

An Application of Lee-Wheaton Conductance Equation to Mixed (Symmetrical and Asymmetrical) Electrolytes in Methanol at Two Different Temperatures

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ABSTRACT

The applicability of (LW) Lee-Wheaton equation is tested for three mixtures I- [Ni(phen)₃]Cl₂ + KBr, II-[Co(phen)₃]Cl₂ + KBr at 298.16K and III-[Co(phen)₃]Cl₂ + KBr at 308.16K. From the association constant K_A and the ionic mobility λ° data for appropriate single electrolytes, detail information about the conductivity parameters are interpreted which have been affected by varying the temperature. A very good agreement is obtained between the experimental and calculated data. It is also found that (LW) equation is applicable to the salts and complexes, at different temperatures under studying.

KBr + -2	KBr + [Ni(phen) ₃]Cl ₂ -1	-	-
308.16	KBr + [Co(phen) ₃]Cl ₂ -3	298.16	[Co(phen) ₃]Cl ₂

INTRODUCTION

The conductance of mixed electrolyte solution can be derived from the association constant (K_A) and the equivalent conductance (Λ) data for the appropriate single electrolytes and used to determine the concentration and conductance of all species present in the solution. The molar conductances of the mixture are calculated theoretically, and the results are compared with the experimental values.

The conductivity of the mixed electrolyte solutions involving symmetrical and asymmetrical electrolytes ($\text{BaBr}_2+\text{NaCl}$), (BaBr_2+KCl), $\text{SrCl}_2 + \text{KI}$, ($\text{Sr}(\text{NO}_3)_2+\text{NaBr}$) and $\text{SrCl}_2+\text{NaBr}$) have been measured in methanol at 25°C (Lee et al., 1978) (Akrawi et al., 1992). Electrical conductivities of the three different mixtures have been measured as (2:1+1:1) which are I- $\{[\text{Ni}(\text{en})_3]\text{Cl}_2+\text{KBr}\}$, II- $\{[\text{Cu}(\text{en})_3]\text{Cl}_2 + \text{NaNO}_3\}$ and III- $\{[\text{Co}(\text{en})_3]\text{Cl}_2+\text{BaBr}_2\}$ in methanol at 298.16K, for each ionic species in the solution, the ionic concentration, activity coefficient, transport number and equivalent conductivity at the best fit value of R have been calculated theoretically by using Lee-Wheaton equation for mixed electrolytes (Al-Tamer, 1999) in methanol at 298.16K, the electrical conductivity of a mixture of both symmetrical and asymmetrical complexes I- $\{[\text{Ni}(\text{en})_3](\text{NO}_3)_2\}+\{([\text{Co}(\text{en})_3]\text{Cl}_2)\text{Cl}\}$ have been measured and the results were analysed using Lee-Wheaton equation. The equivalent conductivities have been compared with the experimental values at the best fit values of (R), ionic concentration, activity coefficient and transport number for each ion present in the solution have been calculated (Akrawi, 2002).

EXPERIMENTAL

In order to prepare the desired complexes (Malik et al., 1986) $[\text{Ni}(\text{phen})_3]\text{Cl}_2$ and $[\text{Co}(\text{phen})_3]\text{Cl}_2$, a mixture of 6mM of 1, 10-phenanthroline in 10 cm^3 of ethanol and 2mM of $\text{NiCl}_2.6\text{H}_2\text{O}$ or $\text{CoCl}_2.6\text{H}_2\text{O}$ in 30 cm^3 of deionized water was refluxed for about 45 min., on a water bath. On cooling and adding excess of absolute ethanol the complex was precipitated, filtered then washed with ice-cold 50% ethanol. The crude product was dissolved in a minimum quantity of hot 50% ethanol and then recrystallized by slow cooling to 0°C followed by addition of excess absolute ethanol. The product was dried under vacuum over anhydrous calcium chloride.

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

Magnetic, electronic spectral (UV), infrared spectra measurements used for analysis of the complexes and also gas chromatography was used to determine water content and other organic impurities of the purified methanol as a solvent. Conductivity measurements were made using a WTW conductivity meter (Model LBR) with frequency range of 50Hz-30KHz and sensitivity between 10^{-1} and 10^{-9}S .

For conductivity measurement in non-aqueous solvent such as methanol which is highly sensitive to atmospheric pressure and carbon dioxide, a special design is required to ensure complete isolation of the system from the outside atmosphere and maintain this 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 $\pm 0.1^\circ\text{C}$ using water circulating ultrathermostat type VHS B radiometer. Purified nitrogen was passed through a known volume of methanol until the conductance of the solvent was constant. Additions of solute were then made. The design of the conductance cell and the nitrogen line was the same as that previously used by Wheaton (Wheaton, 1978). The cell constant for the conductivity cell was measured using the methods of Jones and Bradshaw (Jones et al., 1933). 0.01M KCl solution was prepared from KCl (BDH reagent) recrystallized three times from conductivity water and then dried at 760 Torr and 500°C for 10 hr. The cell constant was checked regularly and found to be 0.0554 cm^{-1} .

A general method has been used for measuring the conductance of mixed electrolytes. The conductivity cell was washed first with conductivity water and then with methanol, then dried, weight empty and kept at constant temperature. Purified nitrogen gas was passed through the cell. 100ml of purified methanol were added and nitrogen gas was passed for 10-15 min. until the conductance of the solvent was constant, whereupon the cell plus the contents were weighed. A certain amount of KCl solution was injected into the conductivity 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. Small increment of known amount of the complex solution were then added (generally 10 additions) and the conductivity of the mixed solution was measured after each addition. After all additions have been made, 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

It was found that Lee-Wheaton equation is applicable to the interpretation of conductance data for simple (2:1 + 1:1) in methanol at 298.16K (Akrawi et al., 1991). This equation is used for complete analysis of mixed symmetrical and asymmetrical electrolyte at different temperatures. The following mixtures are chosen for this study.

I- {[Ni(phen)₃]Cl₂ + KBr}, II- {[Co(phen)₃]Cl₂ + KBr} in methanol at 298.16K and III- {[Co(phen)₃]Cl₂ + KBr} in methanol at 308.16K.

The equivalent conductivity ($\Lambda_{\text{equiv.}}$) at each concentration of each electrolyte solution was calculated by the following equation:

$$(\Lambda_{\text{equiv.}}) = 1000\sigma / C_1C_2 \quad \dots\dots\dots(1)$$

Where σ is the specific conductance obtained experimentally, C_1 and C_2 are the equivalent concentration of 2:1 and 1:1 electrolytes used respectively. Table (1) shows the values of the equivalent conductivity and concentrations of the two electrolytes salts (2:1 and 1:1) determined experimentally.

The Lee-Wheaton equation (LW) for symmetrical electrolytes is used for analyses of the conductance data for mixed electrolyte solutions (I, II and III) using a computer program (Amtest). For each mixture ($\text{MX}_2 + \text{NY}$) there are six ionic species (M^{+2} , X^{-1} , MX^{+1} , N^{+1} , MY^{+1} and Y^{-1}) where X^{-1} and Y^{-1} are halide (chloride) ions. The theoretical equivalent conductance is given by the following equation.

$$\Lambda_{\text{equiv.}} = \sum_{i=1}^n |Z_i| m_i \lambda_i / \sum_n C_n \quad \dots\dots\dots(2)$$

Where Z_i is the charge, m_i molar concentration, λ_i equivalent conductivity for each ionic species present in the solution and C_n is the stoichiometric equivalent concentration of electrolyte species n . It was found earlier that K_A and λ_s° value for single ion and for ion-pair are constant from one system to another for symmetrical, asymmetrical and mixed electrolytes by using LW equation, therefore the value of K_{As} and λ_s° in Table (2) and (3) were taken from (Akrawi thesis) and from the present work.

The input data of computer program (Amtest) are: solvent parameters (T , D , η), charges Z_i and limiting conductivities λ_i° for each ionic species. $K_{\text{association}}$ for each ion

Table 1: The equivalent conductivities ($\Omega^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$) with the molar concentration for $[\text{Ni}(\text{phen})_3]\text{Cl}_2$ (conc. 1, $\text{M} \times 10^{-4}$ and KBr (conc. 2, $\text{M} \times 10^{-3}$) in methanol at 298.16K.

Experiment A			Experiment B			Experiment C			Experiment D			Experiment E		
Conc. 1	Conc. 2	$\Lambda_{\text{equiv.}}$	Conc. 1	Conc. 2	$\Lambda_{\text{equiv.}}$	Conc. 1	Conc. 2	$\Lambda_{\text{equiv.}}$	Conc. 1	Conc. 2	$\Lambda_{\text{equiv.}}$	Conc. 1	Conc. 2	$\Lambda_{\text{equiv.}}$
1.937	0.977	90.995	1.918	1.938	91.161	1.905	2.871	91.416	1.882	3.808	89.131	1.874	4.707	89.243
3.848	0.968	86.487	3.803	1.919	87.250	3.780	2.845	88.746	3.732	3.775	86.172	3.718	4.666	85.791
5.726	0.959	83.291	5.658	1.902	84.620	5.620	2.819	86.688	5.549	3.743	83.154	5.528	4.626	83.694
7.567	0.951	80.849	7.473	1.884	82.717	7.428	2.793	83.910	7.330	3.712	79.547	7.307	4.586	81.248
9.375	0.943	77.817	9.258	1.867	80.395	9.198	2.769	82.616	9.080	3.681	76.954	9.060	4.547	79.104
11.153	0.935	76.463	11.010	1.850	79.545	10.942	2.744	80.576	10.807	3.651	74.698	10.785	4.509	77.052
12.896	0.927	75.757	12.733	1.834	77.652	12.651	2.720	78.562	12.510	3.621	72.726	12.479	4.471	75.478
14.615	0.919	75.396	14.421	1.817	76.131	14.333	2.696	77.444	14.179	3.591	71.013	14.144	4.434	74.164
16.302	0.911	73.902	16.076	1.802	75.343	15.986	2.673	76.233	15.815	3.563	69.105	15.780	4.398	74.004
17.963	0.904	73.271	17.709	1.786	74.192	17.610	2.650	74.757	17.433	3.534	67.785	17.384	4.362	740.637
19.597	0.896	71.877	19.313	1.770	73.332	19.205	2.628	73.909	19.204	3.503	66.019	18.971	4.327	69.548
21.215	0.889	70.917	20.886	1.755	72.725	20.771	2.606	72.126	20.764	3.475	64.869	20.530	4.292	69.242

association equilibrium with their values as shown in Table (2) and (3); for one mixture as an example and the experimental data which are the stoichiometric concentration of the two electrolytes solution within the experimentally determined equivalent conductivities calculated from equation (1).

Table 2: The values of the charges and equivalent conductivity for each ionic species in the solution in methanol at 298.16K.

Mixture I			Mixture II		
Ionic species	Z _i	λ _i ^o	Ionic species	Z _i	λ _i ^o
[Ni(phen) ₃] ⁺²	+2	49	[Co(phen) ₃] ⁺²	+2	60
Cl ⁻¹	-1	52.36	Cl ⁻¹	-1	52.36
{[Ni(phen) ₃]Cl} ⁺¹	+1	1.0	{[Co(phen) ₃]Cl} ⁺¹	+1	1.0
K ⁺¹	+1	52.64	K ⁺¹	+1	52.64
{[Ni(phen) ₃]Br} ⁺¹	+1	1.0	{[Co(phen) ₃]Cl} ⁺¹	+1	1.0
Br ⁻¹	-1	56.5	Br ⁻¹	-1	56.5

Table 3: The association equilibria with their ion association constant K_A for mixtures I and II in methanol at 298.16K, and mixture III at 308.16K.
Mixture I:

$$K_A^{(1)} = \frac{\{[Ni(phen)_3]Cl\}^{+1} \cdot f \{[Ni(phen)_3]Cl\}^{+1}}{[Ni(phen)_3]^{+2}(Cl^{-1}) \cdot f [Ni(phen)_3]^{+2} \cdot f(Cl^{-1})} = 202$$

$$K_A^{(2)} = \frac{\{[Ni(phen)_3]Br\}^{+1} \cdot f \{[Ni(phen)_3]Br\}^{+1}}{\{[Ni(phen)_3]\}^{+2} (Br^{-1}) \cdot f \{[Ni(phen)_3]\} \cdot f(Br^{-1})} = 150$$

$$K_A^{(3)} = \frac{(KBr)}{(K^{+1})(Br^{-1})} \cdot \frac{f(KBr)}{f(K^{+1}) \cdot f(Br^{-1})} = 30$$

$$K_A^{(4)} = \frac{(KCl)}{(K^{+1})(Cl^{-1})} \cdot \frac{f(KCl)}{f(K^{+1}) \cdot f(Cl^{-1})} = 20$$

To calculate Λ_{equiv.} theoretically equation (2) should be used. The values of m_i and λ_i for each ionic species can be calculated by solving a polynomial equation for the three mixtures. The polynomial equation that was derived from the mass and charge balance together with the various K_A equilibria give the values of the concentrations of the six ionic species, their activity coefficient the transport number of each ionic species can be calculated.

The computer program (Amtest) calculate the minimum standard deviation σ_s(Λ) between Λ_{equiv.} (found experimentally) using equation (2) and Λ_{equiv.} (Calculated by using equation (1) as σ_s(Λ) = (Λ_{Cal.} - Λ_{experi.})³ at the appropriate (R) values (R; the over all distance parameter), where R is only the variable parameter, for each set of the data of

each experiment done. Tables (4– 6) show the results of the analysis of some typical examples of mixtures (I, II and III) where each table show the concentration (for all ionic species present), the activity coefficient, transport number, the equivalent conductance and the best fit data at the appropriate values.

Table 4: Results of the set number (9) from mixtures I experiment (B) where conc. 1 $[\text{Ni}(\text{phen})_3]\text{Cl}_2 = 16.07629 \times 10^{-4} \text{ M}$, conc. 2 (KBr) = $1.80205 \times 10^{-3} \text{ M}$, $\Lambda_{\text{equiv.}} = 75.34360$ in methanol at 298.16K.

	$[\text{Ni}(\text{phen})_3]^{+2}$	$[\text{Cl}^{-1}]$	$\{[\text{Ni}(\text{phen})_3]\text{Cl}\}^{+1}$	$[\text{K}^{+1}]$	$\{[\text{Ni}(\text{phen})_3]\text{Br}\}^{+1}$	$[\text{Br}^{-1}]$
Concentration (M)	5.239×10^{-4}	2.956×10^{-3}	1.829×10^{-4}	1.693×10^{-3}	9.010×10^{-4}	8.680×10^{-4}
Activity coefficient	5.847×10^{-4}	8.744×10^{-1}	8.744×10^{-1}	8.744×10^{-1}	8.744×10^{-1}	8.744×10^{-1}
Transport number	1.419×10^{-1}	4.496×10^{-1}	1.063×10^{-4}	2.587×10^{-1}	5.236×10^{-4}	1.417×10^{-1}
$AA_{(j)} = W_i^2$	2.511	11.472	1.674×10^{-4}	11.594	1.674×10^{-4}	13.216
$\lambda_{(j)}$	9.369	78.717	2.922	40.514	2.922	80.826

Table 5: Results of set number (9) from mixture II experiment (D) where conc. 1 $[\text{Co}(\text{phen})_3]\text{Cl}_2 = 16.7796 \times 10^{-4} \text{ M}$, conc. 2 (KBr) = $1.92011 \times 10^{-3} \text{ M}$, $\Lambda_{\text{equiv.}} = 75.86476$ in methanol at 298.16K.

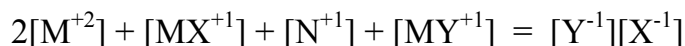
	$[\text{Co}(\text{phen})_3]^{+2}$	$[\text{Cl}^{-1}]$	$\{[\text{Co}(\text{phen})_3]\text{Cl}\}^{+1}$	$[\text{K}^{+1}]$	$\{[\text{Co}(\text{phen})_3]\text{Br}\}^{+1}$	$[\text{Br}^{-1}]$
Concentration (M)	4.458×10^{-4}	3.001×10^{-3}	2.725×10^{-4}	1.799×10^{-3}	9.600×10^{-4}	9.226×10^{-4}
Activity coefficient	5.5869×10^{-1}	8.753×10^{-1}	8.753×10^{-1}	8.753×10^{-1}	8.753×10^{-1}	8.753×10^{-1}
Transport number	1.496×10^{-1}	4.395×10^{-1}	1.524×10^{-6}	2.649×10^{-1}	5.371×10^{-5}	1.458×10^{-1}
$AA_{(j)} = W_i^2$	3.766	11.472	1.674×10^{-6}	11.595	1.674×10^{-6}	13.356
$\lambda_{(j)}$	12.205	81.148	3.901	41.127	3.901	83.312

Table 6: Results of set number (9) from mixture III experiment (A) where conc. 1 $[\text{Co}(\text{phen})_3]\text{Cl}_2 = 17.62710 \times 10^{-4} \text{ M}$, conc. 2 (KBr) = $5.46245 \times 10^{-4} \text{ M}$, $\Lambda_{\text{equiv.}} = 69.49743$ in methanol at 308.16K.

	$[\text{Co}(\text{phen})_3]^{+2}$	$[\text{Cl}^{-1}]$	$\{[\text{Co}(\text{phen})_3]\text{Cl}\}^{+1}$	$[\text{K}^{+1}]$	$\{[\text{Co}(\text{phen})_3]\text{Br}\}^{+1}$	$[\text{Br}^{-1}]$
Concentration (M)	1.060×10^{-3}	3.074×10^{-3}	4.286×10^{-4}	5.201×10^{-3}	2.731×10^{-4}	2.682×10^{-4}
Activity coefficient	3.291×10^{-1}	7.574×10^{-1}	7.574×10^{-1}	7.574×10^{-1}	7.574×10^{-1}	7.574×10^{-1}
Transport number	4.036×10^{-1}	4.711×10^{-1}	1.166×10^{-2}	8.011×10^{-1}	1.486×10^{-4}	4.485×10^{-2}
$AA_{(j)} = W_i^2$	5.126	13.292	4.184×10^{-5}	13.424	1.674×10^{-6}	15.827
$\lambda_{(j)}$	45.881	48.819	5.885	48.814	5.422	53.258

The following Tables (7–9) show the values of $\Lambda_{\text{equiv. (experi.)}}$ and $\Lambda_{\text{experi. (calc.)}}$ with $\sigma_s(\Lambda)$ at the best fit R values for some typical examples from mixtures (I, II, and III respectively) where (R) represent the average distance between the different ionic species present in the solution, and not between any specific pair.

The mass balance equation is used in order to check the concentration of the ionic species present in each mixture. The total concentration of the positive ionic species should be equal to the total concentration of the negative ions in the mixed electrolytes i.e:



Example is shown as following from three mixtures:

Mixture	Experi.	Set No.	Total Concentration of +ve ion	Total Concentration of -ve ion
I	C	12	5.0349×10^{-3}	5.0359×10^{-3}
II	C	5	3.3438×10^{-3}	3.3422×10^{-3}
III	A	9	2.5562×10^{-3}	2.5537×10^{-3}

Another check is that for the total transport number should be equal to unity ($\sum \text{TV}_i = 1$) as an example of each mixture.

Mixture	Experi.	Set No.	Total Transport Number
I	B	9	0.9993
II	D	9	0.9999
III	C	5	0.9998

In order to investigate the variation of distance parameter R, Figure (1) shows the effect of R at the best fit values of $\sigma_s(\Lambda)$ on the concentration ratio of $[\text{Co(phen)}_3]^{+2} / [\text{K}^+]$ and $[\text{Co(phen)}_3]^{+2} / [\text{Br}^{-1}]$ for each set of data.

Table 7: The values of Λ (experimental) and Λ (calculated) with $\sigma_s(\Lambda)$ at the best fit values for the mixture I $[\text{Ni}(\text{phen})_3]\text{Cl}_2 + \text{KBr}$ experiments (A) and (B) at 298.16K.

Experiment (A)				Experiment (B)			
$\Lambda_{(\text{exptl.})}$	$\Lambda_{(\text{cacl.})}$	$\sigma_s(\Lambda)$	R/A°	$\Lambda_{(\text{exptl.})}$	$\Lambda_{(\text{cacl.})}$	$\sigma_s(\Lambda)$	R/A°
83.791	83.795	1.543×10^{-5}	73.40	79.545	79.460	7.129×10^{-3}	46.40
80.849	80.775	5.451×10^{-3}	56.80	77.652	77.720	4.610×10^{-3}	40.60
77.817	77.782	1.253×10^{-3}	46.80	76.131	76.149	3.051×10^{-4}	37.10
76.463	76.493	9.027×10^{-4}	41.00	75.343	75.343	2.028×10^{-7}	34.28
75.757	75.821	4.160×10^{-3}	37.60	74.192	74.192	9.443×10^{-3}	32.00
75.398	75.401	7.399×10^{-6}	33.92	73.332	73.336	1.604×10^{-5}	29.72
73.902	73.919	2.693×10^{-4}	31.96	72.725	72.748	2.768×10^{-4}	27.76
73.271	73.281	1.194×10^{-4}	30.66				
71.877	71.925	2.289×10^{-3}	28.00				
70.917	70.936	3.561×10^{-4}	26.48				

Table 8: The values of Λ (experimental) and Λ (calculated) with $\sigma_s(\Lambda)$ at the best fit values for the mixture II $[\text{Co}(\text{phen})_3]\text{Cl}_2 + \text{KBr}$ experiments (A) and (B) at 298.16K.

Experiment (A)				Experiment (B)			
$\Lambda_{(\text{exptl.})}$	$\Lambda_{(\text{cacl.})}$	$\sigma_s(\Lambda)$	R/A°	$\Lambda_{(\text{exptl.})}$	$\Lambda_{(\text{cacl.})}$	$\sigma_s(\Lambda)$	R/A°
86.163	86.239	5.720×10^{-3}	90.00	84.829	84.839	1.039×10^{-4}	72.80
82.679	82.609	4.834×10^{-3}	63.80	82.182	82.273	8.362×10^{-3}	58.20
79.502	79.452	2.496×10^{-3}	49.00	80.408	80.360	2.265×10^{-3}	48.20
77.466	77.543	5.796×10^{-3}	41.60	79.662	79.723	3.679×10^{-3}	43.40
75.191	75.176	2.203×10^{-4}	37.00	78.324	78.361	1.406×10^{-3}	39.40
72.721	72.719	3.087×10^{-6}	31.60	77.749	77.825	3.186×10^{-3}	37.20
70.883	70.888	3.334×10^{-5}	30.60	76.798	76.868	4.947×10^{-3}	35.40
69.497	69.463	1.124×10^{-3}	29.00	76.052	76.067	2.255×10^{-4}	32.92
68.434	68.387	2.835×10^{-3}	28.13				

Table 9: The values of Λ (experimental) and Λ (calculated) with $\sigma_s(\Lambda)$ at the best fit values for the mixture III $[\text{Co}(\text{phen})_3]\text{Cl} + \text{KBr}$ experiments (A) and (B) at 308.16K.

Experiment (A)				Experiment (B)			
$\Lambda_{(\text{exptl.})}$	$\Lambda_{(\text{cacl.})}$	$\sigma_s(\Lambda)$	R/A°	$\Lambda_{(\text{exptl.})}$	$\Lambda_{(\text{cacl.})}$	$\sigma_s(\Lambda)$	R/A°
86.163	86.088	5.700×10^{-3}	68.2	85.513	84.839	1.721×10^{-3}	60.0
82.679	82.706	7.341×10^{-3}	38.0	83.207	82.273	6.330×10^{-3}	44.8
79.502	79.518	2.461×10^{-4}	25.5	81.108	80.360	1.661×10^{-3}	32.8
77.466	77.480	1.813×10^{-4}	20.0	76.427	79.723	6.455×10^{-6}	24.4
75.191	75.219	8.086×10^{-4}	14.4	74.930	78.361	3.086×10^{-4}	21.0
72.721	72.699	4.619×10^{-4}	10.4	73.336	77.825	1.860×10^{-3}	18.0
70.883	70.828	7.980×10^{-3}	9.0	71.673	76.868	1.655×10^{-3}	15.4
69.497	69.504	5.369×10^{-5}	8.8	71.056	76.067	7.548×10^{-3}	15.2
68.434	68.494	3.505×10^{-3}	8.6				

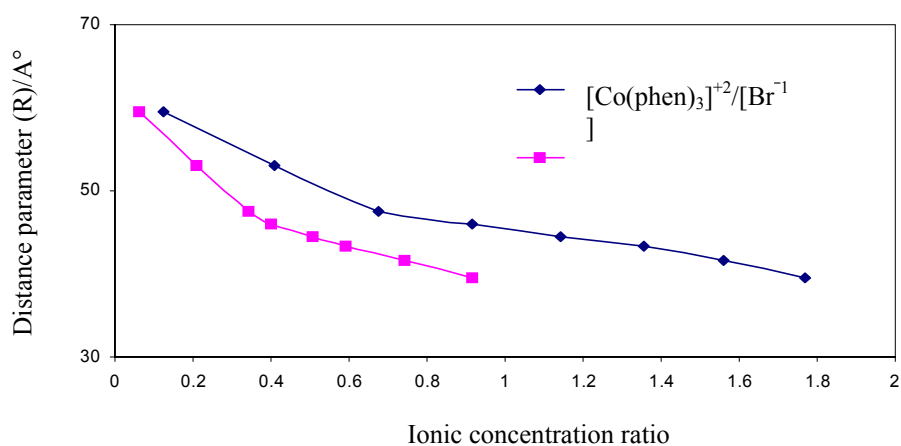


Fig. 1: The plot of distance parameter against the ionic concentration ratio for mixture (II) in methanol at 298.16K.

From this Figure it can be seen that the appropriate R decrease with increasing concentration ratio which shows a similar tendency of ion association of both Cl^- and Br^- since the $[\text{K}^+] = [\text{Br}^-]$ similar behaviour has been obtained by other workers (Akrawi, 1981, Al-Tamer, 1999, Dawood, 1996).

The plot of the concentration of six ionic species of each set data against the mole fraction of $[\text{Co}(\text{phen})_3]\text{Cl}_2$ is shown in Figure (2). It can be seen that the $[\text{Cl}^-]$ increases rapidly with increasing mole fraction of $[\text{Co}(\text{phen})_3]\text{Cl}_2$; $[\text{Co}(\text{phen})_3]^{+2}$ and

$\{[Co(phen)_3]Cl^{+1}\}$ increases slowly; $[K^+]$, $\{[Co(phen)_3]Br^{+1}\}$ and $[Br^{-1}]$ shows similar behaviour and they decrease slowly with increasing the value of the mole fraction. Here one can determine from this Figure the concentration of each ion species present in the mixture for any given mole fraction of $[Co(phen)_3]Cl_2$.

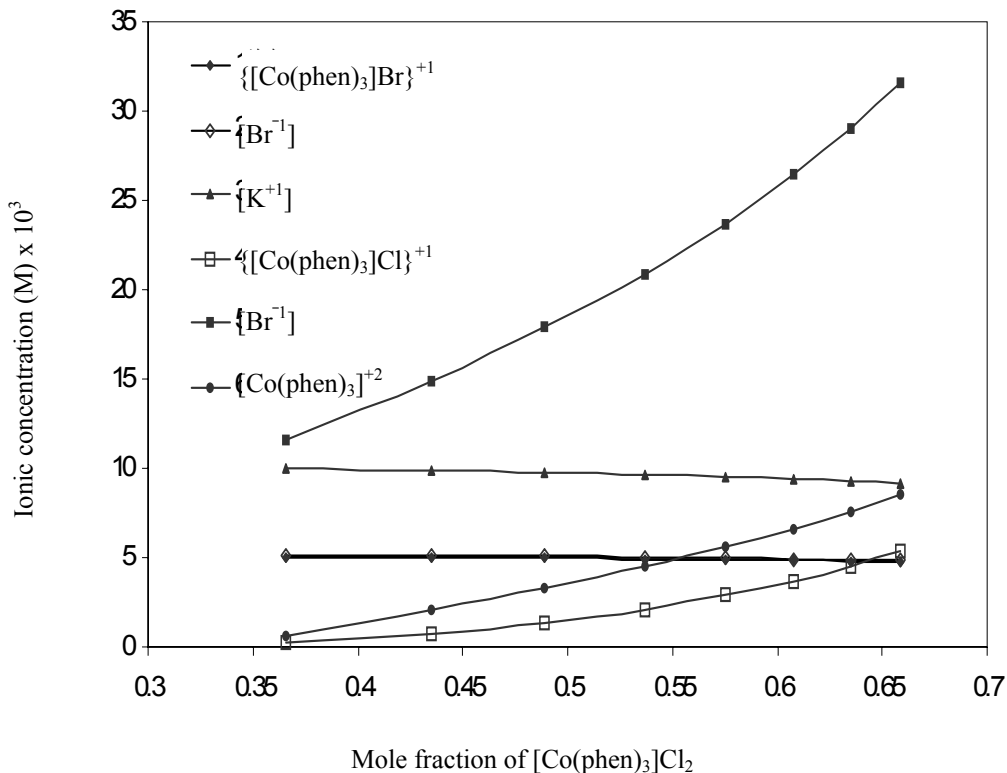


Fig. 2: The plot of ionic species concentration against the mole fraction of $[Co(phen)_3]Cl_2$ in methanol at 298.16K

Comparison between Conductivity Parameters for Mixed Complex Electrolytes at 298.16K in Methanol:

To get an information about the change of each of concentration, activity coefficient, transport number and ionic mobility of each ionic species in the mixed electrolytes we have compared these parameters at two different temperatures and almost at the same condition (concentration, solvent, distance parameteretc.).

Tables (4–6) show that increasing temperature from 298.16 to 308.16K causes a decrease in ACT according to Debye-Hückel equation.

$$\text{Log } \gamma_t = -A|Z_- Z_+| I^{1/2} \dots\dots\dots(3)$$

Where γ_t is the means ACT, A is a constant depends on the temperature, density, viscosity and dielectric constant and I is the ionic strength. So an increase in the temperature causes an increase in the value of A and hence a decrease of the ACT.

Both the transport number and ionic conductivity (λ) are increasing with increasing of the temperature according to the following relation.

$$\lambda_i^\circ = \lambda_{i(25^\circ C)}^\circ [1 + \beta(t - 25)] \dots\dots\dots(4)$$

Where β is a constant.

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