

## The Electrical Conductivity of $[\text{Ni}(\text{Phen})_3]\text{Cl}_2$ in Methanol-Water Mixtures at 298 K

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### Abstract

The aim of this work is to measure the electrical conductivity of  $[\text{Ni}(\text{Phen})_3]\text{Cl}_2$  in different percentages of methanol-water mixtures at 298 K. The data were analyzed using Lee-Wheaton equation for unsymmetrical electrolytes. The conductivity parameters, ionic conductivity  $\lambda_{\text{Ni}^{2+}}^{\circ}$ , association constant  $K_A$  and the distance parameter  $R$  are calculated at the best fit values of the standard deviation  $\sigma_s$  ( $\Lambda$ ). The results indicate that  $\lambda_{\text{Ni}^{2+}}^{\circ}$  decrease on increasing percentage of methanol in the mixture. Maximum association obtained at equal percentage of  $\text{H}_2\text{O}$  and methanol (50:50). The distance parameter was almost 29  $\text{\AA}$  at each percentage forming solvent-separated ion pairs. Walden-product is also calculated for this system.

-	$[\text{Ni}(\text{Phen})_3]\text{Cl}_2$	-	298
$K_A$	$\lambda_{\text{Ni}^{2+}}^{\circ}$	:	
$\lambda_{\text{Ni}^{2+}}^{\circ}$	$\sigma_s(\Lambda)$		$R$
			29
			$(\lambda_{\circ}\eta)$

### Introduction

The analytical applications of this complex  $[\text{Ni}(\text{Phen})_3]\text{Cl}_2$  with other transition metal chlorides ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ) with 1,10-phenanthroline as a ligand as complexes are well known <sup>(1)</sup>. They are now finding extensive use in vulcanization of rubber froth floatation process for concentration of sulphide ores, as antioxidants, lubricants and have been found to possess fungicidal and insecticidal activity <sup>(2)</sup>. The characteristics of metal

chelate electrolytes is of their solute-solvent interactions concerning charge, size and chemical properties of ligand, have been elucidated by the study of electronic spectra <sup>(3)</sup>, racemization <sup>(4)</sup>, optical resolution <sup>(5)</sup>, viscosity and molal volume <sup>(6)</sup> and conductivity <sup>(7,8)</sup>.

Among these, the conductivity measurements are useful as an effective means to understand the nature of solute-solvent interactions since the degree of ion-pairing and ionic mobility is exceedingly sensitive to interactions.

Very few works have been done of 1,10-phenanthroline as a ligand with any metal ion. <sup>(9)</sup> had studied the kinetics and conductivity of tris (3,4,7,8-tetramethyl-1,10-phenanthroline-Fe(II) complex in acetonitrile at 25 °C and the conductivity data were analysed by the Lee-Wheaton equation.

Novel chiral complexes of tin have been synthesized by using amino acids as chiral auxiliary and 1,10-phenanthroline, 3,7-phenanthroline or 1,7-phenanthroline as a secondary ligand <sup>(10)</sup>. It has been found that the complexes are non-electrolytic and are octahedral in shape with a coordination number six around the tin atom. Also the complexes have been screened against a number of fungi and bacteria to assess their growth inhibiting potential.

In this work we have measured the electrical conductivity of  $[\text{Ni}(\text{Phen})_3]\text{Cl}_2$  in methanol-water mixtures at 298 K. Lee-Wheaton equation is used to elucidate the conductivity parameters  $\lambda^\circ$ ,  $K_A$  and  $R$  in the different percentages of the two solvents.

## Experimental

Methanol was purified and dried by the method described by Perrun <sup>(11)</sup> and the procedure was repeated twice to ensure that all water was removed. Conductivity water was prepared by redistilling distilled water three times and condensing it by using a condenser with glass joints. Little potassium permanganate was added to the distilled water to reduce the absorption of carbon dioxide <sup>(12)</sup>.

### Preparation of complexes:

To prepare the complex, a mixture of 6 mM of 1,10-phenanthroline in 30 cm<sup>3</sup> of ethanol and 2 mM of  $\text{NiCl}_2$  in 10 cm<sup>3</sup> of water was refluxed for about 45 minutes on a water bath. On cooling and adding excess of absolute ethanol, a coloured precipitate was formed then suctioned, filtered and washed with ice-cold 50% ethanol. The crude product was dissolved in a minimum quantity of hot 50% ethanol and

recrystallised by slow cooling to 0 °C followed by addition of excess absolute ethanol. The product was dried under vacuum over anhydrous calcium chloride <sup>(2)</sup>. The composition of the complex was determined by using Shimadzu U.V. & Vis Recording UV-160 spectrophotometer and I.R. Spectra by Using A Perkin Elmer 580 B Infrared Spectrometer (200-4000 cm<sup>-1</sup>). The magnetic susceptibility were measured applying Faraday method. The instrument used is of the type Bruker B.M. 6.

### General Procedure:

A special design was used for conductivity measurements in aqueous and non-aqueous solvent to ensure complete isolation of the system from outside atmosphere and during the addition of solute. Nitrogen gas was passed through lime water,  $\text{H}_2\text{SO}_4$  and  $\text{CaCl}_2$  before entering the cell. The temperature of the cell and its contents was kept constant at  $25 \pm 0.1$  °C using a water thermostat type HAAKE NK 22. Purified nitrogen was passed through a known amount of a solvent until its conductivity was constant and addition of solute was then made.

The design of the cell was the same as used previously in our lab <sup>(1)</sup> with its two platinized platinum electrodes. This cell constant was checked regularly and found to be 0.05564 cm<sup>-1</sup>. Conductivity meter is of a type WTW (model LBR) with a frequency range of (50 Hz-3 KHz) and sensitivity between (10<sup>-1</sup>-10<sup>-9</sup> S).

A general method has been used for measuring the conductance of the electrolytes. The conductivity cell was weighted and kept at a constant temperature then purified nitrogen was passed through the cell; 100 ml of purified solvent was added and nitrogen gas was passed for further 10-15 minutes, whereupon the cell plus its contents were weighed. A certain amount of 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 all the additions had been made (generally 15), the cell was reweighed to find the weight change over the half run which was found not more than 0.02%.

## Results and Discussion

$$\lambda_j = \lambda_j^0 \left\{ 1 + z_j \sum_{p=2}^s X_j^p \sum_{v=1}^s t v X_v^p [A_v^p(t)(\beta k) + B_v^p(t)(\beta k)^2 + C_v^p(t)(\beta k)^3] \right\} - \frac{|z_j| (K\tau)}{2(1+t)} \left\{ 1 + V_j^{(1)}(t)(\beta k) + V_j^{(2)}(t)(\beta k)^2 + \pi_j^{(5)} t/6 \right\} \dots \dots \dots (1)$$

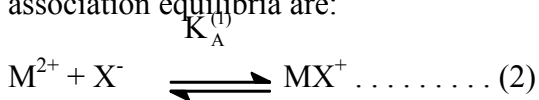
$$\text{with } \Lambda_{\text{equiv.}} = \sum_{j=1}^s (|z_j| m_j \lambda_j) / C \text{ where}$$

s is the number of charged species,  $z_i$  and  $t_j$  are the charge and transference number of species

$$\beta = e^2 / DK T, k = (4\pi / DK T) \sum_{j=1}^s n_j e_j^2 \text{ and is}$$

proportional to the ionic strength,  $t = kR$  and  $T = Fe/6\pi\eta$ ,  $n_j$  is the molar free ion concentration of species  $j$ ,  $C$  is the equivalent stoichiometric concentration of the electrolyte. The plasma coefficients  $A_v^p$ ,  $B_v^p$  . . . etc are functions of  $kR$  and  $q_p$  while the terms  $X_j^p$  and  $q_p$  are functions of the limiting mobilities, the concentration, and charge on all ions present in solution. [All other terms are defined in the original paper <sup>(13)</sup>].

For an unsymmetrical electrolyte  $MX_2$  ionising into  $M^{2+}$  and  $X^-$ , the possible association equilibria are:



and



Thus three ionic species are present in the solution, which are  $M^{2+}$ ,  $MX^+$  and  $X^-$ .

Thus for associated salts:

$$\Lambda_{MX_2} = f (\lambda_{M^{2+}}^0, \lambda_{MX^+}^0, \lambda_{X^-}^0, K_A^{(1)}, K_A^{(2)}, R) \dots \dots \dots (4)$$

The equation derived by Lee and Wheaton <sup>(13)</sup> has been tested extensively in both aqueous and non-aqueous systems and provide a satisfactory explanation of the conductometric behaviour of a variety of systems. Lee and Wheaton obtained an equation for unsymmetrical electrolytes of the form:

where  $R$  is the average centre to centre distance for ion pairs.

The input data to the computer program (RM<sub>1</sub>) are solvent data (Temp.  $T$ , Dielectric constant  $D$  and viscosity  $\eta$ ); the charge  $z_1$  and ionic mobility  $\lambda_i^0$  for each ionic species,  $K_A^{(1)}$ ,  $K_A^{(2)}$ ,  $\lambda_{MX^+}^0$ ,  $\lambda_{M^{2+}}^0$  and  $R$ , all in the form  $K_A^{(1)}$  (min.),  $K_A^{(2)}$  (max),  $\Delta K_A^{(1)}$  . . . etc., then the experimental data (molecular concentrations and the equivalent conductances). This program is used to determine values of  $K_A^{(1)}$ ,  $K_A^{(2)}$ ,  $\lambda_{MX^+}^0$ ,  $\lambda_{M^{2+}}^0$  and  $R$  which minimize  $\sigma_s(\Lambda)$ .

Table (1) shows the molar concentrations and equivalent conductances of  $[Ni(Phen)_3]Cl_2$  in different percentages of methanol-water at 298 K and Figure (1) illustrates the relation between them.

**Table (1): Molar concentrations (M) and equivalent conductances ( $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{equiv}^{-1}$ ) of  $[\text{Ni}(\text{Phen})_3]\text{Cl}_2$  in different percentages of methanol-water at 298 K**

MeOH 100%		MeOH 90%		MeOH 70%		MeOH 50%		MeOH 30%		MeOH 10%		MeOH 0%	
$M \times 10^{-4}$	$\Lambda$	$M \times 10^{-4}$	$\Lambda$	$M \times 10^{-4}$	$\Lambda$	$M \times 10^{-4}$	$\Lambda$	$M \times 10^{-4}$	$\Lambda$	$M \times 10^{-4}$	$\Lambda$	$M \times 10^{-4}$	$\Lambda$
0.762	94.157	0.772	49.155	0.728	42.262	0.737	36.276	0.761	39.410	0.776	55.334	0.748	91.728
1.517	94.047	1.533	48.850	1.454	41.580	1.467	36.151	1.514	39.344	1.551	54.878	1.521	89.342
2.268	91.134	2.283	48.258	2.172	41.484	2.196	36.053	2.259	39.020	2.311	54.054	2.274	89.207
3.011	88.512	3.029	47.666	2.883	40.153	2.924	35.979	2.995	39.010	3.067	53.787	3.019	86.872
4.439	83.507	4.453	45.159	4.251	39.304	4.310	35.798	4.411	38.942	4.511	53.504	4.458	86.765
5.846	81.599	5.857	45.120	5.591	38.006	5.675	35.437	5.799	38.344	5.931	53.430	5.574	86.393
7.218	80.661	7.226	44.736	6.905	37.466	7.019	35.244	7.159	38.223	7.321	52.838	7.260	86.339
8.568	78.016	8.575	44.475	8.198	37.294	8.331	34.878	8.493	37.649	8.693	52.412	8.617	85.661
9.845	75.988	9.895	44.474	9.473	36.833	9.619	34.392	9.808	37.576	10.014	52.470	9.952	85.192
11.197	74.611	11.197	43.992	10.725	36.760	10.893	34.220	11.068	37.379	11.326	52.276	11.262	84.971
11.471	73.671	12.470	43.528	11.957	29.022	12.156	34.122	12.338	37.286	12.618	52.129	12.540	84.905

Table (2) shows the results of analysis of conductance data by using LW equation.

**Table (2): The results of analysis of conductance data of [Ni(Phen)<sub>3</sub>]Cl<sub>2</sub> in methanol-water at 298 K by using LW equation**

Water%	K <sub>A</sub>	λ <sub>MX<sup>+</sup></sub>	λ <sub>M<sup>2+</sup></sub> <sup>o</sup>	R/A <sup>o</sup>	σs(Λ)
100	19	1.0	57.0	29	0.076
90	80	1.0	27.0	29	0.023
70	1250	1.0	17.0	29	0.044
50	10000	1.0	14.0	29	0.038
30	1300	1.0	16.0	29	0.064
10	400	1.0	24.0	29	0.029
100% methanol	202	1.0	50.0	29	0.095

The results of analysis of the complex [Ni(Phen)<sub>3</sub>]Cl<sub>2</sub> in different percentages of methanol and water, show that this complex is associated to form:

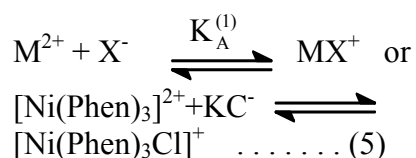


Table (2) shows that the value of λ<sub>M<sup>2+</sup></sub> is the highest in pure water and decrease with increasing methanol percentages till the ratio between the two solvents is 50:50 and then increase with further increase of methanol percentage. The first decrease in Λ<sub>o</sub> is expected since the force between ions increased and hence the mobility of ions decreased with decreasing the dielectric constant of the medium. This behaviour is similar to that obtained <sup>(14)</sup> for NaI and tetraethylammonium iodide in methanol-water mixture which refer the increase of the equivalent conductivity to the effect of the viscosity which plays an important role. Similar observations have also been noted for some electrolytes in other mixed solvents <sup>(15)</sup> and this may be attributed to the selective solvation of ions besides the solvodynamic viscous force.

In methanol a considerable amount of ion-pair formation is to be expected. The values of K<sub>A</sub> obtained (Table 2) confirm this. Association increases with

increasing mole percentage of methanol till equal percentage of the two solvents and then K<sub>A</sub> decrease gradually with increasing amount of methanol. This can be understand from the plot of log K<sub>A</sub> against the reciprocal of the dielectric constant (1/D) (Fig. 2). The explanation of the non-linearity of this relation is due to the difference in solvating properties of the mixtures towards the ion-pairs as for the free ions <sup>(16)</sup>. The results suggest that over the experimental values of the dielectric constant (D ~ 48-78) (30-100% H<sub>2</sub>O), the coulombic association as described by <sup>(17)</sup> who established that when both cation and anion are both solvated, they will exhibit compensating effects, that is to say a maximum in the log K<sub>A</sub> versus 1/D plot is expected to appear, (Fig. 2).

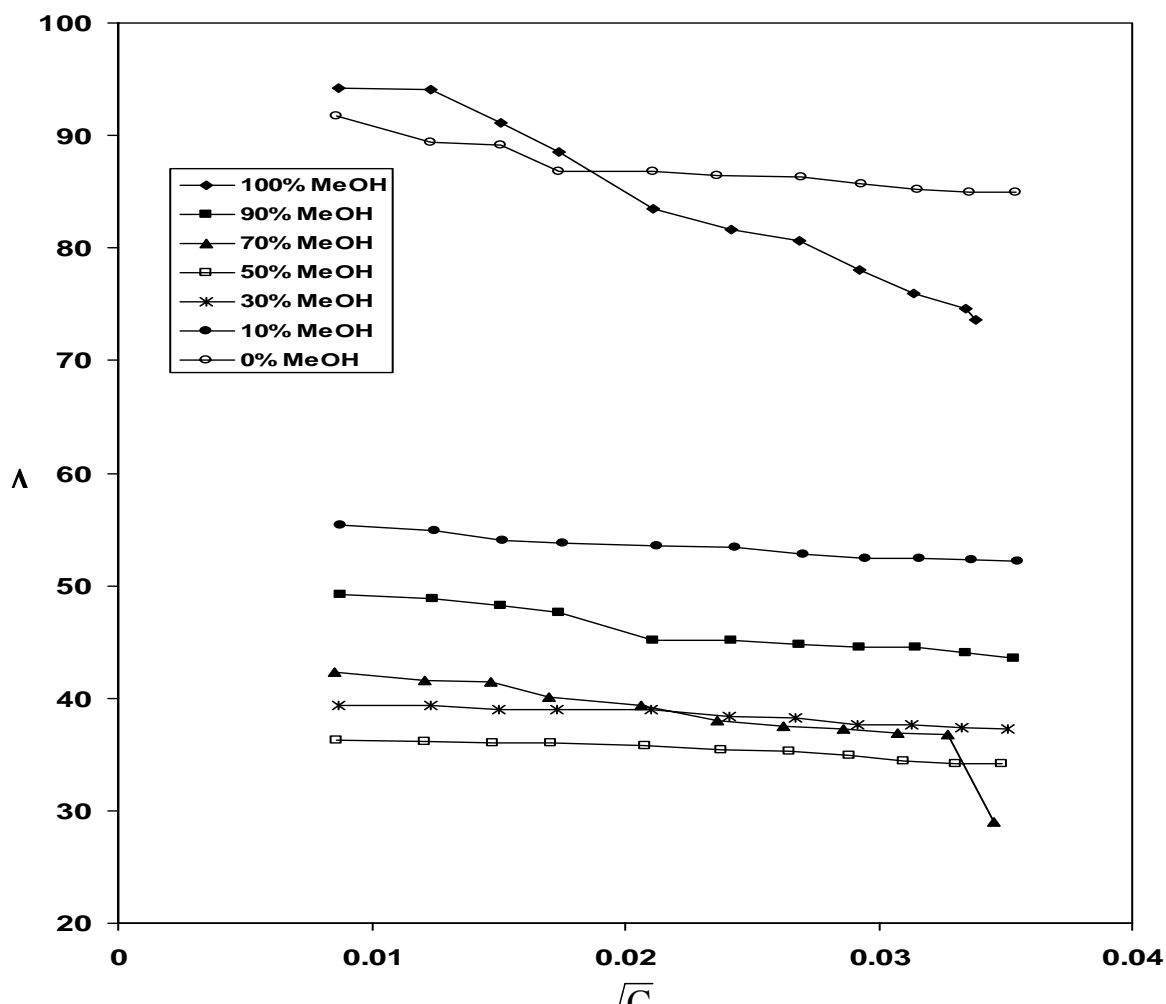
If Stokes law were obeyed in a system <sup>(18)</sup>, the value of the Walden product (η<sub>o</sub>Λ<sub>o</sub>) would be constant only if the effective radius of the ion remains the same in the different media. He suggested that the major deviation in the Walden product is due to the variation of the electrochemical equilibrium between ions and the solvent molecules with the composition of the mixed polar solvents. This is the case in the behaviour of the present system as indicated in Figure (3) where the ions suffer various degrees of solvation with different mixtures of methanol and water. The higher values of R (29 A<sup>o</sup>) indicate the formation of

the same number of solvent separated ion pairs (Table 2). The values of  $\sigma(\Lambda)$  obtained are small (generally less than 0.1).

Table (3) shows some physical constants of methanol-water mixtures and the Walden product ( $\eta\Lambda_0$ ) for this electrolyte.

**Table (3): Dielectric constants (D), viscosities ( $\eta$ ) of methanol-water mixtures at 298 K and the Walden product ( $\eta\Lambda_0$ )**

Water %	D	$\eta$ (cp)	Walden product ( $\eta\Lambda_0$ )
100	78.30	0.890	0.5073
90	70.12	0.870	0.2349
70	64.91	0.790	0.1333
50	55.40	0.720	0.1008
30	46.42	0.650	0.1040
10	37.23	0.575	0.1380
100% meth.	32.64	0.545	0.2725



**Figure (1): The plot of equivalent conductivities against square root of concentration for  $[\text{Ni}(\text{Phen})_3]\text{Cl}_2$  in methanol-water**

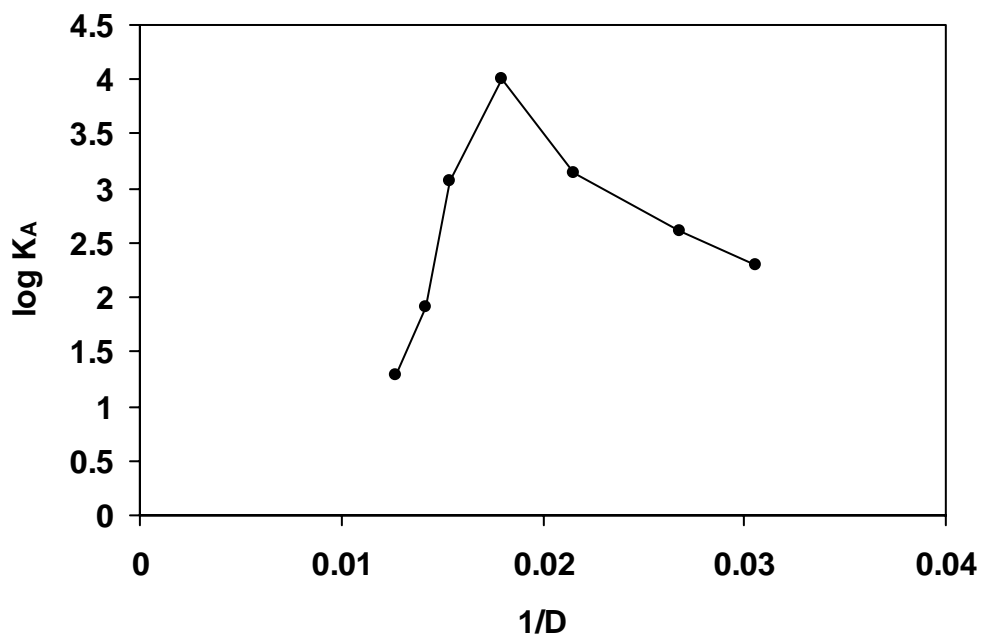


Figure (2): Log  $K_A$  values for  $[\text{Ni}(\text{Phen})_3]\text{Cl}_2$  in methanol-water mixtures of 298 K against the reciprocal of the dielectric constant ( $1/D$ )

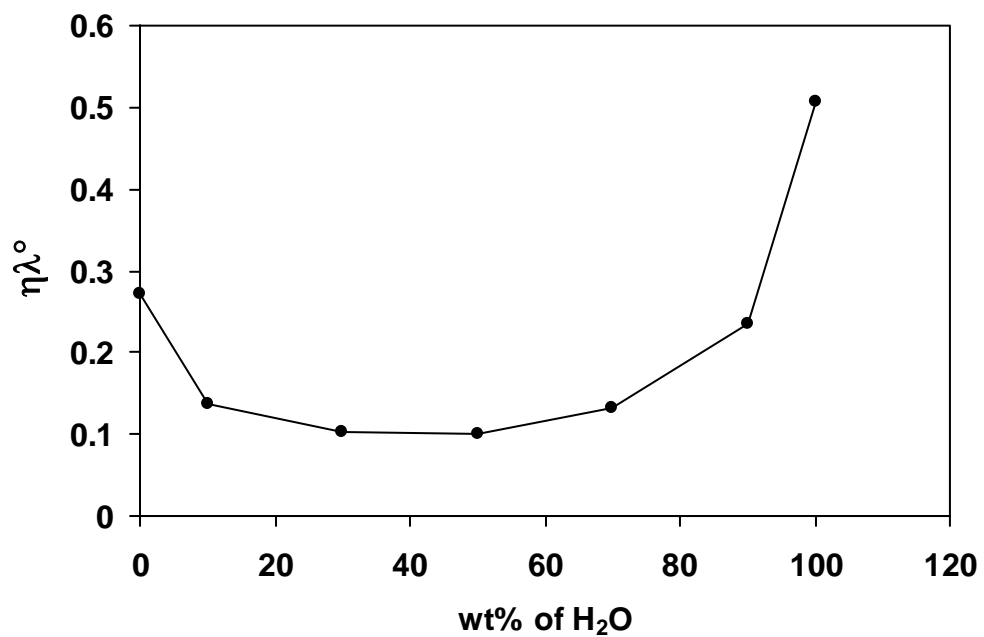


Figure (3): Walden product  $\lambda^o \eta$  for  $[\text{Ni}(\text{Phen})_3]\text{Cl}_2$  in methanol-water mixtures at 298 K versus the composition of the mixtures

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