Conductivity and Thermodynamics of Ion-association of [Ni(phen)₂H₂OCl]Cl in Methanol

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Abstract:

Conductance measurements are reported for $[Ni(phen)_2H_2OCI]Cl$ in methanol at temperatures between (280.15 - 318.15°K). The limiting molar conductances \Box_0 , association constants K_A and the mean distance between the ions in solution R have been derived from Lee-Wheaton (LW) conductivity equation. The investigation of the dependence of ion association behaviour on the properties of the complex ion including detailed information converning ion-ion and ion-solvent interaction especially from thermodynamic point of view and Walden product were also calculated.

Introduction:

Conductance measurements have been made on solutions of chloroaquabis 1,10-phenanthroline Nickel (II) chloride in methanol at (280.15-318.15°K). The limiting molar conductances and association constants were derived from the experimental data by means of Lee-Wheaton equation for (1:1) symmetrical electrolytes.

After taking some interset in the ionic association between divalent metal cations and 1,10-phenanthroline (phen) (Al-Mustawi, Y.O.H., 2002), studied the electrical conductivity of $[Ni(phen)_3]Cl_2$ in water, methanol and ethanol at different temperatures (280.16-318.16) to investigate the dependance of the ion association behaviour on the properties of the complex ion including detailed information concerning ion-ion and ion-solvent interaction, especially from thermodynamic point of view (Yokoyama, H., et al 1988).

The conductivity of oxine (8-hydroxyquinoline) with some transition and alkaline earth salt complexe in methanol were measured. The complexes of [Ni, Mn, Sr and Ba oxanates) show that all of them are associated in methanol to form the new species (MX)⁻. Lee-Wheaton conductance equation was used to analyse the experimental data and found to be very applicable for such type of complexes (Akrawi, B.A, & Sarsam, L.A. 2001).

Molar conductivity.

The electroconductivity of the 1,1-electrolytes in N,Ndimethyl formamide is experimentally determined at 283-318K. The limiting molar electroconductivity Λ_o of salts and constants of ionic association K_A are calculated by using Lee-Wheaton equation (Safonova, L.P. et al 1999).

Conductance measurements are reported for NaSCN, KSCN and NH₄SCN in water, N,N-dimethyl formamide (DMF) and (water+DMF) mixtures at 20°C. The limiting molar conductances and association constants have been drived from Lee-Wheaton conductivity equation (Tsierkezos N.G. et al 2003).

Experimental:

1. Preparation of the complex: in order to prepare the desired complex a mixture of 2mmole of (1,10-phenanthroline) in 10cm³ of ethanol and 2mmole of

NiCl₂.6H₂O in 10 cm³ of water was refluxed for about 45 minutes on a water bath then cooling and adding the excess of absolute ethanol. A coloured precipitate was suctioned, filtered and washed with ice-cold 50% ethanol and recrystalized by slow cooling to 0°C followed by addition of excess absolute ethanol. The product was dried under vaccum over unhydrous calcium chloride (Malik et al., 1980).

2. Methanol was purified and dried by the method described by Perrin (Perrin 1966) and the procedure was reported twice to ensure that all water was removed.

For conductivity measurement 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 mentain the isolation during the addition of the solute.

Nitrogen gas was passed through lime water, sulphuric acid and calcium chloride before enterning the cell. The temperature of the cell and its contents was kept constants at certain temperature using a water thermostate type. HAAKE N K 22. Purified nitrogen gas passed through a known volume of solvent until the conductance of the solvent was constant. Addition of the solute was then made.

The design of the conductance cell and the nitrogen line was the same as that previously used by Wheaton (Lee and Wheaton 1979), the cell constant of the conductivity cell was measured using the method of Jones and Bradshow (Jones and Bradshow 1933). 0.01M KCl solution was prepared from KCl (B.D.H.) reagent recrystalized three times from conductivity water and then dried at 700 Torr at 500°C for 10 hrs. The cell constant was checked regularly and found to be 0.05564 cm⁻¹.

A general method has been used for measuring the conductance of electrolytes, the conductivity cell was washed first with solvent used and then dried, weighed empty and kept at constant temperature. Purified nitrogen gas was passed through the cell; 100ml of purified solvent was added a nitrogen gas was passed for further 10-15min, Whearupon the cell plus the contents were weighed. A certain amount of the complex solution was injected into the cell from a plastic syringe (which was weighed before and after each addition), Nitrogen gas was passed for several minutes and the conductivity of the solution was measured after each addition (Generally (12-15) 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 dependance of the ion association behaviour on the properties of the complex ion, in this work, the conductimetric 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 specially from theromodynamic point of view (Yokoyama et al., 1988). The measured molar conductivities are shown in Table (1) at (280.15-318.15 Kelvin).

Table (1)	Molar co	nductivitie	s (□/S	cm ²	mol ⁻¹) of
[Ni(phe)	n) ₂ H ₂ OCl	ICI at diffe	erent te	mpe	ratures	3

1.04	$\Lambda/S \text{ cm}^2 \text{mol}^{-1}$				
10 mmol 1it ⁻¹	280.15°	288.15°	298.15°	308.15°	318.15°
minor in	K	K	K	K	K
1.04527	155.332	186.987	197.725	228.856	266.864
2.08670	148.319	185.729	190.862	225.461	254.946
3.09486	147.985	178.556	191.947	223.886	251.987
4.10138	146.382	174.680	189.540	220.761	247.490
6.06604	144.464	174.009	188.856	217.958	240.786
7.96610	144.231	170.263	187.214	216.297	240.628
9.85895	140.156	168.715	186.033	211.734	239.726
11.71315	139.679	168.118	185.023	211.629	237.747
13.51729	137.993	167.050	184.202	207.760	234.343
15.31195	137.673	166.735	182.595	206.758	232.213
17.07515	137.174	165.507	180.989	204.819	228.438
18 81855	136 745	164 908	180 828	202 589	227.081

The theromodynamic constant (K_A) is:

where α is the degree of dissociation $(\alpha = \lambda/\lambda_{ex})$, i.e. the relation between the measured molar conductivity for each concentration and the molar conductivity of free ions, y_{\pm} is the mean activity coefficient of free ions, and $c^{\circ}=1 \text{ mol dm}^{-3}$.

For the activity coefficient, we have used the Debye-Hükel expression.

$$y_{+}^{2} = \exp[-e/(1+t)]$$
(2)

where e=2Kq, t=KR; K is the Debye parameter, q is the Bjerrum critical distance, and R is the center-to-center distance between the ions in the ion-pair formed (distance parameter). (Tominic` I. et. al, 1998).

Fig. (1) shows the relation between square root concentration and molar conductance of the complex at different temperature.

Fig. (1) The plot of A against $C^{1/2}$ of different temperatures



For the specific case of a solution containing only a single symmetrical electrolyte:

$$\Lambda_{\text{equiv.}} = f(\Lambda_0, \mathbf{R}, \mathbf{K}_A)$$

where Λ_o is the equivalent conductance at infinite dilution, K_A the pairwise ion association constant:

$$\mathbf{M}_{aq}^{+} + \mathbf{X}_{aq} = (\mathbf{M}_{n.aq} + \mathbf{X})^{\circ}$$

where n may be zero and R is the distance parameter which is defined as the distance between an anion and cation at which short-range forces become strong enough to impede further approach of the ions, allowing the formation of the contact (CIP) or solvent-separation ion pairs (SSIP). The magnitude of R depends upon the extent of ion-solvent interaction in the solution. It was suggested that for both symmetrical and unsymmetrical electrolytes all R_{ji} terms could be replaced by R where R = R_{cation} + R_{anion}; but when more than two species are present, the assumption was made that all cations have the same radius (R_{cation}) and similarly all anions have the radius (R_{anion}). (Lee and Wheaton, 1979).

 $\Lambda = \Lambda_{g} [1 + C_{1}(KR)(\varepsilon K) + C_{2}(KR)(\varepsilon K)^{2} + C_{3}(KR)(\varepsilon K)^{3}] - \dots (3)$ (\rho K)/(1 + (KR)[1 + C_{4}(KR)(\varepsilon K) + C_{5}(KR)(\varepsilon K)^{2} + (KR)/12]

where the concentration depend terms are both the "plasma parameter", (ϵK) and (KR). The concentrationcoefficient are functions of these parameters:

In equation (3):

$$\varepsilon = |Z|^2 e^2 / DKT,$$
 $K^2 = 8\pi N e^2 |Z|^2 C / 1000 DKT,$

 $\rho = F\zeta e|Z|/3\eta$

where F= faraday constant (9.6486×10⁴) and ζ is a conversion factor

(volt \rightarrow e.s.u.) = 1/299.7925. (all terms have been defined previously in details (Lee and Wheaton, 1979).

The input data to the computer program (MR₂) are: solvent data; temperature, dielectric constant and viscosity as (T, D, η). Association constant, equivalent conductance at infinit dilution and the characteristic ion pair distance as (K_A, Λ_o , R), R in the form R_{min}, R_{max}, Δ R together with solution molarities and the corresponding equivalent conductances.

The computer program (MR₂) calculates those values of K_A , Λ_o , and R which gives the best fit of the experimental conductance to the equation (3) as measured by the quantity $\sigma(\Lambda)$:

$$\sigma_{(\Lambda)} = \sum_{n=1}^{Np} \left\{ \sum (\Lambda_{calc.} - \Lambda_{exper.})^2 / Np \right\}^{1/2} \qquad \dots \dots \dots (4)$$

where Np is the number of the pairs of conductance concentration data. $\sigma(\Lambda)$ is sometimes (incorrectly) reffered to as the standard deviation of the data from equation (3).

The results of the analyses of the complex $[Ni(phen)_2H_2OC1]Cl$ are shown in table (2)

Table (2) The results of the analyses (Λ_o, K_A, R) at the best value of $\sigma(\Lambda)$

Т⁰К	Λ_0 mol ⁻¹ .cm ²	K _A	R/Pm	σ(Λ)
280.15	261.937	97.737	2800	0.0285
288.15	153.134	74.349	2800	0.0137
298.15	195.60	42.657	2800	0.0116
308.15	199.70	27.052	2800	0.0070
318.15	230.40	80.879	2800	0.0068

It is clear that the values of Λ_o increases with increasing temperature, this is expected, since the force between the ions decrease and hence the mobility of ions increase with increasing temperature.

The values of K_A obtained confirm the fact that in methanol a considerable amount of ion pair formation is to be expected. Association decreases with increasing temperature. The values of R indicate the forming of

solvent separated ion pair (SSIP). The values of $\sigma(\Lambda)$ obtained are less than 0.1.

The plot of ln K_A against 1/T (Vant Hoff's equation) (ln $K_A=-\Delta H_o/RT+C$) are given in Fig. (2) for the complex which is linear in the temperature range from (280.15-308.15).

Fig. (2) The plot $\ln K_A$ against 1/T



Thermodynamic parameters ΔH , ΔG , ΔS are determined from the following:

 ΔG is determined from (ΔG =-RTlnK_A) (Vant Hoff's equation), ΔS is calculated from these two parameters (ΔG = ΔH -T ΔS) which are given in table (3).

 Table (3) Thermodynamic parameters, from the ion

 association constant of [Ni(phen)₂H₂OCl]Cl in methanol

 at different temperatures

TOLZ	-ΔG	-ΔS	-∆H	
IK	KJmol ⁻¹	Jmol ⁻¹ K ⁻¹	KJmol ⁻¹	
280.15	10.672	80.600		
288.15	10.320	79.597		
298.15	9.303	80.338	33.256	
308.15	8.503	80.327		
318.15	11.617	68.015		

It was found that the value of ΔH of ion association is negative, since ions are rigid and associated in a coulombic interaction in a dielectric continum media (Doe H. et al 1990). The negative values of ΔS in methanol have been considered as due to the orientation of solvent molecules when the ion-pair form, the values of ΔG are negative in methanol according to the relation ΔG =-RTlnK_A and indicates that the reaction is spontaneous.

It is seen from Figure (3) that the Walden product $\Lambda_0\eta_0$ for [Ni(phen)₂H₂OCl]Cl is slightly temperature dependent in methanol, it was found that the solvent structure weakens and the molecules are more easily attracted to secondary solvation shells (Tominic I. et.al. 2004).

Fig. (3) Dependence of Walden product for [Ni(Phen)₂H₂OCl]Cl on the reciprocal value of dielectric constant of methanol.



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توصيلية وثيرموداينميكية التجمع الأيوني للمعقد Ni(phen)₂H₂OCl]Cl] في مذيب الميثانول

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الملخص:

تمت قياسات التوصيلية للمعقد Ni(phen)₂H₂OCl]Cl] في الميثانول للـدرجات الحراريـة بـين (٢٨٠,١٥–٢١٨,١٥) واسـتخدمت معادلـة لـي – ويتـون لاسـتخراج التوصـيلية المولاريـة ٨٥ وثابـت التجمـع الأيـوني K_A والمسافة بين الأيونات في المحلول R. واستخرجت الدوال الثيرموداينميكية

وبصورة مفصلة من ثابت التجمع الأيوني المتعلقة بتداخل أيون – أيون وأيون – مذيب خاصبة من الناحية الثيرموداينميكية وكذلك حاصل ناتج والدن.