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Association Equilibria of Co(II) and Cu(II) Complexes of Salicylidine p-chloroaniline in Different Solvents

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ABSTRACT

The electrical conductivity of cobalt salicylidiene chloroaniline and cupper salicylidiene chloroaniline in water, methanol, ethanol, isopropanol and mixture of water-methanol with different composition (100-20%) were measured at 303K. The molar conductivity of the complexes were treated by Lee-Wheaton equation and Kohlrausch equations. The limiting molar conductivity ($\lambda^{o}_{M^{2+}}$), ($\lambda^{o}_{MX^{+}}$), the ionic association constant (K_A) as well as the main distance between cations and anions (R) were measured. Generally, it was found from the analysis of the results that ($\lambda^{o}_{M^{2+}}$) decreases with decreasing the variation of dielectric constant of the solvents as well as decreasing the percentage of water. The association constants of the two complexes were increased with decreasing the dielectric constants and increasing of viscosity. The distance parameter (R) indicated that the ions existed as solvent separated ion-pairs (SSIP).

Keywords: conductivity, Lee-Wheaton equation, salicylidene chloroaniline, Schiff base, association constant

توازنات التجمعات الأيونية لمعقدات الكوبلت(II) و النحاس(II) مع بارا-كلورو ساليسيلدين انيلين في مذيبات مختلفة

الملخص

تم قياس التوصيلية الكهربائية لمعقدي الكوبلت والنحاس مع كلورو-ساليسيلدين كلوروانيلين في مذيبات مختلفة من الماء، الكحول المثيلي، الكحول الاثيلي والآيزوبروبانول وفي نسب مختلفة من مزيج الماء والميثانول (100-20%) في درجة حرارة 303 كلفن. وقد تم حساب التوصيل المكافئ المولاري للمعقدات باستخدام معادلتي لي – ويتون وكولوراوش. التوصيل المكافئ المولاري الايوني ($\lambda^{o}_{MX^{+}}$) و ($\lambda^{o}_{M^{2+}}$) وثابت التجمع الايوني (K_A) فضلاً عن معدل المسافة بين الايونات الموجبة والايونات السالبة (R) كما تم حساب وبصورة عامة وجد من تحليل النتائج بأن ($\lambda^{o}_{M^{2+}}$) تتناقص مع النقصان في تغير ثابت العازل للمذيبات الحاصل وفي النسبة المئوية للماء. أما ثابت التجمع الايوني للمعقدين فأنه يزداد مع النقصان في

ثابت العازل فضلا عن الزيادة في اللزوجة. وتدل قيم المسافة بين الايونات (R) على أنها مفصولة بعدد من جزيئات المذيب (SSIP).

INTRODUCTION

Various studies (Scozzafava *et al.*, 2001), (Scozzafana and Supuran, 2000) have shown a relationship between antitumar and antibacterial agents, which becomes a subject of great interest. It was seen that the biological active compounds become more bacteriostatic and carcinostatic upon chelation with metal ions. Schiff bases have also attracted a considerable attention in terms of their chelating abilities and analytical applications (Khuhawar *et al.*, 1984). The chlorosalicylidiene aniline Schiff base is also of the same type. The synthesis and characterization of some transition metals complexes of Schiff base ligand N-salicylidene and their electrical conductivity (Maldhure and Aswar, 2009). Protonation constants of some substituted salicylidene aniline by the spectroscopic method in ethanol-water mixtures were also determined (Akaya *et al.*, 2002). Kinetics and mechanism of hydrolysis of N-Salicylidene-p-chloroaniline were determined spectrophotometrically (Kirdant *et al.*, 2012). Recent studies have shown some interest in studying the various properties of salicylidene chloroaniline and its complexes with transition metals (Kirdant *et al.*, 2012), (Bhattacharjee *et al.*, 2011) and (Yong-qian *et al.*, 2011). In the present work, it is of interest to prepare and study the behavior of salicylidene-p-chloroaniline complexes conductometrically in different solvents at a constant temperature and analyze the results by Lee-Wheaton equation.

EXPERIMENTAL

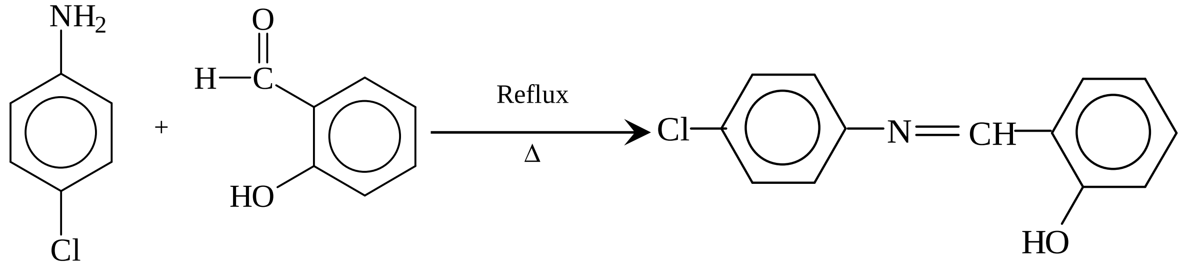
Materials and methods

All chemicals used were of reagent grade and obtained from Fluka and B.D.H chemical companies and were used up as supplied. Methanol, ethanol, isopropanol were taken as absolute from store (Fluka). Conductivity water was prepared by redistilling distilled water three times with the addition of a little amount of potassium permanganate and a small pellets of KOH. The specific conductance of water was less than 1.2×10^{-6} S/cm.

Preparation of complexes

Synthesis of Schiff Base (Iqbal *et al.*, 2006)

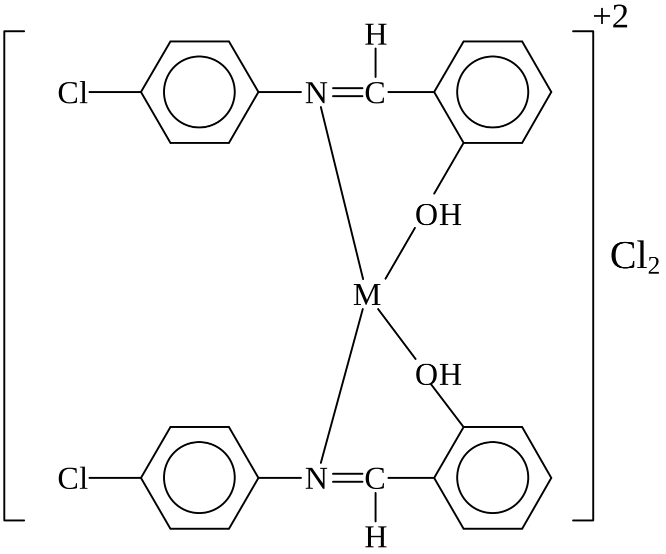
(1.1)g of salicylaldehyde (0.01 M) was mixed with (10 ml) of ethanol and then added to the ethanolic solution of p-chloroaniline (1.28g, 0.01 M). The solution was magnetically stirred during the addition of 2 to 3 drops of concentrated H_2SO_4, refluxed for 2h and left overnight at room temperature. The formed solid coloured product was filtered, washed with ethanol and ether consecutively, and then dried at room temperature and recrystallised from hot ethanol to give the required Schiff base.



P-Chloroaniline **Salicylaldehyde** **P-Chlorosalicylidene aniline**

Synthesis of metal complexes

(4.62)g, (0.02 mol) of Schiff base was dissolved in (25 ml) of ethanol. (0.01 mol) of Cu and Co chloride salts dissolved in (20 ml) of ethanol was added to this solution to form 1:2 metal- ligand. This mixture was magnetically stirred while being refluxed for 2h. The reaction mixture was cooled a room temperature. Upon cooling, coloured precipitate was formed, which was filtered, washed with dry ethanol and vacuum dried (Iqbal *et al.*, 2006), and identified as:



M(II) bis salicylidene chloroaniline dichloride
Where M = Co(II) or Cu(II)

The structure of the complexes are expected to be tetrahedral for Co(II) and distorted tetrahed tetrahedral in case of Cu(II) complex.

Apparatus

Conductivity measurements were made using a digital conductivity meter (Jenway) with sensitivity between 10^{-1} and 10^{-9} Siemens. A general method was used for measuring the conductance of each electrolyte, the cell constant was 1.02 cm^{-1}. The conductivity cell was washed carefully with water and then with each solvent used, dried, weighed empty and kept at constant temperature (303 K). 25 ml of conductivity water (or solvent) was added and the conductance was then measured. Certain amount of the concentrated electrolyte solution was added into the conductivity cell using a micropipette, mixed well using a magnetic stirrer. The conductivity of the solution was then measured. Generally, (10-41) additions were added for each run and the conductivity of the solution (or complex solution) was measured after each addition.

The same procedure was repeated as above using different composition of water-methanol solution (20-100%).

RESULTS AND DISCUSSION

The results of the present work were analyzed using a conductance equation due to Lee and Wheaton (Lee and Wheaton, 1979) based upon a model for ions in solution, describes charge transfer in solutions containing any number of ionic species of any velancy type. This equation is used to analyze the data for some unsymmetrical transition (2:1) metal complexes, $[Co(L_2)]Cl_2$ and $[Cu(L_2)]Cl_2$, where L=Salicylidiene-p-chloroaniline, in water, methanol, ethanol, isopropanol and different percentages of water-methanol (100-20%) measured at 303K.

For unsymmetrical electrolyte MX_2 ionizing into M^{2+}, MX^+ and X^- , the possible association equilibria are :

$$M^{2+} + X^- \underset{}{\overset{K_A^{(1)}}{\rightleftharpoons}} MX^+ \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; (1)$$

$$MX^+ + X^- \underset{}{\overset{K_A^{(2)}}{\rightleftharpoons}} MX_2 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; (2)$$

Therefore, three ionic species are present in the solution, as M^{2+}, MX^+ and X^-

$$\therefore \Lambda_{\text{equiv.}} = \sum_{i=1}^{i=s} |\,Z_i\,|\, m_i \lambda_i \,|\, C \quad \ldots\ldots\ldots\ldots (3)$$

Where Λ equiv. is the equivalent conductivity of the solution, S is the number of ionic species, λi, mi, Zi are the equivalent conductance, molar free ion concentration and charge of the ith-species respectively, C is the stoichiometric equivalent concentration.

For 2:1 Associated salts

The equivalent conductivity (Λ_{MX_2}) is a function of the following parameters :

$$\Lambda_{MX_2} = f\,(\lambda^o_{M^{2+}}, \lambda^o_{MX^+}, \lambda^o_{X^-}, K_A^{(1)}, K_A^{(2)}, R) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where λ^o is the ionic conductivity, K_A is the associate constant and R is the average center to center distance for ion-pairs.

A multi-parameter "least square" curve fitting procedure is used to give the lowest value of the 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 $\sigma(\Lambda)$ (Lee and Wheaton, 1979). In this case :

$$\sigma(\Lambda) = \left\{ \sum_{n=1}^{NP} (\Lambda_{\text{calc.}} - \Lambda_{\text{exp.}})^2 / NP \right\}^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

(NP = number of points)

The input data of the computer program are solvent parameters: [T (temp.), D (dielectric constant), η (viscosity)]; the charge Zi and $\overset{o}{\lambda}i$ for each ionic species, $K_A^{(1)}$ (min.), $K_A^{(2)}$ (max.), $\Delta K_A^{(1)}$ etc., as well as the experimental data which are the molar concentration and the equivalent conductance.

The following results of typical conductivity runs are listed in Tables (1-5) and plotted in Fig. (1-4)

Table 1: Molar concentration (M) and equivalent conductance L equiv. (Siemens equiv^{-1}.cm^{2}) of the complexes in absolute methanol at 303K.

[Co(L_2)]Cl_2		**[Cu(L_2)]Cl_2**	
M ´ 10^{-4}	L **equiv.**	**M ´ 10^{-4}**	L **equiv.**
0.738	143.5	0.738	106.2
1.219	138.8	2.153	98.5
1.690	138.7	4.128	92.6
2.153	135.0	4.751	90.8
2.606	133.0	5.357	88.9
3.051	131.0	5.947	87.4
3.488	129.2	6.521	86.1
3.917	127.0	7.081	85.1
4.337	126.0	7.627	84.2
4.751	124.9	8.158	83.2
5.156	123.8	8.677	82.3
5.555	122.4	9.183	81.7
5.947	121.0	9.677	80.9
6.331	120.3	10.317	80.1
6.709	119.6	10.937	79.3
7.081	118.8	11.538	78.8
7.446	117.9	12.121	78.5
7.805	117.6	13.235	77.1
8.158	116.6	13.768	76.8
8.677	115.1	14.412	76.2
9.183	114.3	15.034	75.7
9.677	113.4	15.635	75.2
10.159	112.4	16.216	74.8
10.629	112.5	16.777	74.5
11.089	111.6	18.253	73.3
11.538	110.8	19.040	72.8
12.121	109.6	19.788	72.5
12.686	108.8	20.501	72.0
13.235	108.0	21.181	71.7
13.768	107.4	21.830	71.4
14.285	106.8	22.451	71.0
14.912	106.0	23.118	70.7
15.517	105.1	23.753	70.5
16.101	104.4	24.358	70.1
16.666	103.8	24.937	69.9
17.213	103.1	25.550	69.5
17.741	102.6		
18.253	102.2		
18.750	101.7		
19.230	101.1		
19.848	100.2		

Table 2: Molar concentration (M) and equivalent conductance L equiv. (Siemens equiv^{-1}.cm^{2}) of the complexes in absolute ethanol at 303K.

[Co(L_2)]Cl_2		**[Cu(L_2)]Cl_2**	
M ´ 10^{-4}	L **equiv.**	**M ´ 10^{-4}**	L **equiv.**
0.738	27.6	2.380	24.4
1.456	23.1	4.545	21.9
2.606	19.9	6.521	20.4
4.128	17.5	8.847	19.0
6.140	15.9	11.240	17.9
9.677	13.7	14.028	16.9
13.369	12.3	17.532	15.9
16.996	11.4	20.845	15.2
20.845	10.7	23.190	14.8
25.186	10.2	26.076	14.4
27.578	10.0	27.168	14.3

Table 3: Molar concentration (M) and equivalent conductance L equiv. (Siemens equiv^{-1}.cm^{2}) of the complexes in Isopropanol at 303K.

[Co(L_2)]Cl_2		**[Cu(L_2)]Cl_2**	
M ´ 10^{-4}	L **equiv.**	**M ´ 10^{-4}**	L **equiv.**
0.248	12.3	1.219	5.0
0.495	8.2	3.488	4.0
0.738	6.9	8.333	3.5
1.219	5.0	12.962	3.1
1.923	3.7	16.666	2.9
3.051	3.0	19.696	2.6
4.337	2.3	30.769	2.02
5.947	2.0	33.333	2.08
7.446	1.9	35.294	2.1
9.016	1.69	35.714	2.2
10.629	1.63		
12.121	1.59		
13.636	1.49		
15.156	1.48		
16.555	1.41		
18.051	1.41		
19.512	1.36		
21.098	1.35		
22.677	1.34		
24.358	1.33		
26.076	1.29		
27.477	1.26		

Table 4: Molar concentration (M) and e equivalent conductance L equiv. (Siemens equiv^{-1}.cm^{2}) for the complex [Co(L_2)]Cl_2 in mixtures of (Water + Methanol) at 303 K.

100% H_2O		**80% H_2O**		**60% H_2O**		**40% H_2O**		**20% H_2O**	
M´10^{-6}	L	**M´10^{-6}**	L	**M´10^{-6}**	L	**M´10^{-6}**	L	**M´10^{-6}**	L
3.984	486.4	5.964	222.3	32.882	192.3	46.892	152.0	5.964	239.4
5.964	478.9	7.936	218.4	34.749	187.8	47.619	149.9	7.936	231.3
7.936	469.1	9.900	216.3	36.608	184.8	49.429	148.5	9.900	226.6
9.900	463.6	11.857	215.0	38.461	182.9	51.233	147.3	11.857	223.6
11.857	455.9	13.806	214.2	40.307	182.2	53.030	146.1	13.806	221.6
15.748	451.1	15.748	213.7	42.145	181.5	54.820	144.4	15.748	220.2
25.341	442.7	17.681	213.4	42.879	181.0	56.603	143.7	417.681	219.1
29.126	441.2	19.607	213.29	43.977	180.9	58.380	143.0	20.376	218.0
31.007	440.8	21.526	213.21	46.892	180.8	60.150	142.4	23.436	217.6
32.882	440.4	23.437	213.26			62.242	142.0	25.341	217.3
34.749	440.3					63.670	141.7	27.237	217.2
36.608	440.1					65.420	141.5	29.126	217.1
						66.118	141.6		
						67.512	141.5		

Table 5: Molar concentration (M) and e equivalent conductance L equiv. (Siemens equiv^{-1}.cm^{2}) for the complex [Cu(L_2)]Cl_2 in mixtures of (Water + Methanol) at 303 K.

100% H_2O		**80% H_2O**		**60% H_2O**		**40% H_2O**	
M´10^{-6}	L	**M´10^{-6}**	L	**M´10^{-6}**	L	**M´10^{-6}**	L
1.996	153.3	3.984	102.4	29.126	91.0	1.996	102.2
3.507	142.8	7.936	96.3	32.882	89.9	5.964	85.5
5.964	136.8	17.681	89.4	36.608	89.1	9.900	82.4
9.900	133.9	32.882	86.8	40.307	88.5	13.857	81.2
13.806	132.9	34.749	85.1	43.997	88.0	17.681	80.7
15.748	132.5	38.461	84.8	47.619	87.8	21.526	80.55
21.437	132.2	45.801	84.6	51.233	87.5	25.341	80.50
25.341	132.02			54.820	87.4	29.126	80.54

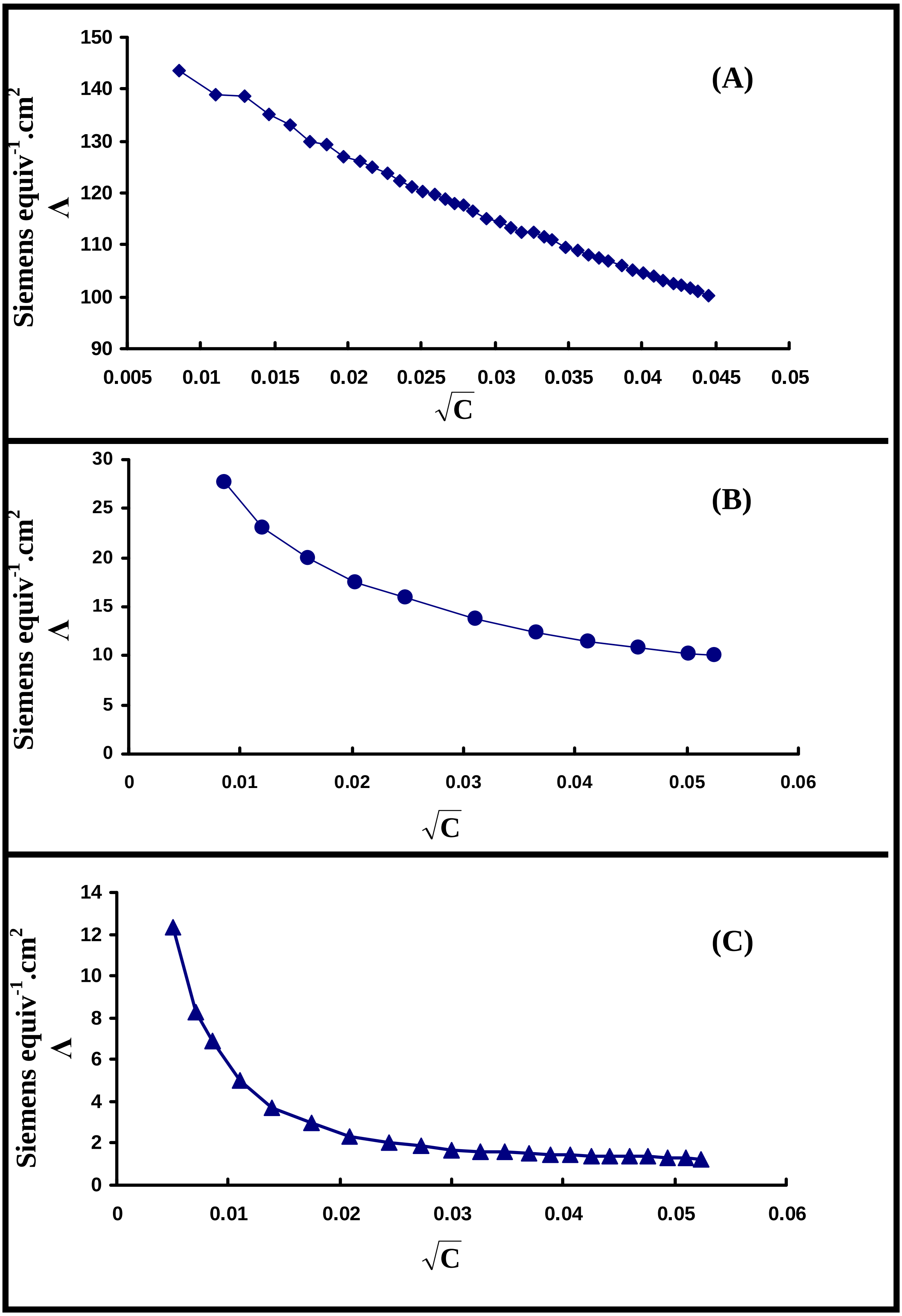


Fig. 1 : Plots of the equivalent conductivity against the square root of molar concentration of $[Co(L_2)]Cl_2$ in different solvent (A-Methanol, B-Ethanol and C-Isopropanol) at 303K.

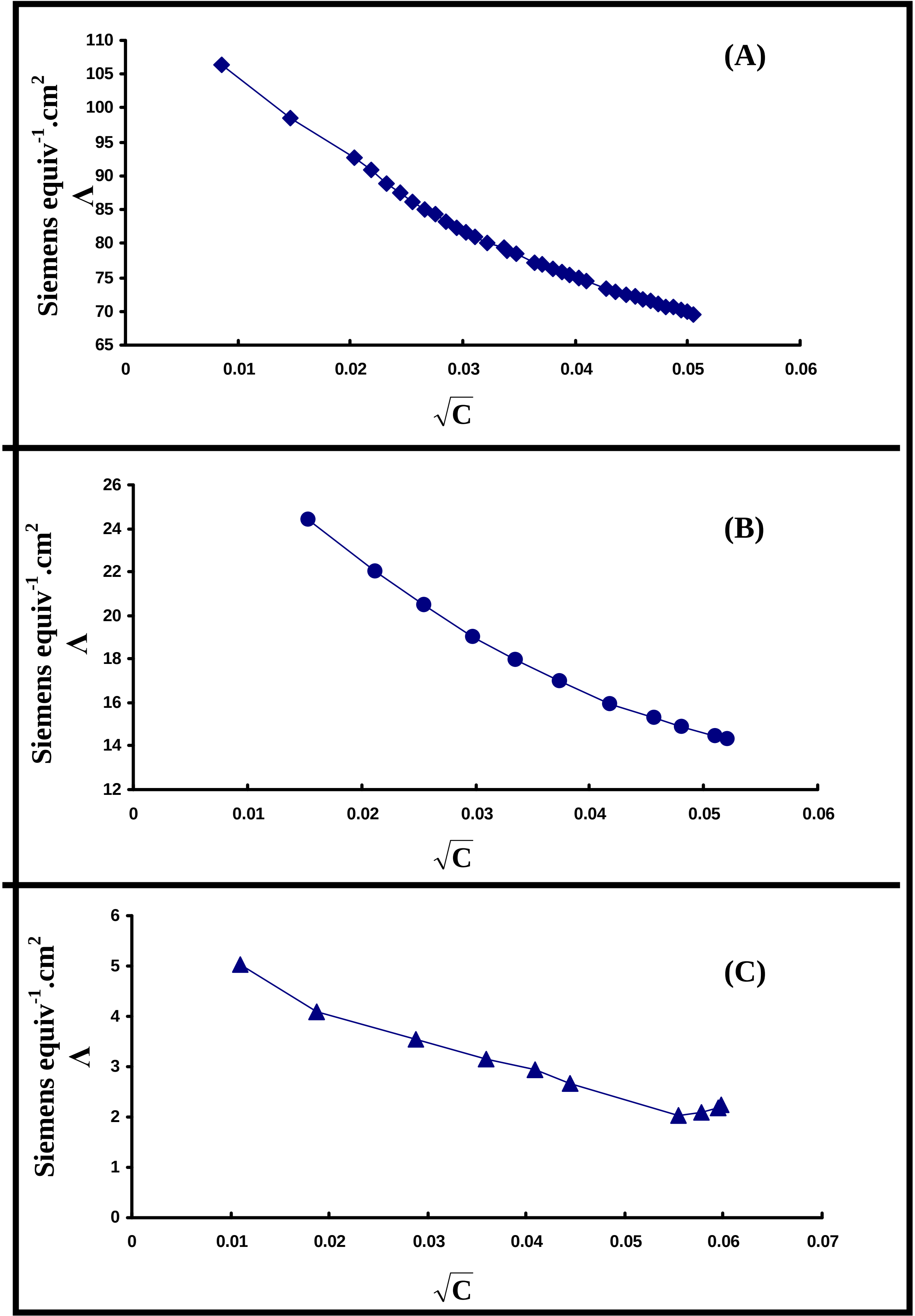


Fig. 2 : Plots of the equivalent conductivity against the square root of molar concentration of $[Cu(L_2)]Cl_2$ in different solvents (A-Methanol, B-Ethanol and C-Isopropanol) at 303K.

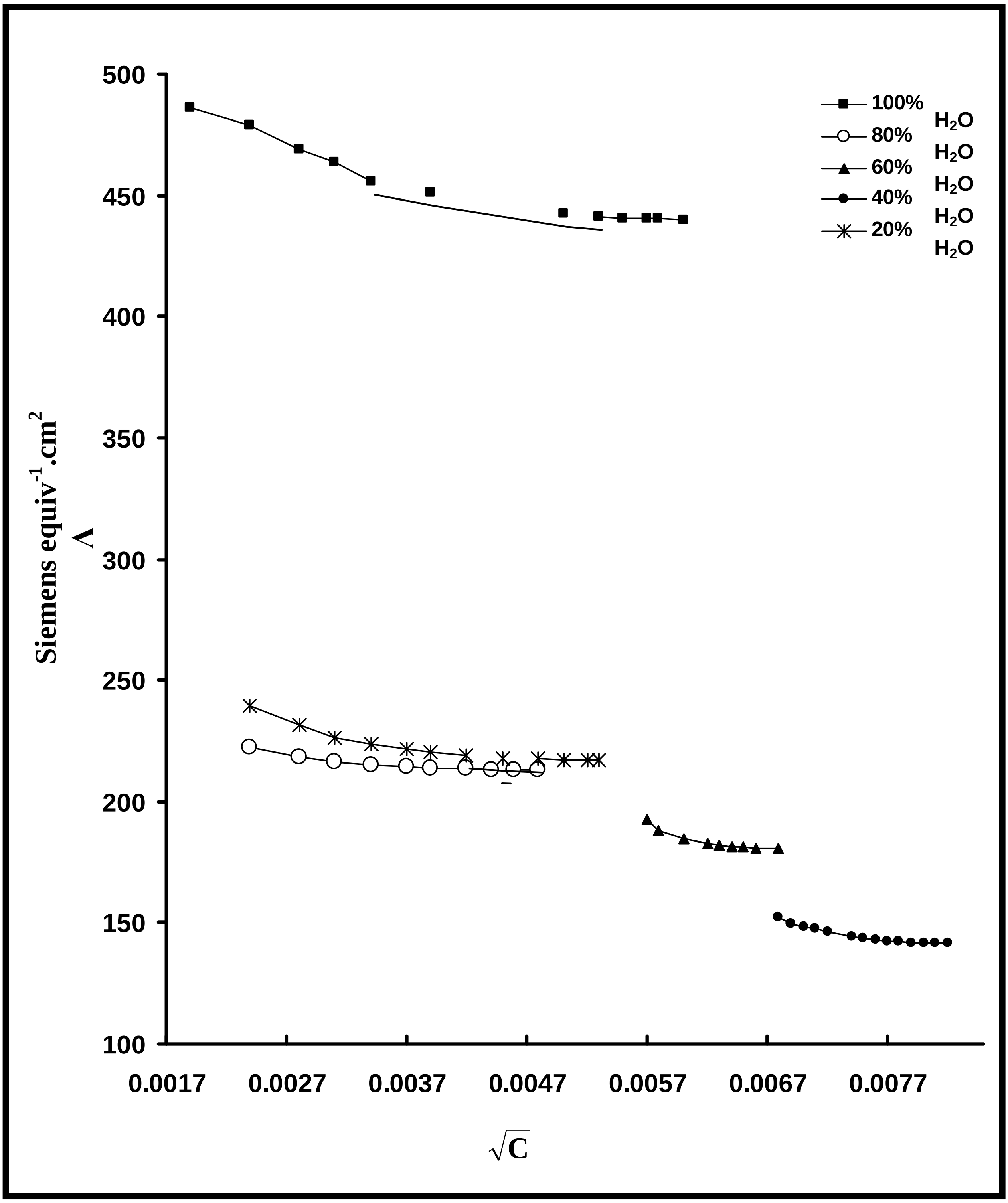


Fig.3 : Plots of the equivalent conductivity against the square root of molar concentration of $[Co(L_2)]Cl_2$ in (Water + Methanol) at 303K.

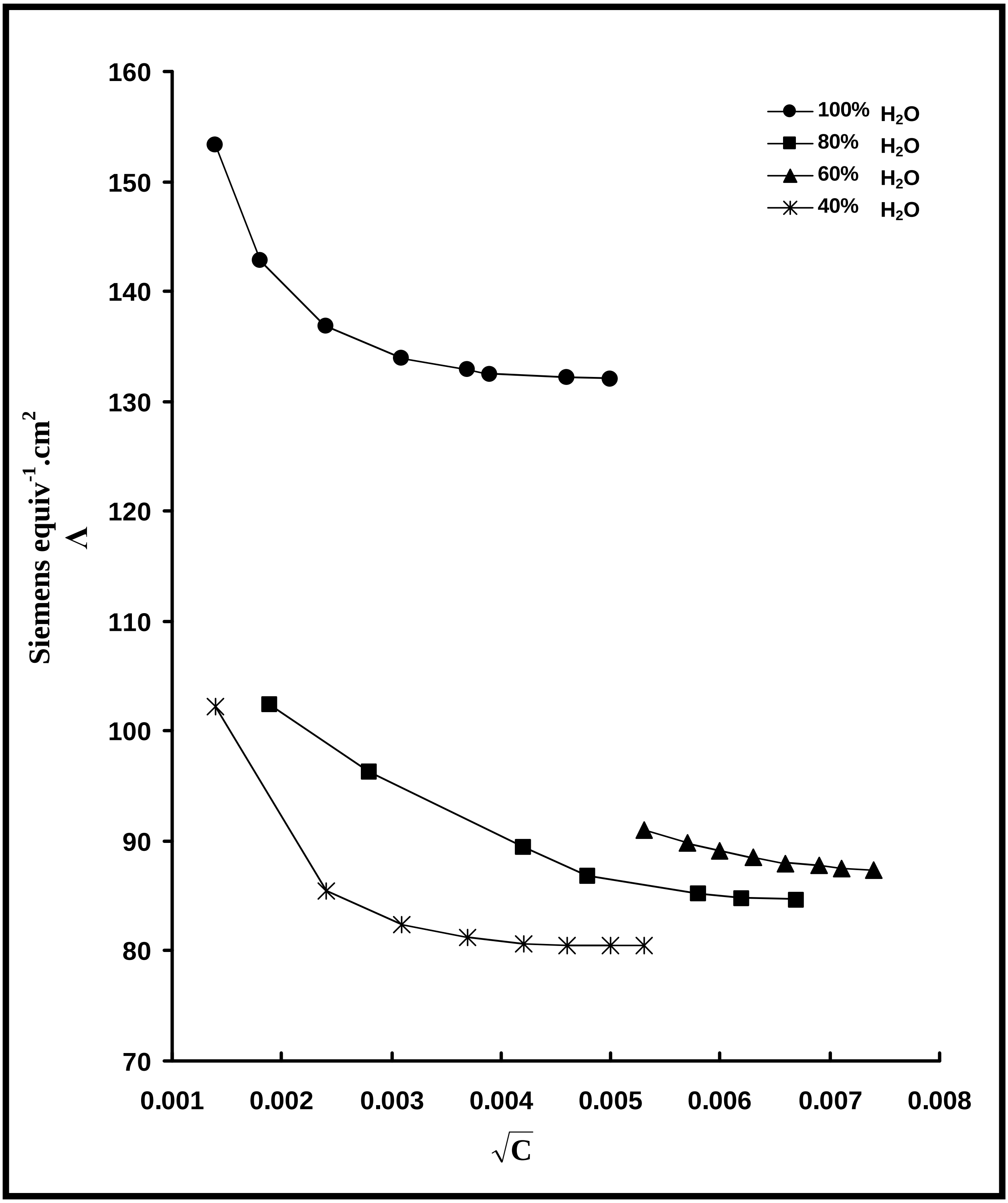


Fig. 4 : Plots of the equivalent conductivity against the square root of molar concentration of $[Cu(L_2)]Cl_2$ in (Water + Methanol) at 303K.

The analysis of the experimental results for the complexes in methanol, ethanol, isopropanol and in different composition of water-methanol (100-20%) by LW equation are shown in Tables (6,7,8) which show that all of the salts are associated to form the new conducting species MX^+ :

Table 6: Best fit parameters of analysis of conductance data for the complexes in a different solvents (Methanol, Ethanol and Isopropanol) at 303K.

$[Co(L_2)]Cl_2$					
Solvents	**K_A**	**$\lambda^o_{M^{2+}}$**	**$\lambda^o_{MX^+}$**	**R/A^o**	s(L)
Methanol	75	40	0.1	29	0.088
Ethanol	10001	9	0.85	34	0.324
Isopropanol	100000	5	0.01	40	0.555
$[Cu(L_2)]Cl_2$					
Solvents	**K_A**	**$\lambda^o_{M^{2+}}$**	**$\lambda^o_{MX^+}$**	**R/A^o**	s(L)
Methanol	100	20	0.085	40	0.683
Ethanol	250000	5	0.1	29	0.522
Isopropanol	1500000	2	0.1	44	0.173

Table (6) shows that the values of the Ka (association constants) of these complexes follow the sequence :
Methanol < ethanol < isopropanol.

K_A for $[Cu(L_2)]Cl_2 > [Co(L_2)]Cl_2$ in the three solvents. It means that the highest charge density of the solvated ion is for Cu complex, which confirmes the trend of the crystallographic radii of the solvated cations.

On the other hand, the values of $\lambda^o_{M^{2+}}$ for both complexs also differ in solvents in the following trend: methanol > ethanol > isopropanol. This propertionation can be explained according to decreasing the dielectric constant of the solvent and increasing its viscosity and also according to stokes law, where the ionic mobility should be inversely proportional to the solvated ionic radius:

$$\overset{0}{\lambda}i = 8.2\times10^{-9}\ zi / \eta ri$$

where $\overset{0}{\lambda}i$ is the ionic conductance, zi is the charge, η is the viscosity and **ri** is the radius. In fact, the present results confirm the trend of the crystallographic radii of the bare cations.

The values of R from (Table 6), show that the two complex electrolytes form solvent separated ion pairs, (R ranges between 29-44 A^o). The value of the standard deviations σ(Λ) gives an indication of good best fit values.

Table 7: Best fit parameters of analysis of conductance data for the complex $[Co(L_2)]Cl_2$ in a mixture of (Water +Methanol) at 303k.

$[Co(L_2)]Cl_2$					
% of water composition	**K_A**	**$\lambda^o_{M^{2+}}$**	**$\lambda^o_{MX^{2+}}$**	**R/A^o**	s(L)
100	1360	400	0.1	28	0.982
80	1750	150	0.8	28	0.316
60	1800	136	0.6	28	0.008
40	2000	110	0.2	28	0.239
20	2000	182	0.2	28	0.981

Table (7) shows the best fit parameters of analysis of conductance data for $[Co(L_2)]Cl_2$ complex in a mixture of (water + methanol) at 303K from 100-20%. It was found that K_A values increase with increasing methanol composition which is due to the decrease in the dielectric constant of the medium and the viscosity was increased (Bregorowicz *et al*., 1998). It was found that the $\lambda^o_{M^{2+}}$ decrease with increasing the composition of methanol and then increase at 20% of water. This behavior can be explained in terms of increasing free ions in this composition i.e. less interactions between ion-solvent.

The values of the distance parameter (R) is 28 A^o, these high values indicate the formation of solvent seperated ion pair (SSIP).

For the other complex $[Cu(L_2)]Cl_2$:

Table 8: Best fit parameters for analysis of conductance data for the complex $[Cu(L_2)]Cl_2$ in a mixture of (Water +Methanol) at 303K.

$[Cu(L_2)]Cl_2$					
% of water composition	**K_A**	**$\lambda^o_{M^{2+}}$**	**$\lambda^o_{MX^{2+}}$**	**R/A^o**	s(L)
100	1000	64	0.1	30	0.350
80	1000	14	0.8	30	0.981
60	1200	25	0.2	30	0.981
40	4400	30	0.8	30	0.981

Table (8) shows the best fit parameters of analysis of conductance data for $[Cu(L_2)]Cl_2$ complex in a mixture of (water + methanol) as 303K from 100-20%. It can be seen from this table that K_A values increase with increasing methanol composition and it is due to the effect of the methanol. The value of $\lambda^o_{M^{2+}}$ decrease can also be explained in terms of interactions between ions and solvent. The distance parameter (R) is constant (30A^o). The values of $\sigma(\Lambda)$ are small and give indication about the useful of Lee-Wheaton equation.

When we have discussed the results in terms of Walden – product ($\lambda^o_{M^{2+}}.\eta$) Fig. (5) as a function of the reciprocal dielectric constant (1/D)in order to analyze the structural change of the solution, we found that the change of ion – solvatoin (minimum) for cobalt complex is at (D=49.66), for cupper complex is at (D=67.69). (Domench and Miro, 1988) and (Hikmat, 2002).

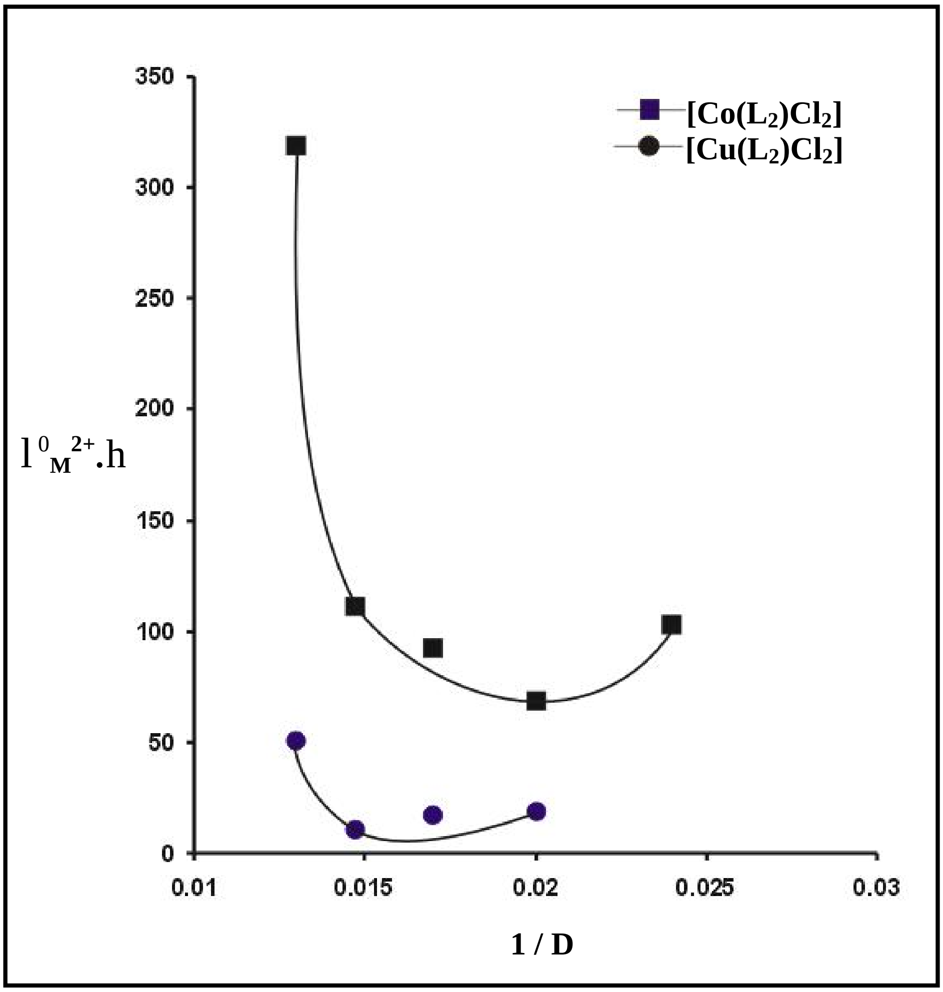


Fig. 5: Plot of the Walden product against 1/D for $[Co(L_2)Cl_2]$ and $[Cu(L_2)Cl_2]$ in a mixture of (water + methanol) at 303 K

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