An Electrical Conductimetric Study of Association Phenomena of 4- Aminoantipyrine (4-AAp) Complexes in Mixtures of Methanol-Water at Different Temperatures

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ABSTRACT

The aim of this work is to measure the electrical conductivity of Co (II) and Ni (II) complexes with 4-amino antipyrine in mixtures of different percentages of methanol and water at different temperatures. The data were analyzed using the Lee-Wheaton equation for unsymmetrical electrolytes, the conductivity parameters: ionic equivalent conductivity λ_M^{+2}, association constant K_A, and the distance parameter R are calculated. The ionic equivalent conductivity λ_M^{+2}, increases with increasing temperature, which may attributed to the breaking of hydrogen bonds between solvated ion. Association constant K_A increase with increasing temperature, which assumed the presences of simple coloumbic interactions between hard sphere ions in continuous medium. The distance parameter R are calculated at the bist fit values of standard deviation $\sigma\Lambda$. Thermodynamic parameters from the relation between LnK_A and 1\T were calculated to examine the nature of interaction. Walden product were calculated which show the variation depending on electrochemical equilibrium between ions and the solvent molecules with the composition of the mixed polar solvents.

Keywords: Electrical conductivity, 4-amino antipyrine, Lee-Wheaton equation, Thermodynamic parameters, Walden product.

دراسة التوصيلية الكهربائية لظاهرة التجمع الايوني لمعقدات 4-امينو انتى بايرين في مزيج من الميثانول والماء وبدرجات حرارية مختلفة

الملخص

يتضمن البحث دراسة التوصيلية الكهربائية لمعقدات النيكل والكوبلت مع 4-أمينو انتيبايرين في نسب مختلفة من مزيج الميثانول والماء وفي درجات حرارية مختلفة. تم تحليل النتائج باستخدام معادلة لـي-ويتون في التوصيلية للاليكتروليتات غير المتجانسة وتم حساب التوصيلية الأيونية المكافئـة، ثابـت التجمـع الايوني ومعدل المسافات بين الايونات حيث ازدادت التوصيلية الأيونية المكافئة مع زيـادة درجـة الحـرارة ويعود السبب إلى كسر الأواصر الهيدروجينية بين الايونات المتناوبة، أما ثابت التجمع الأيوني فيزداد عنـد زيادة درجة الحرارة بسبب التداخلات الكولومبية بين الأجواء الأيونية في وسط عازل مستمر. آما المسافة بين الايونات فقد تم حسابها أيضا عند أحسن قيم للانحراف القياسي فضلا عـن ذلـك تـم حـساب الـدوال الثرموديناميكية من ثابت التجمع الأيوني لمعرفة طبيعة التداخل بين الجزيئات وأخيرا حساب نـاتج والـدن، والذي يبين الاختلاف بين التوازن الكهروكيميائي للايونات مع جزيئات المذيب المتكون من مزيج من مذيبين قطبيين.

الكلمات الدالة: التوصيلية الكهربائية، 4-أمينو انتيبايرين، معادلة لي-ويتون، الدوال الثرموديناميكية، نـاتج والدن.

INTRODUCTION

Conductivity measurements are useful as an effective means to understand the nature of solute - solvent interaction, science the degree of ion pairing and ionic mobility is exceedingly sensitive to interaction. The characteristics of metal chelat electrolytes, is of their solute - solvent interaction concerning charge, size and chemical properties of ligand have been elucidated by the study of electronic spectra (Fukuda and Sone, 1972), racemization (Von Meter and Newman, 1976), optical resolution (Iwamoto *et al.*, 1977), viscosity and molal volume (Tominago, 1975) and conductivity(Newmann *et al.*, 1979)(Ito, *et al.*, 1982). The Molar conductivities (Λ) of solution of n–tetrabutylammomium tetraphenylborate (NBu_4Bph_4) in 3- pentanone has been measured in the temperature range from 283.15 to 329.15 K., the conductance data have been analyzed using Lee-Wheaton conductivity equation with distance parameter (R) set at Pjerrum's pairing distance, the limiting molar conductivities (Λ^o) and derived association equilibrium constant (K_A) (Tsierkezos, 2007).

In this work we have measured the electrical conductivity of 4-amino antipyrine complexes at different temperatures; Lee-Wheaton equation is used to elucidate the conductivity parameters and R. The calculation of association constants (K_A) at different temperature enable calculation of the thermodynamic quantities ($\Delta H, \Delta G and \Delta S$) for the association reaction which can provide detailed information concerning ion-ion and ion-solvent interaction particularly from thermodynamic point of view.

EXPERIMENTAL

Preparation of complexes

A mixture of the ligand (4--AAp) (0.378 g, 20 mmole), for 1:2 molar ratio (0.567gm, 30 mmole) for the 1:3 molar ratio and appropriate metal salt (10 mmole) was refluxed in absolute methanol (100 ml) with continuous stirring for two hours. The solid product formed was filtered of, recrystallized from ethanol, and dried under vacuum. IR spectra were recorded on Unicom SP 2000 spectrometer at the range (700 – 4000 cm^{-1}) using Nujol mall and KBr discs, electronic spectra were recorded on a shimadzu UV/Vis spectrophotometer UV-160 for 10^{-3} M solution of the complexes in ethanol at ambient temperature (25 C). Heat of formation and steric energies of products in addition to the geometry (three dimensional structure) of complexes (11) at minimized energy (mm2) were established by chem..3D ultra ; molecular modeling and analysis (version 6.0.3) by Pentium (IV) computer (Jonan *et al.,* 2011).

Purification of solvent

Methanol was purified and dried by the method of Perrin (Perrin *et al.*, 1966) and the procedure was repeated twice to ensure that all water was removed. Conductivity water was prepared by redistilling distilled water three times and condensing it by using a condenser with glass joints, little potassium permanganate was added to the distilled water to reduce the absorption of carbon dioxide (Daniels *et al.*, 1970).

General procedure

General method has been used for measuring the conductance of the electrolytes. The conductivity cell was weighted and kept at a constant temperature then purified nitrogen passed through the cell: 100 ml of purified solvent was added and nitrogen gas was passed for further (10-15) minutes, where upon the cell plus its content were weighed. Certain amount of complex solution was injected in to the cell from a- plastic syringe (which was weighed before and after each addition), nitrogen gas was passed for several minute and the conductivity of the solution was measured. After performing all additions (generally 15), the cell was reweighed ed to find the weight change over the whole run which was found not to exceed than (0.02%).

RESULTS AND DISCUSSION

The equation derived by Lee-Wheaton has been tested extensively in both aqueous and non-aqueous systems and provide satisfactory explanation of the conductmetric behavior of variety of systems. Lee and Wheaton derived an equation for unsymmetrical electrolytes of the form:

$$\lambda_j = \lambda_j^{\cdot}\left\{1 + Z_j\sum_{p=s}^{s} X_j^p \sum_{v=1}^{s} tvX_v^p\left[A_v^p(t)(\beta k) + B_v^p(t)(\beta k)^2 + C_v^p(t)(\beta k)^3\right]\right\} -$$

$$Z_j(kt)\Big/2(1+t)\left\{1 + v_j^1(t)(\beta k) + v_j^2(t)(\beta k)^2 + \pi_j^5 \frac{t}{6}\right\} - - - - - - - - (1)$$

With $\Lambda_{equiv.} = \sum_{j=1}^{s}(|z_j|m_j\lambda_j/C)$ where s is the number of charged species, Z_j and t_j are the charge and transference number of species

$\beta = e^2$ / DKT, k = (4π/DKT $\sum_{j=1}^{s} n_j e_j^{\ 2}$ and is proportional to the ionic strength. t=KR and T=Fe/6πη, n_j is the molar free ion concentration of species j. C is the equivalent stoichiometric concentration of the electrolyte. The plasma coefficients $A_v^p, B_v^p, ------$ etc are functions of KR and q_p while the terms x_j^p and q_p are functions of the limiting mobility's, the concentration and charge of all ions present in solution [all other terms are defined in the original paper] (Lee and Wheaton, 1978).

For an unsymmetrical electrolyte MX_2 ionizing in to M^{+2} and X^- the possible association equilibrium are

$$M^{2+} + X^- --kA^{(1)} --- MX^+ ----(2)$$

and

$$MX^+ + X^- --kA^{(2)} --- MX_2 --- (3)$$

Thus three ionic species are present in the solutions which are MX^+, M^{2+}, and X^-.
Thus for associated salts:

$$\Lambda_{MX2} = f\,(\lambda^o_{M^{2+}},\ \lambda^o_{MX^+},\ \lambda^o_{X^-},\ K_A^{(1)},\ K_A^{(2)},\ R)\ .\ .\ .\ .\ .\ .\ .\ (4)$$

Where R is the average center-to-center distance for ion pairs.

The input data to the computer program (RM_{11}) are solvent data (temp. T., dielectric constant D and viscosity η); the charge Zi and ionic mobility $\lambda_i^{\cdot}$ for each ionic species, $K_A^{(1)}, K_A^{(2)}, \lambda^{\cdot}_{mx^+}, \lambda^{\cdot}_{m^{2+}}$ and R all in the form $K_A^{(1)}(\min), K_A^{(2)}(\max), \Delta K_A --etc$, then the experimental data (molecular concentration and the equivalent conductance). This program is used to determine values of ($K_A^{(1)}, K_A^{(2)}, \lambda^{\cdot}_{mx^+}, \lambda^{\cdot}_{m^{2+}}$ and R which minimize $\sigma_s(\Lambda)$.

Table (1) (A-H) shows the molar concentration and equivalent conductance's of [Ni (4-AAp)$_3$] Cl_2 in different percentages of methanol water at different temperatures (293.15-313.15 K), and Fig. 1 (A-H) illustrates the relation between them. From both tables and figures it can be seen clearly that the equivalent conductivities increase with increasing temperatures and increasing the percentages of methanol, this is because of the effect of viscosity which play an important role which may be due to the contribution of triple ions which are expected to be present in the solution together with the free ions (Hikmat, 2002), generally the equivalent conductance of Co^{2+} complexes more than that of Ni^{2+} complexes and this is related to the ionic radii of Co which is more than Ni and form small solvated ion in solution.

Table 1 A: Molar concentration (M) and equivalent conductance of [Ni-4-AAp]Cl_2in 50% methanol –water mixture.

Conc. *10-5 M	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**	**T=313 K**
4.3695	80.0877	80.4293	82.2225	89.6471	104.3928
8.3457	78.2619	79.1752	81.2828	85.8090	94.8153
12.7402	77.4813	79.1384	81.1347	84.4257	87.1753
16.5494	77.3524	78.9013	80.6119	83.8332	85.2549
20.7744	77.1599	78.6678	80.2712	82.3550	84.0159
24.9281	76.2972	78.1048	79.8603	82.1022	83.4113
29.1623	75.7246	77.5682	79.7644	82.0781	83.1349
32.9363	75.7245	77.4370	79.4635	80.8634	82.8410
37.0007	75.4950	77.2471	78.9221	80.7946	82.6189
40.4563	73.4408	75.6856	78.3364	80.7240	82.4845
44.4878	70.0552	73.8384	77.9303	80.6360	82.1206
48.2247	67.7582	72.8305	76.2996	80.3792	81.8076
52.2860	57.4113	67.9822	76.2039	80.0644	81.5465
55.8697	47.4333	49.8273	54.6153	59.4034	63.7924
59.8184	42.6079	45.6565	48.0954	50.5344	60.2900

Table 1 B: Molar concentration (M) and equivalent conductance of [Ni-4-AAp]Cl_2in 70% methanol –water mixture.

Conc. *10-5 M	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**	**T=313 K**
4.3695	149.2791	151.9671	159.5425	164.9186	170.7834
8.3457	139.3554	145.8857	152.8241	157.3136	160.9869
12.7402	130.0708	136.3152	138.9170	143.7738	146.6761
16.5494	125.7580	128.2712	131.1270	134.9448	145.6818
20.7744	123.6592	127.7604	130.6444	134.7211	138.5930
24.9281	123.2462	126.1174	129.4974	133.8687	138.0067
29.1623	121.6820	125.0594	127.0405	133.7792	137.9475
32.9363	118.8324	122.2594	126.7482	129.2813	136.0363
37.0007	118.6159	121.1503	124.8639	128.8296	135.9249
40.4563	117.7180	120.3666	123.6846	128.7022	131.6033
44.4878	114.9278	118.8322	122.5587	126.0240	130.2101
48.2247	108.7998	116.9772	121.6476	124.8420	128.4609
52.2860	104.4905	112.4706	118.7705	121.1614	126.5773
55.8697	67.6068	80.4111	96.2641	114.9636	122.9547
59.8184	50.3641	69.1567	92.6474	107.8489	117.6046

Table 1 C: Molar concentration (M) and equivalent conductance of [Ni-4-AAp] Cl_2in 90% methanol –water mixture.

Conc. *10-5 M	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**	**T=313 K**
4.3695	122.1933	124.0200	125.5344	146.6761	178.3886
8.3457	120.8199	122.6192	125.2987	132.2381	148.0910
12.7402	120.5654	122.6124	123.8940	127.0340	130.7072
16.5494	120.0362	122.3569	123.8796	125.4787	128.9520
20.7744	119.5894	122.0095	123.4970	125.4310	128.5397
24.9281	118.5403	121.0744	123.4734	125.3779	127.8858
29.1623	118.5156	120.6265	122.6217	125.0726	126.9681
32.9363	114.9019	118.0001	121.9986	125.0493	126.7861
37.0007	114.8434	116.5919	121.2629	124.5980	126.0240
40.4563	111.6465	116.5020	120.9325	123.5818	125.4123
44.4878	109.9500	112.7253	120.4774	123.0819	125.0594
48.2247	101.8075	106.0637	118.7429	120.5865	123.6592
52.2860	90.1668	105.4100	116.0209	117.7555	119.8369
55.8697	86.5355	99.6947	109.4078	112.1440	117.0081
59.8184	80.9021	93.7175	100.1015	104.8895	115.2636

Table 1D: Molar concentration (M) and equivalent conductance of [Ni-4-AAp]Cl_2in 100% methanol.

Conc. *10-5 M	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**	**T=313 K**
4.3695	161.4975	166.3848	173.4715	187.0838	200.7048
8.3457	151.9717	161.6979	171.9218	179.0266	196.2609
12.7402	151.9695	161.5477	168.0822	178.8475	185.1068
16.5494	151.1915	156.0892	163.1196	178.3886	183.9793
20.7744	143.7738	148.2836	161.3950	176.1386	183.4553
24.9281	140.0984	146.2619	154.1883	169.1497	172.4148
29.1623	138.2978	143.9393	153.4873	157.1299	161.4662
32.9363	133.4030	142.4102	147.9339	153.1575	156.9984
37.0007	130.5559	140.8034	144.3294	147.8935	149.2643
40.4563	129.1894	134.7824	136.9140	141.0520	144.3122
44.4878	122.5263	133.0690	132.8406	136.0391	139.6946
48.2247	119.3682	125.2705	128.4369	131.4978	133.1865
52.2860	119.1793	121.2477	123.8796	125.7316	130.0205
55.8697	118.9083	120.8199	122.7839	125.0895	126.9681
59.8184	117.3127	120.6406	122.5587	123.6547	126.4860

Table 1 E: The relation between equivalent conductance and square root of concentration of $[Co\text{-}4\text{-}AAp]Cl_2$ in 50% methanol –water mixture.

Conc. *10-5 M	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**	**T=313 K**
4.3695	80.0877	80.4293	82.2225	89.6471	104.3928
8.3457	78.2619	79.1752	81.2828	85.8090	94.8153
12.7402	77.4813	79.1384	81.1347	84.4257	87.1753
16.5494	77.3524	78.9013	80.6119	83.8332	85.2549
20.7744	77.1599	78.6678	80.2712	82.3550	84.0159
24.9281	76.2972	78.1048	79.8603	82.1022	83.4113
29.1623	75.7246	77.5682	79.7644	82.0781	83.1349
32.9363	75.7245	77.4370	79.4635	80.8634	82.8410
37.0007	75.4950	77.2471	78.9221	80.7946	82.6189
40.4563	73.4408	75.6856	78.3364	80.7240	82.4845
44.4878	70.0552	73.8384	77.9303	80.6360	82.1206
48.2247	67.7582	72.8305	76.2996	80.3792	81.8076
52.2860	57.4113	67.9822	76.2039	80.0644	81.5465
55.8697	47.4333	49.8273	54.6153	59.4034	63.7924
59.8184	42.6079	45.6565	48.0954	50.5344	60.2900

Table 1F: Molar concentration (M) and equivalent conductance of $[Co\text{-}4\text{-}AAp]Cl_2$in 70% methanol –water mixture.

Conc. *10-5 M	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**	**T=313 K**
4.3695	240.1624	257.3267	287.0781	324.8395	351.1580
8.3457	231.1851	240.1717	259.3433	277.9157	289.2988
12.7402	216.5905	231.8964	244.4551	253.0892	259.7610
16.5494	208.7321	214.1703	220.8171	225.3490	231.6936
20.7744	200.6991	205.9941	212.0111	219.2315	225.0079
24.9281	185.6434	192.9302	199.7616	202.0387	204.9231
29.1623	185.3215	193.3799	198.0091	202.8099	206.2389
32.9363	180.8964	190.3235	194.9368	200.7535	206.7708
37.0007	179.8454	182.6832	186.7372	189.4398	192.2776
40.4563	175.8539	178.2021	181.6627	183.0221	185.4940
44.4878	168.2348	171.1570	174.8659	176.7765	178.6872
48.2247	162.4563	164.8410	167.1220	169.4030	171.0618
52.2860	153.1843	157.1050	158.9220	161.3127	163.0340
55.8697	146.2224	149.7127	152.5765	154.0084	155.9773
59.8184	139.9970	142.1703	145.1794	147.3526	150.0274

Table 1 G: Molar concentration (M) and equivalent conductance of [Co-4-AAp]Cl_2in 90% methanol –water mixture.

Conc. *10-5 M	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**	**T=313 K**
4.3695	212.6996	226.4310	240.1624	259.6153	274.4910
8.3457	164.6837	174.2695	188.6481	195.2384	204.8242
12.7402	145.3424	151.0498	158.1140	171.4576	208.3488
16.5494	144.9931	157.6730	169.4558	183.6557	196.0428
20.7744	144.1725	157.1358	168.9292	182.1666	192.7566
24.9281	142.5667	152.8156	162.8445	170.6670	181.2976
29.1623	141.6307	151.8879	157.8888	163.3754	174.3484
32.9363	140.7082	146.1732	151.0311	159.8360	171.2216
37.0007	136.8732	138.9002	142.0083	150.7919	163.8997
40.4563	133.3938	136.1815	140.8779	152.8661	163.2477
44.4878	132.3502	134.9673	137.4399	147.4426	156.8834
48.2247	130.9371	134.0476	134.9807	141.7200	150.0145
52.2860	127.3648	130.9030	133.0068	136.0669	141.9958
55.8697	123.8489	126.6233	130.9190	133.0668	136.6466
59.8184	121.2737	123.6977	127.8770	130.4682	133.1430

Table 1 H: Molar concentration (M) and equivalent conductance of [Co-4-AAp]Cl_2in 100% methanol.

Conc. *10-5 M	**T=293 K**	**T=298 K**	**T=303 K**	**T=308 K**	**T=313 K**
4.3695	232.1525	248.1724	261.9038	292.7995	339.7152
8.3457	182.6570	192.2428	204.2251	225.1940	244.9646
12.7402	153.0120	166.2817	178.9144	189.5108	202.0695
16.5494	145.8901	162.8235	172.0580	182.7493	190.9067
20.7744	152.0815	159.0335	169.1537	176.6310	187.9430
24.9281	148.8041	158.6296	168.6612	173.6626	185.5097
29.1623	146.2299	157.3708	163.8897	171.8289	184.6357
32.9363	141.9226	151.5067	162.8187	170.8675	173.7644
37.0007	152.5486	151.2021	156.0795	166.8727	173.4988
40.4563	145.9451	147.3877	151.7901	162.6298	167.3262
44.4878	138.7886	142.3851	144.2957	148.6789	153.7365
48.2247	133.3218	135.0844	138.4022	140.5795	143.7936
52.2860	127.8429	129.7555	131.6680	134.5369	137.0232
55.8697	124.2964	125.5493	127.1602	128.4131	130.6505
59.8184	120.0199	122.1096	123.9485	125.9545	127.8770

Table 2(A-B) shows the best fit parameters of analysis of conductance data for both complexes in different percentages of methanol and water at different temperatures.

From Table 2(A-B); the values of λ_M^{+2} increase with increasing temperatures which may be attributed to the breaking of hydrogen bonds between solvated ion, and because of the large size of the complex ion which form small size of solvated ion to move in solution. The value of association constant K_A increase with increasing temperature, which assumed simple columbic interactions between hard sphere ions in continuous medium, the same behavior was obtained by Dawood (Dawood, 1996) for symmetrical (1:1) electrolytes in methanol at different temperatures, the values of R are generally 10A° which indicate that the ions are separated by solvent molecules (SSIP).

Table 2 A: Results of analysis of the conductance data for $[Ni(4\text{-}AAP)_3]Cl_2$ in Methanol – Water mixture at different temperatures.

T (K^o)	K_A	$\lambda^o{}_M$+2	$\lambda^o{}_{MX}$+	R_Ao	σΛ
100 % Methanol					
293.16	699	100	0.1	10	0.081
298.16	650	120	0.1	10	0.068
303.16	560	130	0.2	10	0.059
308.16	473	145	0.1	10	0.056
313.16	400	150	0.2	10	0.095
90 % Methanol					
293.16	749	50	0.1	10	0.091
298.16	850	80	0.3	10	0.064
303.16	943	100	0.3	10	0.069
308.16	1100	110	0.3	10	0.058
313.16	1200	120	0.1	10	0.067
70 % Methanol					
293.16	915	110	0.1	10	0.074
298.16	1043	120	0.1	10	0.078
303.16	1150	125	0.1	10	0.071
308.16	1274	130	0.1	10	0.062
313.16	1325	140	0.1	10	0.055
50 % Methanol					
293.16	1100	55	0.1	10	0.074
298.16	1274	50	0.2	10	0.078
303.16	1400	45	0.2	10	0.071
308.16	1500	35	0.1	10	0.062
313.16	1600	30	0.1	10	0.055

Table 2 B: The results of analysis of the conductance data for $[Co(4\text{-}AAP)_3]Cl_2$ in Methanol – Water mixture at different temperatures.

T/ (K^o)	K_A	$\lambda^o{}_{M}{+2}$	$\lambda^o{}_{MX}{+}$	$R_A o$	σΛ
100 % Methanol					
293.16	650	150	0.1	10	0.091
298.16	727	155	0.1	10	0.082
303.16	790	155	0.2	10	0.071
308.16	850	160	0.2	10	0.09
313.16	900	165	0.1	10	0.072
90 % Methanol					
293.16	1152	150	0.3	10	0.087
298.16	1199	160	0.3	10	0.061
303.16	1248	165	0.2	10	0.083
308.16	1300	170	0.2	10	0.092
313.16	1350	175	0.2	10	0.072
70 % Methanol					
293.16	900	155	0.1	10	0.1
298.16	1000	180	0.1	10	0.085
303.16	1100	190	0.2	10	0.091
308.16	1150	200	0.3	10	0.073
313.16	1200	205	0.1	10	0.069
50 % Methanol					
293.16	699	150	0.1	10	0.095
298.16	796	160	0.1	20	0.079
303.16	850	170	0.1	10	0.082
308.16	925	175	0.2	10	0.093
313.16	1000	180	0.2	10	0.081

Table 3 A: The value of Ln K and 1\T for $[Ni\text{-}4\text{-}AAp]Cl_2$ in different mixed solvent

1/T	Ln K_A 100 %	Ln K_A 90 %	Ln K_A 70 %	Ln K_A 50 %
0.00341111	6.549651	6.618739	6.818924	7.003065
0.0033539	6.476972	6.745236	6.949856	7.149917
0.00329859	6.327937	6.849066	7.047517	7.244228
0.00324507	6.159095	7.003065	7.149917	7.31322
0.00319326	5.991465	7.090077	7.189168	7.377759

Table 3 B: The value of Ln K and 1\T for $[Co\text{-}4\text{-}AAp]Cl_2$ in different mixed solvent

1/T	Ln K_A 100 %	Ln K_A 90 %	Ln K_A 70 %	Ln K_A 50 %
0.00341111	6.476972	7.049255	6.802395	6.829794
0.0033539	6.588926	7.089243	6.907755	6.907755
0.00329859	6.672033	7.129298	7.003065	6.549651
0.00324507	6.745236	7.17012	7.047517	6.679599
0.00319326	6.802395	7.20786	7.090077	6.745236

Table 4 A : Thermodynamic parameters from the ion association constant in different temperatures and mixed solvents for the complex $[Ni(4\text{-}AAP)_3]Cl_2$.

T/(K^o)	-ΔH(kJmol^{-1})	-ΔG(kJmol^{-1})	-ΔS(JK^{-1}mol^{-1})
100 % Methanol			
293.16	0.314	15.965	53.387
298.16	0.314	16.063	52.821
303.16	0.314	15.955	51.593
308.16	0.314	15.782	51.022
313.16	0.314	15.296	48.799
90 % Methanol			
293.16	0.261	16.135	55.928
298.16	0.261	16.733	56.996
303.16	0.261	17.265	57.811
308.16	0.261	17.934	59.044
313.16	0.261	18.460	59.781
70 % Methanol			
293.16	0.214	16.623	57.433
298.16	0.214	17.228	58.499
303.16	0.214	17.769	59.319
308.16	0.214	18.319	60.141
313.16	0.214	18.772	60.627
50 % Methanol			
293.16	0.201	17.061	58.883
298.16	0.201	17.724	60.119
303.16	0.201	18.248	60.856
308.16	0.201	18.729	61.429
313.16	0.201	19.215	62.000

Table 4 B: Thermodynamic parameters from the ion association constant in different temperatures and mixed solvents for the complex $[Co(4\text{-}AAP)_3]Cl_2$.

T /(K°)	**-ΔH(kJmol^{-1})**	**-ΔG(kJmol^{-1})**	**-ΔS(JK^{-1}mol^{-1})**
100 % Methanol			
293.16	12.114	15.794	95.197
298.16	12.114	16.336	95.419
303.16	12.114	16.812	95.414
308.16	12.114	17.294	95.430
313.16	12.114	17.705	95.219
90 % Methanol			
293.16	6.041	17.195	79.260
298.16	6.041	17.575	79.207
303.16	6.041	17.971	79.206
308.16	6.041	18.370	79.215
313.16	6.041	18.772	79.234
70 % Methanol			
293.16	0.158	16.574	57.075
298.16	0.158	17.129	57.979
303.16	0.158	17.643	58.718
308.16	0.158	18.062	59.125
313.16	0.158	18.460	59.452
50 % Methanol			
293.16	0.191	15.965	55.109
298.16	0.191	16.559	56.178
303.16	0.191	17.013	56.749
308.16	0.191	17.499	57.405
313.16	0.191	17.991	58.059

If Stokes law were obeyed in a system, the value of the Walden product ($\eta_o\Lambda_o$) would be constant only if the effective radius of the ion remains constant in the different media. He suggested that the major deviation in the Walden product is due to the variation of the electrochemical equilibrium between ions and the solvent molecules depending on the composition of the mixed polar solvents (Hemes, 1974). This is the case in the behaviour of the present system as indicated in Figure (4) where the ions suffer various degrees of salvation with different mixtures of methanol and water as described by (Hameed *et al.*, 2008). Table (5) shows some physical constants of methanol-water mixtures and the Walden product ($\eta\Lambda_o$) for this electrolyt,the decrease of the Walden product values indicates strong solvent-solute interaction as a result of which the solvent fails to decrease the mobility of the ions and increase the viscosity of the medium (Akrawi, 2002).

Table 5: Dielectric constants (D), viscosities (η) of methanol-watermixtures at 298 K and the Walden product ($\eta\Lambda_o$).

Memetheth %	**D**	**η (cp)**	**Walden product ($\eta\Lambda_o$)**
100	32.64	0.545	0.654
90	37.23	0.575	0.460
70	46.42	0..650	0.780
50	55.40	0.720	0.360

◊=293K.■=298K.▲=303K.x=308K.*=313K

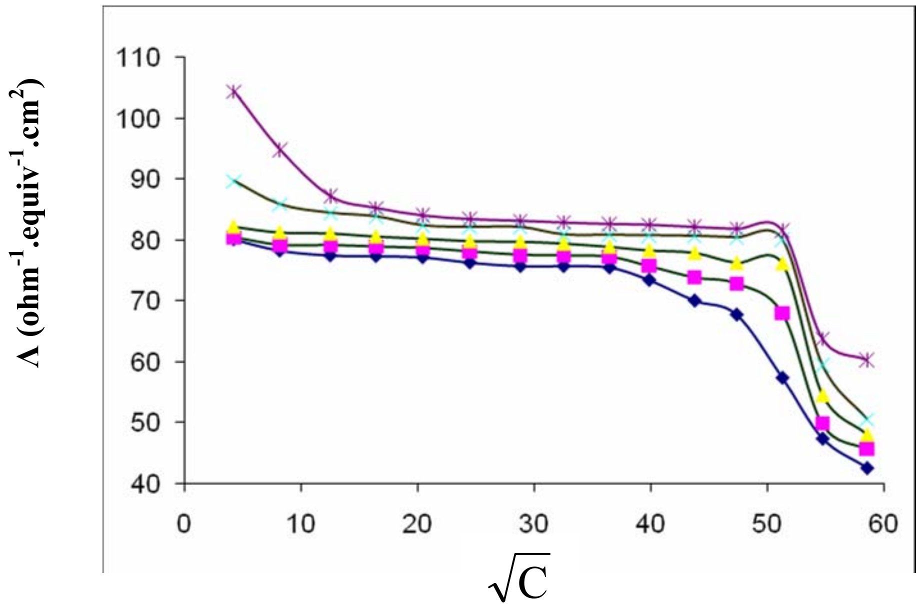

Fig. 1 A: Relation between equivalent conductance and square root of concentration of $[Ni\text{-}4\text{-}AAp]Cl_2$ in 50% methanol –water mixture.

◊ =293 K . ■=298 K. ▲=303 K . x =308K. □ = 313 K

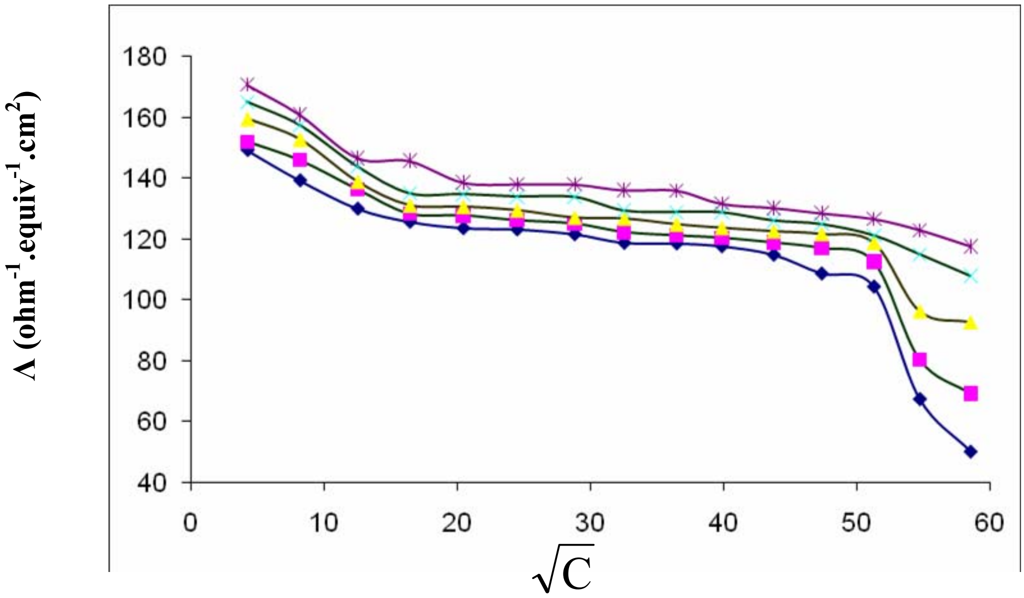

Fig. 1 B: Relation between equivalent conductance and square root of concentration of [Ni-4-AAp]Cl_2 in 70% methanol –water mixture.

◊=293K.■=298K.▲=303K.x=308K.*=313K

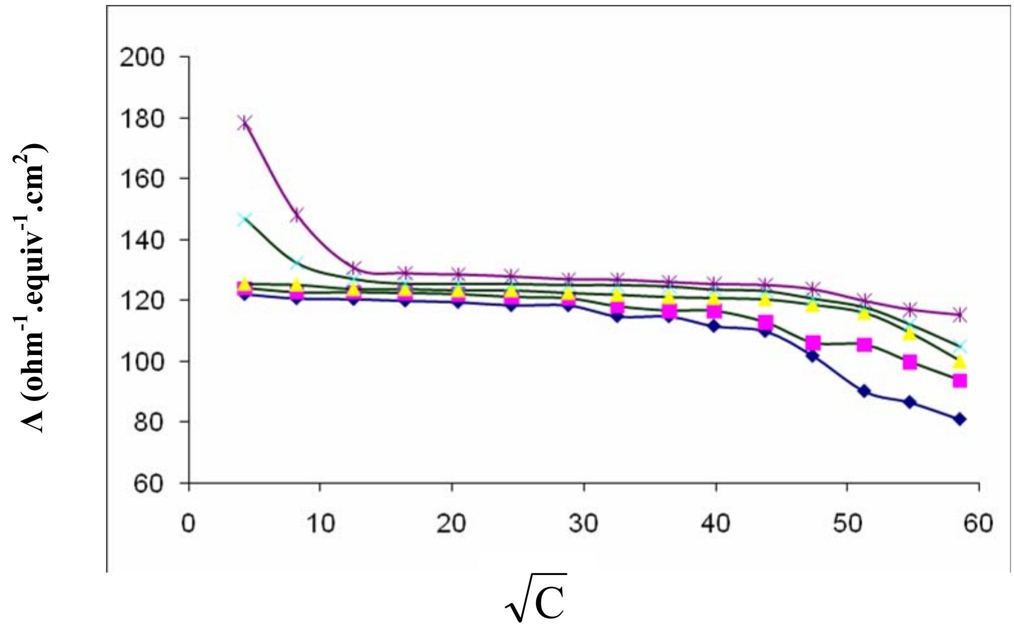

Fig. 1 C: Relation between equivalent conductance and square root of concentration of [Ni-4-AAp]Cl_2 in 90% methanol –water mixture.

◊=293K.■=298K.▲=303K.x=308K.*=313K

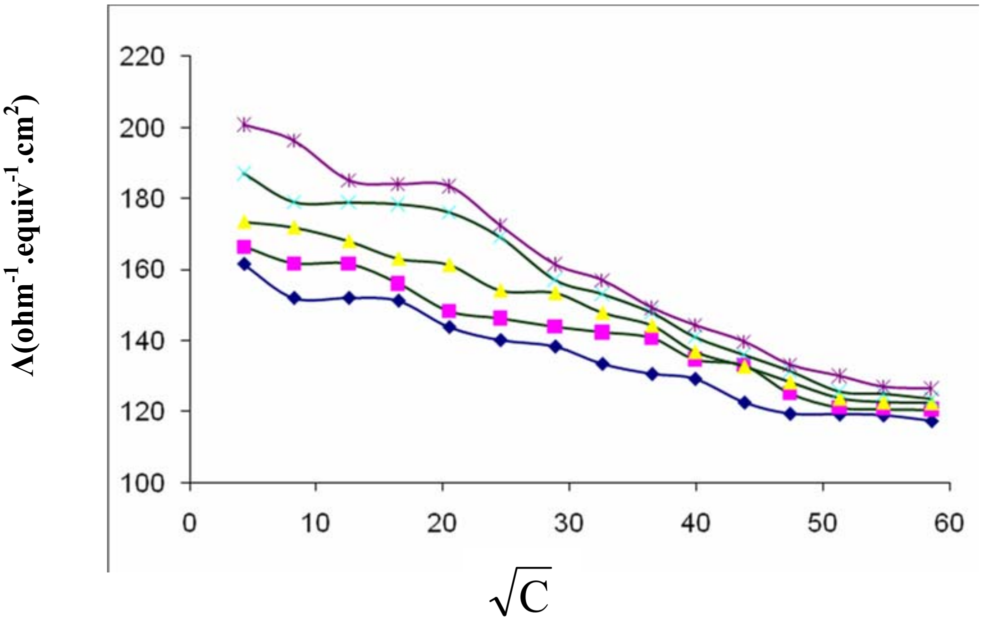

Fig. 1 D: Relation between equivalent conductance and square root of concentration of [Ni-4-AAp]Cl_2 in 100% methanol.

◊=293K.■=298K.▲=303K.x=308K.*=313K

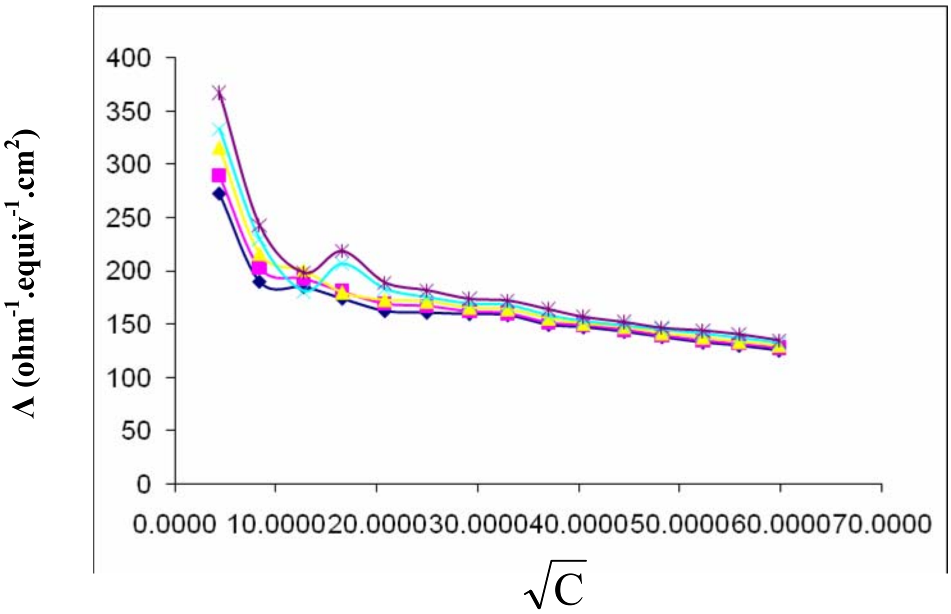

Fig. 1 E: Relation between equivalent conductance and square root of concentration of [Co-4-AAp]Cl_2 in 50% methanol –water mixture.

◊=293K.■=298K.▲=303K.x=308K.*=313K

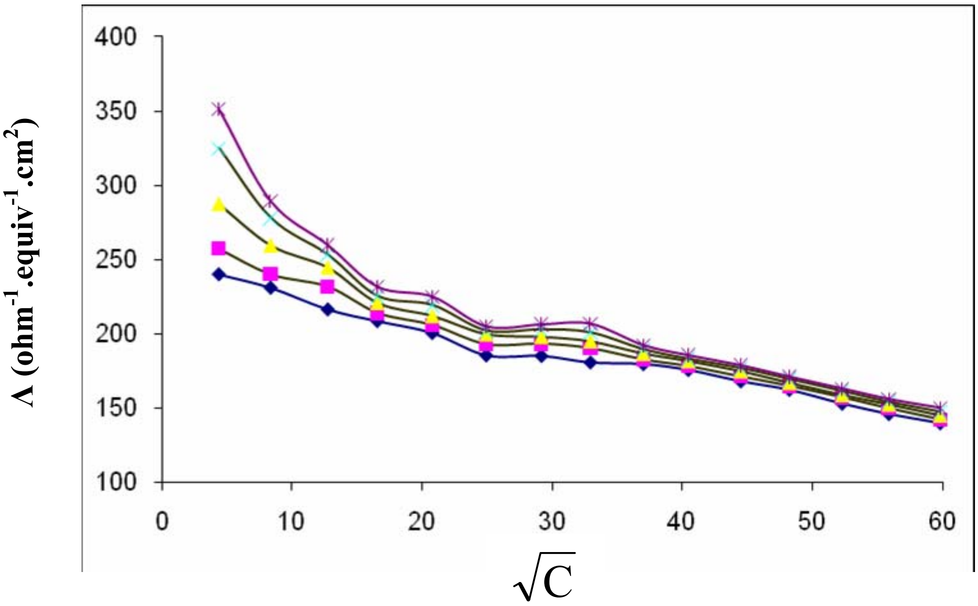

Fig. 1 F: Relation between equivalent conductance and square root of concentration of $[Co\text{-}4\text{-}AAp]Cl_2$ in 70% methanol –water mixture

◊=293K.■=298K.▲=303K.x=308K.*=313K

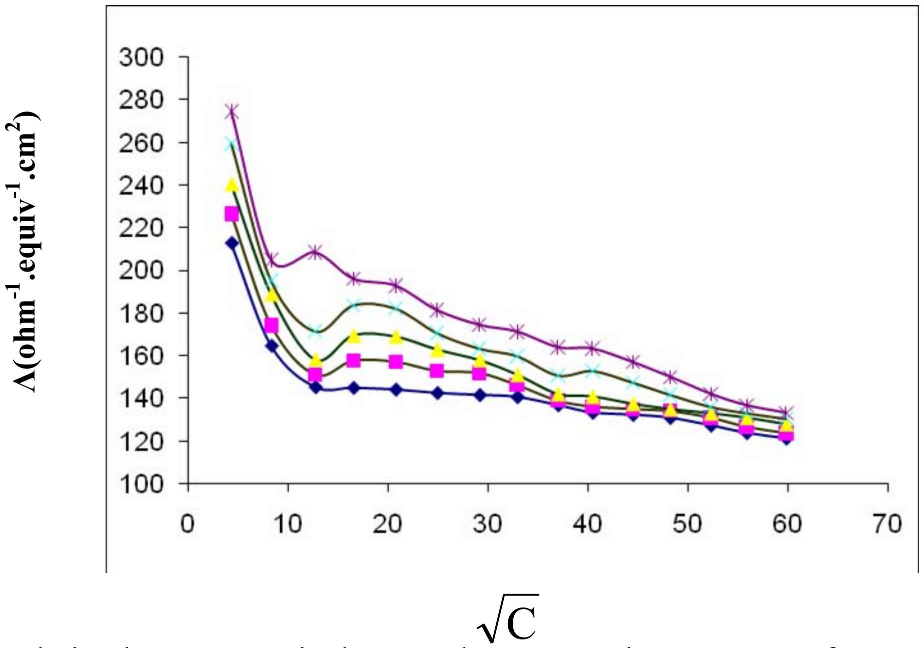

Fig. 1 G: Relation between equivalent conductance and square root of concentration of $[Co\text{-}4\text{-}AAp]Cl_2$ in 90% methanol –water mixture

◊=293K.■=298K.▲=303K.x=308K.*=313K

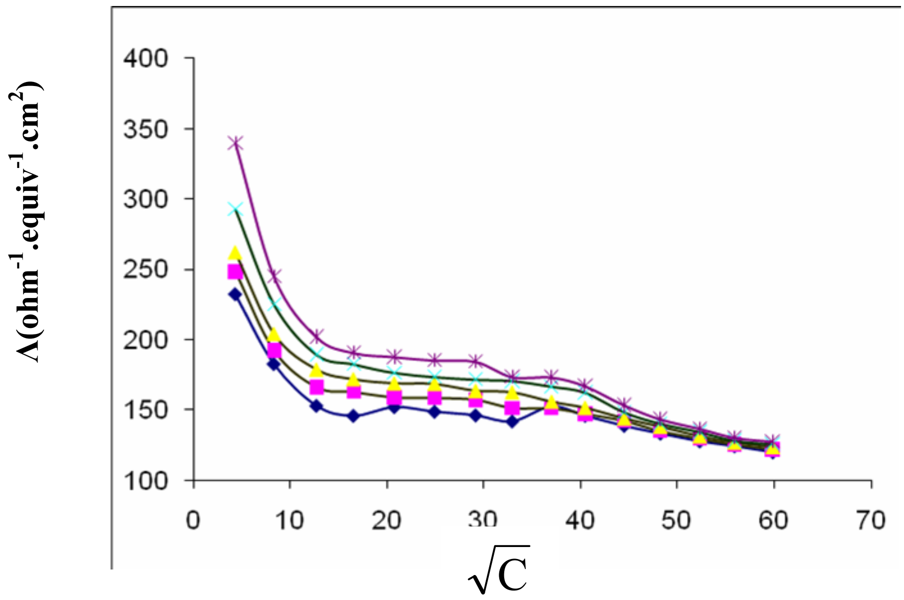

Fig. 1 H: Relation between equivalent conductance and square root of concentration of $[Co\text{-}4\text{-}AAp]Cl_2$ in 100% methanol.

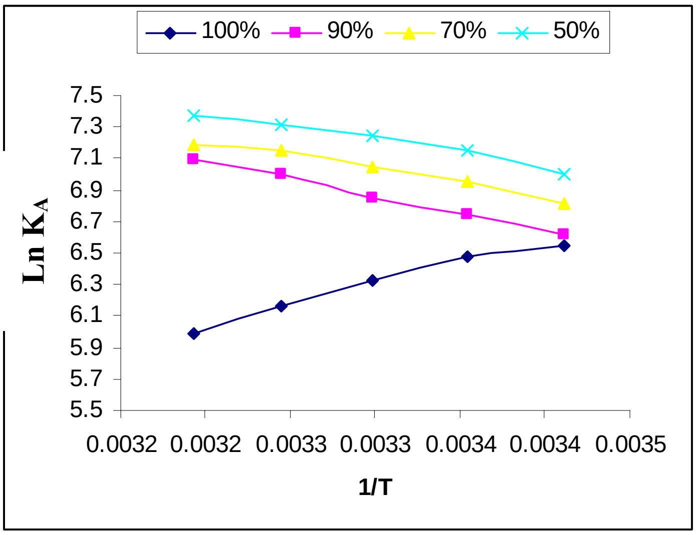

Fig. 2: Relation between LnK_A and 1\T for $[Ni\text{-}4\text{-}AAp]CL_2$ in different percentages of methanol water.

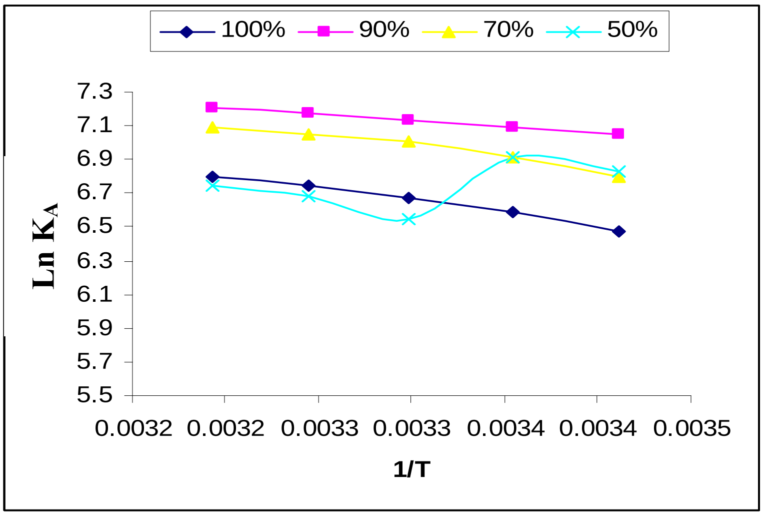

Fig. 3: Relation between LnK_A and 1\T for [Co-4-AAp]CL_2 in different percentages of methanol water.

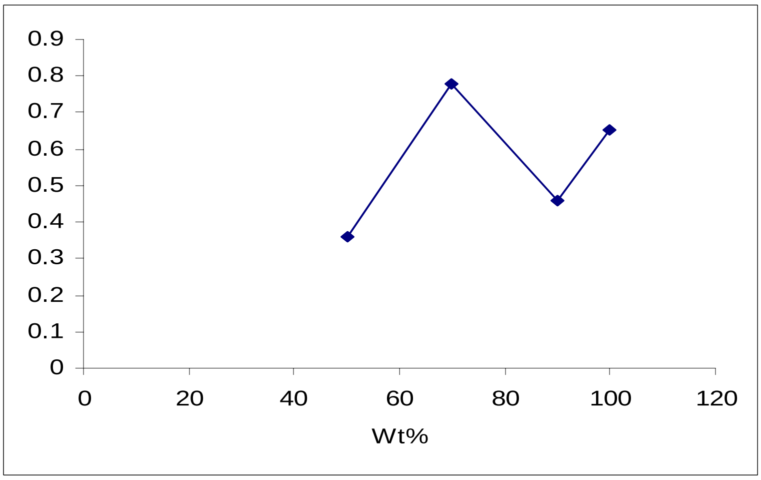

Fig. 4 : The plot of Walden against the weight percent of methanol water mixture

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