Electrical Conductance Study of Aspartic Acid (Asp) Complex Cobalt (Co II) in Different Solvents and Temperatures

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Abstract

The electrical conductivities of Co(II) complex with aspartic acid (Asp) in different solvents (water, methanol and ethanol) at different temperatures were measured by assisting of lee-Wheaton equation at the best fit values of standard deviled $\sigma_{(s)}(\Lambda)$ for analyzing the data of unsymmetrical electrolytes including,the conductivity parameters, the ionic conductivity M^{+2}, the association constant K_A, and the distance parameter R .

Thermodynamic information from association and examining the nature of the interaction was obtained.

Keyword: Aspartic acid, Electrical conductivity , Lee-Wheaton equation, Thermodynamic parameters.

Introduction

The metal complx of Co(II) and other metals with aspartic acid (Asp) based on spectral and other studies was reported by Ehsan and coworkers[1], they suggested that in most compounds both the carboxylic acid group of aspartic acid(Asp) remains deprotonated and participate in the bond formation .

To recognize the interactions between the solutions of this complex in different solvents and the ionic mobility- with ion pairing and because of the features of cobalt chelat electrolytes are it's solute – solvent interaction concerning charge, size of the amino acid aspartic acid ligand, the chemical properties of this ligand.

All these three points were explained by the study of electronic spectra[2]. Racemization[3]. optical resolution[4]. viscosity and molal volume[5]. and conductivity [6,7].

In this work and as continues of our works on the electrical conductmetric studies[**8**] it was of interest to investigate some important measurements of the electrical conductive of aspartic acid (Asp)complexe with cobalt at different temperatures and in different solvents(methanol, ethanol or water) using lee-wheaton equation to explain the conductivity parameters λ°,K_A and R, the association constants (K_A) enable calculation of the thermodynamic quantities (ΔH, ΔG^0 and ΔS^0) for the association reaction which can provide detailed information concerning ion-ion and ion-solvent interaction especially from thermodynamic point of view.

Experimental

Preparation of complexes

To the simultaneously mixed well a solution of cobalt chloride(13gm, 0.1 mole) in ethanol(18 ml), a mixture of Aspartic acid(40gm,0.3mole) in a hot methanol (20 ml)was added and the whole mixture was refluxed for 4 to 5 hours in refluxer unit at 40^0C temperature. After completion of refluxing the solution mixture was transferred into a beaker and then cooled to room temperature. Once the solution cooled the purple color solid product (metal complex) was settled down at the bottom of the beaker. The solid product was obtained through filtration. The solid product was washed with ethanol, ether then with ethanol again. The product was dried in air to afford the desired product (which must handle very carefully due to its hygroscopic [9].

Purification of solvents

Methanol was purified and dried by the method described by Perrin[10]. conductivity water was prepared by distilling twice distilled water with specific conductance of 2×10^{-6} µs. Conductivity measurements were made using Jenway PCM3 conductivity meter with frequency range of 50 Hz-1KHz and accuracy of 0.01 µs. The cell constant for the conductivity cell was measured using the method of Jones and Bradshaw[11]. 0.01 M KCl solution was prepared from potassium chloride (BDH reagent) recrystallized three times from conductivity water and then dried at (760) Torr and 500 ^{0}C for 10 hrs[12]. The cell constant was found to be 1.14 cm^{-1}.

General procedure

A general method has been used for measuring the conductance of the electrolyte. The conductivity cell was washed, dried and then weighed empty and kept at any temperature (± 0.1 ^{0}C) using a water-circulating ultra thermostat type VH5B radiometer. A certain amount of solution was injected into the conductivity cell and the conductivity of the solution was measured. Another known amount of the solution was added and the measurement was repeated as before.

Table (1): The values at constant K_A, λM^{+2}, λMX^{+}, the distance between R(A^0) and Λσ of the complex with different temperatures in water solvent.

T(K)	K_A	λM^{+2} (Ohm^{-1} cm^{2} mol^{-1})	λMX^{+} (Ohm^{-1} cm^{2} mol^{-1})	R(A^0)	Λσ
293.16	335.16	50.17	0.10	9.9	0.203
298.16	328.18	43.71	0.30	9.7	0.194
303.16	310.91	42.61	0.31	8.9	0.215
308.16	292.11	40.35	0.33	8.5	0.198
313.16	283.31	38.61	0.41	8.4	0.211

Table (2): The values of K_A, λM^{+2}, λMX^{+}, R(A^0) and Λσ of complex $[Co(Asp)_3]Cl_2$ with different temperatures in methanol solvent

T(K)	KA	λM^{+2} (Ohm^{-1} cm^{2} mol^{-1})	λMX^{+} (Ohm^{-1} cm^{2} mol^{-1})	R(A^0)	Λσ
293.16	130.18	58.53	0.21	5.9	0.213
298.16	125.61	56.71	0.24	4.7	0.211
303.16	111.31	55.81	0.31	3.6	0.241
308.16	108.46	55.73	0.45	3.5	0.192
313.16	103.71	52.62	0.61	3.4	0.198

Table (3): The values of K_A, λM^{+2}, λMX^{+}, R(A^0) and Λσ of complex $[Co(Asp)_3]Cl_2$ with different temperatures in ethanol solvent

T(K)	KA	λM^{+2} (Ohm^{-1} cm^{2} mol^{-1})	λMX^{+} (Ohm^{-1} cm^{2} mol^{-1})	R(A^0)	Λσ
293.16	98.72	19.71	0.10	2.3	0.099
298.16	95.76	18.13	0.13	2.4	0.081
303.16	91.31	18.0	0.16	1.8	0.099
308.16	86.35	17.67	0.18	1.6	0.15
313.16	84.44	15.13	0.20	1.7	0.16

Results and Discussion

The equation derived by lee-Wheaton has been tested extensively in the three solvents(water, methanol and ethanol), a suitable explanation of the conductmetric behavior of these systems was given. Lee and Wheaton equation for unsymmetrical electrolyte is :

$$\lambda_j = \lambda_j^{\circ}\left\{1 + Z_j \sum_{p=s}^{s} X_j^p \sum_{v=1}^{s} tvX_v^p\left[A_v^p(t)(\beta k) + B_v^p(t)(\beta k)^2 + C_v^p(t)(\beta k)^3\right]\right\} -$$
$$|Z_j|(kt) \Big/ 2(1+t)\left\{1 + v_j^1(t)(\beta k) + v_j^2(t)(\beta k)^2 + \pi_j^5 \frac{t}{6}\right\} --------(1)$$

With Λ enquiv $= \sum_{j=1}^{s}(|Z_j|m_j \, \lambda_j / c$ where s is the number of charged species , Z_j,m_j and λ_j are the charge and transferrance number of species (13).

$\beta = e^2/DKT, K = (4\pi/dKT \sum_{j=1}^{s} njej^2$ and is proportion to the ionic strength, t=KR and $T = Co/\sigma\pi\eta$, nj 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 sunctions of the limiting mobilities , the concentration and charge On all ions present in solution (all other terms are by Lee and Wheaton [13].

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

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

and

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

Thus three ionic species are present in the solution which are MX^+ , M^{2+}, and x^- .

Thus for associated salts:

$$\Lambda mx_2 = f(\lambda_{m^{2+}}^{\circ}, \lambda_{mx}^{\circ}, \lambda_{x^-}^{\circ}, K_A^{(1)}, K_A^{(2)}, R) ---(4)$$

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 λ_i° for each ionic species, $K_A^{(1)}, K_A^{(2)}, \lambda_{mx^+}^{\circ}, \lambda_{m^{2+}}^{\circ}$ and R all in the form $K_A^{(1)}(\min), K_A^{(2)}(\max), \Delta K_A --$etc then the experimental data (molecular constant and equivalent conductance).This program is used to determine values of ($K_A^{(1)}, K_A^{(2)}, \lambda_{mx^+}^{\circ}, \lambda_{m^{2+}}^{\circ}$ and R which minimize $\sigma_s(\Lambda)$. The complex structure is drawn in Fig (1). Also the molar formula of these complex was proved by the IR and UV-Visible spectra in addition to molar conductivity by Azize(14)

Uv spectra for this complex also showed absorption bands attributed to d-d transitions and indicated that this complex was octahedral geometry(14).

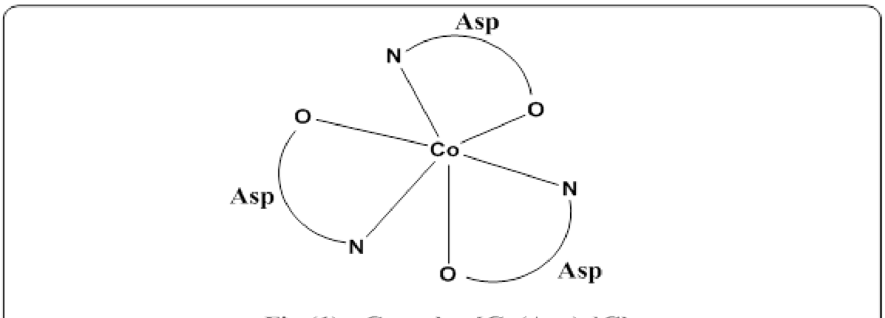

Fig (1) : Complex $[Co(Asp)_3]Cl_2$

The molar concentrations and equivalent conductance's of complex in water at different temperatures (293.15—313.15 K) were shown in Table (1). Figure (2), also shows the plot of the relation between them. The equivalent conductivities increased as the temperatures increased with high equivalent conductance due to the large radii of Co which form small solvated ion in solution [15].

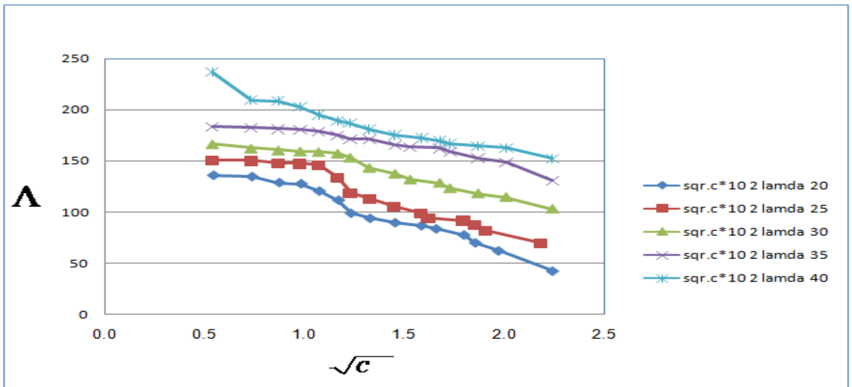

Fig (2) Plots of values of Table (1)

The best fit parameters of analysis of conductance data for complex in methanol at different temperatures were shown in Table (2) and the plots in Fig(3).

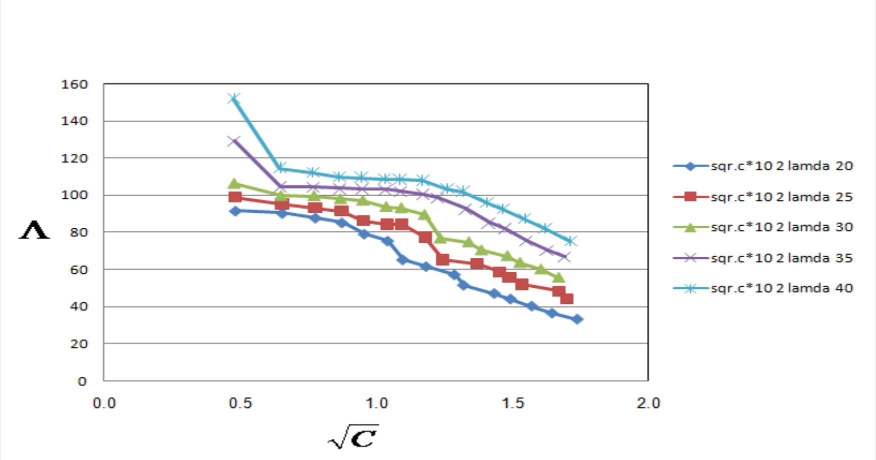

Fig (3) Plots of values of Table (2)

In this table the values of λM^{2+} increase with increasing temperatures which may attributed to the breaking of the hydrogen bonding between solvated ion in addition to the large size of the complex ion which form small size of solvated ion to move in solution[16]. It is found that K_A of the complex in these solvent , follow the sequences K_A (in water) > K_A(in methanol) > K_A(in ethanol) according to decreasing the dielectric constant from water, methanol, ethanol. It is clear from tables that λ^0 M^{+2} of the cation for complex follows the sequence as: λ^0 M^{+2}(in water) > λ^0 M^{+2} (in methanol) >λ^0 M^{+2} (in ethanol) according to decreasing the dielectric constant of the solvent.

Our results of the distance parameter R show that the complex electrolytes form solvent separated ion pairs (R is between 1.6-9.9) in the three solvent. These high values of R indicated that the cathons and anions are separated by many solvent molecules since the association was high. The values of (σΛ) give an indication of good best-fit values[17][18].

According to the equation $\Lambda_0=KC^n$, where n is the slope at log C and K is constant. Table (4) shows the values of each of n and K. It will be seen from this table that the value of n is generally greater for alcohol than for water, it is difficult to say what factors exactly are responsible for this behavior. It is however, likely that this might partly be due to a difference in the dielectric constant of water and alcohols, which might affect the interionic forces to different extents. The variation in the values of n and K for different solvents does not show any regular behavior. The value of K for the complex generally decreases with a decrease in the dielectric constant of the solvents[19],Fig (3) shows the plots of all values in Table (4).

Table(4):Values of n and K

Complex	Water	Methyl alcohol	Ethyl alcohol
$[Co(Asp)_3]cl_2$	n=-0.47 K=84.20	n=-0.64 K=38.4	n=-0.77 K=52.88

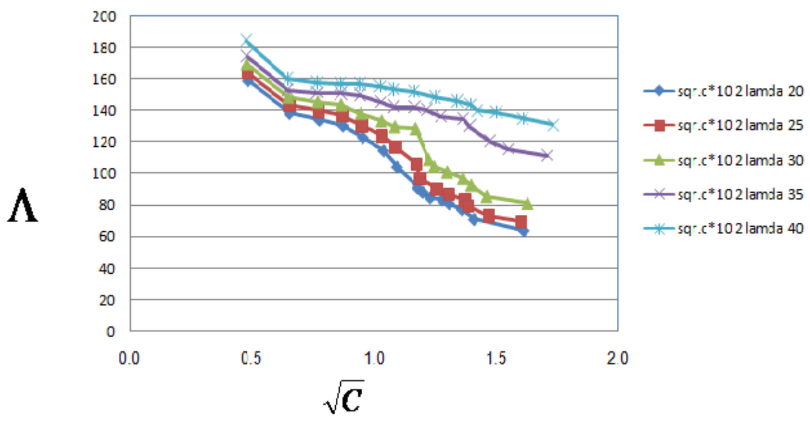

Fig (4) Plotes of values of Table (3)

Conclusion

The electrical conductivities of Co(II) complex with aspartic acid (Asp) in different solvents (water, methanol and ethanol) at different temperatures were measured by assisting of lee-Wheaton equation at the bist fit values of standard deviled $\sigma_{(s)}(\Lambda)$ for analyzing the data of unsymmetrical electrolytes including: The conductivity parameters, the ionic conductivity $M^{+2,}$ the association constant K_A and the distance parameter R .

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دراسة التوصيلية الكهربائية لمعقد الحامض الامينى الاسبارتيك مع الكوبلت فى مذيبات ودرجات حرارية مختلفة

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الملخص

يهدف هذا العمل لحساب التوصيلية الكهربائية لمعقد الكوبالت مع الحامض الأميني الاسبارتيك في مذيبات مختلفة. حللت البيانات باستخدام معادلة لى– ويتون للتوصيلية للاليكترولايتات غير المتجانسة، معلمات التوصيلية، التوصيلية الايونية، ثابت التجمع الأيوني ومعدل المسافات بين الايونات والتي حسبت قيم افضل خط من النقاط، ولحساب المعلومات الديناميكية الحرارية واختبار طبيعة التداخل.