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The Conductance Behaviour of Unsymmetrical Electrolyte of Complex Chloropentammine cobalt(III) Chloride in Water at Different Temperatures

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ABSTRACT

Equivalent conductance of $[Co(NH_3)_5Cl]Cl_2$ in water at 30, 35, 40, 50 and 60°C. The data were analyzed using the Fuoss-Edelson method to obtain the limiting equivalent conductance at infinite dilution (Λ_∞) and the association constant (K_A) simultaneously. The distance of closest approach (a°) was calculated using Stokes' equation.

Key words: Conductivity Co(III) complex chloropentammine chloride, ionic association at different temperatures.

INTRODUCTION

The measurement of electrical conductivity of dilute solutions is considered to be one of the important methods for studying the ion pair formation not only in aqueous solutions but also in nonaqueous solutions (1). It is recognized that ion association occurs by the electrostatic interaction between the cation and the anion and some quantitative relations of predicting the ion association constants are proposed by Bjerrum (2), Fuoss (3) and others (4). In some cases however, tendencies were found to be against the electrostatic theory; therefore, it is necessary to reconsider meaning of ion association theory. In this connection, the conductivity studies to provide valuable information in ionic solvation and solvation effect which may vary with the properties of solvents such as polar or nonpolar, protic or aprotic and protophilic or protophobic (1).

In this work conductivity measurements will be used to study the behaviour of $[Co(NH_3)_5Cl]Cl_2$ in water at different temperatures the data will analyzed using Fuoss-Edelson method to obtain the limiting equivalent conductance (Λ_∞) and the association constant (K_A) at different temperatures.

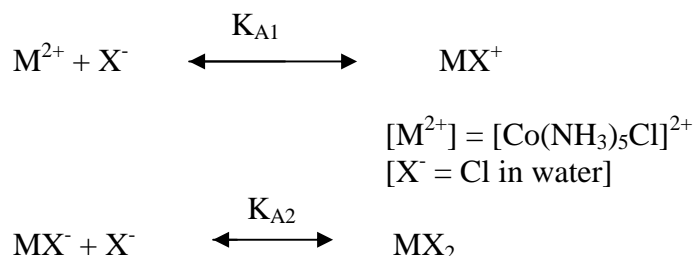
EXPERIMENTAL SECTION

Chloropentammine cobalt(III) chloride, prepared and purified by the published method (5,6). Conductivity water was obtained in reported in the literature (7). Its specific conductance κ amounts to $(2-5) \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. All solvents were taken by weight. Dilution was carried out successively in the cell itself. A "Pye" 11700 conductivity bridge was used for measuring the conductances of solution at 5 KHz. All measurements were carried out at $30 \rightarrow 60 \pm 0.02^\circ \text{C}$ using a water thermostat. The conductivity cell was of pyrex glass and of conventional design (Erlenmeyer type) with unplatinized electrode. The cell constant was found to be $0.05443 \pm 0.0043 \text{cm}^{-1}$. The solvent constants used in all calculations were taken as reported (2), i.e., densities (d_{30°) = 0.99565g mL^{-1} , (d_{35°) = 0.99406g mL^{-1} , (d_{40°) = 0.99224g mL^{-1} , (d_{50°) = 0.98807g mL^{-1} and (d_{60°) = 0.98324g mL^{-1} respectively, the viscosities (η_{30°) = $0.7970 \times 10^{-2} \text{P}$ and (η_{35°) = $0.7190 \times 10^{-2} \text{P}$, (η_{40°) = $0.6530 \times 10^{-2} \text{P}$, (η_{50°) = $0.5470 \times 10^{-2} \text{P}$, (η_{60°) = $0.4660 \times 10^{-2} \text{P}$ respectively and the dielectric constants (D_{30°) = 76.60, (D_{35°) = 74.82, (D_{40°) = 73.15, (D_{50°) = 96.91 and (D_{60°) = 66.81 respectively.

RESULTS AND DISCUSSION

The equivalent conductance Λ ($\Omega^{-1} \text{equiv}^{-1} \text{cm}^2$) measured at the corresponding concentration C (equiv/litre of solution) as shown in Table (1). Approximate values for Λ_∞ were estimated from Λ vs $C^{1/2}$ plots.

Figures (1-2) in water at 30, 35, 40, 50 and 60°C , give straight lines from which Λ_∞ value is estimated from the free hand extrapolation to zero concentration. The data were analyzed using the Fuoss-Edelson (F-E)(7a,b) method to obtain a more accurate value of Λ_∞ and the association constant K_A . In this method two assumptions were made for 2:1 electrolytes. The association equilibrium are represented as follows.



where K_{A1} and K_{A2} refer to the first and the second association constants respectively. The first assumption was that K_{A2} is zero, while the second one was that the mobility of M^{2+} is twice that MX^+ depending on the fact that the chelate cations are considerably large than the anions, according M^{2+} can be through to be hydrodynamically equivalent to MX^+ except in charge type since the ratio of the charges equals that the mobility.

Figures (3-4) represent Λ' vs X plots from the Fuoss-Edelson method for the Co(III) complex chloride in water at different temperatures. All figures follow this equation

$$\Lambda' = \Lambda_\infty - X / K_{D1}\Lambda_\infty$$

Where $\Lambda' = \Lambda$ (exp) F , where F is a function of C and Λ_∞ which corrects the conductance ratio Λ / Λ_∞ for the effect of interionic forces on the mobility

$$\text{Where } X = C' \Lambda' (\Lambda' - \frac{1}{2} \Lambda_\infty), \quad C' = C f_B$$

and f_B is the cationic activity coefficient which can be calculated by Debye-Hückel first approximation:

$$-\log f_B = [1.823 \times 10^6 / (DT)^{3/2}] \times z_B^2 \sqrt{3C}$$

As can readily seen from the previous figures all plots are straight lines from which Λ_0 can be obtained as intercept, while

$1/K_{D1} = K_{A1}$ can be obtained from the slope. The derived constants in water at different temperatures are listed in Table (2- 6).

It is evident from Tables (2-6) that the values of Λ_0 increase with increase the temperatures for Co (III) complex chloride indicating less solvation or higher mobility of ions in all solvent systems studies. This is due to the fact that the increased thermal energy results in greater bond breaking and variation in vibration, rotational and translational energy of molecules that lead to higher frequency and higher mobility of the ions (8).

Table (1): Conductance of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in water at different temperatures

30°C		35°C		40°C		50°C		60°C	
$10^4 \text{ C}^{(1)}$	$\Lambda^{(2)}$	10^4 C	Λ	10^4 C	Λ	10^4 C	Λ	10^4 C	Λ
10.834	157.536	8.7980	201.182	8.7963	212.147	8.8921	253.853	10.349	314.011
10.006	158.676	8.1677	201.894	8.1714	212.705	8.2884	255.694	8.1836	330.256
8.7476	161.268	7.6345	202.502	7.6407	213.214	7.7904	256.636	7.7544	334.354
8.1852	162.696	6.9175	203.541	6.8194	213.962	7.005	259.127	7.0115	342.678
7.3757	165.232	6.3688	204.436	6.1746	214.444	6.3662	261.743	6.4058	348.545
6.6976	167.478	5.8804	205.429	5.6613	214.811	5.8291	263.900	5.8829	355.725
6.1578	168.844	5.4537	206.100	5.2402	215.471	5.3716	265.900	5.4409	362.566

(1) equiv./L

(2) $\Omega^{-1} \text{ equiv.}^{-1} \text{ cm}^2$

Table 2: Fuoss-Edelson equation of $[(\text{Co}(\text{NH}_3)_5\text{Cl})\text{Cl}_2$ in water at 30°C

10^4 C	Λ	F	Λ'	f_B	$10^4 \text{ C}'$	X
10.834	157.54	1.1080	175	0.72944	7.9026	9.97245
10.006	158.68	1.1042	175	0.73847	7.3890	9.44573
8.7476	161.27	1.0969	177	0.75316	6.58832	8.69868
8.1852	162.70	1.0931	178	0.76017	6.2221	8.36548
7.3757	165.23	1.0869	180	0.77082	5.6853	7.89727
6.6976	167.48	1.0816	181	0.78032	5.2263	7.46805
6.1578	168.84	1.0780	182	0.78833	4.8544	7.04702

Table 3: Fuoss-Edelson equation of $[\text{Co}(\text{Co}(\text{NH}_3)_5\text{Cl})\text{Cl}_2$ in water at 35°C

10^4 C	Λ	F	Λ'	f_B	$10^4 \text{ C}'$	X
8.7980	201.18	1.0637	214	0.74435	6.549	14.25871
8.1677	201.89	1.0614	2.14	0.75241	6.145	13.43653
7.6345	202.50	1.0594	2.15	0.75955	5.799	12.72257
6.9175	203.54	1.0564	2.15	0.76966	5.324	11.76324
6.3688	204.44	1.0539	215	0.77786	4.954	11.01430
5.8804	205.43	1.0514	216	0.78554	4.619	10.34899
5.4537	206.10	1.0494	216	0.79259	4.322	9.72552

Table 4: Fuoss-Edelson equation of $[\text{Co}(\text{Co}(\text{NH}_3)_5\text{Cl})\text{Cl}_2$ in water at 40°C

$10^4 C$	Λ	F	Λ'	f_B	$10^4 C'$	X
8.7963	212.15	1.0545	224	0.73684	6.4814	16.04083
8.1714	212.7	1.0524	224	0.74502	6.0879	15.09439
7.6407	213.21	1.0505	224	0.75230	5.7481	14.27752
6.8194	213.96	1.0475	224	0.76423	5.2116	12.97166
6.1746	214.44	1.0452	224	0.77425	4.7807	11.90116
5.6613	214.81	1.0434	224	0.78271	4.4311	11.028311
5.2402	215.47	1.0414	224	0.79001	4.1398	10.34043

Table 5: Fuoss-Edelson equation of $[\text{Co}(\text{Co}(\text{NH}_3)_5\text{Cl})\text{Cl}_2$ in water at 50°C

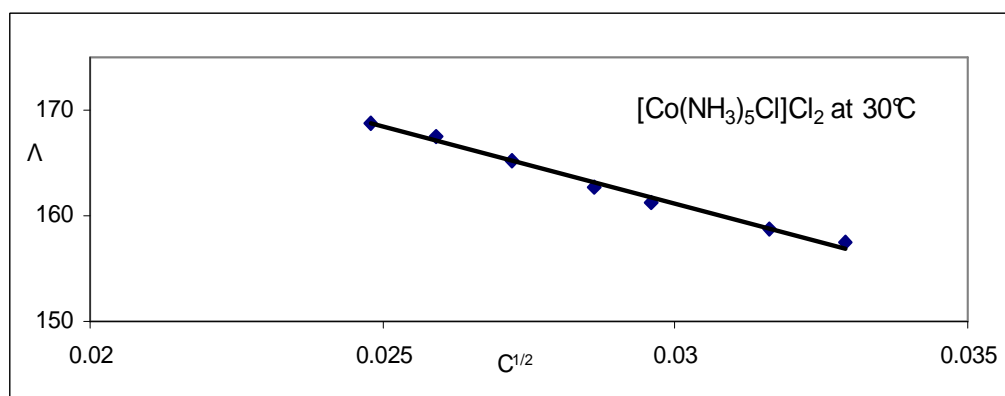
$10^4 C$	Λ	F	Λ'	f_B	$10^4 C'$	X
8.8920	253.85	1.0865	276	0.71990	6.4015	21.54882
8.2880	255.69	1.0831	277	0.72812	6.0350	20.58871
7.7900	256.64	1.0809	277	0.73521	5.7276	19.64590
7.0050	259.13	1.0764	279	0.74699	5.2330	18.26818
6.3660	261.74	1.0720	281	0.75725	4.8207	17.15649
5.8290	263.90	1.0684	282	0.76638	4.4673	16.14557
5.3720	265.90	1.0651	283	0.77459	4.1608	15.25399

Table 6: Fuoss-Edelson equation of $[\text{Co}(\text{Co}(\text{NH}_3)_5\text{Cl})\text{Cl}_2$ in water at 60°C

$10^4 C$	Λ	F	Λ'	f_B	$10^4 C'$	X
10.349	314.01	1.1800	371	0.68421	7.0808	33.19042
8.184	330.26	1.1559	382	0.71358	5.8396	30.70354
7.754	334.35	1.1503	385	0.72000	5.5832	30.19002
7.012	342.68	1.1395	390	0.73171	5.1304	29.3394
6.406	348.54	1.1319	395	0.74188	4.7523	28.21598
5.883	355.73	1.1233	400	0.75117	4.4191	27.47026
5.441	362.57	1.1155	404	0.75945	4.1321	26.80815

Table (7): The Characteristic Parameters for Chloropentaammine Co(III) Chloride in water at different temperatures derived from Fuoss-Edelson equation

Temperature	$\lambda^+ / 2$	Λ_0	λ_{Cl^-}	$\lambda_{[\text{Co(III) complex}]^+}$	K_A	r_{s+}	r_{s-}	$r^+ + r^-$	$a^{\circ}_{\text{ion-pair}}$
30	58.33	200.90	84.23	116.65	542.43	1.76	1.22	2.98	3.53
35	59.56	221.23	92.20	119.03	114.49	1.92	1.24	3.16	3.83
40	62.43	225.35	100.50	124.85	22.45	2.01	1.25	3.26	4.02
50	92.62	300.74	117.50	183.24	351.57	1.64	1.28	2.92	3.27
60	202.92	544.09	138.25	405.84	2861.10	0.87	1.27	2.14	1.73



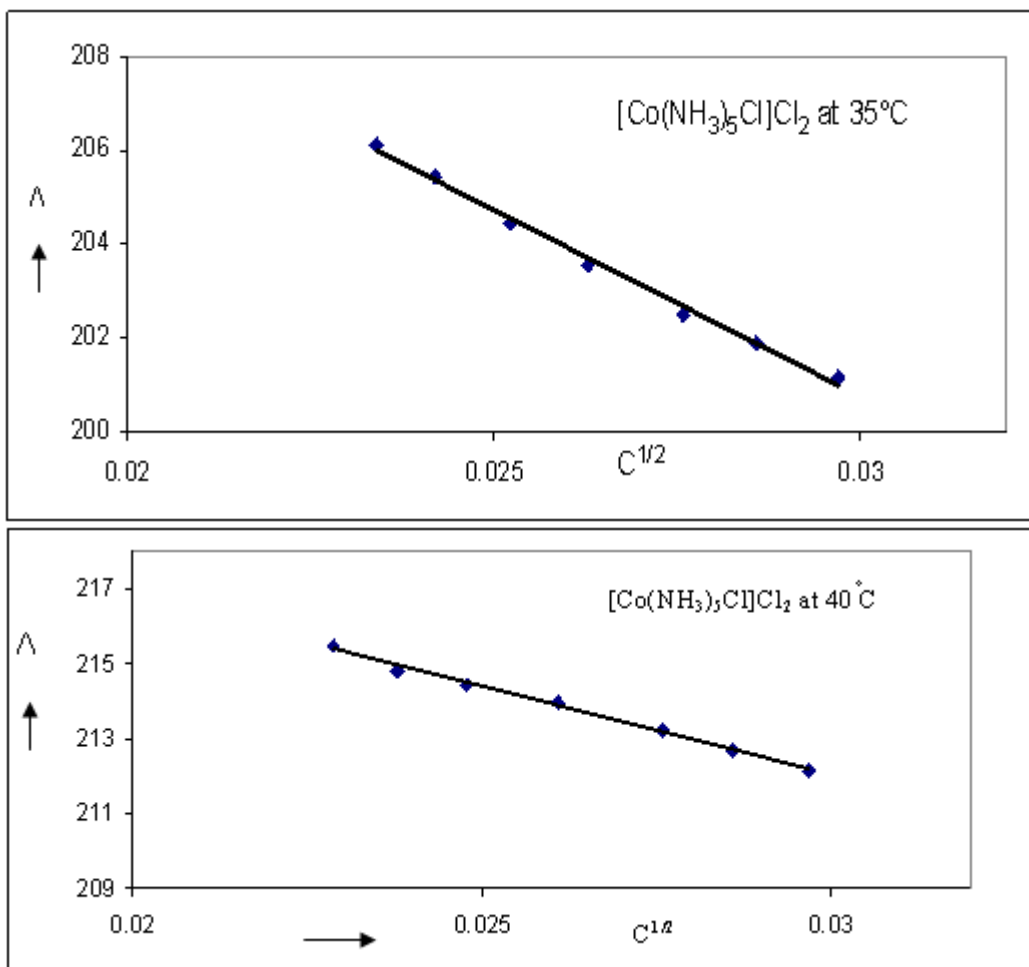
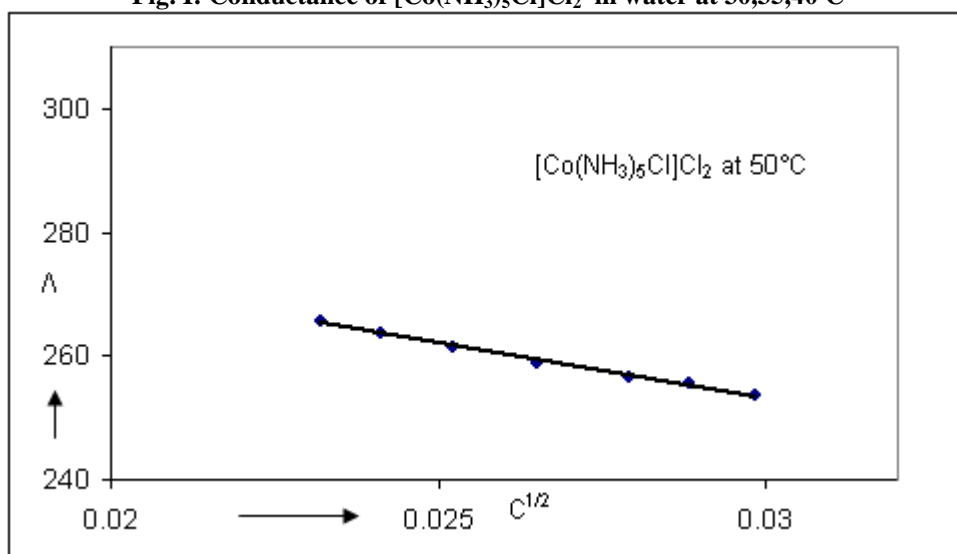


Fig. I: Conductance of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in water at 30,35,40 °C



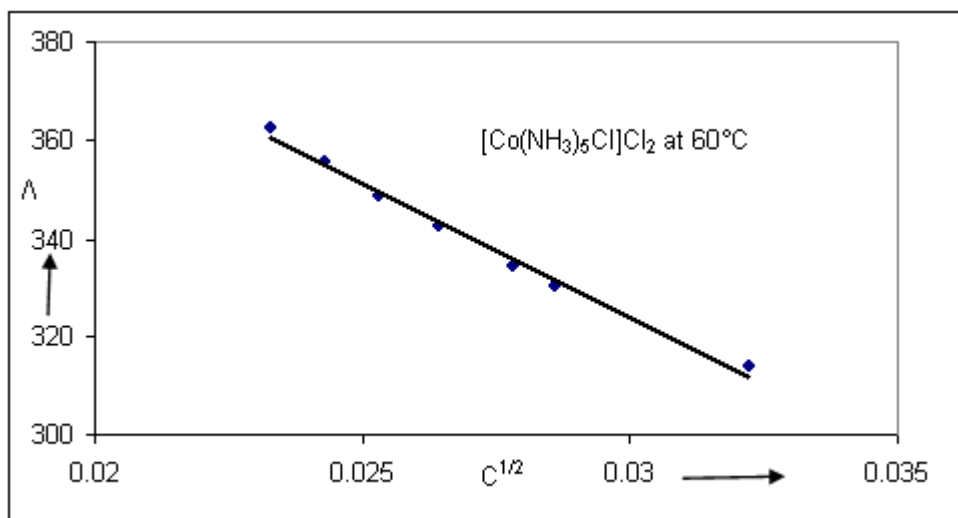
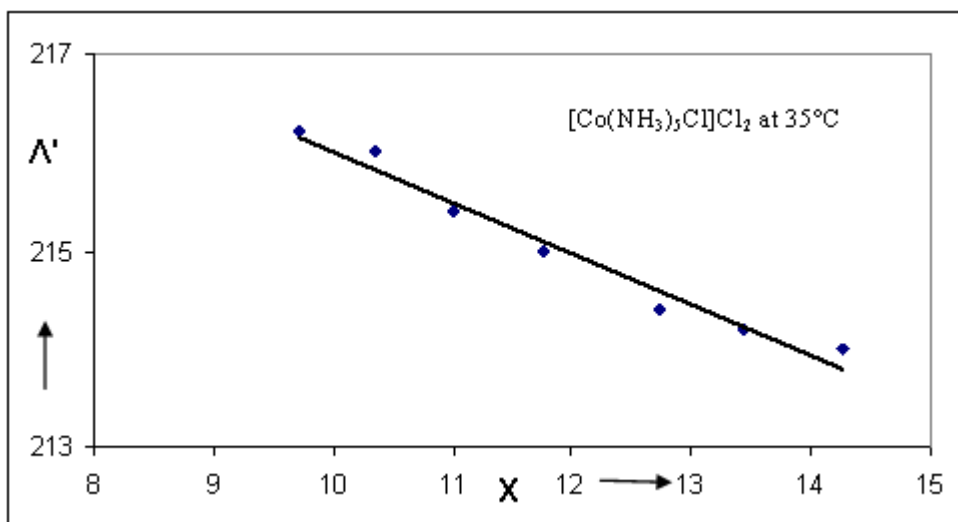
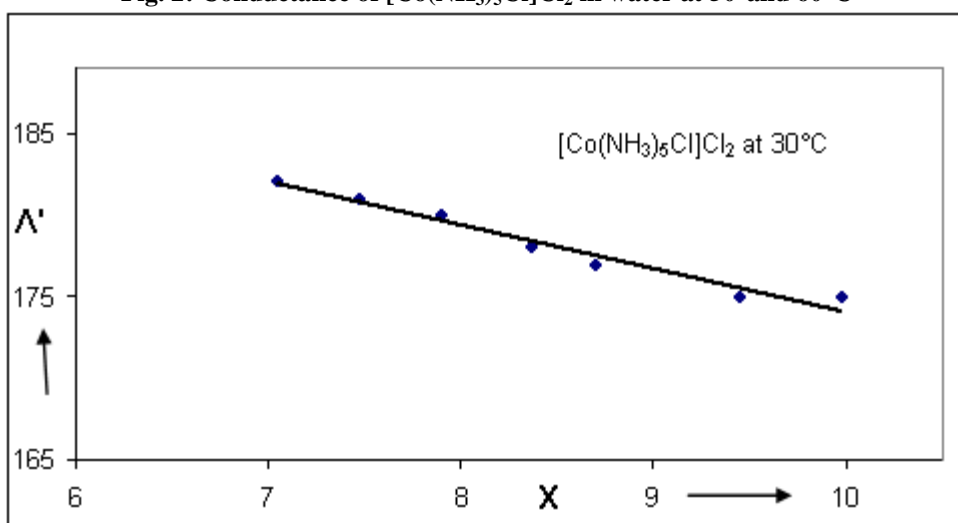


Fig. 2: Conductance of [Co(NH₃)₅Cl]Cl₂ in water at 50°and 60°C



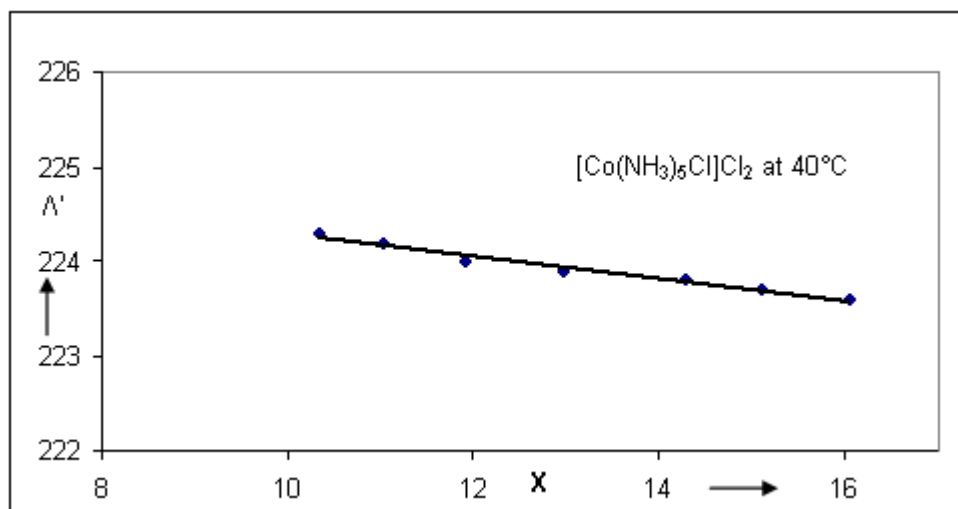


Fig. 3: Test for Fuoss-Edlson equation: for [Co(NH₃)₅Cl]Cl₂ in water at 30, 35, 40°C

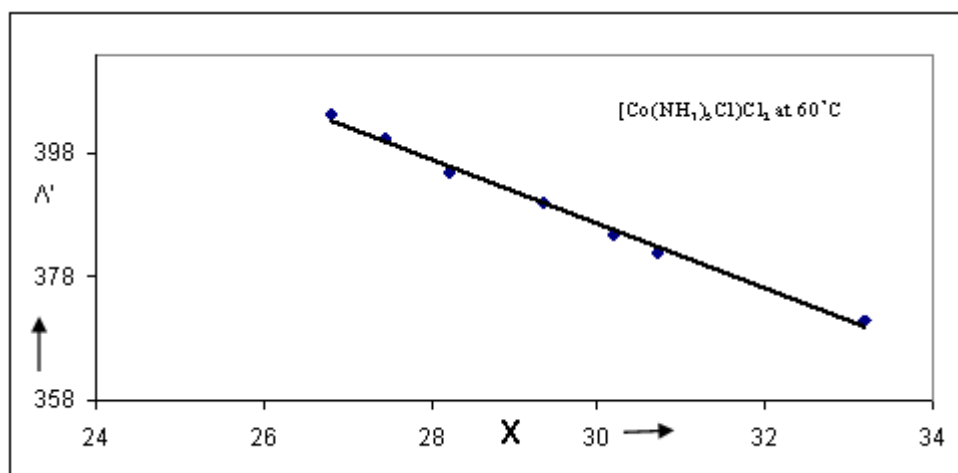
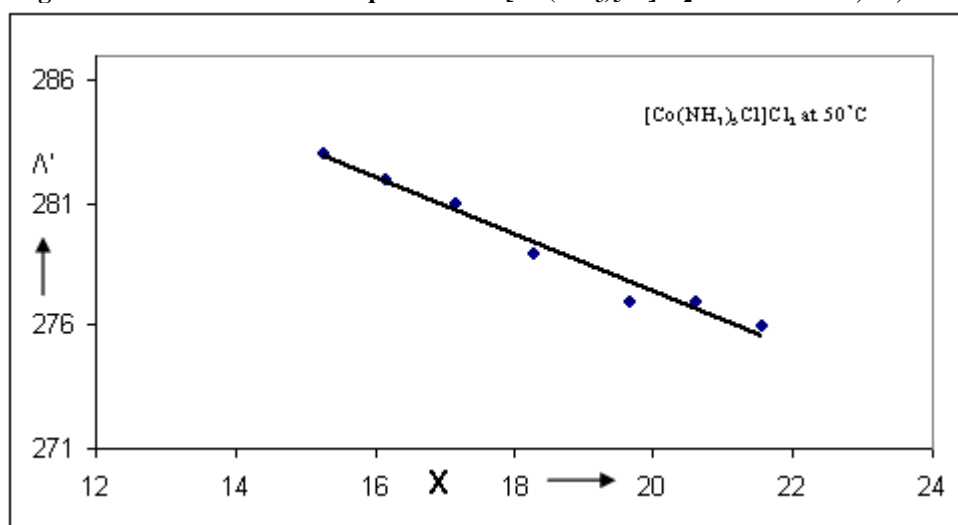


Fig. 4: Test for Fuoss-Edlson Equation : for [Co(NH₃)₅Cl]Cl₂ in water at 50°C and 60°C

Kalugin, et al. (9), measured the conductances of Mg(ClO₄)₂ and Ni(ClO₄)₂ in acetonitrile over the temperature ranges 5-55°C for Mg(ClO₄)₂ and 25-75°C for Ni(ClO₄)₂, they found that the Λ_{∞} , K_{A1} , $\lambda_{ClO_4^-}$, $[KtClO_4]^+$ increase with increasing the temperatures, using the Lee-Wheaton equation for unsymmetrical electrolytes. They shows that the logarithm of the first-step association constant increases by approximate 0.2 units as the temperature grows to 50°C for both $[MgClO_4]^+$ and $[NiClO_4]^+$. Clearly, strengthening of interionic association at higher temperatures

is largely caused by a decrease in the permittivity of the solvent. The log K_{A1} value for nickel perchlorate was smaller than that for magnesium perchlorate by about 0.25 units at equal temperatures, which showed that the nickel cation was better solvated than magnesium (9). Calculation of the distance of closest approach (a°); there are two methods (10) dealing with calculation of the distance of closest approach (a°) for an ion-pair of the form $[MX]^\pm$ there are:

- 1) The ionic radius of both cation and anion is calculated using Stokes' equation:

$$r_{s+} = \frac{0.8194 (z_i)}{\lambda_{2+}^\circ \eta^\circ}, \quad r_{s-} = \frac{0.8194 (z_j)}{\lambda_-^\circ \eta^\circ}$$

- 2) $r_{\text{ion-pair}}$ can be calculated using Stokes' equation directly

$$r_{\text{ion-pair}} = \frac{0.8194 (z_i z_j)}{\lambda_{\text{ion-pair}}^\circ \lambda^\circ}$$

Substituting for $\lambda_{\text{ion-pair}}^\circ = \frac{\lambda_{2+}^\circ}{2}$

Application of the first method requires the values of λ_{2+}° and λ_-° in different temperatures these were obtained as follows:

The values of $a_{\text{ion-pair}}^\circ$ by two methods of calculations are consumed in Table (7) from which one can observe that the values of (a°) obtained from second method of the calculation are more acceptable and indicate solvation.

The trend of (a°) is in agreement with electrostatic (7) theories and it explains the trend of K_{A1} , since (a°) increases with increase the temperature until certain values and decrease again while K_{A1} decreases with increasing the a° until 50°C and decrease the a° with increase K_A at 60°C. The trend of $a_{\text{ion-pair}}^\circ$ solvation with K_{A1} are in agreement with the electrostatic theories (10).

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