionic atmosphere has another effect on the motion of the ions since moving ion experience a viscous drag , when the ionic atmosphere is present this drag is enhanced because the ionic atmosphere moves in an apposite direction to the central ion , The enhanced viscous drag , which is called theelectrophoretic effect reduces the mobilities of the ions and hence also reduces their conductivities which leads to decreasing equivalent conductance [12].

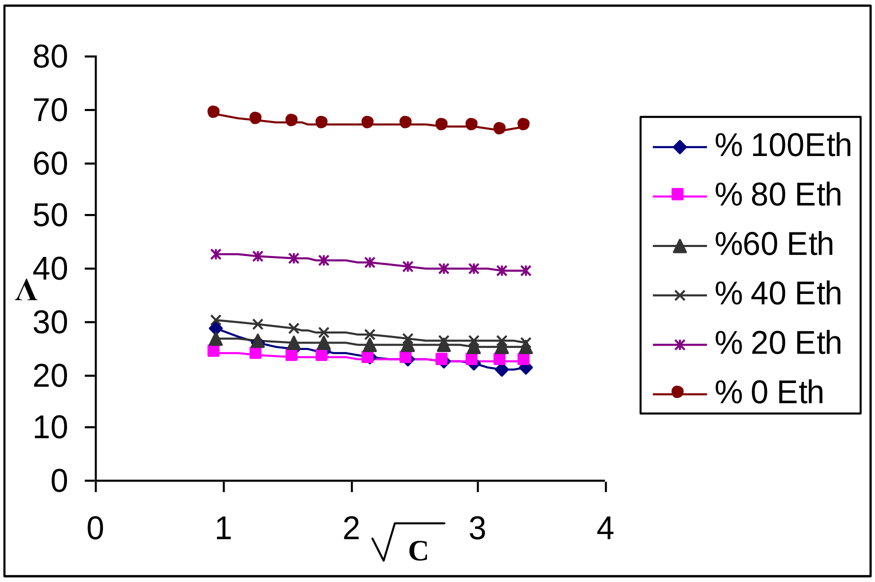

Fig (1): The plot of equivalent conductivity against the square root of molar concentration for [Ni (1,10 – phenathroline)(H_2O)$_4$]Cl_2 ethanol ethanol water mixture at 298.15 K

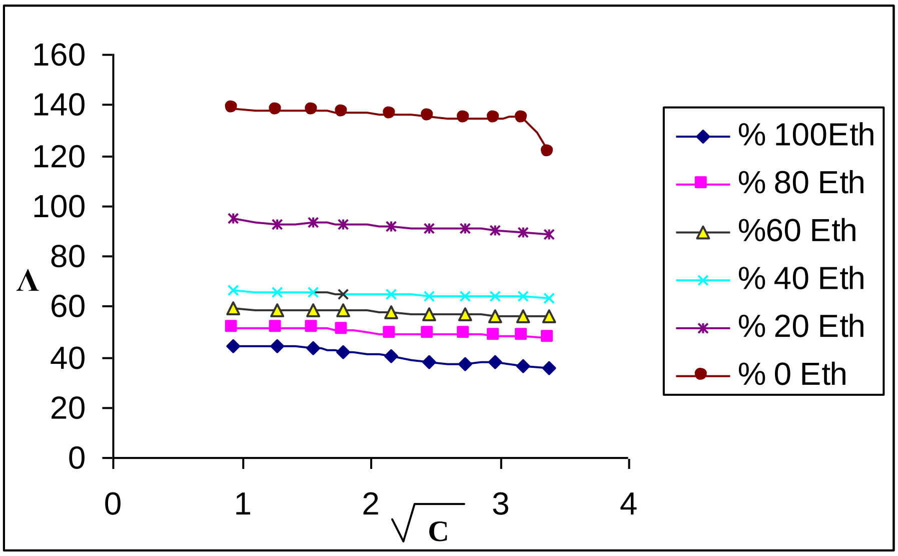

Fig (2): The plot of equivalent conductivity against the square root of molar concentration for [Ni (1,10 – phenathroline)(H_2O)$_4$]Cl_2 in ethanol ethanol water mixture at 318.15 K

Table (6) show the analysis of data by using Lee-Wheaton equation for unsymmetrical electrolyte which indicates that he values of K_A decrease with increasing temperature . This may be attributed to the short range interaction and the hydrogen bonding formed at low temperature . The results of the distances parameter R show that the complex electrolytes form solvent separated generally (49-53.3) which means that the cation is separated by a large numbers of solvent molecules from the anion .

The value of λ_M+2 (the ionic equivalent conductance) increase as water percentage increase and increasing temperature, this also because of broking the hydrogen bond as temperature increase and of increasing dielectric constant of the mixed solvent. And finally the value of λ_{MX}+1 is very small since it is a large ion and convert easily to the product MX_2.

The small values of σ (Λ) give an indication of the good best fit values of less than (0.1).

Table (6): The result of analysis of [Ni(phen)$(H_2O)_4$] Cl_2 at different percentages and temperatures .

EtOH %		278.16 K	288.16 K	298.16 K	308.16 K	318.16 K
100	K_A	1 x 10^8	1 x 10^5	60 x 10^3	1 x 10^4	2000
80		3.5 x 10^7	15 x 10^4	10 x 10^3	1100	70
60		20 x 10^6	1 x 10^4	8 x 10^3	290	10
40		20 x 10^5	6 x 10^3	2000	100	5
20		20 x 10^3	2400	200	50	7
0		1800	700	50	20	5
100	**R A°**	51	50.5	50	49.4	49
80		52	51.8	51.4	51.2	51.1
60		52.5	51.9	51.7	51.4	51.2
40		52.6	52.3	52.1	51.9	51.3
20		52.8	52.5	51.1	52.0	51.9
0		53.3	53.0	52.8	52.5	52.2
100	**σ Λ**	0.084	0.011	0.080	0.079	0.0122
80		0.86	0.027	0.089	0.014	0.059
60		0.068	0.088	0.085	0.048	0.024
40		0.085	0.094	0.062	0.041	0.042
20		0.04	0.087	0.011	0.052	0.034
0		0.012	0.012	0.064	0.061	0.01
100	$\lambda_{M}^{٢+}$	0.1	0.4	0.6	0.8	1
80		0.2	0.9	1	2	3
60		1	2	4	5	9
40		4	6	8	10	18
20		8	16	20	25	45
0		10	26	46	74	91
100	λ_{MX}^{+}	0.001	0.0015	0.0025	0.004	0.006
80		0.01	0.018	0.028	0.03	0.05
60		0.015	0.02	0.03	0.04	0.075
40		0.02	0.025	0.037	0.07	0.088
20		0.03	0.035	0.047	0.085	0.100
0		0.04	0.05	0.06	0.097	0.25

The plot of ln K_A against (1/T) (Arrhenius equation) (ln K_A= $-\Delta H^o$/ RT+C)is shown in figure (3) for the complex in different percentage of ethanol – water mixture which are linear .

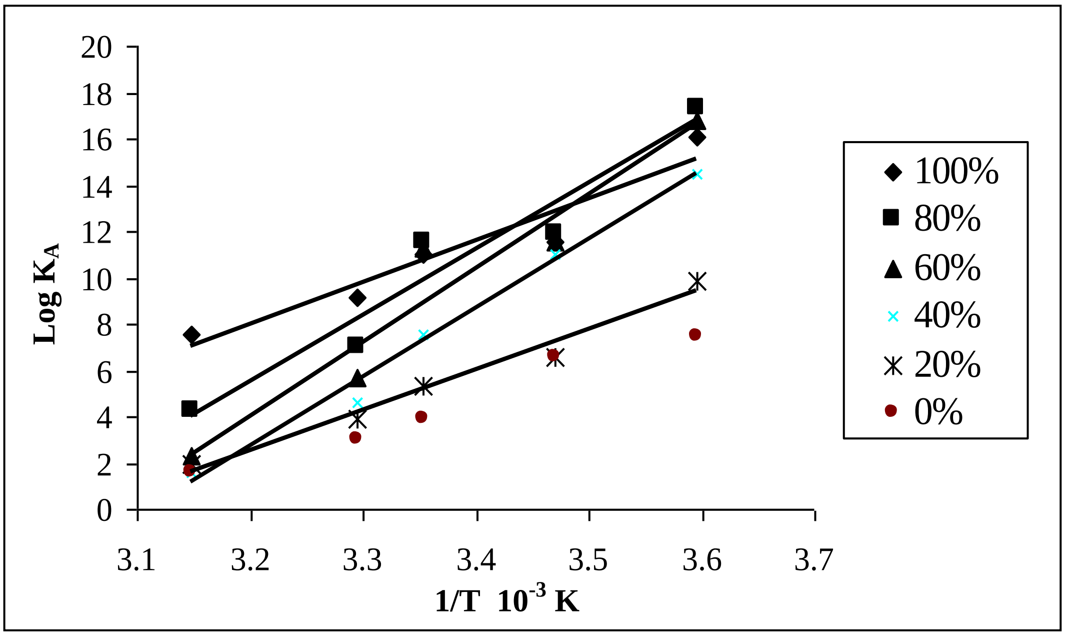

Fig (3) :The plot of Ln K_A against (1/T) for $[Ni(phen)(H_2O)_4]Cl_2$ in ethanol water mixture at different temperatures.

Thermodynamic parameters ΔH^o , ΔG^o , ΔS^o , are determined from the following :
ΔG^o and ΔH^o are determined from values of K_A(ΔG^o=-RT Ln K_A) and temperature, ΔS^o is calculated from these two parameters (ΔG^o= ΔH^o-T ΔS^o)Which are given in table (7) . It is well known that addition of an electrolyte to a solvent causes some structure change due to the rupture of the bonds between the solvent molecules from one side and to the interaction of ions with each other and with the solvent molecules from the other side [12] . 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 decrease in the entropy as temperature increase and decrease with increasing water percentage [13].
The enthalpy of activation according to the activated complex theory [14] is a result of the energies being expended for the destruction of the solvent-solvent bonds and the formation of solvent – ion bonds . As can be noticed from Table (7) , ΔH^o increase with increasing water percentage until %60 and then decrease as water percentage increase due to the broken of ion – ion bond in solution because of increasing the dielectric constant of the solvent [15]. Finally , the values of ΔG^o are negative according to the relation (ΔG^o=-RT Ln K_A)which indicate the reaction is spontaneous .

Table (7): - ΔG^o KJmole^{-1} of ion association in ethanol – wate mixture at different temperatures.

Temp.Ln K	%100 EtOH	%80 EtOH	%60 EtOH	%40 EtOH	%20 EtOH	%0 EtOH
278.16	8.966	9.662	9.315	8.066	5.509	4.169
288.16	6.634	6.868	6.634	6.340	3.775	3.774
298.16	6.560	6.864	6.736	4.531	3.159	2.332
308.16	5.620	4.315	3.493	2.838	2.410	1.845
318.16	4.835	2.703	1.464	1.023	1.237	1.023
- ΔS^o JK $^{-1}$ mole $^{-1}$						
278.16	28.428	38.162	43.896	37.351	22.351	16.727
288.16	24.815	35.380	41.179	35.625	20.617	16.332
298.16	24.711	35.364	41.281	33.816	20.001	14.890
308.16	23.801	32.815	38.038	32.123	19.252	14.403
318.16	23.016	31.203	36.009	30.300	18.079	13.581
- ΔH^o KJ mole $^{-1}$						
	18.181	28.500	34.545	29.285	16.842	12.559

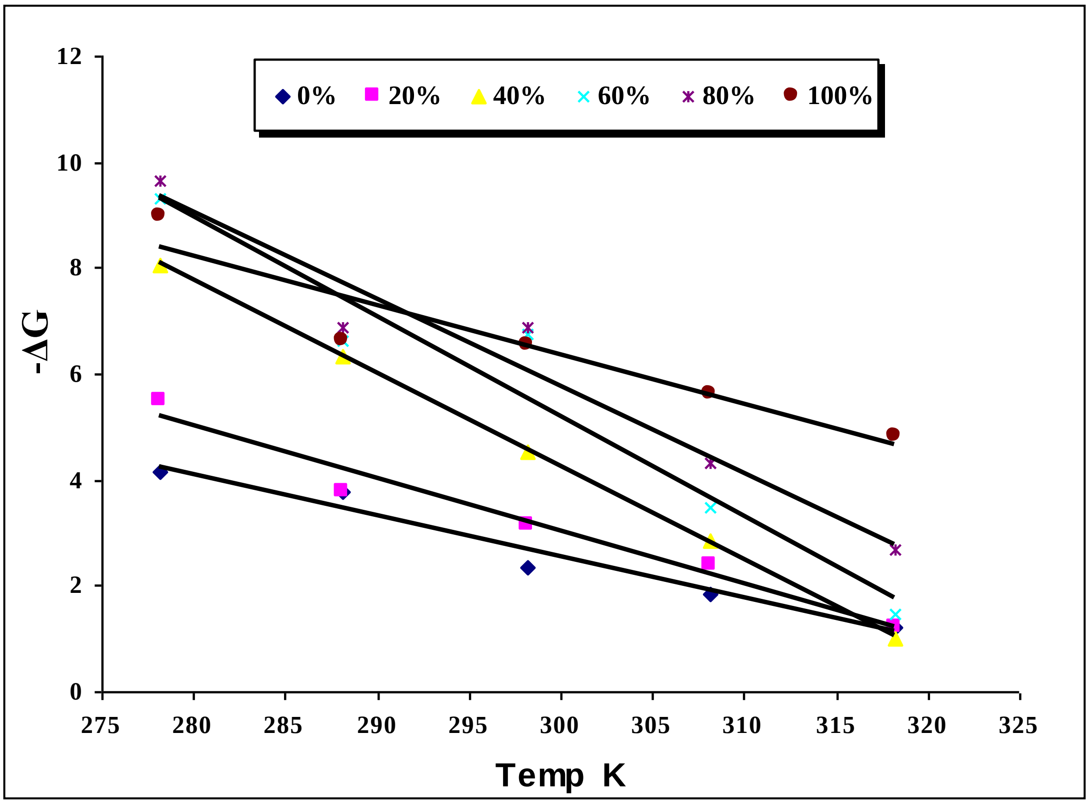

Fig (4) Temperature dependence of ΔG of $[Ni(phen)(H_2O)_4]$ Cl_2in ethanol-water mixture at different temperatures.

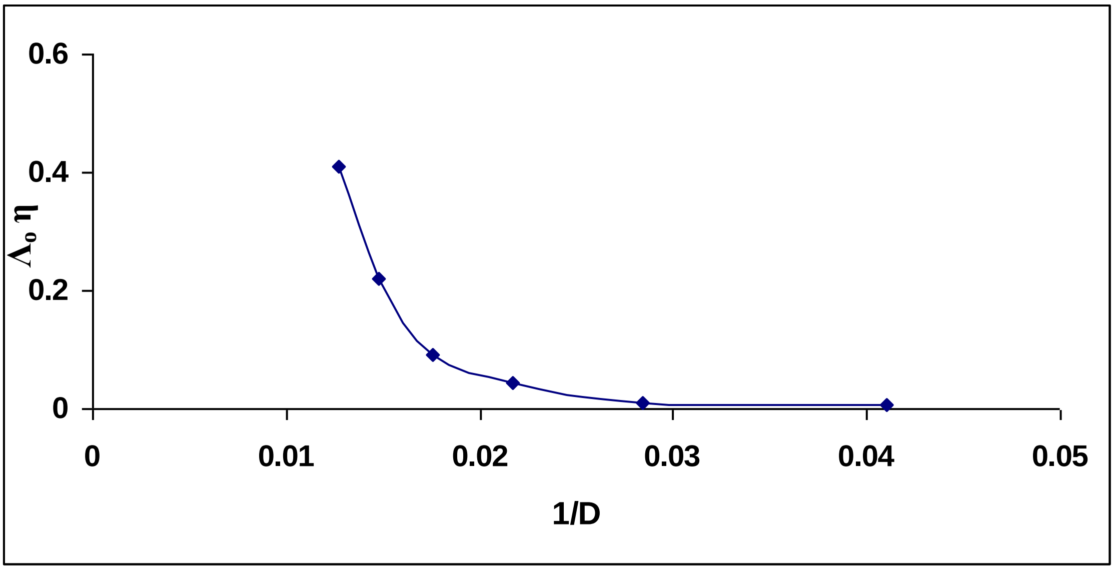

Fig (5): Variation of Walden product with the reciprocal of electric constant of $[Ni(phen)(H_2O)_4]Cl_2$ in ethanol water mixture at 298.15 K

Fig (4) show that the values of –ΔG for the complex gradually decrease with increasing temperature .This is attributed to the fact that the contribution of directional interactions around the nitrogen to ion association is Larger. The directional interactions of $[Ni(phen)(H_2O)_4]$ with Cl^- are more distributed by its rotational motion strengthened with increasing temperature [(16)]. The variation of Walden product (Λ_o η_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 . This is the case in the behavior of the present system as indicate in fig.(4) where the cations are expected to suffer various degree of solvation with increasing amount of ethanol in ethanol – water mixtures [(17)] .

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تأثير درجة الحرارة على ثابت التجمع الايوني للمعقد $[Ni(phen)_2(H_2O)_4]Cl_2$ في مذيب الايثانول والماء بنسب مختلفة

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الملخص

تم قياس ثابت التجمع الايوني للمعقد $[Ni(phen)_2(H_2O)_4]Cl_2$ في مدى لدرجات لحرارة (278.15-318.15 K) بواسطة تقنية التوصيلية وبتطبيق معادلة لي– ويتون لتحديد قيمة ثابت التجمع الايوني (K_A) في كل درجة حرارة ولكل نسبة من مذيب الايثانول والماء ووجد بان قيمة (K_A) تقل كلما قلت نسبة الايثانول وزادت درجة الحرارة ووجد كذلك بان قيمة حرارة التفاعل (ΔH) والطاقة الحرة (ΔG) والعشوائية (ΔS) تزداد بزيادة نسبة الايثانول ودرجة الحرارة ويعود السبب في ذلك الى قلة الناتج الجزيئي لتداخل الايونات المتكون نتيجة الاصرة الهيدروجينية بين المعقد وجزيئة المذيب وحسبت كذلك الدوال التالية (Λ_o , K_A & R) ، Λ_o: التوصيل المكافئ و K_A:ثابت التجمع الايوني ، R: معدل المسافة بين الايونات في المحلول ، فضلا عن حساب ناتج والدن لكل نسبة من المذيب وتم رسم العلاقة بين ($\Lambda_o \eta_o$) التوصيل المكافئ مضروب في اللزوجة ضد مقلوب ثابت العزل والتي تبين ميل الايونات للاتحاد في المحلول.