The Electrical Conductivity of Some Transition Metal Complexes with 2,2`-Bipyridyl in Different Solvents at 298.16K

B.A. Akrawi and A.M.J. Ali
Department of Chemistry, College of Science, University of Mosul, Mosul (Iraq)

(NJC)

Abstract

The aim of this research is a conductivity study of Mn(II), Co(II), Ni(II), Cu(II) complexes with 2,2`-Bipyridyl (bipy) in water, methanol and ethanol as solvents at 298.16K. The data were analyzed by using Lee-Wheaton (LW) conductivity equation for asymmetric electrolytes. The conductivity parameters: ionic conductivity ($\lambda°$), association constant (K_A) and the average distance parameter between the ions (R) at the best fit values of the standard deviation $\sigma s(\Lambda)$ have been calculated.

The results are discussed on the basis of the solvent effect on the conductivity parameters of these complexes.

Key words: 2,2`-bipyridyl complexes, different solvents, conductivity.

(Cu, Ni, Co, Mn)

298.16   -`2,2

.(AM1) 90   .

(R)   (K_A)   ($\lambda°$)   :

.   – $\sigma s(\Lambda)$

.

Introduction

Interest in the 2,2`-Bipyridyl (bipy) and 1,10-phenanthroline (phen) compounds has been renewed because of their interesting redox and photoredox properties [1]. In the case of Cu(I) compounds of these ligands, many systems have been shown to have strong antimicrobial effects. With these ligands, eight-coordinate structures (tetrabidenate) have been proposed for the larger metal ions such as Sr,Ba,Pb and even for Mn(II) [2].Recently have been interested in the catalytic activity of some Cu(I) and Cu(II) complexes with 2,2`-Bipyridylamine[3]. They have also isolated some new complexes of this ligand with Cu(I) halide and investigated their autoxidation in methanol.

Ligand based on six-membered rings belong to the most intensively studied class of chelating ligands with

2,2`-Bipyridyl and 1,10-phenanthroline. In the case of octahedral geometry, the steric effect of the hydrogenes at the six position in bipyridyl is less severe (see figure 1), because the bulky groups are directed to the outside of the molecule.

In fact the octahedral species such as $[M(bipy)_3]^{2+}$ are very stable and often kinetically inert (specially with d^3 and d^6 low-spin metal ions) with Fe^{2+}, low-spin species are observed [2].
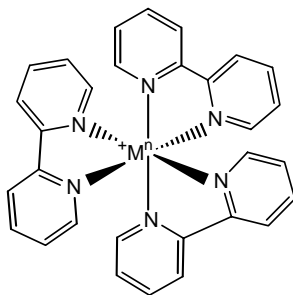

Figure 1

Studies of complexation equilibria of the antibiotic anions natidixate and cinoxacinate with $[Cu(phen)]^{2+}$ and $[Cu(bipy)]^{2+}$ are reported. These studies indicate that the stability of this type of complex is strong related to the metal environment. A correlation between the stability constants, determined with the sigma donation character of the ligand is proposed. This study shows that the stability constant for the reaction between the quinolones and the moiety $[Cu(N-N)]^{2+}$ is dependent on the coordinate diamine to the metal ion. This is in agreement with previous studies where other physical properties as their electronic absorption spectra in the visible region, display similar behaviour. These results suggest that inside the living cells, a possible interaction with some metal ion will be strongly controlled by the type of ligand bound to the cation [4].

New mixed-ligand Cu-(II), complexes: [Cu(cf)(phen)(Cl)](BF$_4$)]. 4H$_2$O, [Cu(cf)(bipy)(Cl)](BF$_4$)].2H$_2$O,

and [Cu(cf)(dafone)(Cl)](BF$_4$)]. 2H$_2$O, [cf= ciprofloxacine and dafone = 4,5-diazofluoren-9-one], have been isolated and characterized. The antimycobacterial activity of ciprofloxacin and the complexes above has been evaluated against Mycobacterium smegmatis, which shows clear enhancement in the antitubercular activity upon copper complexation with N-N donors [5].

Because of widespread emergence of resistant Mycobacterium tuberculosis in AIDS patients, the activity of 2,2`-Bipyridyl was studied in vitro [6], which show great promise in chemotherapy of tuberculosis and M. avium infection.

Lee- etal. [7] studied the structure in oriented wet-spun films and fibers for NaDNA-bipyridyl-(ethylenediamine)platinum (II) (Abbreviated [(bipy)Pt(en)]$^{2+}$ complex, to understand the interaction of DNA with this ligand which is of tremendous importance for developing theoretical models of biological process such as

replication and transcription and for the development of new anticancer drugs that bind to DNA. The author found that the attachment of the $[(bipy)Pt(en)]^{2+}$ changed the winding of the DNA double helix. The data also showed that the $[(bipy)Pt(en)]^{2+}$ compound changes the winding of DNA less than the ethidium ion does.

Electrolytic conductivities for copper (II) and manganese (II) sulfates in ethanol+water, ranging in mole fraction of ethanol from 0 to 0.28, have been measured at 298.16K. The limiting molar conductivity λ_0, and association constant K_A, were derived from concentration – conductivity results with the Lee and Wheaton conductivity equation. The results are discussed on the basis of the solvent effect on the conductivity parameters of these salts [8].

Experimental

Chemicals and Reagents:

2,2`-Bipyridyl & KCl (Fluka analar grade) and the transition metal chlorides were reagent grade (BDH) products and were used without any further purification.

Solvents:

Absolute methanol and absolute ethanol were of (BDH) products.

Conductivity water:

Conductivity water was prepared by redistilling distilled water three times with addition of a little amount of potassium permanganate and small pilletes of KOH. The specific conductance of this water was less than 1.2×10^{-6} μSiemens cm^{-1}.

Instruments Used for the Analysis of the Complexes:

BRUKER B.M. 6.is used for measuring the Magnetic susceptibility. A SHIMADZU UV-Visible spectrophotometer (Computerized UV-1650 PC) is used

for measuring electroning spectra .IR mesurment carried out by two instruments : Perkin-Elmer 590B infrared spectrophotometer (200-4000 cm^{-1}) and Thermo Nicolte, Fourier-Transform infrared (FT-IR) spectrophotometer 2002 (500-4000 cm^{-1}). The conductivity measurements were made using (WTW) conductivity meter (model LBR) with a frequency range of 50Hz-3KHz and sensitivity between 10^{-1} and 10^{-9} Siemens.

Preparation of complexes:

In order to prepare the complexes [9,10], Tris $(L)M^{2+}Cl_2$ where L=2,2`-Bipyridyl and $M^{+2}=Mn^{+2}, Co^{+2}, Ni^{+2}$ and Cu^{2+}, a 6mM (0.9371) of the ligand dissolved in a minimum amount of absolute ethanol added to 2mM of each metal chloride dissolved in a minimum amount of absolute ethanol, then refluxed for 1hr on water bath. The crystals of the complex precipitated by evaporating the excess of solvent to a minimum amount and cooling the solution, then a little amount of diethylether added. The product was filtered and washed with diethylether then dried under vacuum and the yield was identified by magnetic suceptibility by applying Faraday Method. The instrument used is of a type BRUKER B.M.6. The electronic spectral measurements were by Shimadzu (computirized) UV-Vis by using quartz cell with diameter (1cm). The spectrum and data were printed by Epson printer at 298.16K. Infrared spectra for the complexes were obtained using a Perkin-Elmer one B infrared spectrophotometer (model 2000). These measurements confirm the structure and the purity of the complexes.

The apparatus used for measuring the condictivity was (WTW)

conductivity meter (model LBR) with a frequency range 50Hz-3KHz, sensitivity between 10^{-1} and 10^{-9} Siemens .

Conductivity Measurements:

Because the conductivity measurements in water, methanol and ethanol are highly sensitive to atmospheric carbon dioxide, the whole system is completely isolated from the outside atmosphere and isolation was maintained during the addition of solute.

The design of the conductance cell and the nitrogen line was the same as that previously used [11].

The cell constant for the conductivity cell was measured using the method of Johnes and Bradshow [12]. Solution of 0.001M and 0.01M KCl was prepared from KCl. The cell constant was checked regularly and found to be $0.05887cm^{-1}\pm0.001$. The electrodes used were of platinum type (WTW). Plastic syringes (1ml) with a fitting plunger were used for injection the stock solution into the conductivity cell. This syringe was found to be more efficient due to the very small losses of weight (by evaporation) due to closer-fitting plunger.

Nitrogen Line:

A nitrogen gas line was used which passed through several traps: a trap of lime water for carbon dioxide absorption, a trap of pyrogallol in KOH for oxygen absorption, another two traps one for concentrated sulphuric acid and the other for calcium chloride for water absorption.

General Procedure:

A general method has been used for measuring the conductance of the elctrolytes. The conductivity cell was dried, weighed empty and kept at a constant temperature $(25°\pm0.01°C)$. Purified nitrogen was passed through the cell then 100ml of solvent was added to the cell and the nitrogen gas was passes again for 10-15min. until the conductance of the solvent was constant, then the cell plus contents where weighed.

A certain amount of the concentrated complex solution was injected into the conductivity cell from a plastic syringe (which was weighed before and after each addition)[13].

Nitrogen gas was passed for several minutes and the conductivity of the solution was measured. This procedure was repeated for about 15-19 times for each run. After all additions where completed, the cell was dried, reweighed to find the weight change which had taken place through the run. This loss was found to be not more than 0.02%.

Results and Discussion

The results of the present work were analyzed by using a conductance equation due to Lee and Wheaton, based upon a model for ions in solution, describes charge transport in solutions containing any number of ionic species of any velancy type. This equation is used to analyze the data for some unsymmetrical transition (2:1) metal complexes, $[Mn(bipy)_3]Cl_2$, $[Co(bipy)_3]Cl_2$, $[Ni(bipy)_3]Cl_2$, and $[Cu(bipy)_3]Cl_2$ in water and methanol, $[Co(bipy)_3]Cl_2$, $[Ni(bipy)_3]Cl_2$, $[Cu(bipy)_3]Cl_2$ in ethanol at 298.16K.

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

$$M^{2+} + X^- \xrightleftharpoons{K_A^{(1)}} MX^+ \qquad \text{............ (1)}$$

$$MX^+ + X^- \xrightleftharpoons{K_A^{(2)}} MX_2 \qquad \text{............ (2)}$$
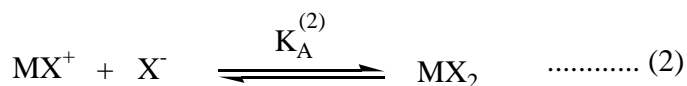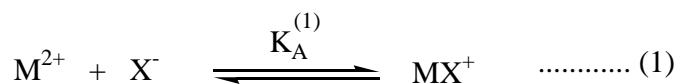
Therefore, three ionic species are present in the solution, which are, M^{2+}, MX^+ and X^-.

$$\therefore \ \Lambda_{equiv.} = \sum_{i=1}^{s} |Zi| mi\lambda i / c \ \ldots\ldots(3)$$

where $\Lambda_{equiv.}$ Is the equivalent conductivity of the solution, s is the

number of ionic species; λi, mi, zi are the equivalent conductance, molar free ion concentration and charge of the ith-species respectively, c is the stoichiometric equivalent concentration. For 2:1 associated salts:

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

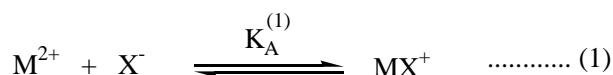where R is the average center to center distance for ion-pairs.

A multi-parameter "least square" curve fitting procedure is used to give the lowest value of the parameter s (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 s (Λ)[14]. In this case:

$$s(\Lambda) \ .) = \{\sum_{n=1}^{NP} (\Lambda_{calcd.} - \Lambda_{expt})^2 / NP\}^{1/2} \qquad \ldots\ldots\ldots (5)$$

(
NP = number of points)

The input data of the computer program are solvent parameters: [T(temp.), D(dielect constant), η(viscosity); the charge Zi and λi^0 for each ionic species, $K_A^{(1)}$ (min.), $K_A^{(2)}$ (max.), $\Delta K_A^{(1)}$ etc., then the experimental data which are the molar concentration and the equivalent conductance.

The following are the results of typical conductivity runs, Tables (1-3)

and plotted in figures (2-4).

The analysis of the experimental results for the complexes in water, methanol and ethanol by LW equation (Table 4) shows that all of the salts are associated to form the new conducting species MX^+:
From table (4) it is found that K_A, the ion pairwise association constants of these complexes, follow the sequences K_A (in water) < K_A (in methanol) < K_A (in ethanol)

$$M^{2+} + X^- \xrightleftharpoons{K_A^{(1)}} MX^+ \qquad \text{............ (1)}$$

according to decreasing the dielectric constant from water $\longrightarrow$ methanol $\longrightarrow$ ethanol, besides in each solvent K_A decreasing in the following way:

$K_A[Mn(bipy)_3]Cl_2 > K_A[Co(bipy)_3]Cl_2 > K_A[Ni(bipy)_3]Cl_2 > K_A[Cu(bipy)_3]Cl_2$.

It means that the charge density of the solvated ion is the highest for Mn complex and decreases from Mn to Cu

495

complex, our results confirm the trend of the crystallographic radii of the bare cations.

According to stokes law, the ionic mobility should be inversely proportional to the solvated ionic radius.

$$\lambda i^0 = 8.2 \times 10^{-9} Z i / \eta r i \ \ldots..(6)$$

where λi^0 is the ionic conductance, Zi is the charge, η viscosity and ri is the radius, our results confirms the trend.

$\lambda^0[Mn(bipy)_3]Cl_2 > \lambda^0[Co(bipy)_3]Cl_2 > \lambda^0[Ni(bipy)_3]Cl_2 > \lambda^0[Cu(bipy)_3]Cl_2$, also it is clear from Table (4) that $\lambda^0 M^{+2}$ of the cation for all complexes follows the sequence as:

$\lambda^0 M^{+2}$ (in water)> $\lambda^0 M^{+2}$ (in methanol)> $\lambda^0 M^{+2}$ (in ethanol)> according to decreasing the dielectric constant of the solvent.

Our results of the distance parameter R show that all the complex electrolytes form solvent separated ion pairs (R is between 28-30A°) in the three solvents. These high values of R indicated that the cations and anions are separated by many solvent molecules since the association was high. The values of $\sigma(\Lambda)$ give an indication of good best-fit values.

Table (1): The molar concentration (M) and the equivalent conductance ($\Lambda_{equiv.}$, Siemens cm^2.equiv.$^{-1}$) of the complexes in water at 298.16K.

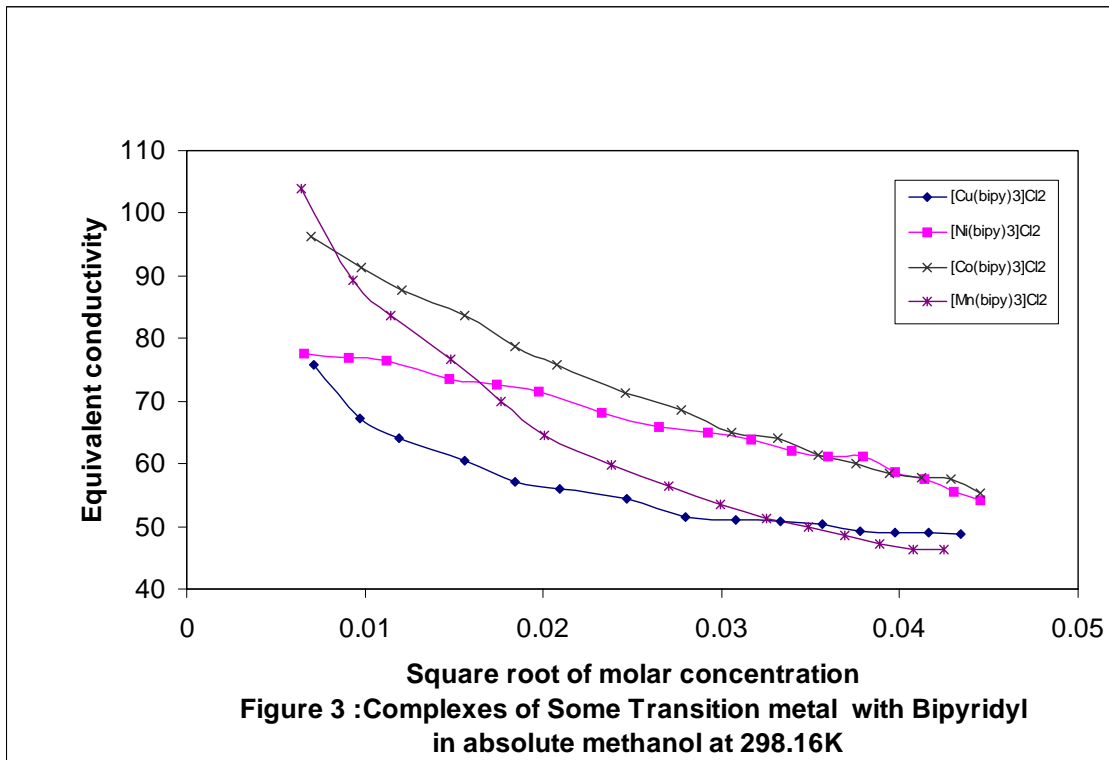| [Mn(bipy)₃]Cl₂		[Co(bipy)₃]Cl₂		[Ni(bipy)₃]Cl₂		[Cu(bipy)₃]Cl₂	
$M \times 10^4$	$\Lambda_{equiv.}$	$M \times 10^4$	$\Lambda_{equiv.}$	$M \times 10^4$	$\Lambda_{equiv.}$	$M \times 10^4$	$\Lambda_{equiv.}$
0.360	170.081	0.466	135.860	0.403	112.047	0.446	127.320
0.720	164.454	0.900	132.124	0.773	108.479	0.937	126.254
1.378	162.546	1.809	129.767	1.849	107.465	1.384	125.352
2.107	162.498	2.726	127.048	2.837	104.226	2.432	124.107
2.798	161.986	3.610	125.754	4.762	103.019	3.441	123.885
4.041	158.613	5.304	124.170	6.498	102.484	4.468	123.271
5.280	157.073	6.921	122.259	8.295	101.879	6.348	123.148
6.468	156.893	8.500	121.188	10.177	101.350	8.228	121.612
7.636	155.012	10.043	120.205	11.914	101.026	10.095	121.320
8.823	154.370	11.532	119.101	13.547	99.989	11.819	121.144
9.947	152.345	13.011	118.862	15.266	99.661	13.500	118.968
11.065	150.731	14.467	118.329	16.579	99.275	15.204	118.693
12.153	143.444	15.893	118.209	18.104	98.105	16.999	118.627
13.219	141.861	17.250	117.699	19.601	97.404	18.718	118.354
14.315	138.943	18.720	117.510	21.215	97.166	20.422	117.403
		20.405	116.960			22.068	117.042
						23.681	117.031
						25.251	116.376

Table (2): The molar concentration (M) and the equivalent conductance ($\Lambda_{equiv.}$, Siemens cm^2.equiv.$^{-1}$) of the complexes in methanol at 298.16K.

[Mn(bipy)$_3$]Cl$_2$		[Co(bipy)$_3$]Cl$_2$		[Ni(bipy)$_3$]Cl$_2$		[Cu(bipy)$_3$]Cl$_2$	
M×10^4	$\Lambda_{equiv.}$	M×10^4	$\Lambda_{equiv.}$	M×10^4	$\Lambda_{equiv.}$	M×10^4	$\Lambda_{equiv.}$
0.417	103.985	0.492	96.263	0.434	77.597	0.504	75.888
0.869	89.375	0.960	91.353	0.830	76.861	0.940	67.303
1.308	83.658	1.450	87.705	1.252	76.428	1.424	63.987
2.202	76.678	2.437	83.632	2.160	73.610	2.439	60.439
3.119	69.936	3.398	78.805	3.034	72.727	3.386	57.092
4.016	64.462	4.327	75.870	3.897	71.533	4.375	56.088
5.685	59.834	6.058	71.387	5.426	68.052	6.089	54.509
7.330	56.404	7.711	68.488	7.023	65.788	7.806	51.391
8.984	53.534	9.327	65.072	8.558	64.943	9.476	51.069
10.587	51.280	10.974	64.031	10.020	63.775	11.087	50.840
12.177	49.898	12.526	61.489	11.503	62.161	12.690	50.386
13.651	48.634	14.062	59.976	12.927	61.191	14.274	49.199
15.120	47.131	15.558	58.549	14.363	61.054	15.799	48.935
16.595	46.331	17.024	57.883	15.768	58.756	17.324	48.930
18.074	46.231	18.363	57.476	17.150	57.446	18.837	48.885
				18.517	55.616		
				19.840	54.117		

Table (3): The molar concentration (M) and the equivalent conductance ($\Lambda_{equiv.}$, Siemens cm^2.equiv.$^{-1}$) of the complexes in ethanol at 298.16K.

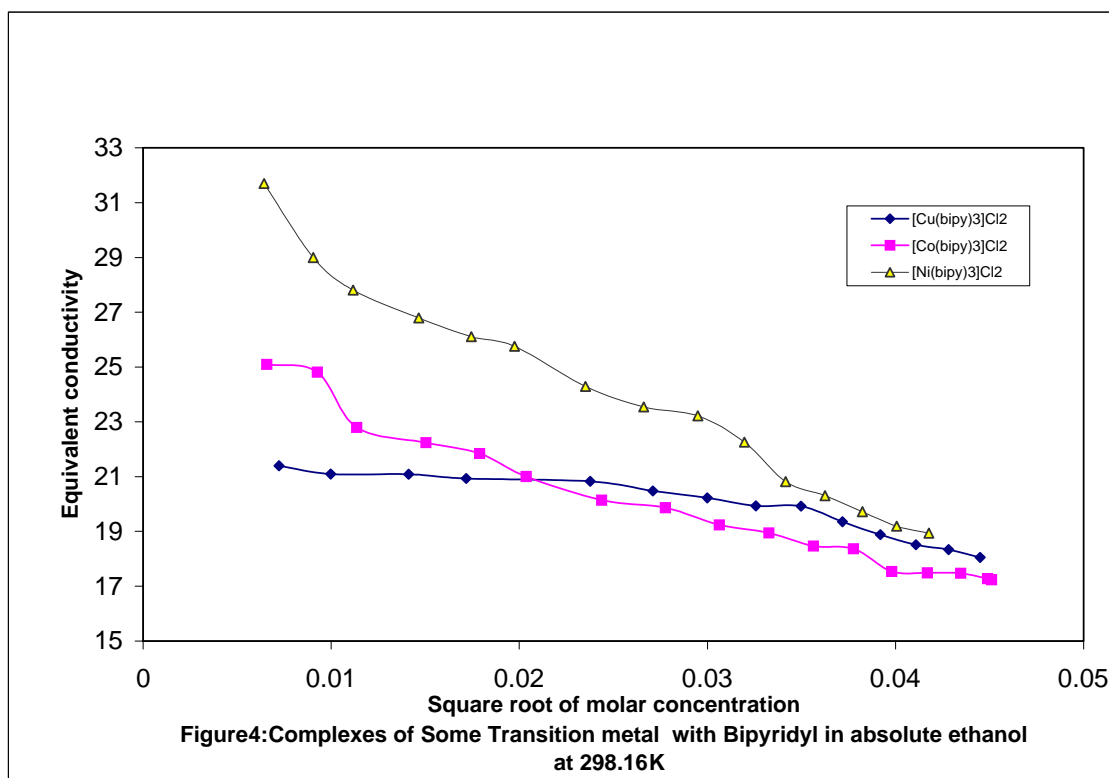| [Co(bipy)$_3$]Cl$_2$		[Ni(bipy)$_3$]Cl$_2$		[Cu(bipy)$_3$]Cl$_2$	
M×10^4	$\Lambda_{equiv.}$	M×10^4	$\Lambda_{equiv.}$	M×10^4	$\Lambda_{equiv.}$
0.432	25.102	0.414	31.702	0.522	21.395
0.856	24.815	0.819	28.996	0.994	21.092
1.291	22.792	1.245	27.809	1.993	21.083
2.259	22.240	2.147	26.792	2.951	20.933
3.202	21.840	3.044	26.108	3.906	20.932
4.147	21.006	3.894	25.758	5.647	20.827
5.945	20.145	5.530	24.296	7.345	20.473
7.714	19.868	7.083	23.541	8.998	20.223
9.385	19.238	8.695	23.222	10.618	19.930
11.062	18.943	10.221	22.260	12.237	19.919
12.691	18.463	11.673	20.818	13.822	19.355
14.270	18.372	13.146	20.305	15.359	18.880
15.842	17.541	14.620	19.720	16.882	18.513
17.385	17.486	16.048	19.194	18.344	18.333
18.888	17.474	17.450	18.942	19.809	18.052
20.351	17.474				

Figure 2 :Complexes of Some Transition metals with Bipyridyl in water at298.16K

Square root of molar concentration
Figure 3 :Complexes of Some Transition metal with Bipyridyl
in absolute methanol at 298.16K

Figure4:Complexes of Some Transition metal with Bipyridyl in absolute ethanol at 298.16K
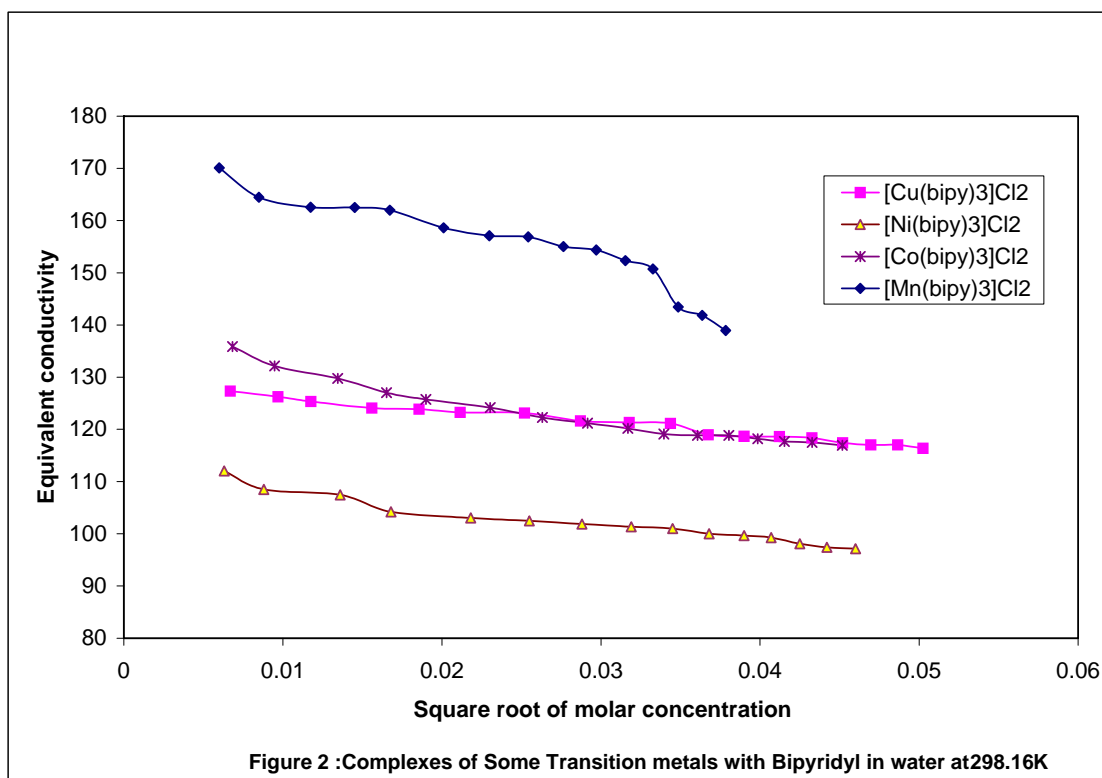
Table (4): The best fit parameters of analysis of conductance data for the complexes, in water at 298.16K

Complex	$K_A^{(1)}$	$K_A^{(2)}$	$\lambda^0 M^{+2}$	$\lambda^0 MX^{+1}$	R/A°	σs(Λ)
[Mn(Bipy)₃]Cl₂	55	<1.0	93	0.01	30	0.1598
[Co(Bipy)₃]Cl₂	54.3	<1.0	58	0.01	28	0.2696
[Ni(Bipy)₃]Cl₂	38.2	<1.0	34.399	0.1	28	0.1890
[Cu(Bipy)₃]Cl₂	18	<1.0	52.4	0.01	28	0.0208

in methanol at 298.16K

Complex	$K_A^{(1)}$	$K_A^{(2)}$	$\lambda^0 M^{+2}$	$\lambda^0 MX^{+1}$	R/A°	σs(Λ)
[Mn(Bipy)₃]Cl₂	1755.4	<1.0	58.5	0.01	29.9	0.2269
[Co(Bipy)₃]Cl₂	599.5	<1.0	57.8	0.1	29.5	0.0710
[Ni(Bipy)₃]Cl₂	189.5	<1.0	30.9	0.1	30.5	0.0594
[Cu(Bipy)₃]Cl₂	273.5	<1.0	17.9	0.9	29.5	0.2706

in ethanol at 298.16K

Complex	$K_A^{(1)}$	$K_A^{(2)}$	$\lambda^0 M^{+2}$	$\lambda^0 MX^{+1}$	R/A°	σs(Λ)
[Mn(Bipy)₃]Cl₂	Insoluble in ethanol					
[Co(Bipy)₃]Cl₂	1000	<1.0	5.0	0.1	29.5	0.1374
[Ni(Bipy)₃]Cl₂	700	<1.0	9.4	0.07	29.5	0.0420
[Cu(Bipy)₃]Cl₂	300	<1.0	1.7	0.01	29.5	0.1355

According to the equation $\Lambda_o = KC^n$, where n is the slope at log Λ_o against log C and K is constant. Table (5) shows the values of each of n and K. It will be seen from this table that the value of n is generally greater for alcohol than for water, it is difficult to say what factors exactly are responsible for this behaviour. It is however, likely that this might partly be due to a difference in the

dielectric constant of water and alcohols, which might affect the interionic forces to different extents. The variation in the values of n and K for different complexes in different solvents does not show any reguallar behaviour. The value of K for all the complexes generally decreases with a decrease in the dielectric constant of the solvents.

Table (5): Values of n and K

Complex	Water	Methyl alcohol	Ethyl alcohol
$[Mn(Bipy)_3]Cl_2$	n=-0.04461 K=109.9375	-0.22433 11.1365	Insoluble
$[Co(Bipy)_3]Cl_2$	n=-0.04073 K=90.8274	-0.15395 22.2444	-0.1067 8.9838
$[Ni(Bipy)_3]Cl_2$	n=-0.04382 K=73.1683	-0.09396 32.5237	-0.13204 8.6601
$[Cu(Bipy)_3]Cl_2$	n=-0.02618 K=99.7739	-0.11789 22.7519	-0.04212 14.5988

References

1- Zeid, M., Wieaer, M., Yoshida, T., Sugio, T., and Nagasawa, T., *Applied and Environmental Microbiology*, 1998, **64(12)**, 4743.

2- Robert, D., Gilard, R.D., and Mecleverty, J.A., "Comprehensive Coordination Chemistry", 1st ed., Pergammon press, Oxford, England, vol. 2, p. 90,1989.

3- Lanfredi, A., Ugozzoli, F., and Canus, A., *J. of Chem. Chrystallo*., 1996, **25(2)**, 141.

4- Mendozadiaz, G., Perezalons, R., and Morenoesparzo, I., *J. of Inorg. Biochem.*, 1996, **64(3)**, 207.

5- Saha, D.K., Padhye, S., Ason, S.E., and Powell, A>K., *Transit. Met. Chem.*, 2003, **28(5)**, 579.

6- Dhople, A.M., Dhople, A.A., and Ibanez, M.A., *Tuber Lung Dis*, 1995, **76(2)**, 136.

7- Lee, S.A., Grim, H., Pohle, W., Scheiding, W., Van Dam, Z., Song, Z., Levitt, M.H., Korolev, N., Szabo, A., and Rupprechi, A., *Physical Review E*, 2000, **26(5)**, 7044.

8- Niazi, M., Hussain, M., *Journal of Chemical and Engineering Data*, 1994, **39(1)**, 48.

9- Palmer R.A. and Piper, t.S., *Inorg. Chem.*, 1966, **5(5)**, 864.

10- Malik, W.U., Bembi, R. and Beardwat, V.K., *J. Indian Chem Soc.*, 1980, **LVII**, 35.

11- Wheaton, R.J., Ph.D. Thesis, University of Surrey Guildford, Surrey,1978.

12- Jones, G. and Bradshow, B.C.J., *J. Amer. Chem. Soc.*, 1933, **55**, 1780.

13- Akrawi, B.A., Ph.D. Thesis University of Surrey Guildford, Surrey,1981.

14- Lee, W.H. and Wheaton, R.J., *J. Chem. Soc. Faraday Trans*, 1978, **II**, 74, 743.