Study of Conductance of the Ionic Association Phenomena of $[Ni(phen)_3]Cl_2$ in Different Solvents and Different Temperatures

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Abstract:

Conductance measurements of $[Ni(phen)_3]Cl_2$ in water, methanol and ethanol at (280.16-318.16K) are reported. Limiting equivalent conductance ($\Lambda_\circ$), association constant (K_A) and distance of closest approach of ions (R) are calculated. The experimental data were analyzed by means of Lee-Wheaton conductivity equation that gives detailed information on ion-ion and ion-solvent interaction and also to obtain thermodynamic information of ion association and examining the nature of the interaction.

Keywords: Electric Conductivity Lee-Wheaton equation, thermodynamic parameters

Introduction:

Many problems concerning ionic solvation have been attracting the attention of chemists in various fields [1]. The ion solvent interaction of $[Ni(en)_3]^{+2}$ complexes depending on the ion association behavior on the properties of the complex ion were studied in methanol at temperatures between (278.16-318.16K) [2]. The interaction between solvent and ions of $CoSO_4$ and $NiSO_4$ with (10, 20 and 30 wt.%) glycerol-glycol and isopropanol-water mixture at different temperatures (30-45°C) had been studied [3]. The temperature effect on the conductance of some alkali halides in n-propanol was studied [4]. and the results were discussed in terms of contact and solvent separated ion pair. After noticing an interest in the ionic association between divalent metal cation and 1,10-phenanthroline, we have made a complete study on $[Ni(phen)_3]Cl_2$in water, methanol and ethanol at different temperatures (280.16-318.16K). In the present work the conductance data were treated using Lee-Wheaton 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 [5].

Experimental:

Preparation of the complex:

In order to prepare the desired complex, a mixture of 6mM of 1,10-phenanthroline in $30cm^3$ of ethanol and 2mM $NiCl_2.6H_2O$ in $10cm^3$ of water was refluxed for about 45 min. on a water bath, then cooling and adding the excess of absolute ethanol. A colored precipitate was sucitioned, filtered and washed with ice cold 50% ethanol. The crud product was dissolved in a minimum quantity of hot 50% ethanol and recrystalised by slow cooling to 0°C followed by addition of excess absolute ethanol. The product was dried under vacuum over anhydrous calcium chloride [6]. The composition of the complex was determined by using Shimadzu (U.V. Vis. Recording U.V. 160) spectrophotometer and IR spectra by using a Perkin Elmer 580 B infrared spectrophotometer ($200\text{-}4000cm^{-1}$). The magnetic susceptibility was measured applying (Faraday Method). The instrument used is of type BRUKER B.M.6.

Conductivity measurement:

Ethanol and methanol were purified and dried by the method described by Perrin (Perrin et al., 1966) and the procedure was repeated twice to ensure that all water was removed.

For conductivity measurements in non-aqueous and aqueous solvents which are highly sensitive to atmospheric pressure and carbon dioxide a special 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 and calcium chloride before entering the cell. The temperature of the cell and its contents was kept constant at certain temperature using a water-thermostat type HAAKE NK 22. Purified nitrogen gas was passed through a known volume of solvent until the conductance of the solvent was constant. Addition of solute was then made.

The design of the conductance cell and the nitrogen line was the same as that previously used by Wheaton [8].

The cell constant of the conductivity cell was measured using the method of Jones and Bradshuw [9]. 0.01M KCl solution was prepared from KCl (BDH reagent) recrystalised three times from conductivity water and then dried at 700 torr and 500°C for 10 hrs. The cell constant was checked regularly and found to be $0.05564cm^{-1}$.

General procedure:

A general method has been used for measuring the conductance of electrolytes. The conductivity cell was washed first with the solvent used and then dried, weighed empty and kept at constant temperature. Purified nitrogen gas was passed through the cell; 100 ml of purified solvent was added and nitrogen gas was passed for further 10-15min. whereupon the cell plus the contents were weighed. A certain amount of the complex solution was injected in to the cell from a plastic syringe (which was weighed before and after each addition), nitrogen gas was passed for several minutes and the conductivity fo the solution was measured. After all the addition have been made (generally 15 addition) 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:

To investigate the dependence of the ion association behavior on the properties of the complex ion we have studied the ion association of $[Ni(phen)_3]^{+2}$ complex ion with mono-valent anion (Cl^-) by measuring the conductivities of $[Ni(phen)_3]Cl_2$ in water, methanol and ethanol at temperatures between (280.16-318.16K). The input data to computer program (RM_1) by using LW equation for asymmetrical electrolytes which was used to analyse the concentration conductivity measurements are (T, D and η) where T is the temperature in Kelvin, D and η are the dielectric constant and the viscosity of the solvent at that temperature [10], [11].

Tables (1,2, and 3) shows the conductivity-concentration data for the studied complex in the three solvents at different temperatures. The plot of $\Lambda_{equiv.}$ Against the square root of the molar concentration ($C^{1/2}$) at different temperatures were shows in Figures (1, 2 and 3).

Table (1): The equivalent conductivity (Ω^{-1} cm^2 $equiv.^{-1}$) and molar concentrations (M) of the complex $[Ni(phen)_3]Cl_2$ in deionized water at different temperatures.

280.16K		288.16K		298.16K		308.16K		318.16K	
M x 10^4	$\Lambda_{eqyiv.}$	M x 10^4	$\Lambda_{eqyiv.}$	M x 10^4	$\Lambda_{eqyiv.}$	M x 10^4	$\Lambda_{eqyiv.}$	M x 10^4	$\Lambda_{eqyiv.}$
0.78842	68.22017	0.79630	77.82651	0.73426	92.19710	0.78289	118.31890	0.78319	142.29230
1.56265	67.66524	1.57738	76.37736	1.54197	90.85986	1.56311	118.29580	1.55823	141.01916
2.33518	66.82362	2.35209	76.17636	2.30113	88.91951	2.33051	117.11730	2.33069	140.89600
3.09925	66.76147	3.11520	76.13572	3.06421	88.49512	3.09156	115.16410	3.09405	139.29758
4.55724	66.39438	4.57846	76.09948	3.81038	88.30590	4.55077	114.67320	4.55840	138.35546
5.99186	66.18849	6.00879	76.03902	5.23519	87.28456	5.98044	114.62156	5.99486	137.68770
7.39554	66.14871	7.41534	75.89645	6.63045	86.64529	7.38520	113.82780	7.39839	137.59330
8.77206	65.96622	8.78877	75.81953	7.99996	86.25976	8.76772	113.58460	8.77173	136.60820
10.1157	65.92934	10.13737	75.55767	9.34636	85.13802	10.11442	113.42250	10.12575	136.46520
11.44056	65.83015	11.46512	75.14301	10.67046	84.99565	11.44385	113.38760	11.45812	136.06340
12.74320	65.65588	12.77392	75.11496	11.96958	84.44076	12.74767	113.19870	12.76262	136.00916
14.01430	65.31030	14.05642	74.67397	13.24658	84.43510	14.02423	113.13040	14.04051	135.82550
15.25743	65.27785	15.31174	74.56603	14.49797	84.33209	15.27913	113.13010	15.29403	135.77787
16.48288	65.26222	16.54806	74.54864	15.73103	84.10004	16.51585	112.63440	16.52866	135.33010
17.69063	65.16988	17.75807	74.41413	16.93712	84.05599	17.72660	112.46710	17.74170	134.96270

Table (2): The equivalent conductivity (Ω^{-1} cm^2 $equiv.^{-1}$) and molar concentrations (M) of the complex $[Ni(phen)_3]Cl_2$ in methanol at different temperatures.

280.16K		288.16K		298.16K		308.16K		318.16K	
M x 10^4	$\Lambda_{equiv.}$	M x 10^4	$\Lambda_{equiv.}$	M x 10^4	$\Lambda_{equiv.}$	M x 10^4	$\Lambda_{equiv.}$	M x 10^4	$\Lambda_{equiv.}$
0.77086	70.88529	0.78334	78.30411	0.75730	90.66321	0.78921	97.88345	0.75759	113.13850
1.53857	70.15669	1.56047	77.64639	1.50707	90.78451	1.54789	97.63205	1.50794	110.71230
2.29233	69.53996	2.32966	77.08315	2.25201	87.31358	2.30634	94.74982	2.25471	107.85156
3.04216	68.50313	3.09059	75.20760	2.98966	85.31175	3.03999	89.54578	2.97415	101.87340
4.47678	64.40418	4.55196	71.23213	4.41097	82.73508	4.46598	89.80852	4.39327	98.72864
5.88353	63.26664	5.98781	69.94724	5.80280	79.67055	5.84999	89.60881	5.79515	97.88824
7.26911	62.68877	7.39698	69.03303	7.17343	78.02156	7.21692	85.51929	7.16321	94.33967
8.62134	60.92341	8.77494	68.02074	8.51223	75.88190	8.53290	83.08927	8.51058	92.47961
9.94878	59.78534	10.13477	66.83458	9.82895	75.39930	9.87056	81.41164	9.83123	90.80968
11.24719	59.06735	11.46787	65.36035	11.12262	72.83018	11.16205	80.21705	11.13200	89.19483
12.53282	58.55756	12.77815	64.99944	12.39344	70.97406	12.45663	79.47375	12.40820	88.76564
13.78925	58.26578	14.06110	64.21246	13.63741	70.61939	13.72574	78.81404	13.65833	88.17735
15.02787	57.16589	15.32377	62.73392	14.86342	70.40994	14.96134	77.88345	14.88655	86.88243
16.24871	57.15108	16.56412	62.43514	16.07045	70.31493	16.19259	77.28738	16.09974	86.58305
17.44315	56.42739	17.78482	62.29981	17.25486	67.90683	17.39159	77.23782	17.28144	85.46694

Table (3): The equivalent conductivity (Ω^{-1} cm^2 equiv.$^{-1}$) and molar concentrations (M) of the complex $[Ni(phen)_3]Cl_2$ in ethanol at different temperatures.

280.16K		288.16K		298.16K		308.16K		318.16K	
M x 10^4	$\Lambda_{equiv.}$	M x 10^4	$\Lambda_{equiv.}$	M x 10^4	$\Lambda_{equiv.}$	M x 10^4	$\Lambda_{equiv.}$	M x 10^4	$\Lambda_{equiv.}$
0.75535	22.83487	0.76385	27.31551	0.75577	34.78532	0.75229	40.12336	0.73671	48.04291
1.50816	22.50438	1.52144	27.24512	1.51151	34.62815	1.49460	39.92623	1.47137	46.25536
2.25873	21.80043	2.26827	26.61463	2.25966	34.41077	2.22391	39.71762	2.19823	46.19307
3.00315	21.49151	3.00553	25.91750	2.99749	33.36545	2.95060	38.32716	2.91224	45.31996
4.41592	20.91574	4.41623	24.88297	4.41549	32.41629	4.35123	37.69023	4.29637	44.67908
5.82001	20.34142	5.80292	24.25831	5.80644	31.59513	5.71959	36.40689	5.65265	42.37986
7.15714	19.90158	7.16221	23.73290	7.17250	30.42839	7.03677	34.88977	6.98311	40.47640
8.48567	19.57245	8.49530	23.61095	8.54139	29.72757	8.36292	33.51536	8.28773	39.81128
9.79114	19.23590	9.79906	22.93956	9.82367	29.15477	9.63973	32.82792	9.57228	38.53765
11.07412	18.88294	11.08462	22.46767	11.11764	28.51352	10.92965	32.00803	10.83494	38.41159
12.34000	18.53164	12.34259	22.13412	12.38605	27.84011	12.17687	31.69966	12.07460	37.69361
13.579391	18.27434	13.58075	21.30428	13.63217	27.33600	13.39566	31.09997	13.28902	37.17982
14.79350	17.99692	14.79912	21.05423	14.85355	29.96115	14.60823	30.80378	14.48535	36.41383
15.99148	17.68362	15.99681	21.04308	16.05352	26.67881	15.76986	30.47526	15.66061	36.16815
17.16886	17.53246	17.17601	20.89415	17.23114	26.47003	16.92944	29.86683	16.81182	35.67723

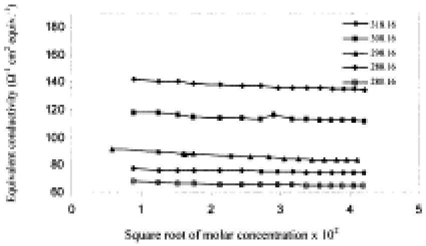

Figure (1): The plot of equivalent conductivity against the square root of molar concentration for $[Ni(phen)_3]Cl_2$ in water at different temperatures.

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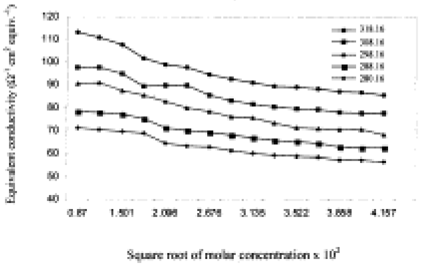


Figure (2): The plot of equivalent conductivity against the square root of molar concentration for $[Ni(phen)_3]Cl_2$ in methanol at different temperatures.

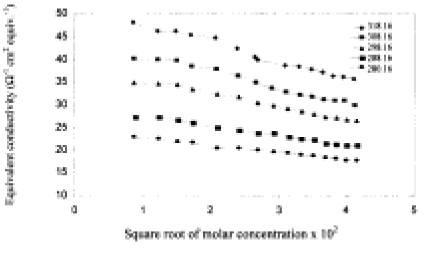


Figure (3): The plot of equivalent conductivity against the square root of molar concentration for $[Ni(phen)_3]Cl_2$ in ethanol at different temperatures.

From both tables and figures it can be seen clearly that the equivalent conductivities increase with increasing temperature. Table (4) shows the best fit parameters of analysis of conductance data for $[Ni(phen)_3]Cl_2$ in water, methanol and ethanol at different temperatures.

Table (4): The best fit parameters of analysis of conductance data for $[Ni(phen)_3]Cl_2$ in de-ionized water at different temperatures.

Temp/K	$K_A^{(1)}$	$K_A^{(2)}$	$\lambda°_{MX}{}^{+}$	$\lambda°_M{}^{+2}$	R/A°	σ_s (A)
280.15	22	< 1.0	0.02	18	29x10^{-8}	0.0726
288.15	9	< 1.0	0.1	28	29x10^{-8}	0.1367
298.15	2.3	< 1.0	0.1	40	29x10^{-8}	0.0735
308.15	2	< 1.0	1.2	68	29x10^{-8}	0.0412
318.15	0.3	< 1.0	30	92	29x10^{-8}	0.0176

The best fit parameters of analysis of conductance data for $[Ni(phen)_3]Cl_2$ in methanol at different temperatures.

Temp/K	$K_A^{(1)}$	$K_A^{(2)}$	$\lambda°_{MX}{}^{+}$	$\lambda°_M{}^{+2}$	R/A°	σ_s (A)
280.15	79	< 1.0	9.5	20	29x10^{-8}	0.442
288.15	106	< 1.0	18	31	29x10^{-8}	0.061
298.15	135	< 1.0	6	47	29x10^{-8}	0.137
308.15	150	< 1.0	24	55	29x10^{-8}	0.169
318.15	238	< 1.0	20	70	29x10^{-8}	0.127

The best fit parameters of analysis of conductance data for $[Ni(phen)_3]Cl_2$ in ethanol at different temperatures.

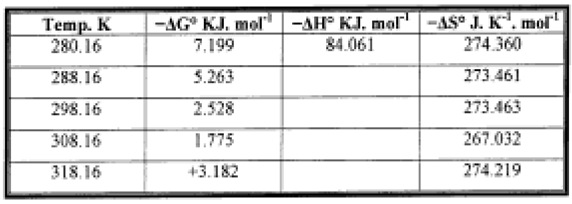
Temp/K	$K_A^{(1)}$	$K_A^{(2)}$	$\lambda°_{MX}{}^{+}$	$\lambda°_M{}^{+2}$	R/A°	σ_s (A)
280.15	9x10^{8}	< 1.0	0.008	0.06	29x10^{-8}	0.348
288.15	35x10^{5}	< 1.0	0.001	0.12	29x10^{-8}	0.572
298.15	4580	< 1.0	0.004	0.15	29x10^{-8}	0.276
308.15	2510	< 1.0	0.004	0.06	29x10^{-8}	0.253
318.15	767	< 1.0	0.002	0.90	29x10^{-8}	0.044

From Table (4) the values of $\lambda°M^{+2}$ in water increase with increasing temperature which may attributed to the high value of the dielectric constant of water and also because of the large size of the complex ion $[Ni(phen)_3]^{+2}$ which form small size of solvated ion to move in solution. In the other hand $\Lambda_{equiv.}$ In Table (1) greatly increase with increasing temperature, so the association constant K_A decreases as shown in Table (4) due to short-range interaction and the hydrogen bonding formed at lower temperatures. [12]. The value of λ° of $[Ni(phen)_3]^{+2}$ ion slightly increases with increasing temperature which may attributed to the decrease in the viscosity of methanol [13], in the other hand $\Lambda_{equiv.}$ In Table (2) and Figure (2) increases with temperature.

The value of association constant K_A in methanol increase with increasing temperature which assumed a simple coulombic interactions between hard sphere ions in continuous medium. The same behavior was obtained by Dawood [14] for symmetrical (1:1) electrolytes in methanol at different temperatures. The high value of K_A association constant in ethanol were due to the low value of dielectric constant which leads to high association and low value of λ° of $[Ni(phen)_3]^{+2}$ ion. The value of $\Lambda_{equiv.}$ also increase with increasing temperature but found to be lower than in methanol and water as shown in Table (3) and Figure (3).

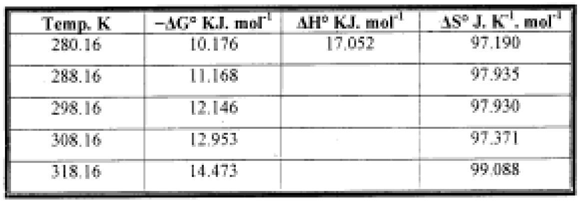
Thermodynamic parameters ΔG°, ΔH° are determined from the values of K_A ($\Delta G° = -RT\ln K_A$) , ($\ln K = -\Delta H/RT + C$) and temperature (Arrhanius equation), then ΔS° is calculated from these two parameters ($\Delta G° = \Delta H° - T\Delta S°$) and are given in Table (5).

Table (5): Thermodynamic parameters from the ion association constant of $[Ni(phen)_3]Cl_2$ in water at different temperatures.



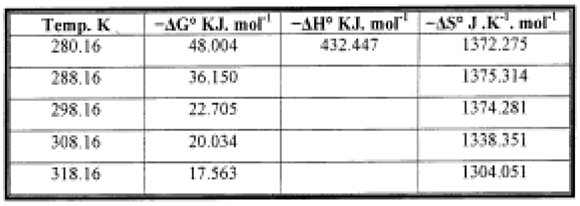
Temp. K	$-\Delta G°$ KJ. mol^{-1}	$-\Delta H°$ KJ. mol^{-1}	$-\Delta S°$ J. K^{-1}. mol^{-1}
280.16	7.199	84.061	274.360
288.16	5.263		273.461
298.16	2.528		273.463
308.16	1.775		267.032
318.16	+3.182		274.219

Thermodynamic parameters from the ion association constant of $[Ni(phen)_3]Cl_2$ in methanol at different temperatures.



Temp. K	$-\Delta G°$ KJ. mol^{-1}	$\Delta H°$ KJ. mol^{-1}	$\Delta S°$ J. K^{-1}. mol^{-1}
280.16	10.176	17.052	97.190
288.16	11.168		97.935
298.16	12.146		97.930
308.16	12.953		97.371
318.16	14.473		99.088

Thermodynamic parameters from the ion association constant of $[Ni(phen)_3]Cl_2$ in ethanol at different temperatures.



Temp. K	$-\Delta G°$ KJ. mol^{-1}	$-\Delta H°$ KJ. mol^{-1}	$-\Delta S°$ J .K^{-1}. mol^{-1}
280.16	48.004	432.447	1372.275
288.16	36.150		1375.314
298.16	22.705		1374.281
308.16	20.034		1338.351
318.16	17.563		1304.051

In water, the values of ΔH° are negative and ΔS° are small, this will ascribed to specific short-range interaction such as hydrogen bonding. From the same table the values of ΔS° and ΔH° in methanol are positive and in agreement with theoretical ΔH° values containing the ($T^{-1} + \partial\ln D/\partial T$) term: since the experimental value of $\partial\ln D/\partial T$ makes the theoretical ΔH° value positive ($\partial\ln D/\partial T$)<-1 [12].

$\Delta H°_{eq.} = -bRT^2(T^{-1} + \partial\ln D/\partial T)\ (d\ln K_A/db)$

This agreement of the experimental and theorical values of ΔH° may mean that the temperature dependence of D, $\partial\ln D/\partial T$ represent how much the ion salvation is weakened by ion association. The positive value of ΔS° in Table (5) has been considered as due to the decreasd orientation of solvent molecules when the ion pair performed [2].

In ethanol the values of ΔH° and ΔS° are negative and small because of the low value of the dielectric constant of ethanol which leads to ion solvent interaction, and the high value of association constants leads to very low value of λ° of $[Ni(phen)_3]^{+2}$ ion and more orientation due to ion solvent interaction.

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دراسة توصيلية لظاهرة التجمع الايوني لمعقدات $Ni(phen)_3]Cl_2$ في مذيبات مختلفة وبدرجات حرارية مختلفة

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الملخص:

تم اجراء القياسات التوصيلية لمعقد $[Ni(phen)_3]Cl_2$ في مذيبات الماء، الميثانول والايثانول في درجات حرارية مختلفة. وتم حساب المواصلة المكافئة عند التخفيف اللانهائي(Λ_O) وثابت التجمع الايوني (K_A) والمسافة بين الايونات (R) في المحلول .وقد اجري تحليل النتائج باستخدام معادلة لي–ويتون في التوصيلية والتي اعطت معلومات مفصلة عن التداخلات بين ايون–ايون وايون– مذيب فضلاً عن إعطاء معلومات عن الدوال الثرموداينمكية وطبيعة التداخلات.

الكلمات الدالة: التوصيلية الكهربائية، معادلة لي–ويتون، الدوال الثرموداينميكة.