

# Conductivity measurements of ChloropentaammineCobalt (III)chloride Complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in Water(1) +Methanol(2)Mixtures at different Temperatures

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( Received 14 / 1 / 2009 , Accepted 22 / 4 / 2009 )

## Abstract

The electrolytic conductance of ChloropentaammineCobalt(III)chloride Complex  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  Complex in a different percentages of Water (1) + Methanol (2) Mixtures at (288.15,293.15,298.15 and 303.15) K are reported . The limiting equivalent conductance  $\lambda_o$ , association constant  $K_A$  and distance of closest approach of ions (R) are evaluated by means of

Lee –Wheaton equation .

The association constants obtained at different temperatures were used in determining the thermodynamic quantities of the association reaction of  $[\text{MX}]^{2+}$  ions and  $\text{Cl}^-$  ions (where  $[\text{MX}]$  is the coordination complex ) and the results are discussed on solvent effect on the conductivity parameters of this complex.

**Keyword:** ChloropentaammineCobalt(III)Chloride Complex , Association constant, Conductivity measurements , Lee–Wheaton equation.

## Introduction:

Conductance measurements provide useful and sensitive indications of ion-solvent interaction, ion-ion association, and solvent structure. Although numerous conductance measurements have been reported in the literature, extensive studies on electrical conductivities in various mixed organic solvents have been performed in recent years [1-4]. To examine the nature and magnitude of ion-ion and ion-solvent interactions, solvent properties as the viscosity and the relative permittivity have also been taken into consideration, which help in determining the extent of ion association and the solute-solvent interactions. Methanol is known to be extensively self-associated through hydrogen-bonding in the pure state [5]. Studies on the equivalent conductance of electrolytes in mixed solvents are useful for the understanding of the theory. Methanol + water mixtures have many special properties, which are different from that of the other alcohol +water mixtures.

In this work we have measured the electrical conductivity of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  Complex in methanol +water mixture at different temperatures (288.15-303.15 K).Lee-Wheaton equation is used to elucidate the conductivity parameter  $\lambda_o$ ,  $K_A$  and R in the different percentages and temperatures of the two solvents

## Experimental:

### Preparation of complex:

5 g of cobalt(II) chloride hexahydrate is dissolved in 5 ml of water. 10 g of ammonium chloride is dissolved in 30 ml of concentrated ammonia. The two solutions are mixed in a 100 ml conical flask. Then 2 ml of 30% hydrogen peroxide is added and the conical flask is shaken (vigorously) for three minutes. This addition of 2 ml of hydrogen peroxide and shaking of the conical flask is repeated three times, and the reaction mixture is transferred to a 250 ml beaker and stirred at room temperature for 15 minutes. 35 ml of concentrated hydrochloric acid is added dropwise while the mixture is stirred, and after this addition, the mixture is heated while still stirred - OBS be careful: bumping may occur - until it boils for about three minutes. Cooling in the air results in purple crystals, which are separated using a glass filter funnel. The crystals are washed with 15 ml of

4 M hydrochloric acid and then with 96% ethanol and dried in the air at room temperature.[6]

### Purification of solvents:

Methanol was purified and dried by the method described by Perrin [7]. Conductivity water was prepared by distilling twice distilled water to obtain specific conductance less than  $3 \times 10^{-6} \mu\text{S}$ . Conductivity measurements were made using Jenway PCM3 conductivity meter with frequency range of 50 Hz -1KHz and accuracy of 0.01  $\mu\text{S}$ .

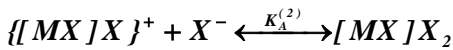
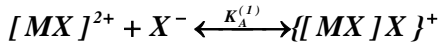
The cell constant of the conductivity cell was measured using the method of Jones and Bradshaw [8], 0.01 M KCl solution was prepared from potassium chloride (BDH reagent ), recrystallized three times from conductivity water and then dried at (760) Torr and 500 C° for 10 hrs [9].The cell constant was checked regularly and found to be  $1.14 \text{ cm}^{-1}$ .

### General Method :

A general method has been used for measuring the conductance of the electrolytes . The conductivity cell was washed ,dried and then weighed empty and kept at any temperature( $\pm 0.1^\circ\text{C}$ ) using a water –circulating ultra thermostat type VH5B radiometer . A certain amount of solution was injected into the conductivity cell and the conductivity of the solution was measured . Another known amount of the solution was added and the measurement was repeated as before. Generally [15] addition have been made.

### Results and discussion:

Experimental values obtained for the equivalent conductance  $\Lambda$  and the concentrations  $C$  (equivalents per liter) for dilute solutions of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  in various Water (1) +Methanol (2) solvent mixtures at 288.15, 293.15,298.15 and 303.15 K are listed in Table 1. Solvent correction was made to get the exact values of specific conductance's of the complex solutions. The experimental data were analyzed by Lee and Wheaton equation for unsymmetrical electrolytes which is an extended form of the Debye-Hukel equation for the calculation of equivalent conductance, association constant and main distance between ions in solution [10, 11] . For an unsymmetrical electrolyte  $\text{MX}_2$  ionizing to  $[\text{MX}]^{2+}$  and  $\text{X}^-$  the possible association equilibrium are:



Thus, three ionic species are present in the solution which are  $[MX]^{2+}$ ,  $\{[MX]X\}^+$  and  $X^-$ . All such solutions are in effect "mixed electrolyte" since the ion pair  $\{[MX]X\}^+$  is a conducting species.

$$\Lambda_{equiv.} = \sum_{i=1}^s |z_i| m_i \lambda_i / C$$

This equation is derived as follows:

$$\lambda_i = f(\lambda_i^0, \epsilon, R)$$

$$\sigma_i = i \lambda_i / 1000 = |z_i| m_i \lambda_i / 1000$$

$$\text{And } \sigma_{solu} = \sum_{i=1}^s |C_i|$$

$$\text{or } 1000 \sigma_{solu} = \sum_{i=1}^s |C_i \lambda_i|$$

$$\text{and } \Lambda_{solu} = \sum_{i=1}^s |z_i| m_i \lambda_i / \sum C_i$$

where (s) is the number of ionic species,  $\sigma$  is specific conductance, C stoichiometric equivalent concentration,  $\lambda_i$ ,  $m_i$ ,  $C_i$  and  $z_i$ , are the equivalent conductance, equivalent free ion concentration, equivalent concentration and charge of the species respectively. Thus for 2:1 associated salts

$$\Lambda\{[MX]X\}^+ = f(\lambda_{[MX]^{2+}}^0, \lambda_{\{[MX]X\}^+}^0, \lambda_{X^-}^0, K_A^{(1)}, K_A^{(2)}, R)$$

where R is the average center to center distance for the ion pairs. A multi parameter "least square" curve-fitting procedure is used to give the lowest value of curve fitting parameter  $\sigma(\Lambda)$  between the experimental and calculated points. An iterative numerical method which was found to be very successful has been used to find the minimum  $\sigma(\Lambda)$ . [8] where :

$$\sigma\Lambda = \left[ \frac{\sum_{n=1}^{NP} (\Lambda_{calc} - \Lambda_{exp})^2}{NP} \right]^{1/2}$$

A computer program is used to analyse the concentration - conductivity measurements in which the input data are (T, D,  $\eta$ ) where T is the temperature in Kelvin, D and  $\eta$  are the dielectric constant and viscosity (poise) of the solvent at that temperature.

From Table (1) and figures (1-5) the equivalent conductivities decrease rapidly with increasing methanol percent suggesting an increasing tendency of the ions to associate into ion pairs ,

Table (2) show the results of analysis of conductance data by using Lee-Wheaton equation. The values of  $\lambda_M^{2+}$  decrease rapidly, and the association constant  $K_A$  increase with increasing the methanol percent since addition of methanol to water promotes a breakdown of the water structure so the oxygen centers of the water molecules become free for interaction with the protons of methanol molecules.[12] . The association constants increase, as the methanol content of the mixture increases, The bivalent cations form ion pairs and water-separated pairs with the chloride ions. As the methanol

content is increased (dielectric constant of the solvent mixture decreases), the hydration becomes less strong and a short range interaction is possible. Therefore, it can be clearly considered that electrostatic ion pairs are formed.

An examination of molecular models suggests that when methanol solvates the ions, perhaps a steric hindrance occurs.[13] Because of this steric hindrance, the oxygen atoms of methanol are not in direct contact with the ions; consequently, the ions move freely and they have a tendency to associate through ion-ion interactions.

The values of  $\lambda\{[MX]X\}^+$  are almost Low values since they are large ion and more stable than the other ions ( $[MX]^{2+}$ ,  $X^-$ ). The small values of  $\sigma(\Lambda)$  give an indication of good best fit values

The values of  $K_A$  decrease with increasing temperatures because of the short range interaction and the hydrogen bond formed at Low temperatures.

The co-sphere diameter (R) values in the water (1) + methanol (2) mixtures are also reported in Table 2. No systematic trend in R values for the complex has been observed. Because the best-fit conductivity parameters are reproduced equally well over a wide range of arbitrarily chosen R values, a comprehensive correlation of the co-sphere diameter of the studied systems could not be made in the present situation.

This type of behavior has also been reported earlier. [1,14,15]

Thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$  are determined from the following :

$\Delta H^\circ$  and  $\Delta G^\circ$  are determined from the values of  $K_A$  ( $\Delta G^\circ = -RT \ln K_A$ ) and temperature (Arrhenius equation),  $\Delta S^\circ$  is calculated from these two parameters ( $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ ) which are given in the Table(3).

Fig(6) show the plot of  $\ln K$  versus  $1/T$  which give a linear relation.

It is well known that addition of an electrolyte to a solvent causes some structural changes due to the rupture of the bonds between solvent molecules from one side and to the interaction of ions with each other and with solvent molecules from the other side [16]. The negative entropy provides a good indication of ionic association which has an ordering effect on the solution. The solvation effect may exert on the solution structural in the same manner leading relatively to increase in the entropy as temperature increase and decrease with decreasing water percentage [17].

The enthalpy of activation according to the activated complex theory is a result of the energies being expended for the destruction of solvent-solvent bonds and the formation of solvent ion bonds. As can be noticed from Table (3), it was found that the values of  $\Delta H^\circ$  of ion association in all compositions are negative since ions are rigid and associated in a coulombic interaction.

Finally the values of  $\Delta G^\circ$  are negative which indicate the reaction is spontaneous.

Table(4) and Fig. (7) show the variation of Walden product (W) against solvent composition,. It seems to be nearly constant with temperature, but it changes with solvent composition. Changes in the Walden product with solvent composition are common[18] where the cationes are expected to suffer various degree of

solvation with increasing the amount of water in the water-methanol mixtures.

and the solvent molecules with the composition of the mixed polar solvents[9]

The major deviation in Walden product is due to the variation of the electrochemical equilibrium between ions

**Table1: The equivalent conductivities (S.cm<sup>2</sup>.equiv<sup>-1</sup>)with equivalent concentration for [Co (NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> in 100% Water at different temperatures.**

288.15 k		293.15 k		298.15 k		303.15 k	
C*10 <sup>4</sup>	A	C*10 <sup>4</sup>	A	C*10 <sup>4</sup>	A	C*10 <sup>4</sup>	A
<b>100%</b>							
0.797	185.991	2.37	186.756	0.797	200.298	2.37	204.298
3.92	183.432	4.69	185.152	1.59	200.378	3.15	203.054
4.69	183.130	6.95	183.588	3.15	200.158	6.95	202.581
5.45	182.694	7.69	182.767	5.45	198.599	7.69	202.441
6.20	182.171	8.43	181.858	6.95	196.84	8.43	202.598
8.43	180.958	9.16	181.315	8.43	195.835	9.16	201.63
9.89	179.200	9.89	180.246	9.89	195.114	9.89	200.533
<b>90%</b>							
1,13	144.001	1.13	163.134	1.13	177,172	1.48	170.060
2,37	138.813	2.46	160.129	1,82	166.782	1,82	179,290
3,10	138.811	3.33	158.004	2,57	166.163	2,77	178,707
4.69	135.083	3.61	157.729	3,71	165.316	3,00	178,024
5.45	136.614	4.13	157.452	3,87	165.215	3,71	178,170
8,43	136.693	4.38	157.385	4,38	164.681	4,13	177,772
9,17	133.86	4.62	157.092	4,72	164.502	4,38	177,047
<b>80%</b>							
3,92	117,443	4,31	127,729	3,92	133,722	4,31	141,773
4,79	110,020	0,07	127,311	0,07	132,209	4,79	141,042
0,07	110,170	0,83	127,718	7,90	131,391	0,83	141,100
0,40	114,003	7,90	120,107	8,43	130,337	8,43	140,791
0,83	112,723	7,79	124,933	9,17	129,304	9,17	138,772
6.20	111.398	9,89	123,003	9,89	128,923	9,89	138,724
7,90	112,373	10,7	123,287	10,7	128,778	10,7	137,082
<b>70%</b>							
0,07	83,247	5.45	97.374	0,40	100,000	4,79	111,142
0,40	83,102	7,90	97,993	0,83	99,318	0,83	110,972
0,83	82,700	7,79	97,771	7,90	98,994	7,90	110,230
7,20	82,188	9,17	97,711	7,79	98,770	9,17	108,779
7,79	81,979	9,89	97,208	8,43	98,207	9,89	108,177
8,43	81,972	10,7	90,270	9,17	98,129	11,3	108,102
11.13	67881,	11,3	94,788	11.3	96.216	12,0	107,934
<b>60%</b>							
0,07	88,848	0,07	90,197	4,79	93,147	0,07	101,894
0,40	87,470	0,40	88,940	0,07	93,121	0,40	101,707
7,20	87,133	7.69	88.327	7,20	92,097	0,83	100,981
7,90	87,710	8,43	88,401	7,90	92,779	7,90	100,002
7,79	87,797	9,17	88,230	7,79	92,032	7,79	99,739
9,17	80,124	9,89	88,217	8,43	91,977	8,43	98,729
10,7	84,004	10,7	87,701	1.06	92.975	9,89	98,018

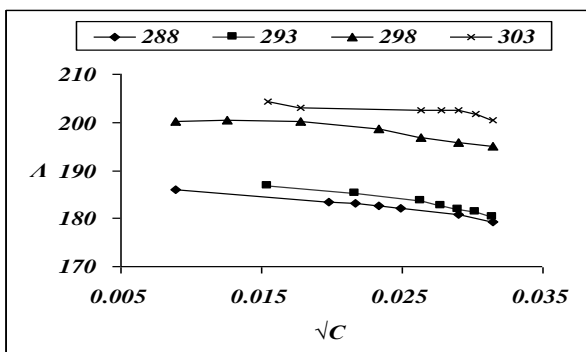


Fig1: The plot of equivalent conductivities ( $S.cm^2.equiv^{-1}$ ) against Square root of concentration for  $[Co(NH_3)_5Cl]Cl_2$  in 100% Water at different temperatures

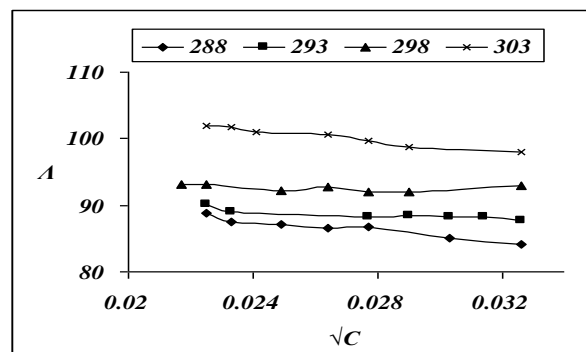


Fig5: The plot of equivalent conductivities ( $S.cm^2.equiv^{-1}$ ) against Square root of concentration for  $[Co(NH_3)_5Cl]Cl_2$  in 60% Water at different temperatures

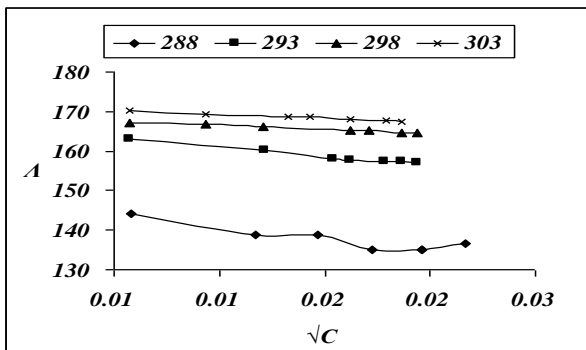


Fig2: The plot of equivalent conductivities ( $S.cm^2.equiv^{-1}$ ) against Square root of concentration for  $[Co(NH_3)_5Cl]Cl_2$  in 90% Water at different temperatures

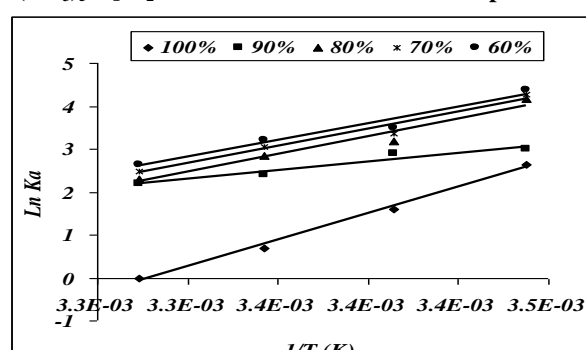


Fig 6: The plot of Log KA against 1/T for the complex at different solvent composition

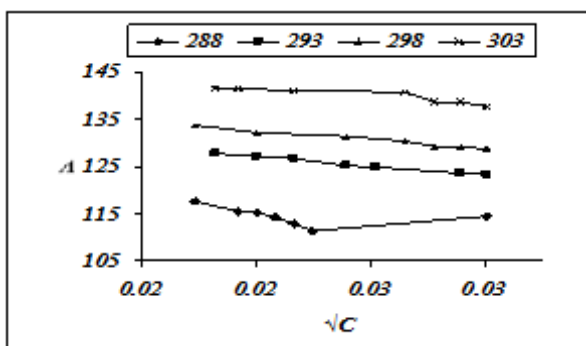


Fig3: The plot of equivalent conductivities ( $S.cm^2.equiv^{-1}$ ) against Square root of concentration for  $[Co(NH_3)_5Cl]Cl_2$  in 80% Water at different temperatures

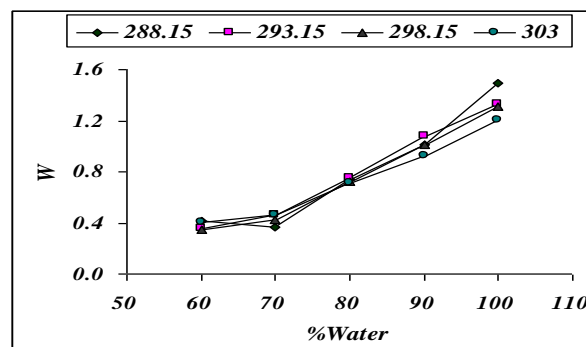


Fig7: Walden product (W) for the complex in methanol-water mixture versus percentage of solvent mixture at different temperatures

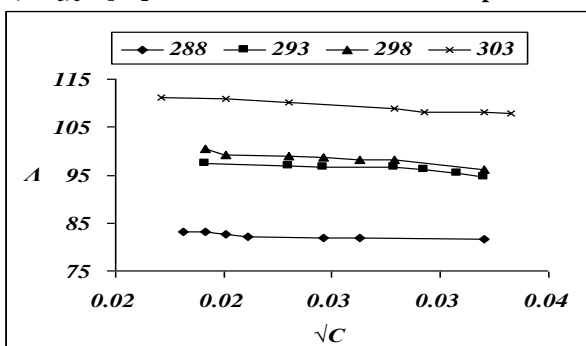


Fig4: The plot of equivalent conductivities ( $S.cm^2.equiv^{-1}$ ) against Square root of concentration for  $[Co(NH_3)_5Cl]Cl_2$  in 70% Water at different temperatures

**Table(2):The results of analysis of conductance of [Co(NH3)5Cl]Cl2 in different parentage and temperatures of methanol water using L-W equation**

T/ K	KA	$\Lambda/M^{1/2}$	$\Lambda/[MX]X^{1/2}$	R(A°)	$\sigma$
<b>100% Water</b>					
288.15	14	137.59	0.2	30	0.0026
293.15	5	138.80	0.29	19	0.0060
298.15	2	153	0.2	18	0.0047
303.15	1	157	0.1	34	0.0050
<b>90% Water</b>					
288.15	20	93	9	11	0.0110
293.15	18	112.39	4.9	2.4	0.0017
298.15	11	118	0.29	58	0.0009
303.15	9	120.79	0.009	68	0.0030
<b>80% Water</b>					
288.15	64	72	0.49	24	0.0063
293.15	23.79	82.07	2.9	24	0.0020
298.15	17	88	3.99	18.9	0.0022
303.15	10	96.59	3.9	25	0.0053
<b>70% Water</b>					
288.15	72	37	0.1	88	0.0016
293.15	29	53	7.9	23	0.0051
298.15	21	54.4	0.1	29	0.0025
303.15	12	65.39	1.9	30	0.0023
<b>60% Water</b>					
288.15	80	44	0.0001	58	0.0315
293.15	33	43	0.1	64	0.0030
298.15	25	46	0.019	69	0.0021
303.15	14	59.2	0.00001	2	0.0013

**Table(3): Thermodynamic parameters (  $\Delta H_o$  ,  $\Delta G_o$  ,  $\Delta S_o$ )of the complex in different solvent composition.**

% Water	T/ K	$\Delta G_o$ (cal/ mol)	$\Delta S_o$ (cal/ mol)	$\Delta H_o$ (cal/ mol)
<b>100% Water</b>	288.15	-1505.7	-21.854	
	293.15	-934.18	-23.431	-7803
	298.15	-409.19	-24.799	
	303.15	0	-25.74	
<b>90% Water</b>	288.15	-1709.18	-2.90013	
	293.15	-1677.68	-2.95811	-2544.85
	298.15	-1415.57	-3.78763	
	303.15	-1318.86	-4.04418	
<b>80% Water</b>	288.15	-2372.8	-9.89219	
	293.15	-1839.56	-11.5425	-5223.23
	298.15	-1672.55	-11.909	
	303.15	-1382.1	-12.6707	
<b>70% Water</b>	288.15	-2440	-9.01398	
	293.15	-1954.5	-10.5164	-5037.37
	298.15	-1797.29	-10.8673	
	303.15	-1491.53	-11.6967	
<b>60% Water</b>	288.15	-2500.1	-8.2145	
	293.15	-2029.5	-9.6798	-4867.1
	298.15	-1900.2	-9.951	
	303.15	-1584.1	-10.83	

**Table (4) Values of the Walden product (W)for the complex in methanol (1) –water (2) at different temperatures.**

%water	$eq^{-1}mPa s)^{-1}W(S.cm$			
	288.15	293.15	298.15	303.15
<b>100%</b>	1.50	1.33	1.31	1.21
<b>90%</b>	1.01	1.08	1.01	0.93
<b>80%</b>	0.75	0.75	0.72	0.71
<b>70%</b>	0.36	0.46	0.43	0.47
<b>60%</b>	0.41	0.36	0.35	0.40

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## قياسات التوصيلية لمركب الكلوريد كلورو خماسي أمين الكوبلت ( III ) في مزيج الكحول الميثيلي - الماء

### بدرجات حرارية مختلفة

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( تاريخ الاستلام: ١٤ / ١ / ٢٠٠٩ ، تاريخ القبول: ٢٢ / ٤ / ٢٠٠٩ )

### الملخص:

تم قياس التوصيلية الالكترونية لمعدد الكلوريد كلورو خماسي أمين الكوبلت ( III ) في مزيج من الكحول الميثيلي - الماء في درجات حرارة (٢٨٨,١٥-٣٠٣,١٥) مطلقاً وحسبت الحدود  $\lambda_0$ ،  $K_A$ ،  $R$  أي التوصيلية المكافئة وثابت التجمع الأيوني ومعدل المسافة بين الأيونات في المحلول باستخدام معادلة لي - ويتون ومن حساب ثابت التجمع الأيوني للمعدد في درجات حرارية مختلفة تم حساب الدوال الترموديناميكية لتفاعل التجمع بين ايونات  $[MX]^{2+}$  وايون الكلوريد  $Cl^-$  والنتائج كذلك نوقشت من جهة تأثير المذيب على معطيات التوصيلية لهذا المعدد .

**الكلمات الدالة :** التوصيلية ، الكلوريد كلورو خماسي أمين الكوبلت ( III ) ، قياسات التوصيلية ، ثابت التجمع ، لي ويتون .