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Conductance and ion association studies of unsymmetrical electrolytes of complexes bromopentamine cobalt (III) halides and perchlorate in water at different temperatures

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ABSTRACT

Conductance of complexes bromopentamine cobalt (III) halides and perchlorate has been measured in water at different temperatures (25^oc → 35^oc). The limiting equivalent conductance (Λ_0) and ion association constant (K_A) for complexes in water have been evaluated using Fuoss-Edelson equation. The influence of solvent on the solvation of ions has been discussed. Temperature variation of the association constant has been studied to evaluate the thermodynamic parameters.

Key words: limiting equivalent conductance (Λ_0), Ion association, thermo-dynamics and activation energy.

INTRODUCTION

The measurement of electrical conductivities of dilute solutions of salts or complexes are considered to be one of the important methods for studying the ion-pair or multiple- ion association not only in aqueous solutions but also in non-aqueous, or mixed ones ⁽¹⁻⁴⁾. Also, conductivity measurements were used to evaluate the hydration free energy of some electrolytic solutions and to study the nature of the solute-solvent interaction ⁽⁵⁾. The present work aims to determine the conductance values of complexes of bromopentamine cobalt (III) halides and perchlorate has been measured in water at different temperatures (25^oc → 35^oc), to examine the validity of Fuoss-Edelson equation ⁽⁶⁾. The limiting equivalent conductance (Λ_0), the association constant (K_A) and the solvation for complexes have been evaluated. These values have been used to discuss qualitatively the nature of the

ion-ion, ion-solvent and solvent-solvent interaction of complexes. Temperature variation of (K_A) has been studied to get the thermodynamic parameters as a function of the solvent structure.

EXPERIMENTAL SECTION

All chemicals used were of analar grade. Bromopentammine cobalt (III) bromide was prepared as recommended ⁽⁷⁾ and converted to the perchlorate salt; $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ by precipitation from a hot concentrated solution of acidified LiClO_4 by cooling in ice-water ⁽⁸⁾, and converted to chloride salt; $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{Cl})_2$ by precipitation from a hot concentrated solution of HCl by cooling in ice-water ⁽⁷⁻⁸⁾.

Conductivity water was obtained by passing ordinary distilled water from a tin still over a 60 cm long Elgastat deionizer, and kept CO_2 free using soda lime tubes. Its specific conductance amounts to $(2-5) \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. 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 K c/s. All measurements were carried out at 25, 30 and $35^\circ\text{C} \pm 0.02^\circ\text{C}$ using a water thermostat. The conductivity cell was of Pyrex glass and of conventional design (Erlenmeyer type) with unplatinized electrodes. 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 ⁽⁹⁻¹²⁾, i.e. densities (d_{25}) = $0.99704 \text{ g ml}^{-1}$, (d_{30}) = $0.99565 \text{ g ml}^{-1}$ and (d_{35}) = $0.99406 \text{ g ml}^{-1}$ respectively. The viscosities (η_{25}) = $0.8903 \times 10^{-2} \text{ P}$, (η_{30}) = $0.7977 \times 10^{-2} \text{ P}$ and (η_{35}) = $0.7194 \times 10^{-2} \text{ P}$, respectively, and the dielectric constants (D_{25}) = 78.54, (D_{30}) = 76.60 and (D_{35}) = 74.82 respectively.

RESULTS AND DISCUSSION

The equivalent conductance Λ ($\text{ohm}^{-1} \text{ equiv}^{-1} \text{ cm}^2$) measured at the corresponding concentration C (equiv/litre of solution) as shown in Tables(1-3). Approximate values for Λ_0 were estimated from Λ vs. $C^{1/2}$ plots. Figures (1-3) in water at 25, 30 and 35°C , give straight lines from which Λ_0 value is estimated from the free hand extrapolation to zero concentration.

Table (1): Conductance of Co(III) complexes in water at 25°C

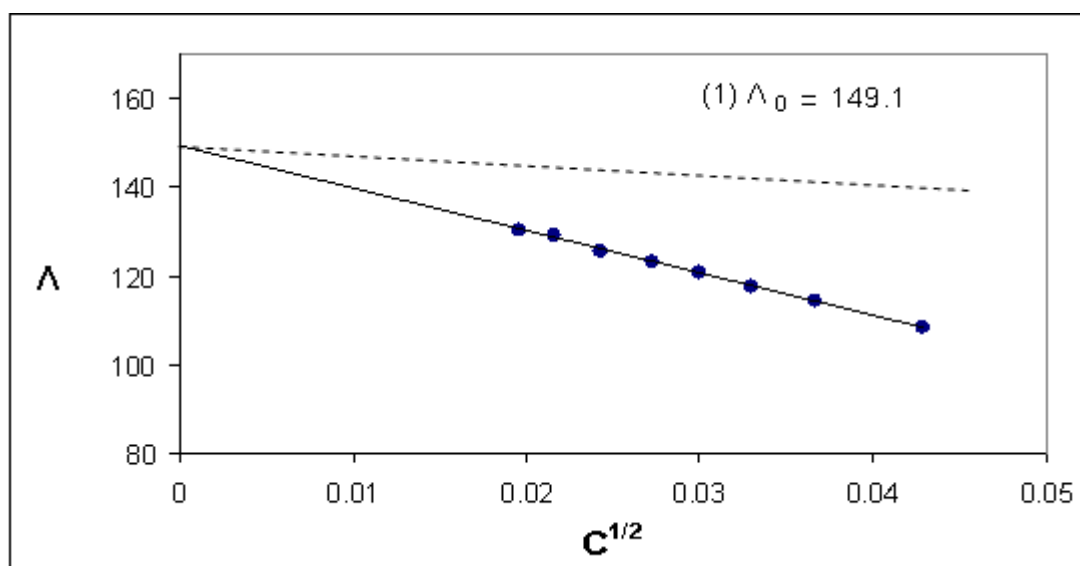
$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$		$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$		$[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$	
$C \times 10^4$ equiv l^{-1}	Λ $\text{ohm}^{-1} \text{ equiv}^{-1} \text{ cm}^2$	$C \times 10^4$ equiv l^{-1}	Λ $\text{ohm}^{-1} \text{ equiv}^{-1} \text{ cm}^2$	$C \times 10^4$ equiv l^{-1}	Λ $\text{ohm}^{-1} \text{ equiv}^{-1} \text{ cm}^2$
18.3649	108.30	18.2363	115.24	18.2931	108.07
13.4473	114.08	13.5440	120.47	13.1838	112.53
10.838	117.25	10.7895	123.38	10.3842	115.99
8.99144	120.71	8.6452	126.27	8.4714	118.14
7.47172	122.95	7.1489	128.73	6.5230	121.39
5.87568	125.52	5.8097	130.90	5.2924	123.18
4.66587	128.87	5.0787	132.16		
3.85674	130.36	4.1168	134.47		

Table (2): Conductance of Co(III) complexes in water at 30°C

[Co(NH ₃) ₅ Br]Cl ₂		[Co(NH ₃) ₅ Br]Br ₂		[Co(NH ₃) ₅ Br](ClO ₄) ₂	
C×10 ⁴ equiv I ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	C×10 ⁴ equiv I ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	C×10 ⁴ equiv I ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²
13.9476	133.36	18.3121	131.23	17.3270	121.96
11.0815	136.44	10.2592	138.86	14.4663	124.21
8.6234	139.66	8.4014	141.10	11.8412	126.98
6.9342	141.86	6.8958	143.37	9.7600	129.11
5.9142	143.38	5.8816	144.94	7.7746	131.60
5.0164	144.94	4.8168	146.72	6.2031	133.62
4.1936	146.46	3.9731	148.40		
		3.3712	149.71		

Table (3): Conductance of Co(III) complexes in water at 35°C

[Co(NH ₃) ₅ Br]Cl ₂		[Co(NH ₃) ₅ Br]Br ₂		[Co(NH ₃) ₅ Br](ClO ₄) ₂	
C×10 ⁴ equiv I ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	C×10 ⁴ equiv I ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	C×10 ⁴ equiv I ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²
18.8374	146.66	18.5379	150.66	18.3423	135.73
15.3625	149.92	15.2185	152.75	15.1402	138.54
12.5483	152.04	12.4153	155.47	12.7760	140.20
10.3702	153.95	10.1817	157.88	10.4353	142.18
9.0168	155.78	8.1270	159.80	8.6891	144.02
7.8730	157.21	7.0157	161.23	7.2185	145.48
6.6021	158.71	6.1563	162.57	5.8593	147.19
5.7272	160.11			4.7958	148.39



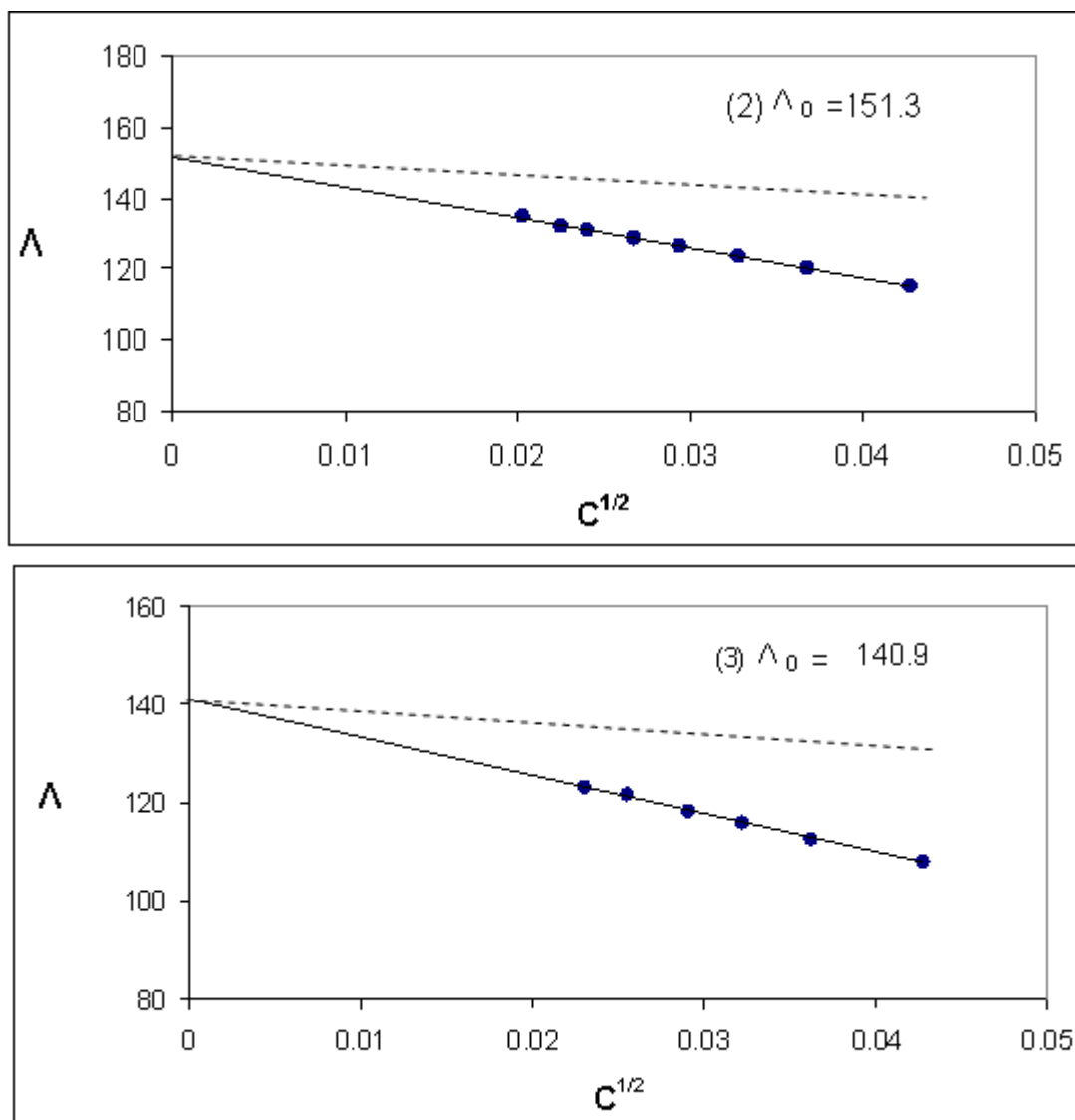
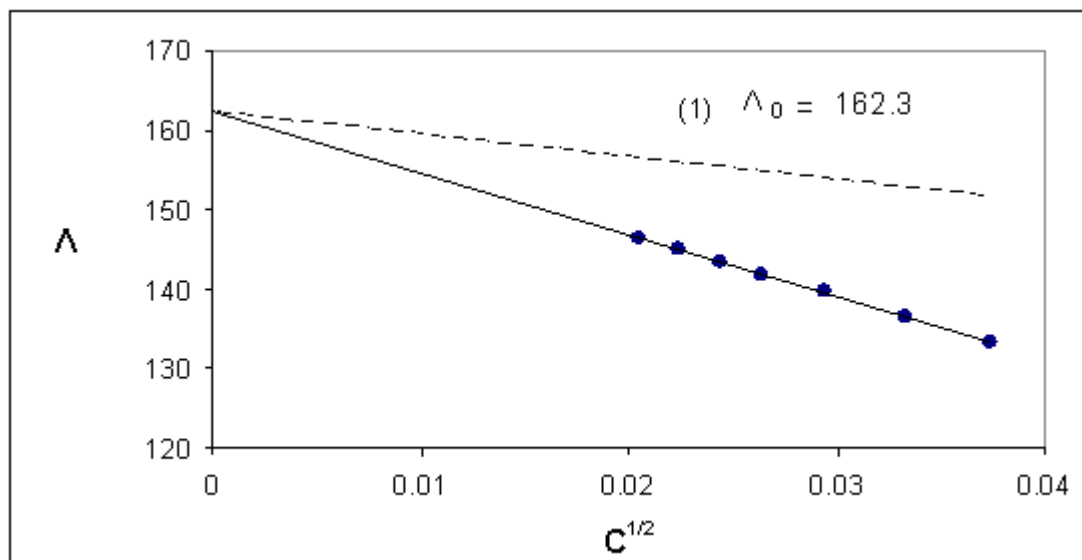


Fig. (1): Conductance of (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$, (3) $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at 25°C



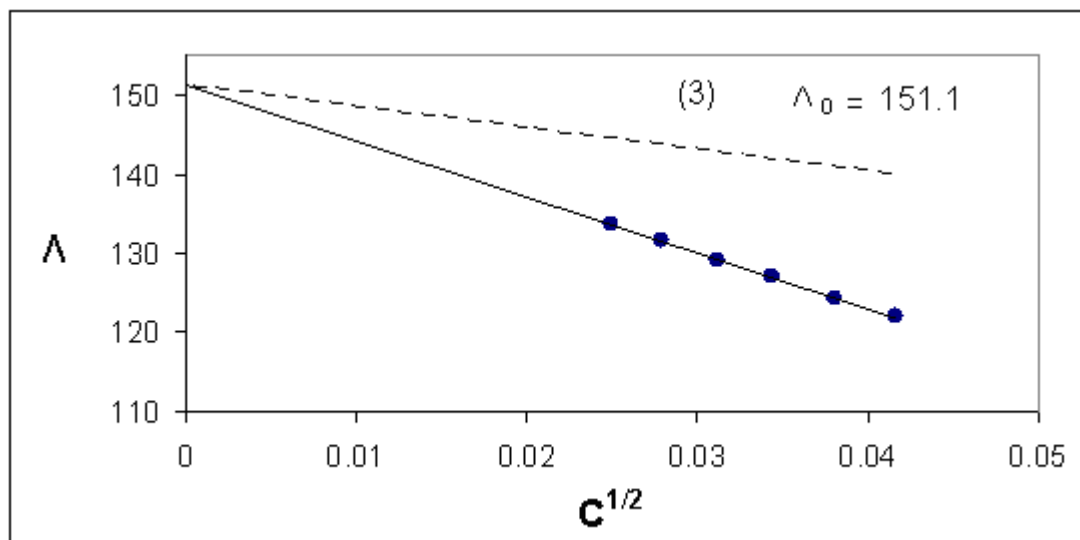
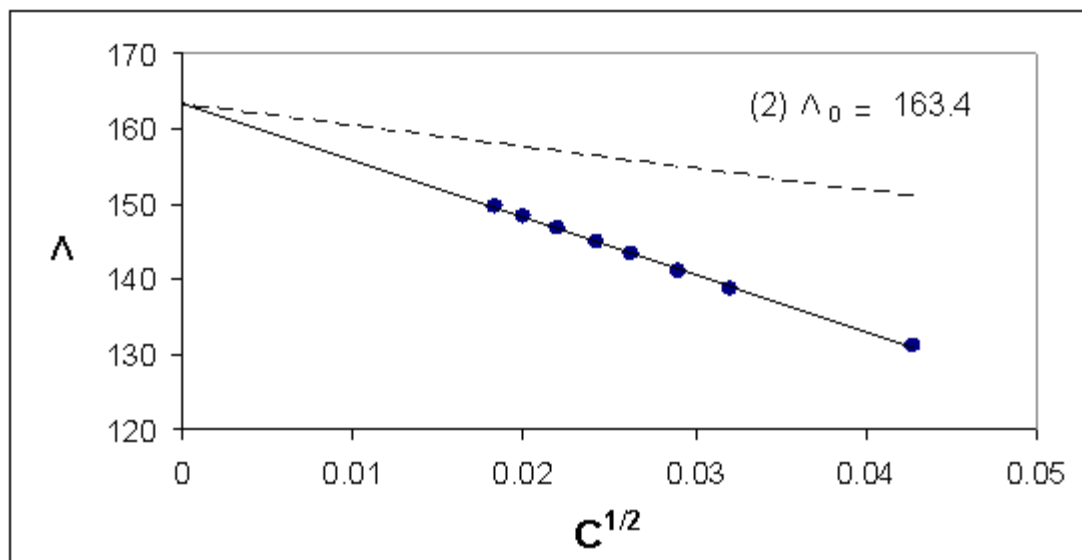
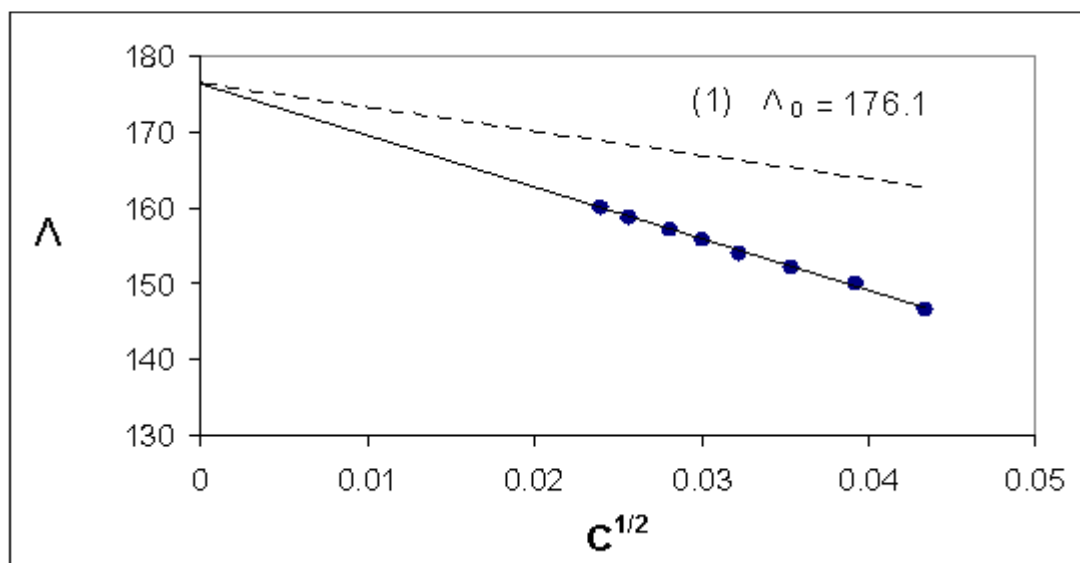


Fig. (2): Conductance of (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$, (3) $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at 30°C .



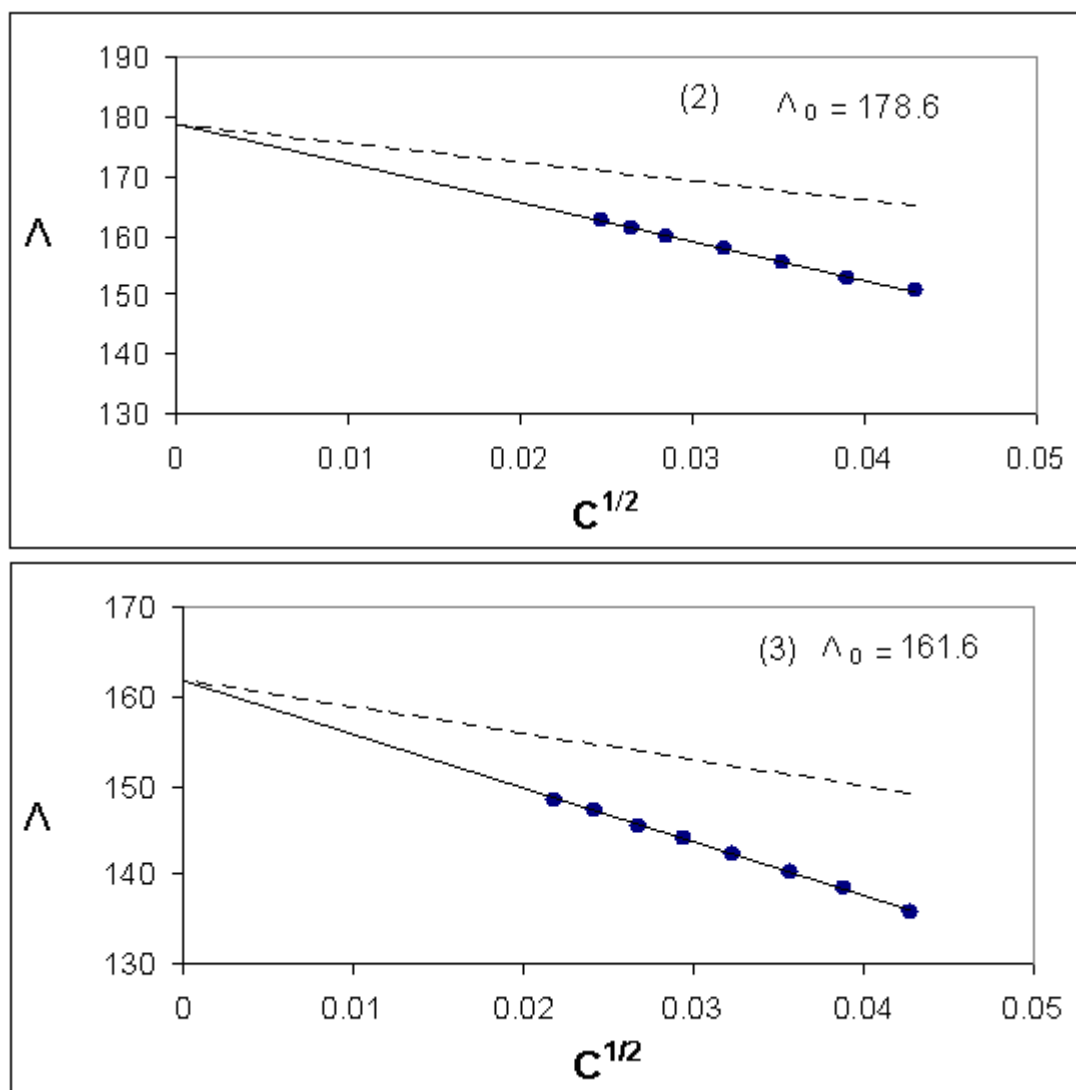
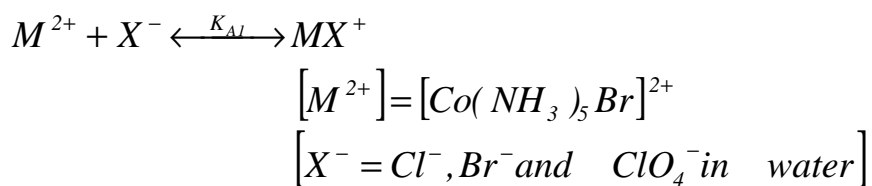


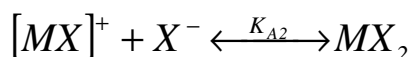
Fig. (3): Conductance of (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$, (3) $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at 35°C .

Figures (1-3) illustrate these plots in which the solid lines represent the experimental data, while the dotted ones represent the theoretical Onsager slopes. It can be seen that in all cases the experimental lines are below the theoretical one indicating ion association.

The data were analyzed using the Fuoss-Edelson⁽⁶⁾ (F-E) method to obtain a more accurate value of Λ_0 and the association constant K_A .

In this method two assumptions were made for 2:1 electrolytes. The association equilibrium is 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 of MX^+ depending on the fact that the chelate cations are considerably large than the anions, accordingly M^{2+} can be thought to be hydro-dynamically equivalent to MX^+ except in charge type since the ratio of the charges equals that of the mobility. Figures (4-6) represents Λ' Vs. X plots from the Fuoss-Edelson method for the cobalt (III) complexes halides and perchlorate in water at different temperatures.

All Figures follow this equation:

$$\Lambda' = \Lambda_0 - \frac{X}{K_{D1}\Lambda_0}$$

Where $\Lambda' = \Lambda$ except F, where F is a function of C and Λ_0 which corrects the conductance ratio Λ/Λ_0 for the effect of interionic forces on the mobility, and is given by the equation:

$$F = \left[\frac{I}{I + \lambda_2^0/2\Lambda_0} \right] \left[\frac{I}{I + \delta\sqrt{c}} + \frac{\lambda_2^0}{2\Lambda} \right]$$

Where λ_2^0 is the ionic equivalent conductance of the divalent cation and δ is the Onsager slope (S) for (2:1) salt divided by Λ_0 ; S_(2:1) can be calculated from the following equation:

$$S_{(2:1)} = \left[\frac{6.86 \times 10^6}{(DT)^{3/2}} \cdot \frac{q^*}{C I + \sqrt{q^*}} \Lambda_0 \right] + \frac{151.6}{\eta (DT)^{1/2}},$$

And

q^* is calculated from the equation

$$q^* = \frac{2}{3} \left(I + \frac{\lambda_a^0}{\Lambda_0} \right)$$

$$S = A\Lambda_0 + B$$

Where $X = C'\Lambda'(A' - \frac{1}{2}\Lambda_0)$, $C' = C f_B$

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

$$\begin{aligned}
 -\log f_B &= AZ_B^2 \sqrt{I} \\
 I &= \frac{1}{2} C(2\alpha + 1) = 3C \\
 Z_B^2 &= 4 \\
 A &= \frac{1.823 \times 10^6}{(DT)^{3/2}} \\
 -\log f_B &= \left[\frac{1.823 \times 10^6}{(DT)^{3/2}} \right] \times Z_B^2 \sqrt{3C} \\
 -\log f_B &= \left[\frac{1.823 \times 10^6}{(DT)^{3/2}} \right] \times 4\sqrt{3C}
 \end{aligned}$$

Where Z_B is 2 and $3C$ is the ionic concentration since,

$$\begin{aligned}
 A' &= A_0 - \frac{[C'A'(A' - \frac{1}{2}A_0)]}{K_{D1A_0}}, \\
 A' &= A_0 - \frac{X}{K_{D1A_0}}
 \end{aligned}$$

$$\text{Where } X = C'A'(A' - \frac{1}{2}A_0), \quad C' = C f_B$$

The plot of A' Vs. X gives A_0 intercept and $\frac{1}{K_{D1}} = K_{A1}$ as the slope. To obtain sensitive and accurate results, the intercept and slope must be obtained by least square method. All calculations in (F-E) were determined by a computer program.

As can be readily seen from the previous Figures all plots are straight lines from which A_0 can be obtained as the intercept; while $\frac{1}{K_{D1}} = K_{A1}$ can be obtained from the slope. The derived constants in water at different temperatures are listed in Tables (7-15).

It is evident from Tables (4-6) that the values of A_0 increase with increase the temperatures for Co(III) complexes halides and perchlorate indicating less solvation or higher mobility of ions in all solvent systems studies⁽¹³⁾.

This is due to the fact that the increased thermal energy results in greater bond breaking and variation in vibration, rotational and translation energy of molecules that lead to higher frequency and higher mobility of the ions⁽¹³⁾.

A perusal of Tables (4-6) shows that the A_0 values of Co(III) complex bromide are higher than those of Co(III) complex chloride in different temperatures in aqueous solutions and in all solvent systems studies⁽¹³⁾.

Table (4): The characteristic parameters for Co(III) complexes halides and perchlorate in water at 25° C derived from Fuoss-Edelson equation

Complex	Λ_0	λ^-	λ^+	The Average value	$K_D \times 10^3$	K_A	f_{\pm}^+	f_{\pm}^-	$f_{\pm}^+ f_{\pm}^-$	a^{\pm} ion-pair
[Co(NH ₃) ₅ Br]Cl ₂	146.7	76.42	70.28	70.11± 0.24%	2.188	456.971	2.626	1.204	3.830	5.251
[Co(NH ₃) ₅ Br]Br ₂	148.4	78.65	69.75		3.107	321.880		1.170	3.796	
[Co(NH ₃) ₅ Br](ClO ₄) ₂	138.3	68.00	70.30		3.326	300.664		1.353	3.979	

Table (5): The characteristic parameters for Co(III) complexes halides and perchlorate in water at 30° C derived from Fuoss-Edelson equation

Complexes	Λ_0	λ^-	λ^+	The Average value	$K_D \times 10^3$	K_A	f_{\pm}^+	f_{\pm}^-	$f_{\pm}^+ f_{\pm}^-$	a^{\pm} ion-pair
[Co(NH ₃) ₅ Br]Cl ₂	159.0	84.25	74.75	74.65± 0.23%	4.645	215.286	2.752	1.219	3.971	5.504
[Co(NH ₃) ₅ Br]Br ₂	160.3	86.00	74.30		4.866	205.505		1.194	3.947	
[Co(NH ₃) ₅ Br](ClO ₄) ₂	148.4	73.50	74.9		5.018	199.301		1.398	4.150	

Table (6): The characteristic parameters for Co(III) complexes halides and perchlorate in water at 35° C derived from Fuoss-Edelson equation

Complexes	Λ_0	λ^-	λ^+	The Average value	$K_D \times 10^3$	K_A	f_{\pm}^+	f_{\pm}^-	$f_{\pm}^+ f_{\pm}^-$	a^{\pm} ion-pair
[Co(NH ₃) ₅ Br]Cl ₂	173.4	92.2	81.2	81.07± 0.71%	7.669	130.397	2.810	1.235	4.045	5.620
[Co(NH ₃) ₅ Br]Br ₂	176.0	94.0	82.0		8.596	116.336		1.212	4.022	
[Co(NH ₃) ₅ Br](ClO ₄) ₂	159.3	79.5	80.0		8.804	113.581		1.433	4.243	

This is reasonable in view of the difference in transport properties of solvated bromide which reflects factors affecting its effective size and strength of columbic field in the range of the solvation shell ⁽¹³⁾.

The factors which affect the size of bromide can be the radii of the nonsolvated cation and the interionic distance between bromide and Co(III) complex cation. Both the factors influence the solvodynamic radii of the ions and thus influence the Λ_0 values ⁽¹³⁾.

Tables (4-6) shows that the values of cationic conductance [Co (NH₃)₅Br]²⁺ in water at different temperatures are taken as average values from the conductance measurements of three complexes chloride, bromide and perchlorate at different temperatures.

Table (7): Fuoss-Edelson equation of [Co(NH₃)₅Br]Cl₂ in water at 25° C

$C \times 10^4$ equiv l ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	F	Λ'	f_B	$c' \times 10^4$	X
18.3649	108.30	1.1374	123.18	0.6726	12.3520	7.3983
13.4473	114.08	1.1139	127.07	0.7122	9.5772	6.3923
10.838	117.25	1.1012	129.11	0.7374	7.9914	5.6294
8.99144	120.71	1.0895	131.52	0.7577	6.8124	5.1045
7.47172	122.95	1.0811	132.92	0.7765	5.8016	4.5016
5.87568	125.52	1.0716	134.50	0.799	4.6949	3.7857
4.66587	128.87	1.0616	136.81	0.8188	3.8204	3.2541
3.85674	130.36	1.0561	137.67	0.8338	3.2158	2.7945

The previous behaviour is in agreement with that obtained for a complex with different anions since the obtained Λ_0 (bromide complex) $>$ Λ_0 (chloride complex) $>$ Λ_0 (perchlorate complex), were in different temperatures. This trend is also attributed to ionic solvation⁽¹⁴⁾. Tables (4-6) show that the values of ionic association K_{AI} decrease with increase the anionic size and temperatures, since the obtained⁽⁷⁻¹⁴⁾; K_A (chloride Co(III) complex) $>$ K_A (bromide Co(III) complex) $>$ K_A (perchlorate Co(III) complex) at different temperatures.

Table (8): Fuoss-Edelson equation of [Co(NH₃)₅Br]Br₂ in water at 25° C

A=0.9667		B=111.2756			q*=1.0132	
C×10 ⁴ equiv l ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	F	Λ'	f _B	c'×10 ⁴	X
18.2363	115.24	1.1238	129.51	0.6735	12.2826	8.5669
13.5440	120.47	1.1034	132.93	0.7113	9.6343	7.3354
10.7895	123.38	1.0916	134.68	0.7379	7.9611	6.3291
8.6452	126.27	1.0809	136.48	0.7618	6.5855	5.4678
7.1489	128.73	1.0724	138.05	0.7808	5.5817	4.8086
5.8097	130.90	1.0647	139.37	0.8001	4.6480	4.1276
5.0787	132.16	1.0602	140.12	0.8117	4.1226	3.7240
4.1168	134.47	1.0531	141.61	0.8288	3.4119	3.1870

Table (9): Fuoss-Edelson equation of [Co(NH₃)₅Br](ClO₄)₂ in water at 25° C

A=0.9489		B= 111.2756			q*=0.9884	
C×10 ⁴ equiv l ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	F	Λ'	f _B	C'×10 ⁴	X
18.2931	108.07	1.1263	121.71	0.6731	12.3132	7.6826
13.1838	112.53	1.1054	124.38	0.7146	9.4210	6.3198
10.3842	115.99	1.0913	126.58	0.7421	7.7063	5.4749
8.4714	118.14	1.0819	127.82	0.7639	6.4709	4.7454
6.5230	121.39	1.0700	129.88	0.7895	5.1498	3.9751
5.2924	123.18	1.0627	130.90	0.8082	4.2774	3.3848

Table (10): Fuoss-Edelson equation of [Co(NH₃)₅Br]Cl₂ in water at 30° C.

A= 0.9786		B=124.7144			q*=1.0127	
C×10 ⁴ equiv l ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	F	Λ'	f _B	c'×10 ⁴	X
13.9476	133.36	1.0982	146.4505	0.6985	9.7420	9.3165
11.0815	136.44	1.0864	148.2294	0.7262	8.0478	8.0021
8.6234	139.66	1.0749	150.1177	0.7541	6.5033	6.7330
6.9342	141.86	1.0667	151.3205	0.7764	5.3840	5.7168
5.9142	143.38	1.0613	152.1611	0.7916	4.6818	5.0587
5.0164	144.94	1.0560	153.0530	0.8064	4.0451	4.4516
4.1936	146.46	1.0508	153.9042	0.8214	3.4445	3.8569

Table (11): Fuoss-Edelson equation of [Co(NH₃)₅Br]Br₂ in water at 30° C

A=0.9822		B=124.7144			q*=1.0178	
C×10 ⁴ equiv l ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	F	Λ'	f _B	C'×10 ⁴	X
18.3121	131.23	1.1121	145.9351	0.6629	12.1383	11.3875
10.2592	138.86	1.0816	150.1918	0.7351	7.5413	7.7634
8.4014	141.10	1.0732	151.4283	0.7569	6.3591	6.7192
6.8958	143.37	1.0655	152.7548	0.7770	5.3580	5.8196
5.8816	144.94	1.0600	153.6377	0.7921	4.6589	5.1528

4.8168	146.72	1.0538	154.6208	0.8099	3.9010	4.4014
3.9731	148.40	1.0484	155.5751	0.8257	3.2805	3.7729
3.3712	149.71	1.0441	156.3237	0.8383	2.8259	3.2987

Table (12): Fuoss-Edelson equation of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at 30° C.

A=0.9627

B= 124.7144

q*=0.9910

$C \times 10^4$ equiv l ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	F	Λ'	f_B	$C' \times 10^4$	X
17.3270	121.96	1.1128	135.7200	0.6703	11.6149	9.4850
14.4663	124.21	1.1023	136.9153	0.6939	10.0377	8.4335
11.8412	126.98	1.0910	138.5308	0.7185	8.5074	7.4225
9.7600	129.11	1.0819	139.6846	0.7407	7.2290	6.4761
7.7746	131.60	1.0720	141.0787	0.7650	5.9473	5.4981
6.2031	133.62	1.0638	142.1461	0.7872	4.8829	4.6223

Table (13): Fuoss-Edelson equation of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$ in water at 35° C.

A=0.9913

B=138.7838

q*=1.0157

$C \times 10^4$ equiv l ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	F	Λ'	f_B	$c' \times 10^4$	X
18.8374	146.66	1.1062	162.2361	0.6492	12.2291	14.7186
15.3625	149.92	1.0941	164.0328	0.67696	10.3998	12.9619
12.5483	152.04	1.0848	164.9332	0.7029	8.8196	11.1838
10.3702	153.95	1.0768	165.7658	0.7258	7.5262	9.6957
9.0168	155.78	1.0707	166.7877	0.7416	6.6872	8.7820
7.8730	157.21	1.0656	167.5160	0.7563	5.9545	7.9265
6.6021	158.71	1.0598	168.1925	0.7743	5.1122	6.8909
5.7272	160.11	1.0551	168.9362	0.7880	4.5132	6.1671

Table (14): Fuoss-Edelson equation of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ in water at 35° C

A=0.9926

B=138.7838

q*=1.0175

$C \times 10^4$ equiv l ⁻¹	Λ ohm ⁻¹ equiv ⁻¹ cm ²	F	Λ'	f_B	$c' \times 10^4$	X
18.5379	150.66	1.1022	166.0605	0.6514	12.0763	15.3935
15.2185	152.75	1.0924	166.8575	0.6782	10.3212	13.3567
12.4153	155.47	1.0823	168.2576	0.7042	8.7425	11.6146
10.1817	157.88	1.0735	169.4873	0.7279	7.4110	10.0722
8.1270	159.80	1.0655	170.2686	0.7529	6.1192	8.4361
7.0157	161.23	1.0604	170.9688	0.7682	5.3897	7.5256
6.1563	162.57	1.0560	171.6726	0.7812	4.8091	6.8006

Table (15): Fuoss-Edelson equation of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at 35° C.
 $A=0.9489$ $B=138.7838$ $q^*=0.9884$

$C \times 10^4$ equiv l ⁻¹	A ohm ⁻¹ equiv ⁻¹ cm ²	F	A'	f_a	$C' \times 10^4$	X
18.3423	135.73	1.1066	150.1989	0.6529	11.9760	12.4833
15.1402	138.54	1.0950	151.7025	0.6789	10.2784	11.0555
12.7760	140.20	1.0869	152.3841	0.7006	8.9511	9.7641
10.4353	142.18	1.0779	153.2561	0.72503	7.5659	8.4014
8.6891	144.02	1.0703	154.1459	0.7457	6.4796	7.3258
7.2185	145.48	1.0638	154.7638	0.7653	5.5246	6.3239
5.8593	147.19	1.0569	155.5660	0.7859	4.6047	5.3558
4.7958	148.39	1.0514	156.0204	0.8041	3.8565	4.5259

Table (16) Thermodynamic Parameters of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$

T (K)	a° (A°)	Λ_∞ (ohm ⁻¹ equiv ⁻¹ cm ²)	K_A	ΔE_s° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
298	3.83	146.7	456.971	12.77	-95.79	-15.17	-270.54
303	3.97	159.0	215.286			-13.53	-271.49
308	4.05	173.4	130.397			-12.47	-270.52

Table (17) Thermodynamic Parameters of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$

T (K)	a° (A°)	Λ_∞ (ohm ⁻¹ equiv ⁻¹ cm ²)	K_A	ΔE_s° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
298	3.80	148.4	321.880	13.01	-77.60	-14.31	-212.38
303	3.95	160.3	205.505			-13.42	-211.82
308	4.02	176.0	116.336			-12.18	-212.40

Table (18) Thermodynamic Parameters of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$

T (K)	a° (A°)	Λ_∞ (ohm ⁻¹ equiv ⁻¹ cm ²)	K_A	ΔE_s° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
298	3.98	138.3	300.664	10.79	-74.21	-14.14	-201.58
303	4.15	148.4	199.301			-13.34	-200.89
308	4.24	159.3	113.581			-12.12	-201.59

Table (19): the values of limiting equivalent conductance Λ_0 (ohm⁻¹ cm² eq⁻¹) association constant K_A and thermodynamics parameters of the $\text{Co}(\text{III})$ complex in water using Shedlovsky method at different temperatures (25,30,35,40°C)

Temperature °C	Λ_0 (ohm ⁻¹ cm ² eq ⁻¹)	K_A	(ΔH°) (KJ K ⁻¹ mol ⁻¹)	ΔG° (KJ mol ⁻¹)	$(\Delta S^\circ) 10^3$ (J K ⁻¹ mol ⁻¹)	ΔE_s (KJ mol ⁻¹)
25°C	138.66	344.78	-37.84	-14.48	-145.43	9.37
30°C	148.48	308.40		-14.44	-143.16	
35°C	155.15	161.36		-13.02	-145.45	
40°C	164.88	95.73		-11.87	-146.80	

Table (20): Results of conductometric data processing for solutions of $Mg(ClO_4)_2$ and $Ni(ClO_4)_2$ in acetonitrile; $\Lambda_0[\frac{1}{2}Kt(ClO_4)_2]$, $\lambda_0[Kt(ClO_4)_2]$, association constants, and R is in P m.

$Mg(ClO_4)_2$				
$T^\circ C$	Λ_0	$\lambda_0 [Kt(ClO_4)_2]^+$	$\log K_{AI}$	R
5	153.1	89	2.35	860
15	171.5	98	2.41	863
25	190.3	99	2.45	865
35	209.3	100.6	2.4759	868
45	228.0	105	2.513	871
55	248.5	108	2.568	873
$Ni(ClO_4)_2$				
$T^\circ C$	Λ_0	$\lambda_0 [Kt(ClO_4)_2]^+$	$\log K_{AI}$	R
25	231	160.7	2.21	865
35	254.4	173	2.26	868
45	280	182.1	2.30	871
55	304	194.8	2.32	873
65	329.9	209	2.34	876
75	358	229	2.39	879

Table (21): Limiting molar conductivities of equivalents in acetonitrile and coulomb interionic association constants for formation of contact (CIP) and solvation separated (SSIP) ion pairs

$T^\circ C$	$\lambda_0(\frac{1}{2}Mg^{2+})$	$\lambda_0(\frac{1}{2}Ni^{2+})$	$\lambda_0(ClO_4^-)$	$\log K_A^{CIP}$	$\log K_A^{SSIP}$
5	68.90	-----	82.97(84.94)	2.92	1.88
15	77.20	-----	93.41(94.16)	2.95	1.89
25	85.64	129.64	103.86(103.62)	2.98	1.90
35	94.17	142.77	114.31	3.01	1.92
45	102.60	156.93	124.76	3.05	1.94
55	111.82	170.36	135.21	3.09	1.96
65	-----	184.76	145.66	3.14	1.98
75	-----	200.71	156.10	3.18	2.00

Calculation of the distance of closest approach (a^0); there are two methods⁽¹⁵⁾ dealing with calculation of the distance of closest approach (a^0); for an ion-pair of the form $[MX]^+$, these are:

- (1) the ionic radius of both cation and anion is calculated using stokes equation:

$$r_{s^+} = \frac{0.8194(Z_i)}{\lambda_{2^+}^0 \eta^0} \quad r_{s^-} = \frac{0.8194(Z_j)}{\lambda_-^0 \eta^0}$$

- (2) $r_{ion-pair}$ can be calculated using stokes equation directly,

$$r_{ion-pair} = \frac{0.8194(Z_i Z_j)}{\lambda_{ion-pair}^0 \eta^0} \quad \text{Substituting for}$$

$$\lambda_{ion-pair}^0 = \lambda_{2^+}^0 / 2$$

Application of the first method requires the values of $\lambda_{2^+}^0$ and λ_-^0 in different temperatures, these were obtained as follows:

The values of (a^0) ion-pair by two methods of calculations are consumed in Tables (16-18) from which one can observe that the values of (a^0) obtained from second method of calculation are more acceptable and indicate solvation.

The trend of (a^0) is in agreement with electrostatic ⁽¹⁴⁾ theories and it explains the trend of K_A , since (a^0) increases with increase the temperature; indicating a decrease in K_A values with increase the temperature.

This can be explained mainly by anionic solvation which increases as crystallo-graphic radius decreases, and the anionic solvation increases with increase the temperatures. $a_{ion-pair}^0$ (solvation) increases with increase the temperatures but K_A decreases with increase temperatures. The trend of anionic solvation, $a_{ion-pair}^0$ (solvation) with K_A are in agreement with electrostatic theories ⁽¹⁶⁾.

The experimental data of conductance measurement of 2:1 complexes of bromopentamine cobalt (III) halides and perchlorate in water at different temperatures were analyzed using Fuoss-Edelson ⁽⁶⁾. Since the conductance of an ion depends on its mobility, it is reasonable to treat the conductance data similar to the one that employs for rate processes taking place with change of temperature ⁽¹⁷⁾, i.e.,

$$A_0 = A e^{-\Delta E_s / RT} \quad \text{or} \quad \ln A_0 = \ln A - \Delta E_s / RT$$

Where A is the frequency factor, R is the ideal gas constant and ΔE_s is the Arrhenius activation energy of transport processes.

Thus from the plot of $\log A_0$ vs. $1/T$ for complexes of bromopentamine halides and perchlorate in water at different temperatures, the ΔE_s values have been computed from the slope ⁽¹⁸⁾ and recorded in Tables (16-18) and Fig (7).

A perusal of Tables (16-18) show that the values of ΔE_s increase from chloride to bromide and decrease from bromide to perchlorate. This indicates lower mobilites of ions in solutions and hence lowers A_0 values.

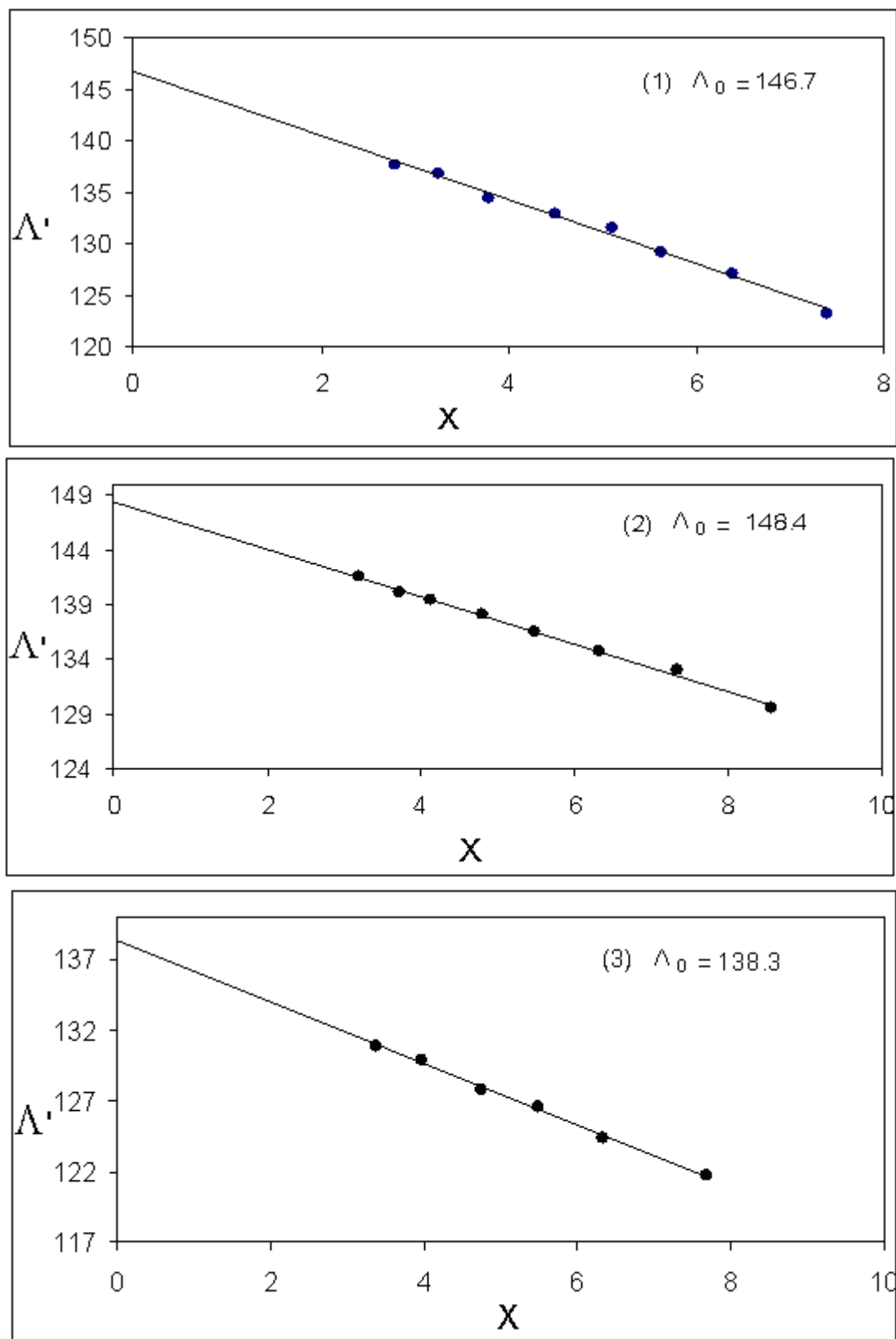


Fig. (4): Fuoss-Edelson plot for (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$, (3) $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at 25°C

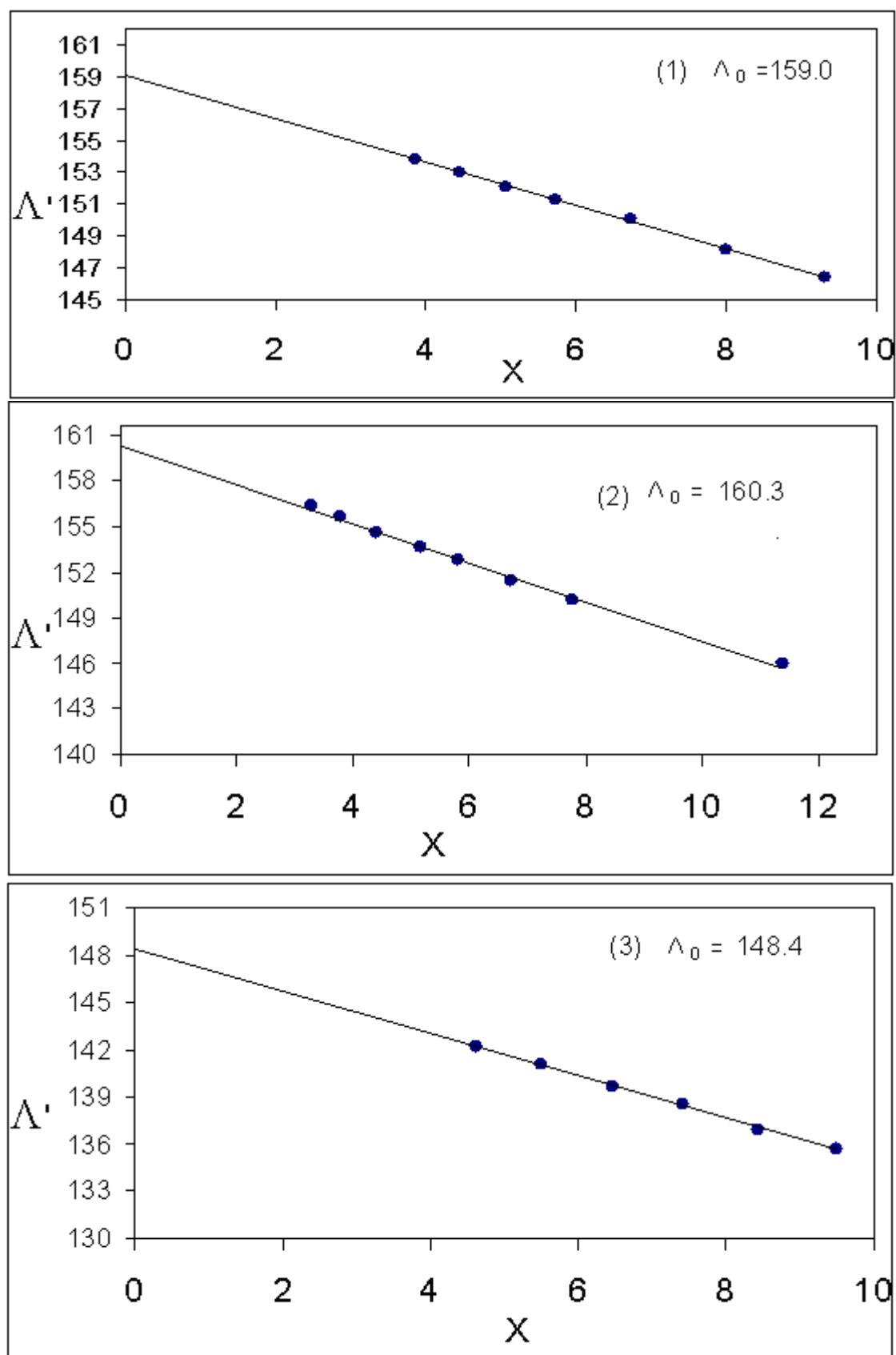


Fig. (5): Fuoss-Edelson plot for (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$, (3) $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at 30°C.

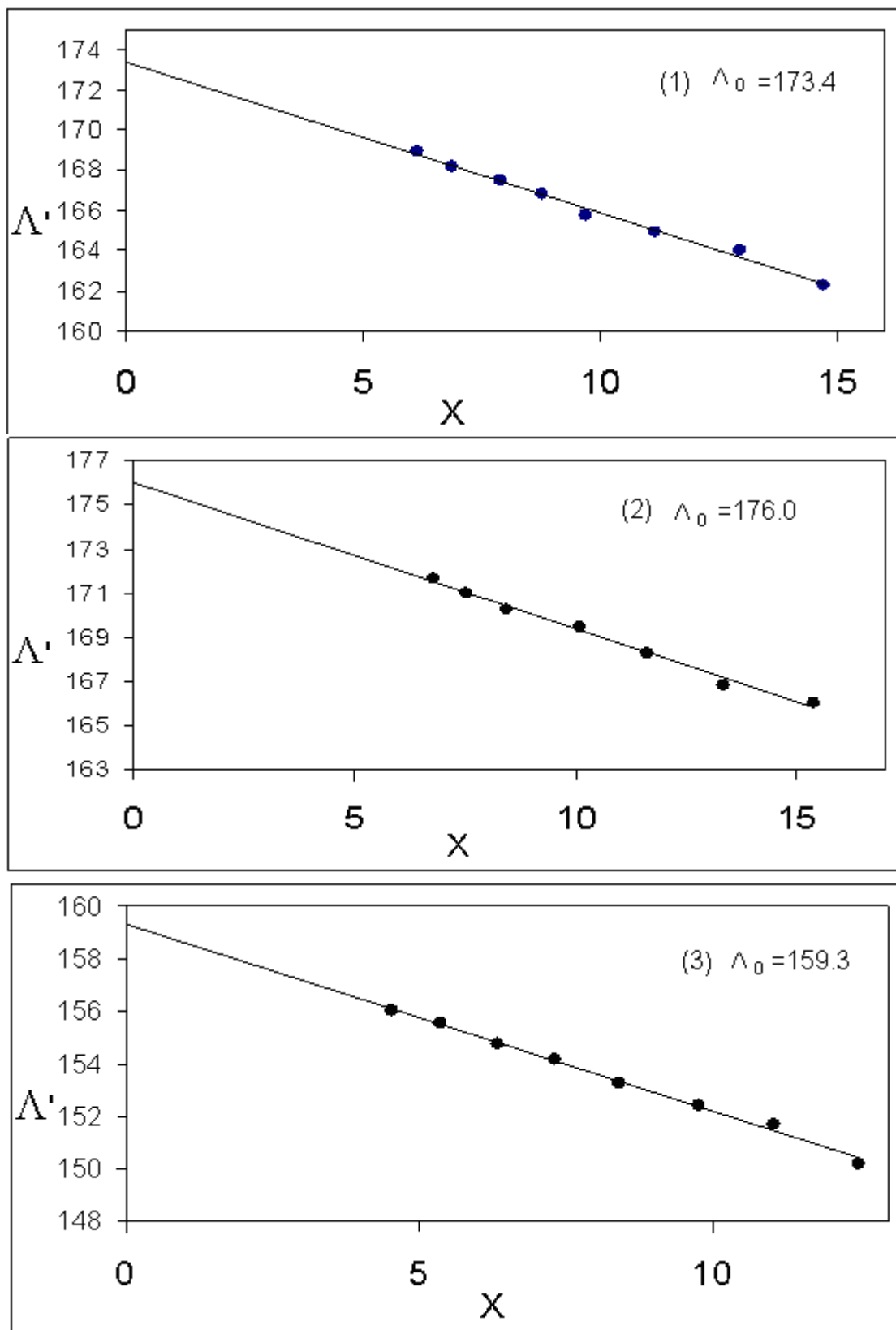


Fig. (6): Fuoss-Edelson plot for (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$, (3) $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at 35°C.

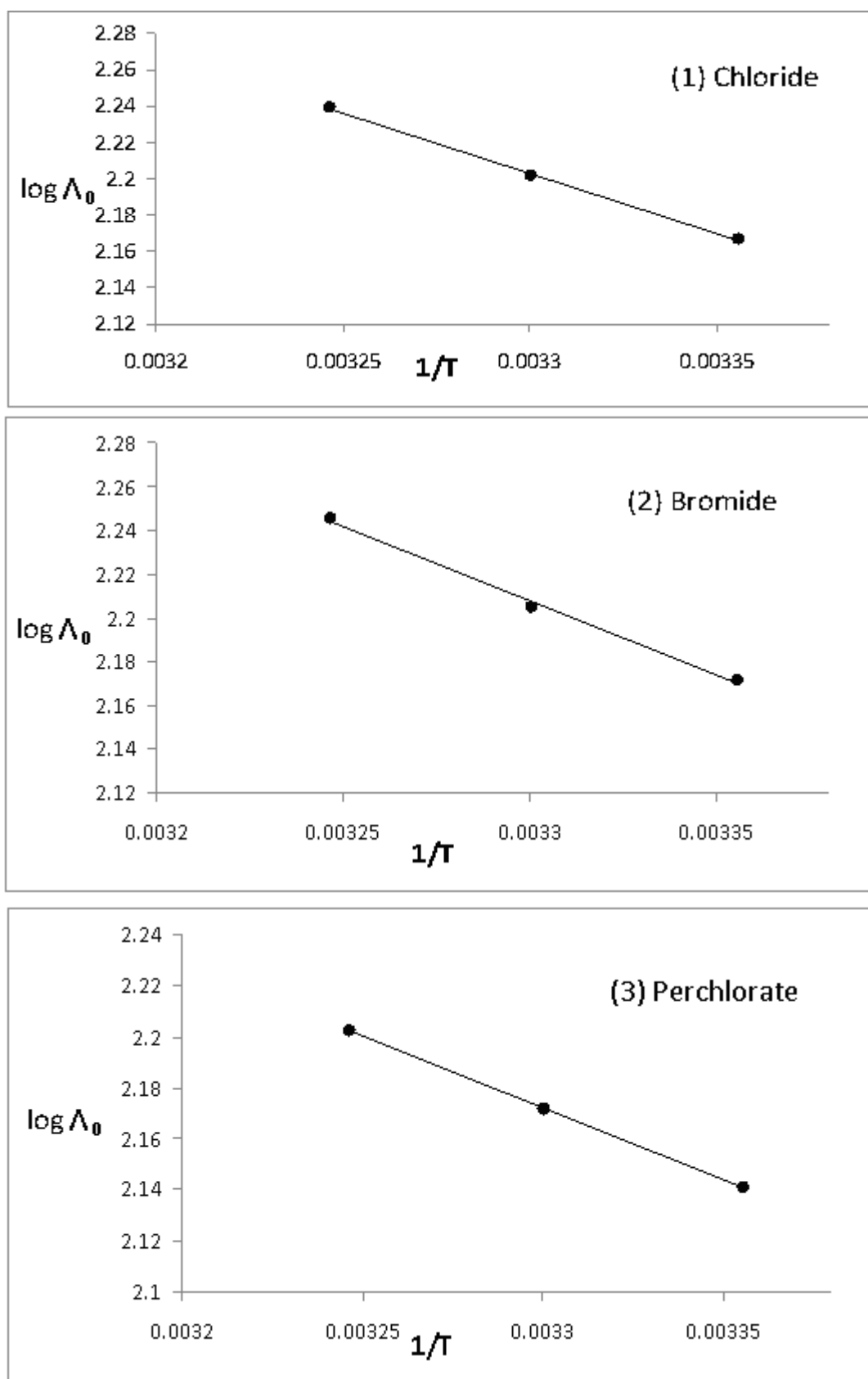


Fig. (7): The variation of $\log \Lambda_0$ Vs $1/T$ for (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$, (3) $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at different Temperatures.

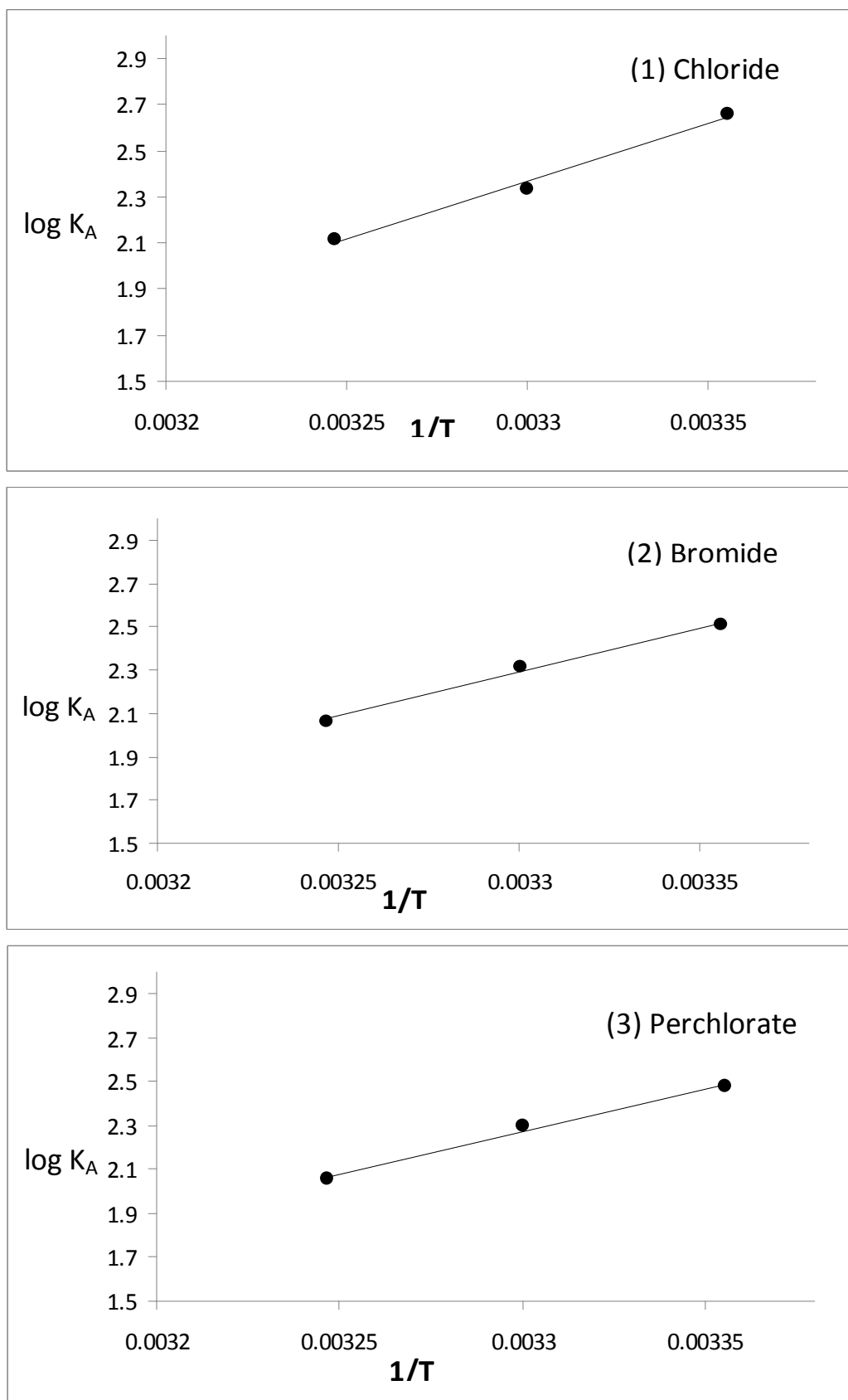


Fig. (8): The variation of $\log K_A$ Vs $1/T$ for (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$, (3) $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in water at different Temperatures.

The free energy change (ΔG^0) for association is calculated from the relation ⁽¹⁹⁾ ($\Delta G^0 = -RT \ln K_A$). The heat of association (ΔH^0) is obtained from the slope of the plot of $\log K_A$ vs. $1/T$ (Fig.8).

The entropy change (ΔS^0) is calculated from Gibbs-Helmholtz equation; ($\Delta G^0 = \Delta H^0 - T\Delta S^0$).

The values of these thermodynamic functions are given in Tables (16-18). The negative values of (ΔH^0) indicate that ion association processes are exothermic in nature in water at all temperatures.

The effect of temperature Tables(16-18) can be noticed from the decreasing in the negative values of the associating free energy as the temperature is raised.

Also, the solvated radii are increased with temperature indicating a higher solvation process due to increase in the electronic clouds around the solvated molecules as a result of increase in their vibration and rotation motion ⁽²⁰⁾.

The limiting equivalent conductance and dissociation degree were also increased as the temperature increased indicating higher solvation process ⁽²⁰⁾.

The negative values of different thermodynamic parameters ($\Delta G^0, \Delta H^0, \Delta S^0$) for all complexes under consideration in the used solvents, indicate exothermic association process, i.e., the association process is less energy consuming and more stabilized ⁽¹⁷⁾.

Bag et al. ⁽²¹⁾ measured the conductance and ion association of diammino-bis-1-amidino-*o*-methylurea cobalt (III) monochloride in aqueous solutions at different temperatures (25, 30, 35 and 40 °C) and evaluated the thermodynamic parameters ($\Delta G^0, \Delta H^0, \Delta S^0$) and activation energy are given in Table (19). It was found that, Λ_0 increases while K_A decreases with increasing the temperatures. The negative values of (ΔH^0) indicates that ion association processes are exothermic in nature in all solvents at all temperatures. At a particular temperature ΔG^0 becomes more negative with the increase in temperatures. This indicates that ion-pair association is favoured with lowering the dielectric constant of the medium ⁽²²⁾, in agreement with our results.

Kalugin et al. (23), studied the conductometric data on solutions of $Mg(ClO_4)_2$ and $Ni(ClO_4)_2$ in acetonitrile over the temperature ranges (5-55 °C) for $Mg(ClO_4)_2$ and (25-75 °C) for $Ni(ClO_4)_2$. The extended Lee-Wheaton equation for unsymmetrical electrolytes was used to determine the limiting equivalent conductivities of the Mg^{2+} , Ni^{2+} , and $(ClO_4)^-$ ions and first-step ionic association constants with the formation of $[KtClO_4]^+$ ion pairs. It was found that from Tables (20,21) the Λ_0 , $\lambda_0 [KtClO_4]^+$, $\log K_{A1}$ and R (solvation) increases with the increasing of the temperature values for two complexes $Mg(ClO_4)_2$ and $Ni(ClO_4)_2$. An analysis of Table (21) shows that the logarithm of first-step association constant increases by approximately 0.2 units as the temperature grows to 50 °C for both $[Mg(ClO_4)_2]^+$ and $[Ni(ClO_4)_2]^+$. Clearly, strengthening of interionic association at high 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.

$a = r_+ + r_-$ is the sum of the radii of the ions, and R is the sum of the radii of the ions including their solvation shells. We used the experimental $\log K_{A1}$ values Table(21) and Ebeling model for the coulomb ionic association constant $(K_A)^{coul(24)}$ to determine $d \pm$.

In absence of short range interionic interaction caused by solvation effects over the range of interionic distance $a < r < R$, that is as $d \pm \rightarrow 0$, the K_A value is actually determined by coulomb constant of formation of a contact ion pair (CIP)

$$K_A^{CIP} = \frac{4\pi N_A}{10^3} K_A^{Coul} (a) .$$

However, if ions are very stable solvation shells, which prevent their approach to each other by distance shorter than R because $d \pm \rightarrow \infty$, the experimental association constant should be equal to the coulomb constant of formation of a solvation separated ion pair (SSIP)

$$K_A^{SSIP} = \frac{4\pi N_A}{10^3} K_A^{Coul} (R) .$$

The calculated K_A^{CIP} and K_A^{SSIP} values for $[Mg (ClO_4)_2]^+$ and $[Ni (ClO_4)_2]^+$ ion pairs are listed in Table (20).

A comparison of the experimental first-step ionic association constant (Table) with the corresponding K_A^{CIP} and K_A^{SSIP} values Table (21) and an analysis of the $d \pm$ values. Since the experimental K_{A1} values are larger than K_A^{SSIP} , the formation of contact ion pairs $[Mg (ClO_4)_2]^+$ and $[Ni (ClO_4)_2]^+$ in dilute solutions in acetonitrile is thermodynamically possible, in spite of the expected strong binding in of acetonitrile molecules with doubly charged ions⁽²⁵⁾. Short range non coulomb $d \pm N_A$ values are positive and are several times higher than the kinetic energy of thermal motion of particles ($RT=2.5KJ \text{ mole}^{-1}$) over the whole temperature range studied for $[Mg (ClO_4)_2]^+$ and $[Ni (ClO_4)_2]^+$. It follows that the existence of a fairly solvation shells of the Mg^{2+} and Ni^{2+} cations. Even though the perchlorate ion is weakly solvated is an important factor that prevents interionic association with the formation of contact ion pair. The $d \pm N_A$ values for nickel perchlorate are approximately 1.5 times larger than those for magnesium perchlorate because of the formation of a stronger solvate complex between the Ni^{2+} cation and acetonitrile compared with the Mg^{2+} ion.

El-Hammamy *et al.*⁽¹²⁾, studied the conductance and ion association of S-acetylthiocholine halides and perchlorate in water at different temperatures (25, 30, 35 °C). These temperatures evaluated the thermodynamic parameters and activation energy for all salts. It was found that A_0 increase with the increasing of the temperatures while K_A decrease with the increase of the temperature range. The values of ΔE_s followed the order Iodide > bromide > perchlorate

> chloride, with the reverse order of ionic mobility. The free energy change ΔG^0 for association process was obtained from the relation

$$\Delta G^0 = -RT \ln K_A.$$

The heat of association (ΔH^0) was obtained from the slope of the plot of $\log K_A$ vs. $1/T$. The entropy change (ΔS^0) is calculated from Gibbs-Helmholtz equation: ($\Delta G^0 = \Delta H^0 - T\Delta S^0$). The negative values of (ΔH^0) indicated that ion association processes were exothermic in nature in all solvents at all temperatures. The solvation radii were also increased with temperature indicating a higher solvation process due to increase in the electronic clouds around the solvated molecules as a result of an increase in their vibrational and rotational motion. The limiting equivalent conductance and dissociation degree were also increased as the temperature increased indicating higher solvation process⁽²⁰⁾. The negative values at different thermodynamic parameters ($\Delta G^0, \Delta H^0, \Delta S^0$), for all salts under test in the used solvent, indicating exothermic association process, i.e., the association process was less energy-consuming and more stabilized⁽¹⁷⁾.

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