Conductivity Measurements of 4-Amino Salicylic Acid and with some Transition Metal Chlorides in Different Solvents and at Different Temperatures

Banan A. Akrawi **Ahlam M. J. Ali*** **Alaa H. Jalil**
Department of Chemistry/ College of Science/ University of Mosul
***Email: pro_ahlam@yahoo.com**

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ABSTRACT

In the first part of this work we have measured the electrical conductivity of 4-amino salicylic acid (4-ASA) solution in water, methanol and ethanol at different temperatures (293.16-313.16 K). The experimental results were analyzed using Lee-Wheaton equation (LW) for symmetrical electrolytes (1:1). The conductivity parameters were calculated: the equivalent conductivity at infinite dilution (Λ_o), the association constant (K_A) and the mean distance values between ions (R) at the best standard deviation $\sigma s(\Lambda)$. It is found that by increasing the temperature, the values of Λ_o increased, in contrast of that the values of K_A decreased in ethanol only, R are found to be between (2-29)A^o which indicates the formation of solvent separated ion pairs in solution. By Vant Hoff equation we have calculated the thermodynamic parameters (ΔG, ΔH and ΔS) of ion association in solution.

The second part of this work is the measurement of electrical conductivity of (4-ASA) in water with chlorides of each of nickel, cobalt and manganese at different temperatures (293.16-313.16 K) and calculation of conductivity parameters by Lee-Wheaton equation for unsymmetrical electrolytes (2:1), besides the thermodynamic parameters were also performed. The Walden-product ($\Lambda_o\eta$) was also determined and discussed.

Keywords: Conductivity, Lee-Wheaton equation, 4-amino salicylic acid, association constant

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قياسات توصيلية 4- امينو حمض السالسيليك ومع كلوريدات العناصر الانتقالية في مذيبات مختلفة وفي درجات حرارية مختلفة

الملخص

في الجزء الأول من هذا البحث تم قياس التوصيلية الكهربائية لمحلول 4-امينو حمض السالسيليك في مذيبات كل من ماء قياس المواصلة والميثانول فضلا عن الايثانول وفي درجات حرارية مختلفة (293.16-313.16 k). وتم تحليل النتائج العملية بتطبيق معادلة لي_ويتون في التوصيلية للاليكتروليتات المتناظرة (1:1) وحساب متغيرات التوصيلية: المواصلة المكافئة عند التخفيف إلى ما لانهاية (Λ_o)، ثابت التجمع الايوني (K_A) ومعدل المسافة بين الايونات (R) عند أحسن قيم من الانحراف القياسي (Λ) σ_S. ولوحظ أن قيم Λ_o تتناقص مع ازدياد درجة الحرارة في المذيبات الثلاثة بينما قيم K_A تزداد في كل من الماء والميثانول في حين انها تقل في مذيب الايثانول وان قيم R ($2-29A^o$) مما يدل على تكوين مزدوجات ايونية مفصولة بجزيئات المذيب في المحلول. وباستخدام معادلة فانت هوف تم حساب الدوال الثرموداينميكية (ΔG, ΔH, ΔS) للتجمع الايوني في المحلول.

والجزء الثاني من البحث يتضمن قياس التوصيلية الكهربائية لمحلول 4-امينو حمض السالسيليك في الماء مع كلوريدات كل من النيكل والكوبلت والمنغنيز وفي درجات حرارية مختلفة (293.16-313.16 k) وحساب متغيرات التوصيلية

باستخدام معادلة لي_ويتون للاليكتروليتات غير المتناظرة (2:1) فضلا عن حساب الدوال الثرموداينميكية وأيضا نوقشت النتائج المستحصلة من علاقة والدن (Walden-Product).

الكلمات الدالة: التوصيلية الكهربائية، 4-امينو حمض السالسيليك، معادلة لي_ويتون، ثابت التجمع الايوني، مزدوجات ايونية.

INTRODUCTION

4-amino salicylic acid is an antibiotic used to treat tuberculosis (Wikipedia, 2013). This organic compound has also been used since 1940, for the treatment of inflammatory bowel disease, where it has shown a greater potency in ulcerative colitis and Crohn's disease. 4-ASA has been investigated for the use in manganese chelating therapy and a 17-year follow-up study shows that it might be superior to other chelating protocols such as EDTA. With heat amino salicylic acid is decarboxylated to produce CO_2 and 3-amino phenol (daily med, 2013).

The dissociation constant of salicylic acid in 1-propanol-water mixtures at 25^{o}C has been determined from conductance measurements. The experimental data have been analyzed by means of (LW) equation (Papadopoulos and Avranas, 1991). The ionization constants of acids are influenced by the nature of the solvent and especially in alcohol-water mixtures vary with solvent composition in a manner which is not completely understood (Niazi and Khan, 1993). Conductance provides a simple and accurate method for the determination of the dissociation constant of a relatively strong acids (Niazi *et al*., 1993).

In the present works the conductivity parameters have been calculated for (4-ASA) with their mixtures of some transition metal chlorides in different solvents and at different temperatures.

EXPERIMENTAL

Chemicals and reagents:

4-amino salicylic acid (analar grade) and the transition metal chlorides were reagent grade (BDH) products used without any further purification.

Solvents:

Absolute methanol and absolute ethanol were of (BDH) products. Conductivity water was prepared by redistilling distilled water three times with the addition of a little amount of potassium permanganate and small pellets of KOH.

Instruments:

The conductivity measurements were made using a digital conductivity meter (Jenway) with sensitivity between 10^{-1} and 10^{-9} Siemens.

General procedure:

A general method has been used for measuring the conductance of the electrolytes. The conductivity cell was dried and kept at a contrast temperature (± 0.1 ^{o}C). A certain volume (25 ml) of conductivity water (or any solvent used) was placed in the conductivity cell, then a small volume of (4-ASA) (1×10^{-3} M) was added and the conductivity of the solution was measured. This procedure was repeated by different additions of (4-ASA) for about (12-16) times for each run. The whole procedure was repeated at each temperature.

The second part of this work was as following: in a clean dried conductivity cell, a certain amount (10 ml of 5×10^{-5} M) of each metal chloride solution was placed in the conductivity cell and then a small known volume of (5×10^{-5} M) (4-ASA) was added and the conductivity was measured followed by (12-16 times) of (4-ASA) additions and measuring the conductivity for each solution. This procedure was repeated again at different temperatures.

RESULTS AND DISCUSSION

The results of the present work were analyzed according to (LW) equation for the specific case of solution containing only a single symmetrical electrolyte indicates that $\Lambda_{equiv.}$ is a function of many parameters as:

$$\Lambda_{equiv.} = f\,(\Lambda_o, R, K_A)$$

Where Λ_o is the equivalent conductance at an infinite dilution, K_A is the pair-wise ion association constant:

$$M^{+}_{aq} + X^{-}_{aq} \xrightarrow{K_A} M^{+}_{n.aq}\,X^{-}$$

Where n is the number of solvent molecule and may be zero, and R is the distance parameter between anion and cation.

The input data to the computer program {(LW) equation for (1:1) symmetrical electrolytes} are: solvent data (Temp. T, Dielectric constant D, Viscosity η); K_A; Λ_o; and R in the form of $R_{min.}$, $R_{max.}$, the minimum and maximum distance between ions), ΔR, together with the solution molarities ($mol.L^{-1}$) and the corresponding equivalent conductance (Siemens $equiv^{-1}.cm^2$).

This program calculates the values of Λ_o, K_A, and R (the characteristic ion-pair distance parameter) which gives the "best fit " of the experimental conductance.

Table (1) shows the variation of the equivalent conductivity with molar concentration of 4-amino salicylic acid in different solvents at different temperatures.

Table 1: Variation of the equivalent conductivity ($\Lambda_{equiv.(Siemens\ equiv.^{-1} cm^{2})}$) with molar (M) concentration (mol./l) of *4*- Amino Salicylic acid in different solvents at different temperatures.

Solvent	Water					Methanol					Ethanol				
Temp./ K	293.16	298.16	303.16	308.16	313.16	293.16	298.16	303.16	308.16	313.16	293.16	298.16	303.16	308.16	313.16
$M \times 10^4$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$
0.19	319.40	288.19	267.38	251.78	236.17	26.01	23.41	19.77	16.65	13.01	4.68	4.16	3.64	3.12	2.60
0.38	260.96	237.09	218.52	207.92	194.66	16.71	13.53	11.14	9.28	7.69	3.18	2.65	2.12	1.86	1.59
0.56	231.38	215.16	198.94	186.33	173.71	12.43	9.55	7.93	6.67	5.59	2.52	1.98	1.62	1.44	1.26
0.74	216.74	201.59	186.45	174.05	161.66	9.64	7.57	6.33	5.23	4.54	2.07	1.65	1.38	1.24	1.10
0.90	205.77	190.07	176.60	165.38	154.16	8.30	6.28	5.39	4.38	3.93	1.80	1.46	1.23	1.12	1.01
1.07	196.49	184.12	170.79	159.36	147.94	7.24	5.43	4.86	4.00	3.52	1.62	1.33	1.14	1.05	0.95
1.23	188.87	175.58	163.95	154.82	144.02	6.48	4.90	4.40	3.74	3.32	1.50	1.25	1.08	1.00	0.91
1.38	182.21	168.90	158.55	150.41	139.32	5.84	4.51	4.07	3.48	3.11	1.41	1.18	1.04	0.96	0.89
1.53	176.13	162.75	154.06	146.71	136.68	5.35	4.28	3.81	3.21	2.94	1.34	1.14	1.00	0.94	0.87
1.67	170.38	158.14	148.96	142.23	133.66	5.02	4.10	3.61	3.12	2.88	1.29	1.10	0.98	0.92	0.86
1.80	166.52	152.95	145.59	139.37	132.02	4.86	3.96	3.45	3.00	2.77	1.24	1.07	0.96	0.91	0.85
1.94	162.00	149.35	140.92	135.65	129.33	4.64	3.79	3.32	2.90	2.69	1.21	1.05	0.95	0.90	0.84
2.06	158.38	145.52	139.10	134.16	127.23	4.45	3.66	3.21	2.82	2.62	1.19	1.04	0.94	0.89	0.84
2.19	154.99	142.40	136.81	132.15	125.62	4.24	3.59	3.12	2.75	2.56	1.17	1.03	0.93	0.89	0.84
2.31	151.78	139.41	134.99	130.57	125.26	4.07	3.45	3.05	2.70	2.52	1.15	1.02	0.93	0.88	0.84
2.42	149.11	136.91	132.70	128.50	124.29	3.96	3.32	2.99	2.65	2.44	1.14	1.01	0.93	0.88	0.84
2.54	146.49	134.83	131.21	127.19	123.17	3.82	3.22	2.93	2.61	2.37	1.13	1.01	0.92	0.88	0.84
2.65	144.27	132.71	129.24	125.39	121.53	3.70	3.12	2.89	2.58	2.31	1.12	1.00	0.92	0.89	0.85
2.75	142.39	130.17	127.94	124.24	120.54	3.63	3.04	2.85	2.59	2.26	1.11	1.00	0.93	0.89	0.85
2.86	140.09	128.31	126.52	122.95	119.38	3.57	2.96	2.82	2.61	2.21	1.11	1.00	0.93	0.89	0.86

The plot of $\Lambda_{equiv.}$ against the square root of the molar concentration ($C^{1/2}$) is shown in Figs. (1-3).

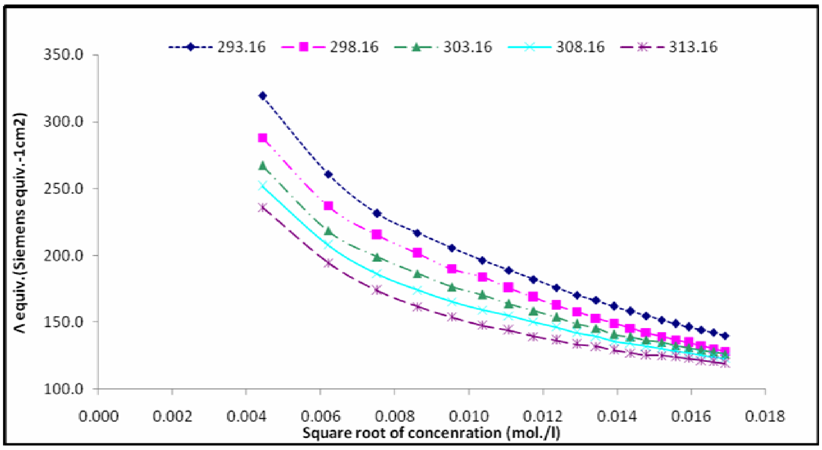


Fig. 1: The relation between equivalent conductivity and the square root of concentration of *4*-Amino Salicylic acid in water at different temperatures

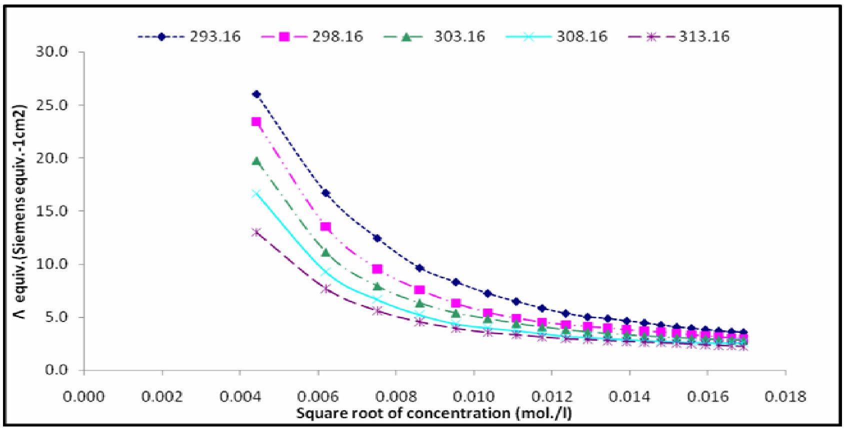


Fig. 2: The relation between equivalent conductivity and the square root of concentration of 4-Amino Salicylic acid in methanol at different temperatures

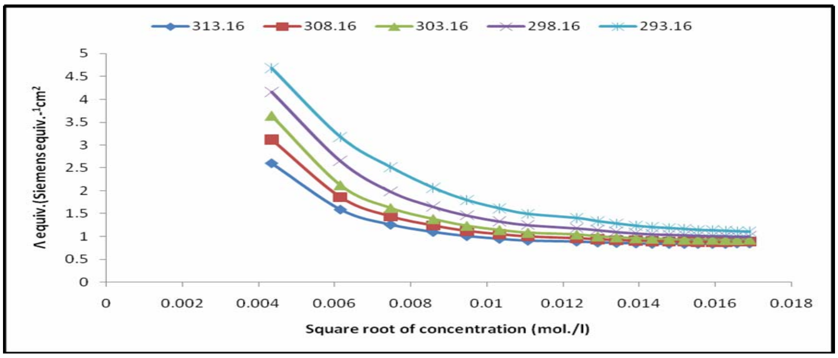


Fig. 3: The relation between equivalent conductivity and the square root of concentration of 4-Amino Salicylic acid in ethanol at different temperatures

It is clear from the plot that the compound behaves as a weak electrolyte at different temperatures in each solvent. Table (2) shows the best fit parameters of analysis of conductance data by using (LW) equation.

Table 2: Best fit parameters of analysis of conductance data for 4-ASA in water, methanol and ethanol at different temperatures

Solvent	Water				Methanol				Ethanol			
Temp. (K)	Λ_o Siemens equiv^{-1}.cm^2	K_A	R/A^o	σs(Λ)	Λ_o Siemens equiv^{-1}.cm^2	K_A	R/A^o	σs(Λ)	Λ_o Siemens equiv^{-1}.cm^2	K_A	R/A^o	σs(Λ)
293.16	357.37	13981	9	0.035	41.95	195763	2	0.066	5.32	----	19	0.095
298.16	355.30	17374	9	0.025	39.47	200728	2	0.730	4.86	56786	19	0.009
303.16	309.90	13494	19	0.035	58.24	274555	10	0.316	4.35	46538	19	0.002
308.16	281.66	11533	19	0.043	33.38	300448	10	0.804	3.8	36720	26	0.002
313.16	257.92	10528	29	0.053	29.54	343951	10	0.026	2.11	1746	26	0.170

The analysis shows that Λ_o decreases with the increasing temperature. In methanol the increasing of K_A assumes a simple coulombic interaction between hard sphere ions in continuous medium. Besides the dielectric constant of the solvent which play an important role on the ionic conductivity, it decreases with increasing temperature, since oppositely charged ions tend to form ion-pairs and the interionic forces in an electrolytic solution are assumed in the various theoretical treatments, to follow coulombs law and so to be inversely proportional to the dielectric constant of the solution which have an important effect on the values of the association constant (K_A) as the K_A values increase with increasing temperature assuming a simple coulombic interaction between hard sphere ions in a continuous medium (Akrawi *et al*., 2006) (Fuoss, 1958). In other words, it is expected that such an increase of (K_A) is partly due to a decrease in the dielectric constant and can partly be explained in terms of diminution in dielectric constant in the vicinity of an ion-pair and decreasing the density of solvent (Weast, 1974).

In both water and ethanol each of K_A and Λ_o decreased with increasing temperature. This behavior can be explained as that the coulombic interactions cannot explain the acid association constants and that some form of short range interaction is required to explain the results for the compound in different temperatures (Niazi *et al*., 1993), (Ali, 2006).

Standard thermodynamic quantities for the association were evaluated by the least-square treatment of the plot of ln K_A against 1/T, Fig. (4).

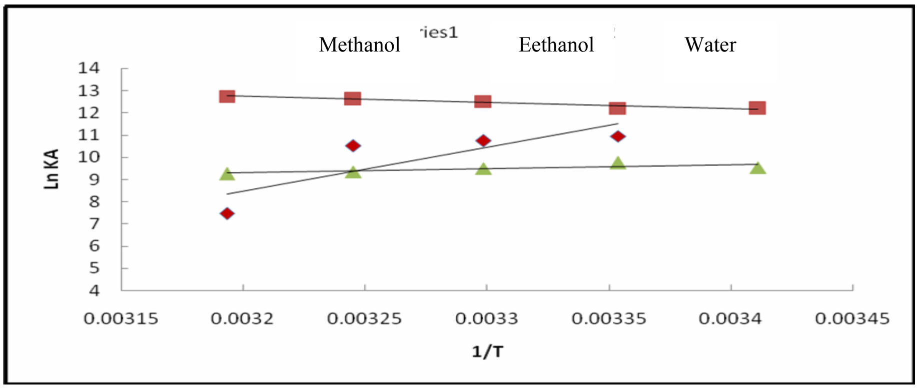


Fig. 4: The plot of Ln K_A against 1/T for 4-ASA in different solvents

$$\ln K_A = -\Delta H^{\circ} / RT + C \;\dots\dots \qquad (1)$$

The standard entropy of ion-pair formation is a linear combination of two variables:

$$\Delta S^{\circ} = \frac{(\Delta H^{\circ} - \Delta G^{\circ})}{T} \;\dots\dots (2)$$

The standard Gibb's energy calculated from the relationship

$$\Delta G^{\circ} = -RT \ln K_A \;\dots\dots\dots\dots (3)$$

The results of calculation are gathered in (Table 3).

Table 3: Thermodynamic parameters from the ion-association constant of (4-ASA) in different solvents at different temperatures

Solvent	Water			Methanol			Ethanol		
Temp. (K)	-ΔH KJ.mol^{-1}	-ΔG KJ.mol^{-1}	-ΔS J. K^{-1}mol^{-1}	ΔH KJ.mol^{-1}	-ΔG KJ.mol^{-1}	ΔS J.K^{-1}mol^{-1}	-ΔH KJ.mol^{-1}	-ΔG KJ.mol^{-1}	-ΔS J. K^{-1}mol^{-1}
293.16	25.848	23.265	0.009	23.358	29.698	0.181	164.39	----	----
298.16		24.200	0.005		30.266	0.180		27.136	0.460
303.16		23.969	0.006		31.563	0.181		27.09	0.452
308.16		23.962	0.006		32.315	0.180		26.929	0.446
313.16		24.114	0.006		33.191	0.182		19.436	0.463

We have found that the values of ΔH of ion-association in water and in ethanol are negative since ions are rigid and associated in a columbic interaction in a dielectric continuum media when the ion-pairs formed (Akrawi and Ali, 2009).

The values of ΔG are negative indicating that the process occurs spontaneously. The negative values of ΔS of 4-ASA in water, and ethanol have been considered as due to the increase in the orientation of solvent molecules when the ion – pairs formed (Akrawi and Ali, 2009).

The value of ΔH for 4-ASA in methanol is positive and represents how much the ion-solvation is weakened by ion association. The positive value of ΔS for 4-ASA in methanol has been considered as due to the decrease in the orientation of solvent molecules when the ion-pairs formed (Ali, 2006).

Table (4) shows the values of the equivalent conductivity with molar concentration of the three mixtures, (4-ASA+$NiCl_2$), (4-ASA +$CoCl_2$) and (4-ASA + $MnCl_2$), at different temperatures in water. It is clear from this table that the values of $\Lambda_{equiv.}$ decrease with increasing concentration of the metal added and increase with increasing of temperatures. From Figs. (5-7) it is clear the equivalent conductivity decreases with increasing metal concentration added.

Table 4: Variation of the equivalent conductivity (Λ $_{equiv.(Siemens\ equiv.^{-1} cm^2)}$) with molar (M) concentration (mol./l) of *4*- Amino Salicylic acid with some transition metals ions at different temperatures in water

Metal ions	Ni^{2+}					Co^{2+}					Mn^{2+}				
Temp./K	**293.16**	**298.16**	**303.16**	**308.16**	**313.16**	**293.16**	**298.16**	**303.16**	**308.16**	**313.16**	**293.16**	**298.16**	**303.16**	**308.16**	**313.16**
M x 10^5	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$	$\Lambda_{equiv.}$
4.76	174.63	196.05	210.44	234.30	252.66	68.54	95.17	112.61	120.56	139.84	109.55	121.18	137.39	149.94	161.57
4.55	123.92	130.28	140.01	152.72	161.14	48.43	65.26	74.43	86.02	95.93	78.54	82.65	89.39	100.61	111.08
4.35	102.91	106.77	111.19	119.60	122.23	40.02	52.85	62.24	72.04	77.97	64.45	67.48	72.31	80.18	88.60
4.17	92.66	92.77	93.88	101.34	101.45	35.72	46.07	54.97	63.87	67.81	56.53	58.31	62.87	67.99	75.55
4.00	83.46	82.89	81.76	89.41	88.66	33.34	42.41	51.09	57.99	62.52	50.72	52.98	57.42	61.48	67.43
3.85	76.55	76.63	75.06	81.19	79.54	31.16	39.37	47.82	53.70	56.94	47.16	48.73	51.63	56.27	61.24
3.70	71.80	71.43	69.05	75.01	73.22	30.15	36.77	46.45	50.54	54.26	43.77	45.85	48.31	51.88	55.45
3.57	67.91	67.64	64.44	70.36	68.25	29.38	34.68	44.47	48.08	51.48	42.02	43.45	45.70	49.50	53.45
3.45	64.62	64.30	61.03	66.57	64.81	28.38	33.04	42.29	46.07	49.34	40.15	41.60	43.68	47.14	50.79
3.33	62.01	62.01	58.30	63.42	61.95	27.89	32.25	41.25	44.25	47.84	38.90	40.07	41.90	45.25	48.72
3.23	59.89	59.67	56.57	60.78	59.84	27.46	31.29	40.44	42.99	46.88	37.61	38.78	40.61	43.66	46.76
3.13	57.95	57.79	55.16	58.63	57.68	26.95	30.17	39.85	41.54	45.80	36.48	37.69	39.38	42.33	45.17
3.03	56.15	56.05	53.44	56.75	55.90	26.58	29.24	39.24	40.49	44.91	35.17	36.72	38.38	41.15	43.91
2.94	54.56	54.70	52.39	55.04	54.12	26.20	28.85	38.77	40.17	44.12	34.25	35.45	37.47	40.17	42.77
2.86	53.17	53.35	52.47	53.72	52.75	25.64	28.47	38.25	39.46	43.81	33.57	34.87	37.14	39.27	41.82
2.78	52.11	52.20	52.38	52.51	51.80	25.08	27.99	37.79	39.18	42.99	32.73	34.21	36.45	38.56	40.93
2.70	51.26	51.17	51.13	51.30	50.74	24.81	27.42	37.52	38.30	42.60	32.19	33.40	35.66	37.83	40.17
2.63	50.16	50.29	50.00	50.29	49.95	24.48	27.09	37.03	37.66	41.84	31.56	32.69	35.31	37.24	39.48
2.56	49.53	49.20	49.28	49.41	49.32	24.32	26.86	36.66	36.91	40.97	31.04	32.11	34.57	36.66	38.88
2.50	48.31	48.51	48.71	48.59	48.35	23.92	26.52	36.28	36.32	40.24	30.56	31.64	33.92	36.16	38.28

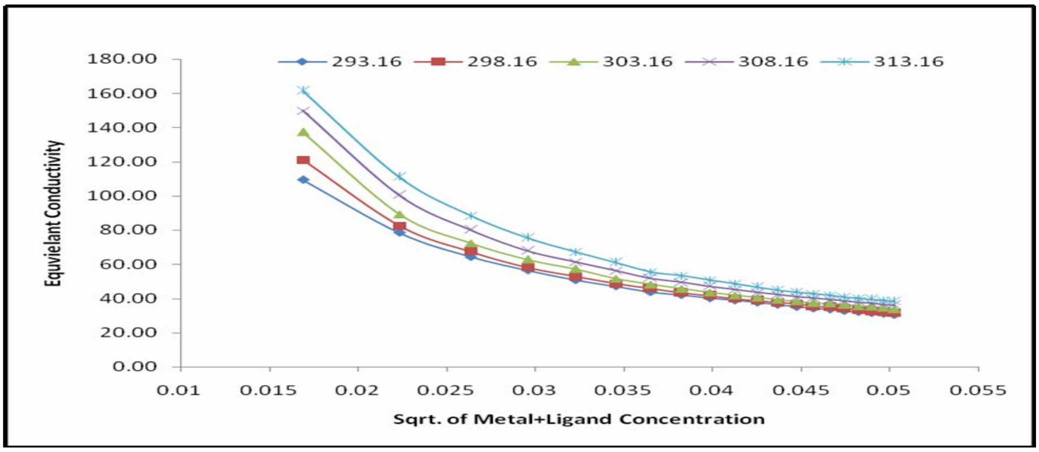


Fig. 5: Equivalent conductivity and the square root of Manganese chloride and ligand concentration (mol.l^{-1})

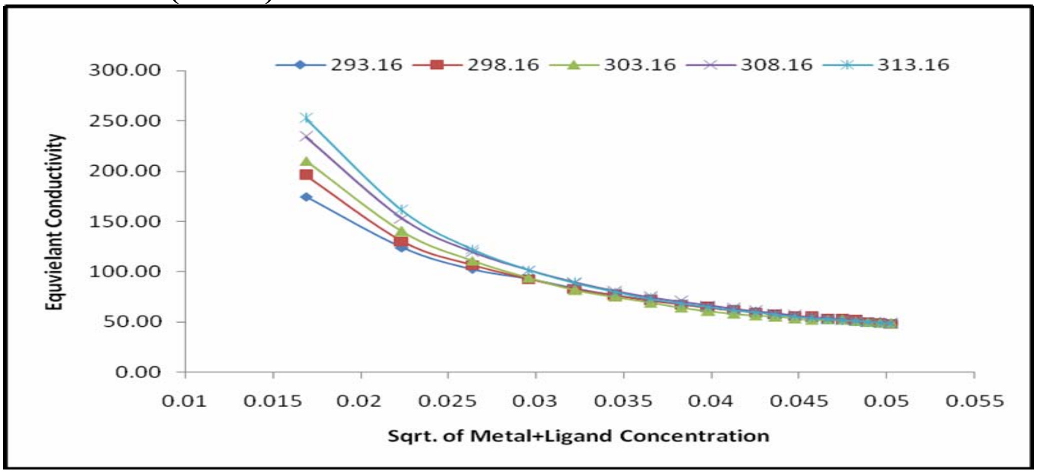


Fig. 6: Equivalent conductivity and the square root of Nickel chloride and ligand concentration (mol.l^{-1})

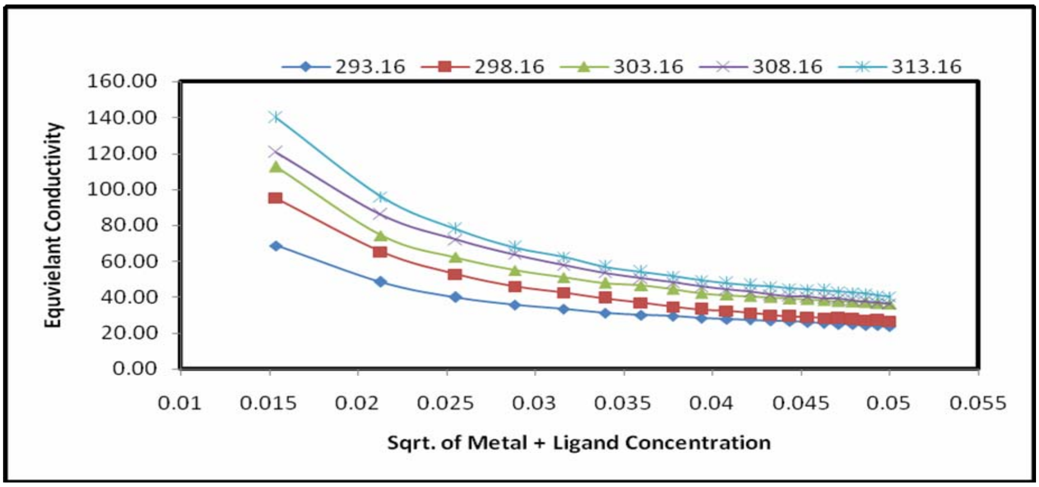


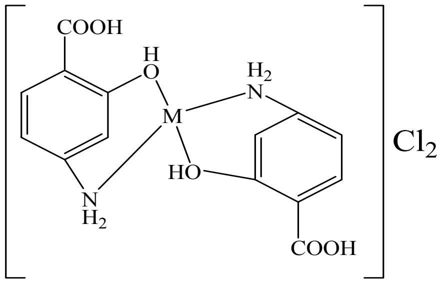
Fig. 7: Equivalent conductivity and the square root of Cobalt chloride and ligand concentration (mol.l^{-1})

The chemical equation which shows the expected complexes resulted from the addition of 4-ASA to the metals chlorides

$$MCl_2.6H_2O + L \longrightarrow [ML_2]Cl_2$$

Where M = Co^{+2}, Ni^{+2}, Mn^{+2}, L=4-ASA

The structure of the complexes expected to be tetrahedral is



M(II) bis 4-Amino Salicylic Acid chloride

For the analysis of the electrolytes (4-ASA +$CoCl_2$), (4-ASA+$NiCl_2$) and (4-ASA + $MnCl_2$), a computer program (RM_1) was used for asymmetrical electrolytes in conductivity water for the data of concentration – conductivity measurements in which the input data are (T, D, η) where T is the temperature in Kelvin, D and η are the dielectric constant and viscosity (poise) of the solvent at that temperature, z_i (charge) and λ_i (ionic conductivity) for each species, $K_A^{(1)}$, $K_A^{(2)}$, $\lambda°_{MX}{}^{+}$, $\lambda°_{M}{}^{2+}$, and R according to (LW) equation for MX_2 electrolyte.

The analysis of the data shows that the cations an associated with anion to form a new species $(MX)^+$

$$M^{+2} + X^- \xrightarrow{K_A^{(1)}} (MX)^+$$

$$(MX)^+ + X^- \xrightarrow{K_A^{(2)}} MX_2$$

Tables (5-7) show the best fit parameters of analysis of conductance data using (LW) equation for the complex solutions of (4-ASA+$CoCl_2$), (4-ASA+$MnCl_2$) and (4-ASA+$NiCl_2$) in water at different temperatures.

Table 5: Best fit parameters of analysis of conductance data for [4-ASA+$CoCl_2$] in water at different temperatures

Temp. (K)	$\lambda_M{}^{2+}$	$\lambda_{MX}{}^{+}$	$K_{A(1)}$	$K_{A(2)}$	R/A°	σs(Λ)
293.16	10	0.2	0.0	10^7	30	1.040
298.16	20	0.2	0.0	250000	10	0.317
303.16	50	0.2	0.0	11500	8	1.102
308.16	69	0.2	0.0	5550	8	2.427
313.16	120	0.2	0.0	5000	8	6.384

Table 6: Best fit parameters of analysis of conductance data for [4-ASA+$MnCl_2$] in water at different temperatures

Temp. (K)	$\lambda_M{}^{2+}$	$\lambda_{MX}{}^{+}$	$K_{A(1)}$	$K_{A(2)}$	R/A°	σs(Λ)
293.16	135	0.2	0.0	11000	8	1.367
298.16	180	0.2	0.0	13500	10	8.897
303.16	220	0.2	0.0	15000	10	3.350
308.16	250	0.2	0.0	13000	10	5.470
313.16	135	0.2	0.0	15000	8	5.461

Table 7: Best fit parameters of analysis of conductance data for [4-ASA+$NiCl_2$] in water at different temperatures

Temp. (K)	λ_M^{2+}	λ_{MX}^{+}	$K_{A(1)}$	$K_{A(2)}$	R/A^o	$\sigma s(\Lambda)$
293.16	580	0.2	0.0	12000	30	1.042
298.16	680	0.2	0.0	10500	30	5.196
303.16	650	0.2	0.0	13000	30	1.371
308.16	1000	0.2	0.0	18500	30	5.606
313.16	1000	0.2	0.0	21000	30	7.196

The above tables show generally that λ_M^{2+} for the three ions increases with increasing temperatures for the three electrolytes, where λ_M^{2+} for (4-ASA+$NiCl_2$) > λ_M^{2+} (4-ASA+$MnCl_2$) > λ_M^{2+} (4-ASA+$CoCl_2$), since Co^{2+} is the smallest cation and the more solvated ion. For the (4-ASA+$CoCl_2$) electrolyte the value of $K_{A(2)}$ decreases with increasing of temperature. This may be due to the effect of short range interaction and the hydrogen bonding formed at low temperature. For the other two electrolytes, $K_{A(2)}$ increases with increase of temperature which assumed a simple coulombic interaction between hard sphere ions in a continuous medium. Besides, such an increase of K_A is partly due to a decrease in the dielectric constant and partly can be explained in term of diminution in dielectric constant in the vicinity of an ion-pair and decreasing the density of solvent (Weast, 1974). The R values obtained are generally (8-30)A^o which indicates that the cations and anions are separated by many water molecules. The relative values of $\sigma s(\Lambda)$ indicate the good applicability of (LW) equation for such a study. The thermodynamic parameters (ΔG, ΔH and ΔS) for 4-ASA complex in water are calculated as mentioned before. Table (8) shows the calculated values.

Table 8: Thermodynamic parameters from the ion association constant of 4-ASA with $CoCl_2$, $NiCl_2$ and $MnCl_2$ in water at different temperatures

Metal chloride	$CoCl_2$			$NiCl_2$			$MnCl_2$		
Temp. (K)	-ΔH KJ.mol^{-1}	-ΔG KJ.mol^{-1}	-ΔS J. K^{-1}mol^{-1}	ΔH KJ.mol^{-1}	-ΔG KJ.mol^{-1}	ΔS J. K^{-1}mol^{-1}	-ΔH KJ.mol^{-1}	-ΔG KJ.mol^{-1}	ΔS J. K^{1}mol^{-1}
293.16	286.397	39.285	0.843	22.938	22.893	0.156	18.531	22.680	0.141
298.16		30.810	0.57		23.384	0.155		23.576	0.141
303.16		23.566	0.866		23.875	0.154		24.236	0.141
308.16		22.088	0.857		25.173	0.156		24.801	0.141
313.16		22.176	0.844		25.911	0.156		28.17	0.149

For 4-ASA with $CoCl_2$ the negative value of ΔH and ΔG values (Table 8) can be explained by interaction in the ion-association process. But the binding entropy (ΔS) between the ions was found to be negative to unfavour the ion-association process and thus favoring ion solvation process (Sarkar *et al*., 2009).

For 4-ASA with $NiCl_2$ (Table 8) the value of (ΔH) is positive which may mean that the temperature dependence of dielectric constant which represents how much the ion –solvation is weakened by ion-association. The positive values of (ΔS) have been considered as due to the decreased orientation of solvent molecules when the ion-pair forms. The values of ΔG of the ion-association are negative and should depend on the kind of the ion (Doe *et al*., 1990). For 4-ASA with $MnCl_2$ (Table 8), it was found that the value of ΔH of ion-association is negative since ions are rigid and associated in a coulombic interaction in a dielectric continuum media. The values of ΔG are negative indicating that the process occurs spontaneously. The positive value of ΔS has been considered as due to the decrease in the orientation of solvent molecules when the ion-pair form, is explained by the fact of the solvent of M^{2+} and weakened by the ion pairing of MX^{+} (Doe *et al.*, 1990).

The plot of Walden-product against reciprocal dielectric constant is shown in Figs. (8- 10). It is clear that $\Lambda_o\eta$ decreases with increasing the dielectric constant. This variation in Walden-product reflects the change of the total solvations. The decrease of the Walden-product indicates an increase of the total solvation with increasing of the dielectric constant. The decrease of dielectric constant of the solvent will increase the solvating power of that solvent, and causes the ion to move with only the primary solvation shell in the solvent and the effect of the secondary solvation appears to be very small.

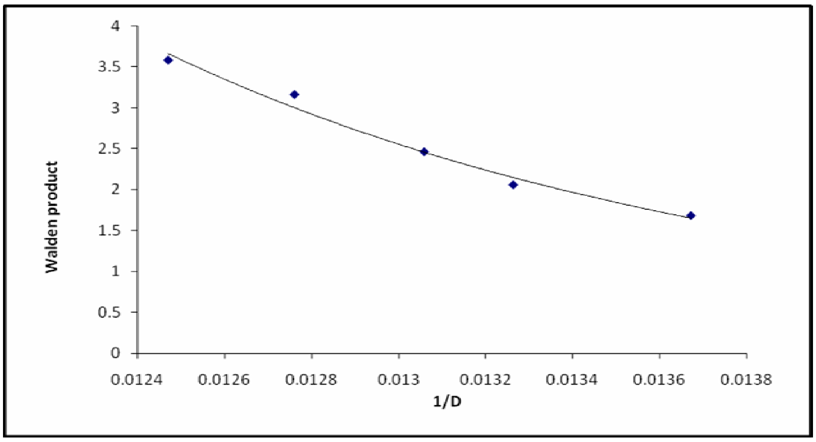


Fig. 8: Walden – product for 4-ASA in water

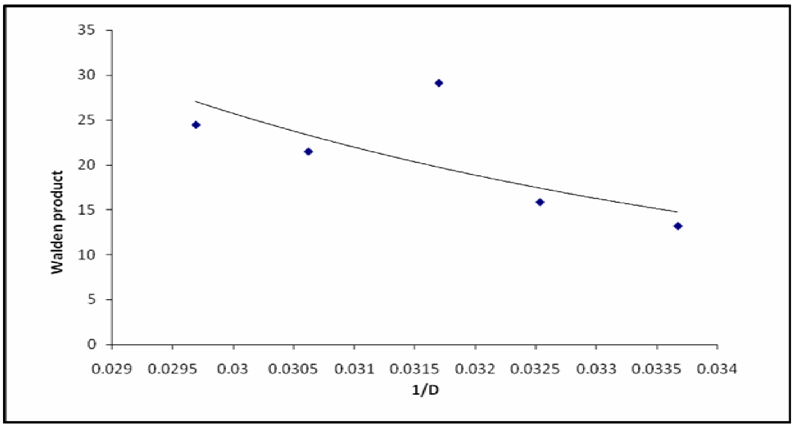


Fig. 9: Walden – product for 4-ASA in methanol

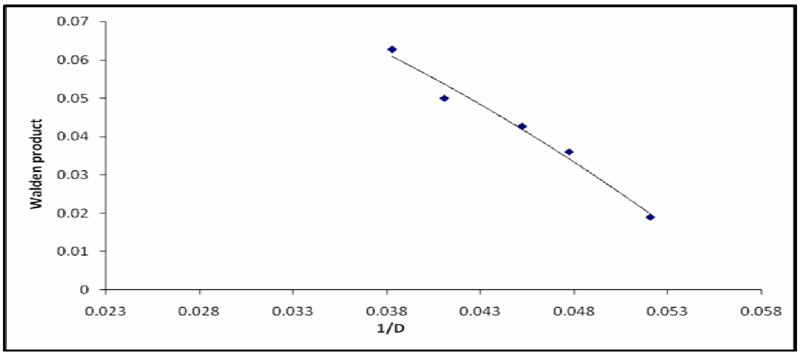


Fig. 10: Walden – product for 4-ASA in ethanol

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