The Electrical Conductivity of a Mixture of Both Symmetrical and Unsymmetrical Complexes in Methanol At 25 °C

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ABSTRACT

We have measured the electrical conductivity of a mixture of both symmetrical and unsymmetrical complexes: $\{[Ni(en)_3](NO_3)_2\}$ + $\{[Co(en)_2Cl_2]Cl\}$ in methanol at 298K. The results are analysed using Lee-Wheaton equation. The equivalent conductivities have been compared with the experimental values at the best-fit values of (R) and they are found to be in a good agreement. Besides, we have calculated the ionic concentration, activity coefficient, transport number for each ion present in the solution.

° **25**

: (2:1) + (1:1)

(298 K) $\{[Ni(en)_3](NO_3)_2\}$ + $\{[Co(en)_2Cl_2]Cl\}$

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(R)

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–   (2:1) + (1:1)

INTRODUCTION

It is well known that Lee & Wheaton (LW) equation gives some information on the ion mobility λ_i^o at infinite dilution, degree of ion association K_A, distance parameter R and the degree of stability of two solvated ions which approach each other to form a complex which is refered to as a solvent separated ion pair (SSIP) (Akrawi 1981).

We have applied this equation on many systems of solution in our research work such as single and mixed electrolytes in different solvents and different temperatures. For mixtures we used it for simple (1:1) + (2:1) electrolytes (Akrawi, 1981), (Akrawi & Khalil, 1992), (Akrawi etal, 1991), (Dawod, 1996) and for a mixture of simple and complex solution (Akrawi & Al-Tamer, 2000). It is now interesting to test the applicability of Lee & Wheaton equation for a mixture of two complexes, which

are{[Ni(en)$_3$](N0$_3$)$_2$}+{[Co(en)$_2$Cl$_2$]Cl} and we have found it is very applicable for also this
kind of a mixture complex solutions.

EXPERIMENTAL

The complex Tris(ethylenediamine)nickel (II) nitrate {[Ni(en)$_3$](NO$_3$)$_2$} was prepared by the method used by (Swink and Atoji, 1973). Ethanolic solution of (2.0 g, 0.005 mole)nickel (II) nitrate was added to a solution containing (0.9 g, 0.015 mole) of ethylenediamine in (10)cm^3 of 85% ethanol. The obtained mixture was then stirred for about 30 minutes and then filtered. The pale violet crystals were washed with a little portion of acetone, dried under vacuum and the yield was 2.8 g (73%), m.p. 285. Trans-dichlorobis(ethylenediamine)cobalt (III) chloride [Co(en)$_2$Cl$_2$]Cl was prepared by the following, (Fernelius, 1946): 12 g. of 10% solution of ethylenediamine were added with stirring to a solution of 13.2 g, 0.02 mole)cobalt chloride 6-hydrate in (10)cm^3 of water in a 100 cm^3 beaker. A vigorous stream of air is passed through the solution for 2 hrs. Then (7cm^3) of concentrated hydrochloric acid is added, and the solution was evaporated on steam bath until a crust forms over the surface (15 cm^3). This solution was allowed to cool and stand overnight before the bright-green square plates of the hydrochloride of the trans form were filtered. The crystals then washed with alcohol and ether, then dried at 110 ^{o}C. At this temperature, the hydrogen chloride was lost, and the crystal crumble to a dull-green powder. The yield was 1.5 g, m.p. 241. For the two complexes C.H.N analysis was used for analysis by using Elemental Analyzer Model 1106. Magnetic susceptibility were also measured by the instrument Bruker B.M.6. A Shimadzu U.V. Vis recording UV-160 Spectrophotometer was used at 25 ^{o}C using quartz cell of 1 cm diameter. I.R spectra for the complexes were obtain using a Perkin Elmer 580 B infra-red Spectrophotometer in the wave number region of 200-400 cm^{-1}. Methanol was purified and dried by using the method of Perrin (Perrin et.al, 1966) with physical properties at 25 ^{o}C: density: 0.78658, dielectric constant: 32 62, viscosity: 0.005445 poise, B.P: 337.76 and specific conductance $< 1 \times 10^{-6} \Omega^{-1}$ cm^{-1}. Gas chromatography type Pye Unicam Pue 4550 was used to determine the water content and other organic impurities of the purified methanol. A water thermostat of type Haake NK22 was used for controlling the temperature of the conductance cell with sensitivity of -$^+$ 0.01 ^{o}C Because methanol is sensitive to carbon dioxide and atmospheric humidity a nitrogen gas line was used which is passed through several traps of limewater, concentrated sulphuric acid and other for calcium chloride.

The conductivity cell has the same design as used before (Akrawi, 1981) with cell constant of 0.0529 cm -1. The electrodes used were platinum electrodes type WTW. Conductivity meter used was of the type WTW model LBR with a frequency range of 50Hz-3KHz and sensitivity between of 10^{-1} and $10^{-9} \Omega^{-1}$ (Siemens or ohm^{-1}). A plastic syringe (1ml) was used for injection the stock solution into the conductivity cell.

For conductivity measurements all stock solutions were generally prepared by weighing, the required amount of each complex was placed in a weighed volumetric flask, then certain amount of the solvent was added to the appropriate volume and the whole content of the flask was then reweighed again. A known amount of methanol was placed in a dried and weighed conductivity cell, and the cell was reweighed again, the cell was thermostated at 25°C for about 15 minutes. To ensure that there is no weight

loss, the cell was weighed again, then the conductance of the solvent was measured. Small amount of the stock solution at 25°C was injected by using a plastic syringe (which was weighed before and after each addition) into the cell. Nitrogen gas was passed for about 2-3 minutes for mixing the solution then the conductance of the solution was measured. This procedure was repeated for about 12 times for each run.

After all additions were completed the cell was dried, reweighed to find the weight change through the run which was found not more than 0.02%.

RESULTS AND DISCUSSION

Table (1) shows the values of the molar stiochiometric concentration of the two electrolyte salts (2:1 & 1:1) and their equivalent conductivity determined experimentally. The equivalent conductivity ($\Lambda_{equiv.}$) at each concentration of mixed electrolyte solution was calculated by the following equation:

$$\Lambda_{equiv.} = 1000\sigma/C_1 + C_2 \quad\text{............................(1)}$$

Where σ is the specific conductance($\Omega^{1-} cm^{-1}$) obtained experimentally. C_1 and C_2 are the equivalent concentration of the 2:1 and 1:1 electrolytes used respectively. (the *LW* equation for mixed electrolytes) is used for analysis the conductance data by using a computer program (Am5). The results are given in Table (1).

They are six ionic species in the mixture: ($MX_2 + YZ$) which are:
(M^{2+}, X^{-1}, MX^{1+}, Y^{1+}, Mz^{1+}, z^{1-}). Since the theoretical equivalent conductance is given by:

$$\Lambda_{equiv.(calc.)} = \sum_{i=1}^{n} |Z_i| m_i \lambda_i / C_n \qquad \text{………................ (2)}$$

Where Z_i is the charge, m_i molar concentration, λ_i equivalent conductance for each ionic species present in the solution, and C_n is the stiochiometric equivalent concentration of electrolytes species. Each of these terms can be calculated by using LW equation for mixed electrolytes. This is done first by calculating the concentration of each ionic species m_i by solution of a polynomial equation for one of the six ionic species, which are derived from the mass and charge balance, and all the ion-association equilibrium (K_A). After obtaining the actual concentration of the six ionic species, the actual ionic strength and hence the six activity coefficients can be obtained. The equivalent conductance λ_i for 1th ionic species were also calculated. For symmetrical electrolyte usually the symmetrical factor is equal to 1/2 , but for such a system of n ions there are n-1 such factors q_p , p =2,n where:

$$q_p = \sum_{i=1}^{S} \overline{w}_i \, t_i \, w_i / (w_i^2 - \alpha_p^2) \qquad \text{………................ (3)}$$

where $\overline{w}_i$,w_i are the mobility and mean mobility of the i_{th} ion respectively and ti is the transference number defined by:

$$t_{i} = n_i.e_i^2 \, \lambda_{i.} \sum_{i=1}^{S} n_i.e_i^2. w_i \qquad \text{………................ (4)}$$

The values of α_p are the solution of the equation:

$$\alpha_p = \sum_{i=1}^{n} t_i \, / \, (w_i^2 - \alpha_p^2) = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

(*Reference* : Akrawi, 1981)

The values of α_p are the solution of this equation and must be found by an interative procedure once the ions have sorted into a sequence of increasing mobility. Thus by obtaining q_p p =2,6 , λ_i can be calculated by using a computer program by varying the distance values R for minimizing the $\sigma_s(\Lambda)$ where:

$\sigma_s(\Lambda) = (\Lambda_{\text{equiv.(calc.)}} - \Lambda_{\text{equiv.(exptl)}})^2$ is used .

It was found eralier (Akrawi, 1981) that the K_A values and the λ_i^{o}'s for single ions and for ion pairs are constant from one system to another, therefore, the input data for the *LW* equation were the temperature, dielectric constant and viscosity of the solvent, charges (z_i),the limiting equivalent conductance for ionic species λ_i^{o}, and the ion-association constant (K_A) for each ion association equilibria, Table(2) shows the charges and λ_i^{o}'s for each ionic species present in the solution for one set of one experiment as an example.

Table 2: The charges and the equivalent conductivity for each ionic species present in the solution.

Mixture: $[Ni(en)_3](NO_3)_2$ + $[Co(en)_2Cl_2]Cl$		
Ionic species	**Charge Z_i**	**Equivalent conductivity λ_i (*)**
$[Ni(en)_3]^{2+}$	+2	55.4
$[NO_3]^{1-}$	-1	61.0
$\{[Ni(en)_3]N0_3\}^{1+}$	+1	1.0
$[Co(en)_2Cl_2]^{1+}$	+1	50.0
$\{[Ni(en)_3]Cl\}^{1+}$	+1	1.0
Cl^{1-}	-1	56.6
(*) References : (Akrawi, 1981) and (Al-Tamer, 1999) .		

Scheme (1): The association equilibria with their ion association constant K_A for the mixture in methanol at 298 K :

$$K_A^{(1)} = \frac{\{[Ni(en)_3]NO_3\}^{1+}}{[Ni(en)_3]^{2+}.(NO_3)^{1-}} * \frac{f\{[Ni(en)_3]NO_3\}}{f[Ni(en)_3]^{2+}.f(NO_3)^{1-}} = 410$$

$$K_A^{(2)} = \frac{\{[Ni(en)_3]Cl\}^{1+}}{[Ni(en)_3]^{2+}.(Cl)^{1-}} * \frac{f[Ni(en)_3]Cl}{f[Ni(en)_3]^{2+}.f(Cl)^{1-}} = 300$$

$$K_A^{(3)} = \frac{\{[Co(en)_2Cl_2]Cl\}}{[Co(en)_2Cl_2]^{1+}.(Cl)^{1-}} * \frac{f\{[Co(en)_2Cl_2]Cl\}}{f[Co(en)_2Cl_2]^{1+}.f(Cl)^{1-}} = 200$$

$$K_A^{(4)} = \frac{\{[Co(en)_2Cl_2]NO_3\}}{[Co(en)_2Cl_2]^{1+}.(NO_3)^{1-}} * \frac{f\{[Co(en)_2Cl_2]NO_3\}}{f[Co(en)_2Cl_2]^{1+}.f(NO_3)^{1-}} = 100$$

Scheme (1) shows the association equilibria and the K_A values for this mixture. The input data to the computer program for this mixture:
temp. =298.16K. , **D** =32.62, η=0.005445 poise, the charges and λ_i^{o} for each ionic species [**Table (2)**]; K_A values (Scheme 1), no. of sets of data and then the sets of concentration. For 2:1 and 1:1 electrolyte solutions and their $A_{\text{equiv.}}$ (found exptl.), each. set as conc1 (for 2:1), conc2 (for 1:1) and $A_{\text{equiv.}}$ Which are given in Table (1).

Table (3) shows a typical example for values of cone., Act. Coeff., Trasport no., λ_i^o for each ionic species present in the mixture at the best fit value of $\sigma_s(\Lambda)$ at the appropriate value of the overall distance parameter R. From this table and under the double line the values of the five roots [number in each parenthesis refers to the value of P (p =1,5) and not to the jth ion] which are $\alpha_p(\alpha_1 \rightarrow \alpha_5)$, q_p as $[Q_{(1)}...Q_{(5)}$ & $SQ_{(p)}]$ where:

$$SQ_{(p)} = \sum_{J=1} \frac{TV(J)}{W^2(J) - \alpha_{(p)}} \quad ....(6)$$

(gives an indication of how much this equation close to zero)

The values of equivalent conductances obtained experimentally and that calculated theoretically with the best-fit value of $\sigma_s(\Lambda)$ at the appropriate value of (R) for each set of data of this mixture are listed in Tables (4)-(8).

For the mixture we have noticed that when the concentration of the complex (1:1) or conc 1 is more than twice of the concentration of the complex (2:1) or conc 2, the values of R obtained are unreliable. So one should deal with these limits of the concentration of the two complex of this kind.In the future we have to extend these limits in this equation and do it as a point of research.

Checking of result taken from **Table (3):**
1. The concentration of the ionic species calculated from the program were checked by applying the mass equation:
$2[M^{2+}] + [MX^{+1}] + [Y^{+1}] + [MZ^{1+}] = [X^{-1}] + [Z^{-1}]$ (result of **Table (3)**)
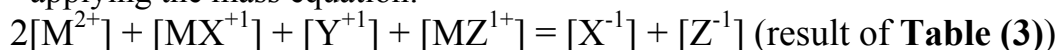
$$\frac{\text{Total conc. of +ve ions}}{4.1626 \times 10^{-3}} = \frac{\text{Total conc. of -ve ions}}{4.1626 \times 10^{-3}}$$

2. For checking the values of transport number of the summation of The six ionic species which must be equal to unity , it found that
$\sum TV_{(1 \rightarrow \sigma)}$ is equal to 1.0004603 .

3. Comparing the stiochimetric ionic concentrations of the mixed salt solution (1:1 & 2:1) with ionic concentration obtained theoretically:

Stoichiometric concentrations:
cone 1 =1.734 x 10^{-3}, cone 2 =1.787 x 10^{-3}
 i.e $[Ni(en)_3]^{2+} = 1.734 \times 10^{-3}$
       $[NO_3]^{1-} = 3.468 \times 10^{-3}$
       $[Co(en)_2Cl_2]^{1+} = 1.787 \times 10^{-3}$
       $[Cl]^{1-} = 1.787 \times 10^{-3}$

Table 4: The values of $\Lambda_{(experimentai)}$ and $\Lambda_{(calculated)}$ with $\sigma_s(\Lambda)$ at the best fit R values
for the mixture.

Experimental A			
$\Lambda_{(exptl.)}$	$\Lambda_{(calc.)}$	$\sigma_s(\Lambda)$	R/A^o
73.954	----	----	----
64.398	64.416	6.513×10^{-4}	86.8
60.626	60.625	5.042×10^{-6}	54.0
56.469	56.573	1.063×10^{-4}	16.8
54.636	54.637	2.442×10^{-7}	5.8
52.999	53.000	3.494×10^{-5}	2.8
51.530	51.526	6.999×10^{-4}	2.8
50.161	50.171	2.457×10^{-2}	2.6
50.142	50.139	8.508×10^{-4}	2.6
48.342	48.329	4.847×10^{-3}	2.0
47.478	47.329	1.206×10^{-2}	2.0
47.118	47.130	5.598×10^{-3}	2.0

Table 5: The values of $\Lambda_{(experimentai)}$ and $\Lambda_{(calculated)}$ with $\sigma_s(\Lambda)$ at the best fit R values
for the mixture.

Experimental B			
$\Lambda_{(exptl.)}$	$\Lambda_{(calc.)}$	$\sigma_s(\Lambda)$	R/A^o
79.039	----	----	----
68.543	----	----	----
64.017	64.047	3.479×10^{-3}	67
58.225	58.215	3.878×10^{-3}	28
55.432	55.418	2.667×10^{-3}	5.6
53.456	53.439	4.971×10^{-3}	2.0
50.626	50.802	1.868×10^{-1}	2.0
49.311	49.417	5.814×10^{-1}	2.0
47.959	47.799	4.788×10^{-1}	2.0
47.324	47.200	3.812×10^{-1}	2.0
45.057	45.189	5.964×10^{-2}	2.0
43.732	43.805	2.751×10^{-2}	2.0

Table 6: The values of $\Lambda_{(experimentai)}$ and $\Lambda_{(calculated)}$ with $\sigma_s(\Lambda)$ at the best fit R values for the mixture.

Experimental C			
$\Lambda_{(exptl.)}$	$\Lambda_{(calc.)}$	$\sigma_s(\Lambda)$	R/A^o
80.365	----	----	----
75.731	----	----	----
69.968	----	----	----
66.282	----	----	----
62.204	62.228	9.889×10^{-3}	42.4
59.226	59.231	7.057×10^{-4}	31.6
56.762	56.758	1.605×10^{-6}	22.0
54.853	54.828	7.231×10^{-4}	14.0
52.972	52.959	2.699×10^{-4}	8.2
50.734	50.597	5.893×10^{-3}	4.4
48.161	48.093	3.953×10^{-2}	2.0
45.965	45.832	9.087×10^{-2}	2.0

Table 7: The values of $\Lambda_{(experimentai)}$ and $\Lambda_{(calculated)}$ with $\sigma_s(\Lambda)$ at the best fit R values for the mixture.

Experimental D			
$\Lambda_{(exptl.)}$	$\Lambda_{(calc.)}$	$\sigma_s(\Lambda)$	R/A^o
82.370	----	----	----
79.648	----	----	----
77.079	----	----	----
73.647	----	----	----
71.597	----	----	----
70.263	----	----	----
68.612	68.704	1.678×10^{-3}	40.4
66.884	66.712	2.204×10^{-2}	35.6
66.118	66.305	2.187×10^{-2}	32.4
64.774	64.587	1.238×10^{-2}	29.6
62.836	62.779	2.949×10^{-3}	26.8
61.816	61.830	1.983×10^{-4}	25.0

Table 8: The values of $\Lambda_{(experimentai)}$ and $\Lambda_{(calculated)}$ with $\sigma_s(\Lambda)$ at the best fit R values for the mixture.

Experimental E			
$\Lambda_{(exptl.)}$	$\Lambda_{(calc.)}$	$\sigma_s(\Lambda)$	R/A^o
63.921	----	----	----
63.074	----	----	----
61.778	----	----	----
60.215	----	----	----
59.310	----	----	----
58.228	----	----	----
57.590	----	----	----
56.180	56.300	7.469×10^{-4}	26.0
54.981	54.789	1.009×10^{-2}	21.6
54.444	54.502	2.848×10^{-3}	18.4
53.912	54.018	4.010×10^{-4}	16.4
52.997	52.991	1.525×10^{-5}	14.0

Results obtained theoretically:

$[Ni(en)_3]^{2+}$ $[Ni(en)_3]^{2+} + \{[Ni(en)_3NO_3]\}^{1+} + \{[Ni(en)_3]Cl\}^{1+} = 1.734 \times 10^{-3}$

$[NO_3]^{1-} = [NO_3]^{1-} + [Ni(en)_3NO_3]^{1+} = 3.468 \times 10^{-3}$

$[Co(en)_2Cl_2]^{1+} = 1.759 \times 10^{-3}$

$[Cl]^{1-} = [Cl]^{1-} + [Ni(en)_3]Cl^{1+} = 1.777 \times 10^{-3}$

It can be seen from this check that there is a good agreement between the stiochiometric concentrations and that obtained theoretically.

From the above checking we can say that *LW* equation is very applicable to such type of mixture complex solutions.
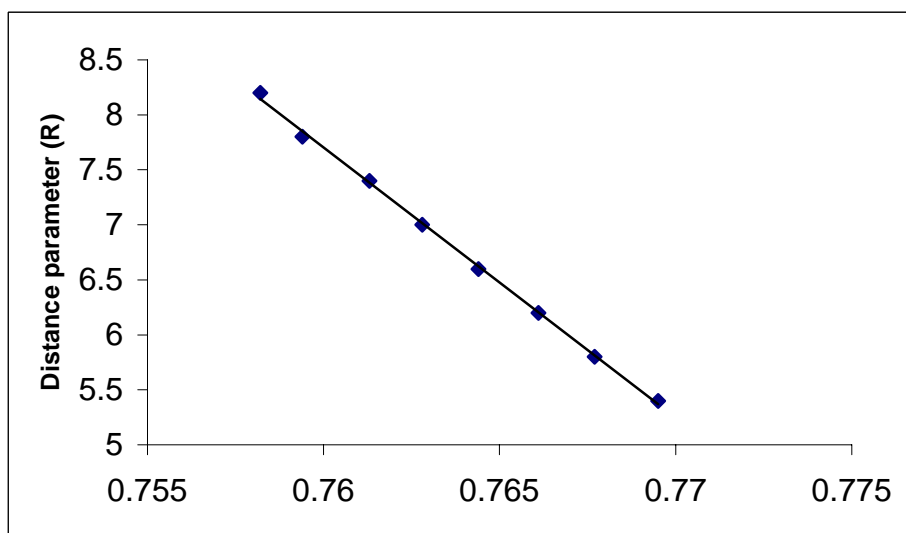
Effect of distance parameter on concentration:

In order to investigate the variation of the distance parameter (R), **Figure (1)** shows the effect of (R) at the best values of as (Λ) of the concentration ratio of $[Ni(en)_3]^{2+} / [Co(en)_2Cl_2]^{1+}$ and $[Ni(en)_3]^{2+} / [Cl]^{1-}$ of set (9) experimental C.

It can be seen from this figure that the values of R decrease with increasing the concentration ration. This can be explained by the similar tendency of ion-association for $[NO_3]^{-1}$ and $[Cl]^{1-}$, since the concentration of $[Co(en)_2Cl_2]^{1+} = [Cl]^{l-}$.

Figure (2) shows the relation between the standard deviation $\sigma_s(\Lambda)$ and the distance parameter (R) for set number (9), experiment (C) as an example. It is clear that the values of $\sigma_s(\Lambda)$ decrease as R increases reaching the best fit value at R = 8.2 A^o and $\sigma_s(\Lambda) = 2.399 \times 10^{-4}$ as we have mentioned before.
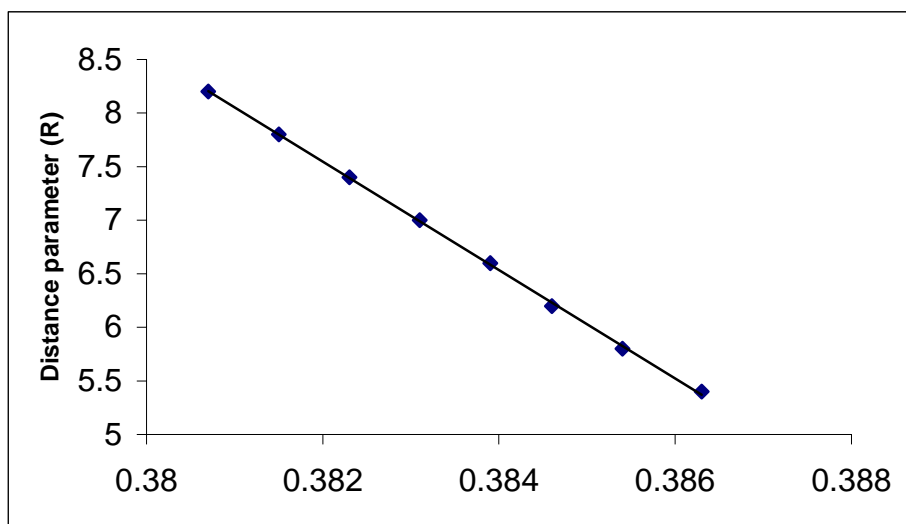
Ionic concentration ratio of $[Ni(en)_3]^{2+} / [Co(en)_2Cl_2]^{1+}$

(A)

Ionic concentration ratio of $[Ni(en)_3]^{2+} / [Cl]^{1-}$

(B)

Fig.1: The plot of the distance parameter against ionic concentration ratio for the mixture at 25^oC:
(A) for $[Ni(en)_3]^{2+} / [Co(en)_2Cl_2]^{1+}$, (B) for $[Ni(en)_3]^{2+} / [Cl]^{1-}$.

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