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Thermodynamic Parameters calculations for Vanadyl Sulfate in the absence and Presence of Beta-alanine (amino acid) in Mixed (EtOH–H_2O) Solvents

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Abstract:

A set of conductometric measurements were conducted using vandyl sulfate ($VOSO_4$) with different percentages of ethanol (EtOH) and water in the presence of β-alanine (ligand) at four temperatures. The present work aims to estimate diverse thermodynamic parameters for nano VO (II) sulfate alone and with amino acid to form complexes in the solutions. All the data for the used electrolytes and ions are very important for analyzing the salt and explaining the different ion-ion and ion-solvent interactions behavior. The isolated metal complexes derived from the interaction of amino acids with VO (II) are characterized by chemical and physical methods. On the basis of spectral data (IR, and UV-Vis), a structure for separated solid complexes is presented and magnetic studies. Furthermore, biological activity measurements are executed, which benefits in determining the factors impacting the thermodynamic parameters and physical properties of the formed complexes in the solution.

Keywords: Ion-pair association Constants; Binary Mixed solvents; Limiting molar conductance; Amino acid

1. Introduction

Studies of thermodynamic and transport properties of binary liquid mixtures provide information on the nature of interactions in the constituent binaries [1]. Physical chemistry and chemical physics (if they are, indeed, fields apart) of *liquids* and *liquid mixtures* or *solutions* are indispensable parts of many areas of the pure and applied sciences, such as chemistry, physics, biophysics, chemical engineering, and geoscience, among others. Beta-alanine is an amino acid needed for the production of collagen and cartilage. It keeps muscles and joints flexible and helps reduce sagging and wrinkling that accompany UV exposure and normal aging of the skin [2]. Thermodynamic properties are very useful study of the intermolecular interactions and geometrical effects in the systems, thermo-physical and bulk properties of solutions. Also its necessary in theoretical and applied areas of research and used in many other fields of industry [3-5]. Studying the information of the transport properties (conductance, viscosity, ionic mobility) of electrolytes in aqueous and partially aqueous media tell us all about ion-ion and ion-solvent interactions in these solutions [6-9]. The Fuoss-Shedlovsky is one of the mathematic equation of conductivity theories, which has been successfully used to investigate many electrolytes in solutions [9-15]. Recently, a study of the properties of vandyl sulphate is essential in many fields such as biochemistry and in other different industry. The more uses of vandyl sulphate as a coloring ingredient in artworks, especially glasses and potteries.

The present article show the effect of all parameters on the transport properties of vandyl sulphate in a binary mixed solvent with alcohol mass fraction 0.0, 0.2 and 0.4 (W/W)

(EtOH-H_2O) at four different temperatures from 298.15 to 313.15K

Materials and Methods

1.1 Materials

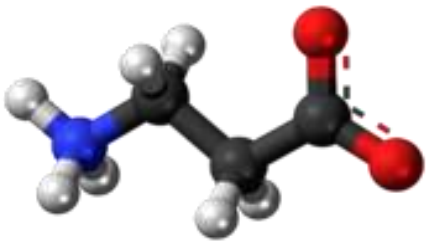
The mixed solvents are synthesized using bidistilled water, which has a specific conductance of 0.09 S cm^{-1} at 298.15 K.

Table 1: The specifications of the chemicals functioned for samples synthesis.

Chemicals	Suppliers	Mass fraction purity	Purification method
Ethanol (EtOH)	Sigma-Aldrich	99.5%	None
Vanadyl sulfate ($VOSO_4$)	Sigma-Aldrich	≥99.9%	None
Potassium Chloride (KCl)	Sigma-Aldrich	99.9%	None

All chemicals were exploited without any former purification. The used amino acids (ligands) are ($H_2\beta$-A) supplied from BDH chemicals Ltd as solids. The metal salt used is purchased from Nice Laboratory, India. The water contents were determined through the (Mettler DL 18 Karl Fischer Titrator) and were showed to be smaller than 0.01%. All the glassware was left in the chromic mixture for a day, and then cleansed many times with water, distilled water, and finally with bidistilled water and then kept in an electric oven to dry. Bidistilled water was obtained by redistillation of the ordinary distilled water over $KMnO_4$ and KOH. The first 25 ml were excluded. Measured specific conductance was found to be 2^{-5} x10^{-7} S cm^{-1}.

Table (2): Structure and properties of Trans-4-hydroxy proline.

Properties	**Beta-alanine**
Structure in 3D	
Chemical formula	$C_3H_7NO_2$
Molar mass	**89.093 g.mol^{-1}**
Density	**1.437 g/cm^3**
Melting point	207 °C (405 °F; 480 K) (decomposes)
Apperance	white bipyramidal crystals

1.2 Solutions

Ethanol and water binary mixtures with alcohol mass fractions of 0%, 20%, and 40% were utilized as solvent media in this study. They were created by combining the needed amount of methanol and water (with an error of ± 0.01 percent) according to the continuity formula:

Alcohol percentage = $(V_1d_1)100/ (V_1d_1+ V_2d_2)$ (1)

Where d1 and d2 are the relative densities of alcohol and water, alcohol is supplied to water in the amount of V1 in order to achieve the required alcohol concentration in V2. At temperatures ranging from 298.15 to 313.15K associated with alcohol mass fractions of 0%, 20%, and 40%, relative permittivity (ε), viscosity (ηo) of (ethanol-water), the physical characteristics, and density (ρ) were studied. The equivalent as (with a 5K step).

1.3 Transmission electron microscope (TEM)

TEM is a wide-spread device to investigate the particle size and morphology of the synthesized solutions. TEM provides a decent resolution down to the nanometer scale. Images were acquired using JEOL HRTEM-JEM -2100 (Japan).

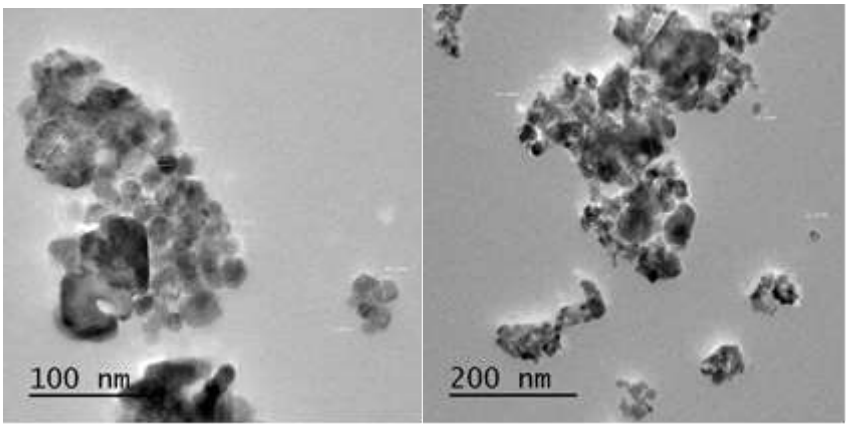


Fig (1): TEM images and electron diffraction of nano vanadyl sulfate.

2.4 Conductance Measurement

A conductance Meter of type (Adwa, AD3000, EC/TDS and Temperature Meter).(with an electrode of cell constant of 1) connecting with ultra-thermostat of the type Kottermann 4130 (to keep the temperature constant at the desired value) were used for the conductivity of different metal salt (nano) solutions of vanadyl (II) sulfate. The conductivity titration measurements of ligands used

(Beta-alanine) as a titrant solution, with (nano) metal salt solutions as a titrant in the solvents (EtOH-H_2O) mixtures and H_2O were carefully achieved. All conductivity measurements using JENCO EC3175

2.5 Analysis of complexes

To suggest the formula of the isolated complexes, elemental analyses are performed. The analyses of metal content are carried out according to standard methods [16, 17]. i. The divalent metal ions, VO^{+2} was determined complexometrically with 0.01 M EDTA using xylenol orange, murexide, or eriochrome black T as an indicator.

ii. Elemental analyses (C and H) are carried out in the Microanalytical Unit, Cairo University.

2.6 Working procedure

2.6.1 Infrared spectra(IR)

The infrared spectra of the studied ligand and its metal complexes were obtained with KBr discs on a Mattson 5000 FTIR spectrometer. At Mansoura University, the spectrum measurement is calibrated using polystyrene film.

2.6.2 Electronic spectra

The electronic spectra of the complexes in Nujol are recorded by Unicam

UV-V is spectrometer UV2 using 1 cm stoppered silica cells, at Mansoura University.

3 Results and Discussion

3.5 Thermodynamic parameters calculations

Fuoss-Shedlovsky conductivity formulas were used to evaluate the experimental conductance data. In H_2O and (EtOH-H_2O) mixed solvents, the limiting molar conductance (Λ_m) of copper sulfate solutions was established by extrapolating the linear Onsager plot at various temperatures [18-24].

$$\Lambda_m = \frac{(K_s - K_{solv}) \cdot K_{cell} \cdot 1000}{C} \quad (3)$$

Here, K_s and K_{solv} denote the solution's and solvent's specific conductances, consecutively; Kcell denotes the cell constant, and C denotes the metal salt solution's molar concentration.

$$\frac{1}{\Lambda_m S(Z)} = \frac{1}{\Lambda_o} + \left(\frac{K_\Lambda}{\Lambda_o^2}\right)\left(C\Lambda_m \gamma_\pm^2 S(Z)\right) \quad (4)$$

$$S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \ldots\ldots \text{ etc.} \quad (5)$$

$$Z = \frac{S(\Lambda_m C)^{1/2}}{\Lambda_o^{3/2}} \quad (6)$$

The value of (Λ_o) was exploited to determine the Onsager slope (S) from the Eq. (7)

$$S = aL_o + b \quad (7)$$

$$a = 8.2 \times 10^5 / (eT)^{3/2} \quad (8)$$

$$b = 82.4/ h((eT)^{1/2} \quad (9)$$

Where (e) is the solvent's relative permittivity, (ηo) is the solvent's viscosity, and (T) is the temperature. The values of (e) and (o) were used to determine the (S) values. utilization the data from (Λm), S (z), and (Λo), the magnitudes of dissociation degrees were calculated using the following equation (Eq. (10)):

$$(\alpha) = \Lambda m\, S(Z) \Lambda o \qquad \alpha = \Lambda m\, S(Z) \Lambda o \quad (10)$$

The use of these (α) and (e) readings, the mean activity coefficients ($\gamma\pm$) were assessed by Eq. (11).Equation]

$$\log \gamma_\pm = -\frac{Z_+ Z_- A\sqrt{I}}{I + Br^\circ\sqrt{I}} \quad (11)$$

Where Z_-, and Z_+ are the charges of ions in the solutions A, B delivers the Debye-Hückel constant.

$$A = 1.824 \times 10^6 (eT)^{-3/2} \quad (12)$$

$$B = 50.29 \times 10^8 (eT)^{-1/2} \quad (13)$$

The relation between Λ_m and $C^{1/2}$ for nano $VOSO_4$ at four different temperatures in absence of ligands and at (0%, 20% and 40%) EtOH-H_2O mixed solvents are presented in Fig. (2-5)

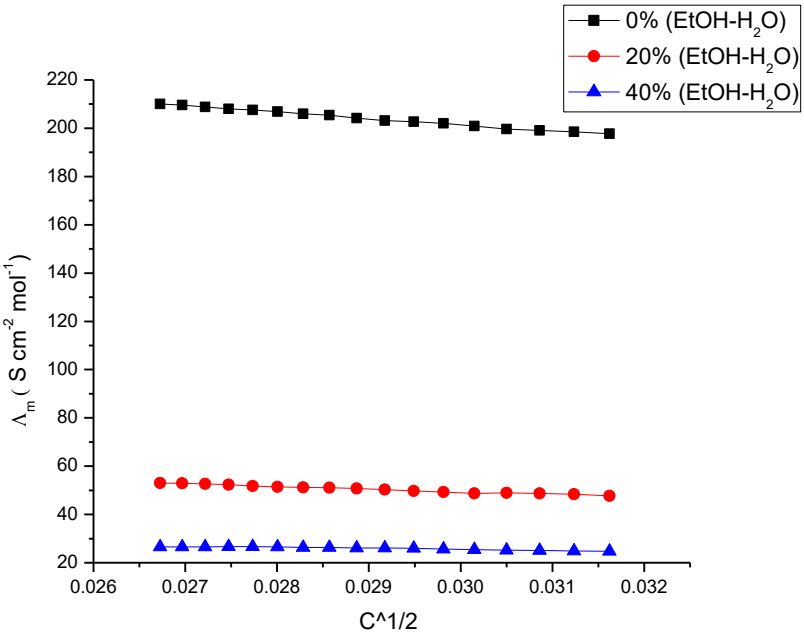


Fig (2): The correlation between molar conductance (Λ_m) and $C^{1/2}$ of nano $VOSO_4$ at 298.15 K temperature.

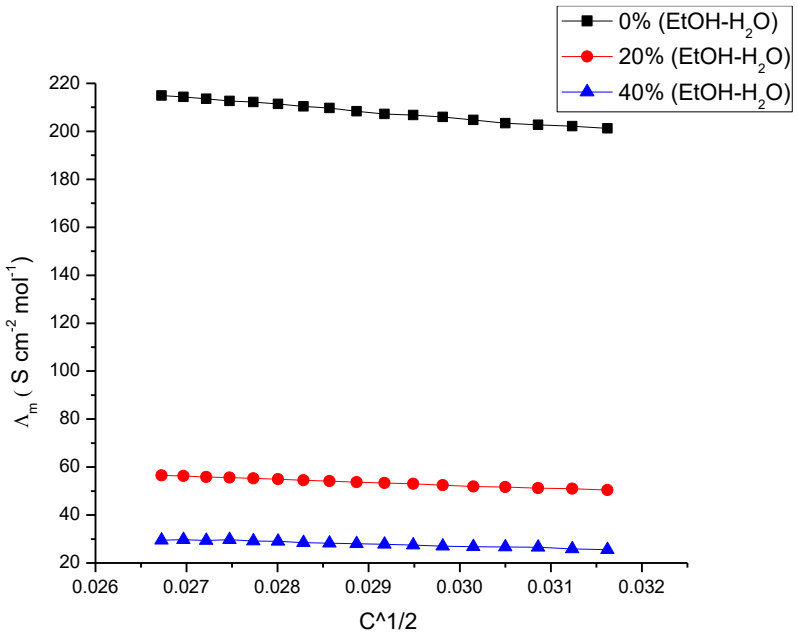


Fig. (3): The correlation between molar conductance (Λ_m) and $C^{1/2}$ of nano-$VOSO_4$ at 303.15 K temperature.

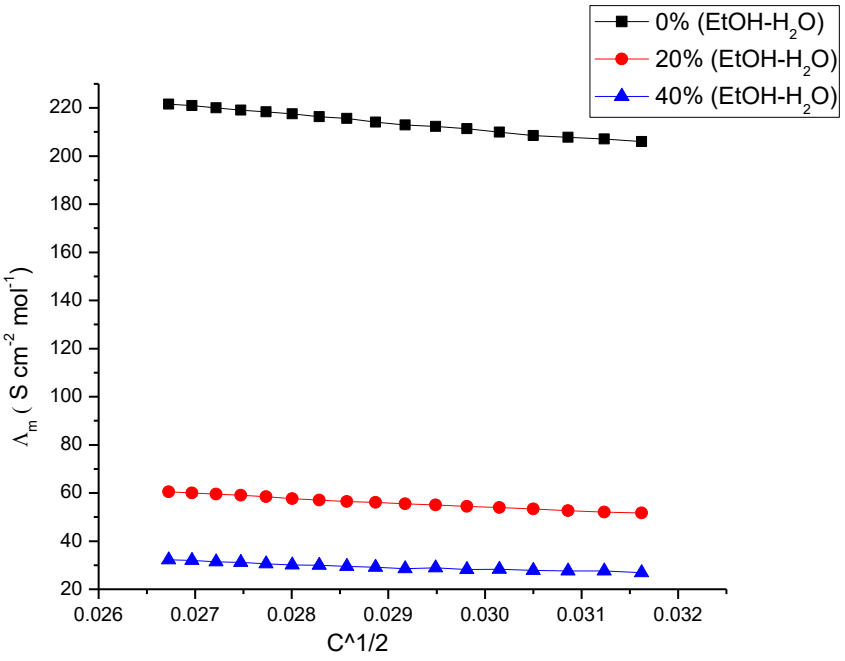


Fig (4): The correlation between molar conductance (Λ_m) and $C^{1/2}$ of nano $VOSO_4$ at 308.15 K temperature.

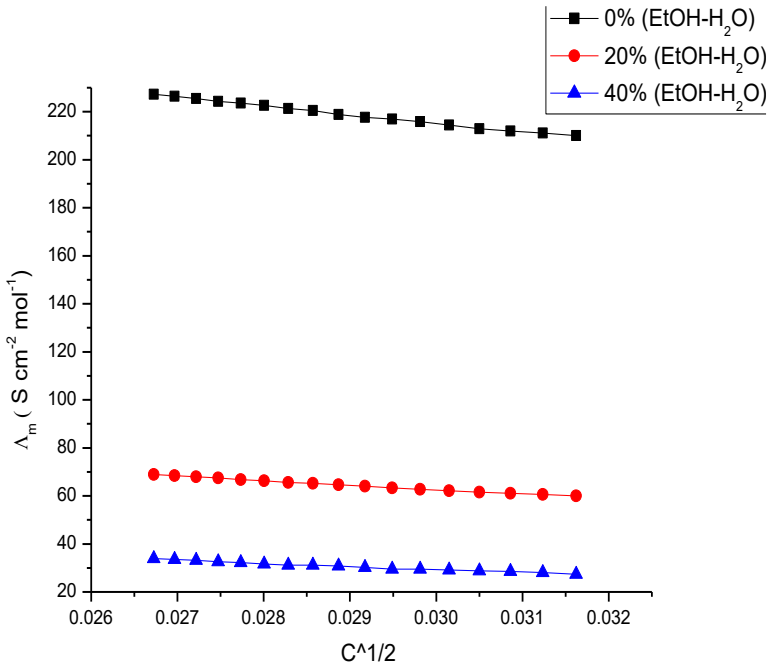


Fig (5): The correlation between molar conductance (Λ_m) and $C^{1/2}$ of nano $VOSO_4$ at 313.15 K.

Table (3): The mole fractions (X_S), the viscosity, the limiting molar conductance, the molar conductance (Λm), the Walden product ($\Lambda_o\eta_o$), the Fuoss-Shedlovsky parameters (S, Z, and S(z)), the activity coefficient($\pm\gamma$), and the dissociation constant (K_D) for nano $VOSO_4$ in a mixed solvent (EtOH-H_2O) are plotted at various temperatures.

T (K)	X_S	$10^2\eta_o$ (poise)	Λ_o	Λ_m	$\Lambda_o\eta_o$	S	Z	S(z)	$\pm\gamma$	10^3 K_D
298.15K	0	0.8921	281.74	198.61	2.5134	125.2217	0.0110	1.0111	0.943	1.36
	0.0717	0.9042	113.97	58.77	1.0305	86.1367	0.0160	1.0161	0.950	0.45
	0.1708	0.9209	63.75	38.76	0.5870	76.8933	0.0277	1.0281	0.941	0.80
303.15K	0	0.8001	291.24	202.63	2.3302	135.5875	0.0114	1.0115	0.942	1.29
	0.0717	0.8082	118.31	61.32	0.9561	94.7113	0.0169	1.0171	0.950	0.85
	0.1708	0.8193	67.08	40.94	0.5495	85.8196	0.0294	1.0299	0.939	0.47
308.15K	0	0.7222	311.37	208.15	2.2487	149.1045	0.0115	1.0116	0.942	1.09
	0.0717	0.7329	128.25	63.94	0.9399	104.5924	0.0169	1.0171	0.950	0.41
	0.1708	0.7478	71.85	41.52	0.5372	98.1280	0.0306	1.0310	0.935	0.29
313.15K	0	0.6211	325.6547	212.75	2.0226	166.4213	0.0121	1.0122	0.942	0.99
	0.0717	0.6911	144.74	68.54	1.0002	116.2927	0.0163	1.0164	0.949	0.34
	0.1708	0.7092	80.19	45.54	0.5687	106.0128	0.0293	1.0298	0.934	0.28

Λ_o in (S $cm^2.mol^{-1}$), Λ_m in (S $cm^2.mol^{-1}$)

The conductometric thermodynamic parameters for nano $VOSO_4$ alone in mixed EtOH-H_2O solvents are presented in Table (3), The molar conductance values for nano $VOSO_4$ are increased with rise temperature favoring more dissociation.

The decrease in values of Walden product with increasing proportion of ethanol in the order: 0% > 20% > 40% can be explained from the fact that increasing the content of organic solvent leads to a bigger size of solvation shells around cation which reduces its mobility as well as Walden product.

3.6 **Free energies of association of nano $VOSO_4$ in the absence of ligands**

free energies, enthalpies, the association constants, and entropies of association for nano $VOSO_4$ at different concentrations of methanol-water at different temperatures is tabulated in Table (4).

Table (4): Association constants, activation energy, enthalpies, and entropies of correlation for nano $VOSO_4$ at various temperatures in the absence of ligands

T (K)	X_s	Ea (kJ.mol^{-1})	ΔH_A (kJ.mol^{-1})	$T\Delta S_A$ (kJ.mol^{-1})	ΔS_A (J.mol^{-1})
298.15	0	3.8095	17.2787	33.6287	112.79
	0.0717	4.2093	15.7625	34.8503	116.88
	0.1708	4.8516	14.4704	32.1426	107.80
303.15	0	3.8095	17.2787	34.0468	112.31
	0.0717	4.2093	15.7625	33.5695	116.73
	0.1708	4.8516	14.4704	33.7811	107.43
308.15	0	3.8095	17.27877	34.7537	112.68
	0.0717	4.2093	15.7625	35.7491	116.02
	0.1708	4.8516	14.4704	35.37417	107.14
313.15	0	3.8095	17.2787	35.2725	112.63
	0.0717	4.2093	15.7625	36.4852	116.51
	0.1708	4.8516	14.4704	35.7862	107.07

All the thermal energy parameters Ea activation energy, ΔH_A enthalpy of association and ΔS_A entropy of association are mainly increased with rise of temperature and decrease of ethanol mole fraction other E_A favoring more solvation by increase of temperature and less solvation by adding more alcohol to nano $VOSO_4$ in absence of ligands

Association parameters of the nano metals in the presence of ligands (Beta-alanine)

The relation between Λ_m and $C^{1/2}$ for nano $VOSO_4$ at various temperatures in the exitance of β-alanine at (0%, 20%, and 40%) EtOH-H_2O as shown in Fig.(6-9).

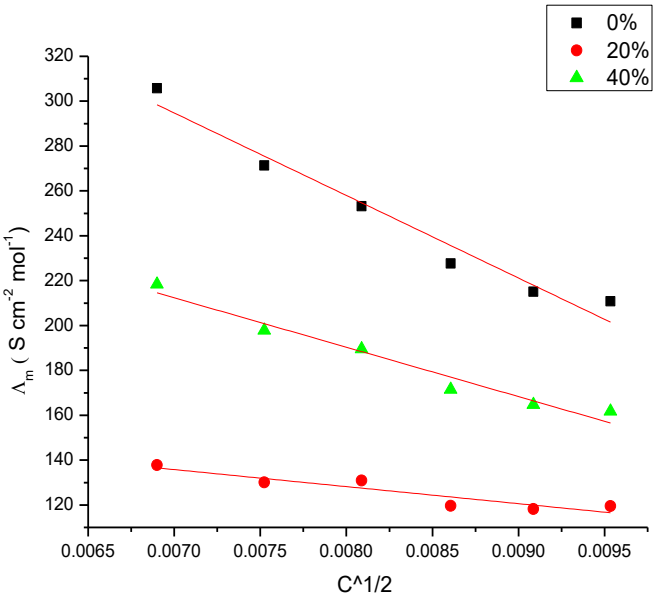


Fig (6): The correlation between nano $VOSO_4$ molar conductance (Λ_m) and $C^{1/2}$ at a temperature of 298.15 K.

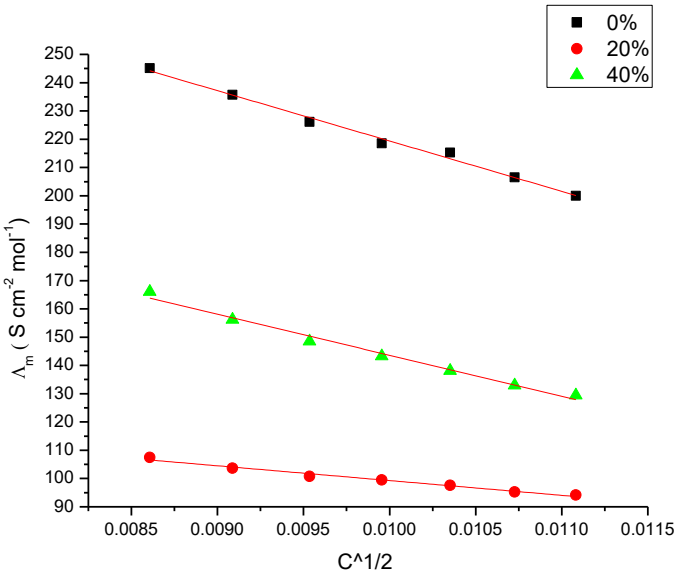


Fig (7): The relation between nano $VOSO_4$ molar conductance (Λ_m) and ($C^{1/2}$) at 303.15 K temperature.

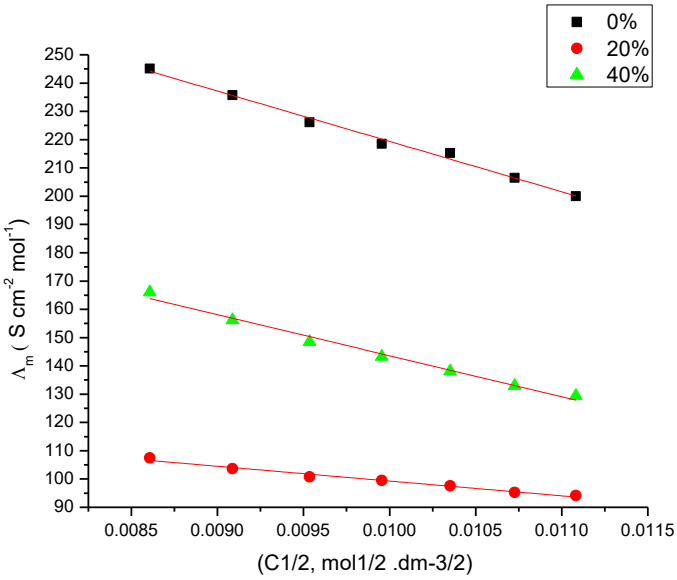


Fig (8): The association between molar conductance (Λ_m) and $C^{1/2}$ of nano $VOSO_4$ at 308.15 K temperature.

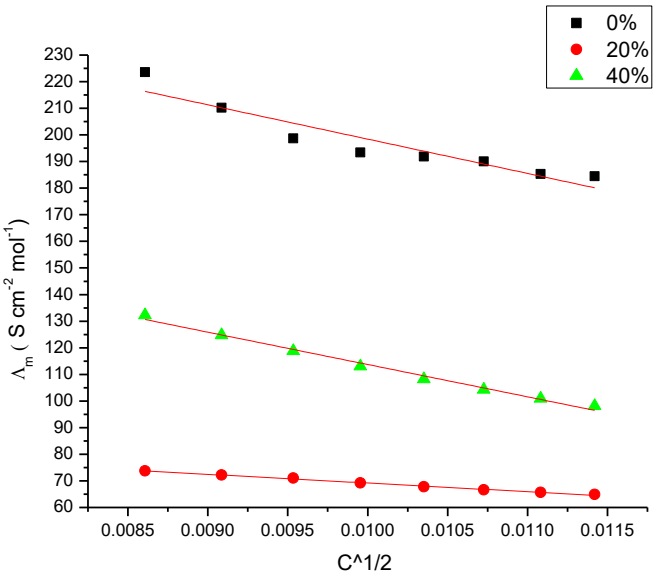


Fig (9): The correlation between molar conductance (Λ_m) and $C^{1/2}$ of nano $VOSO_4$ at 313.15 K.

Table (5): The importance of mole fractions (X_S), activity coefficient ($\gamma\pm$), the values of viscosity (η_o), limiting molar conductance (Λ), molar conductance (Λ_m), Walden product ($\Lambda_o\eta_o$), Fuoss-Shedlovsky parameters (S, Z, and S(z)), and dissociation constant (K_D) for nano $VOSO_4$ in the existence of β- alanine in a mixture solution (EtOH-H_2O) at various temperatures.

T K	X_S	$10^2\eta_o$ (poise)	Λ_o	Λ_m	$\Lambda_o\eta_o$	S	Z	S(z)	$\pm\gamma$	10^3 K_D
298.15K	0	0.8921	255.6	168.46	2.1550	118.7296	0.0053	1.0053	0.993	0.69
	0.0717	0.9042	213.65	190.16	2.9078	111.7127	0.0134	1.0134	0.997	0.357
	0.1708	0.9209	242.01	198.06	1.3588	95.4692	0.0070	1.0070	0.948	0.25
303.15K	0	0.8001	261.28	152.46	2.0905	128.6038	0.0044	1.0044	0.957	0.25
	0.0717	0.8082	209.60	173.36	1.6770	116.5596	0.0053	1.0053	0.95	0.27
	0.1708	0.8193	233.65	194.55	1.8694	122.1646	0.0050	1.0050	0.95	0.20
308.15K	0	0.7222	335.06	193.16	2.3457	157.091	0.0037	1.0037	0.962	0.21
	0.0717	0.7329	231.33	197.22	1.6195	132.5387	0.0055	1.0055	0.954	0.17
	0.1708	0.7478	274.42	210.61	1.921	142.7378	0.0047	1.0047	0.956	0.15
313.15K	0	0.6211	365.85	210.76	2.1687	180.2917	0.0039	1.0039	0.961	0.19
	0.0717	0.6911	272.61	209.66	1.6160	157.8767	0.0053	1.0053	0.955	0.14
	0.1708	0.7092	299.57	222.82	1.7758	164.3579	0.0055	1.0056	0.950	0.13

Λ_o in (S cm^2.mol^{-1}), Λ_m in (S cm^2.mol^{-1})

Table (6): Nano $VOSO_4$ association constants, activation energy, enthalpies, and entropies of the association at various temperatures in the presence of β-alanine

T (K)	X_s	Ea (kJ.mol^{-1})	ΔH_A (kJ.mol^{-1})	$T\Delta S_A$ (kJ.mol^{-1})	ΔS_A (J.mol^{-1})
298.15	0	6.9781	51.1954	70.0875	235.0747
	0.0717	7.1665	31.3408	51.8839	170.6657
	0.1708	8.1247	41.6281	62.1457	208.4377
303.15	0	6.9781	51.1954	72.0832	237.7806
	0.0717	7.1665	31.3408	52.0318	171.6373
	0.1708	8.1247	41.6281	62.9889	207.7815
308.15	0	6.9781	51.1954	72.8452	236.3954
	0.0717	7.1665	31.3408	53.4833	173.5626
	0.1708	8.1247	41.6281	64.0495	207.8517
313.15	0	6.9781	51.1954	73.4193	234.4544
	0.0717	7.1665	31.3408	54.3497	173.5583
	0.1708	8.1247	41.6281	64.6876	206.5709

3.7 **Isolation of metal complexes**

Chemical and physical approaches were used to create and characterize complexes of (H_2β-A) with VO (II) metal ions. All solid complexes were purified. Tables provide the results of elemental analysis and physical properties of metal complexes (7, 8). The comparison of experimental and theoretical data demonstrated that the isolated complexes' compositions were established using the proposed formula. Organic solvents were unable to dissolve any of the solid complexes; however, DMF and dimethyl sulphoxide (DMSO) could dissolve them efficiently.

Table (7): H_2 β-A with metal complexes: elemental characterization and physical properties.

NO	Compound	Formula	M.Wt	Yield	color	m.p		
							C	H
1	H_2β-A	$C_3H_7NO_2$	89.09	80	white	207	40.45 (39.81)	(7.75) (7.74)
2	[VO(Hβ-A)$_2$]	$VOC_6H_{14}N_2O_4$	243.74	70	Dark green	>300	38.89 (39.12)	(6.61) (6.59)

Table (8): The most significant infrared bands for H_2 β-A and related metal complexes

Compound	υ(OH)	$\upsilon(NH)_{as}$	$\upsilon(C=O)_s$	M-N	M-O
H_2β-A	3420	3095	1639	---	---
[VO(Hβ-A)$_2$]	3420	2926	1620	419	482

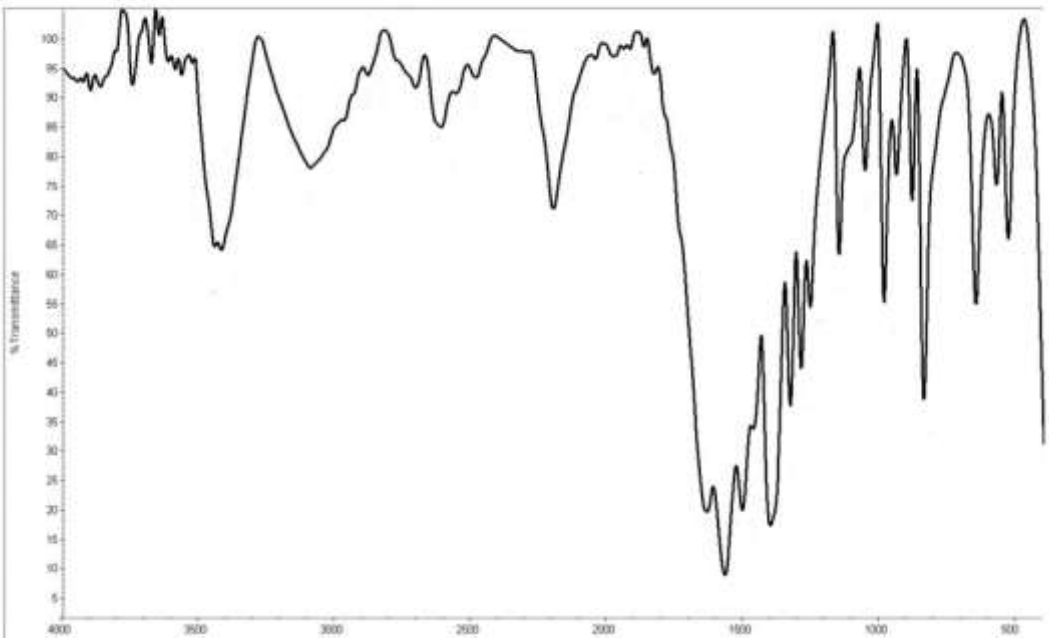


Fig (10): IR spectrum of $H_2\beta$-A ligand.

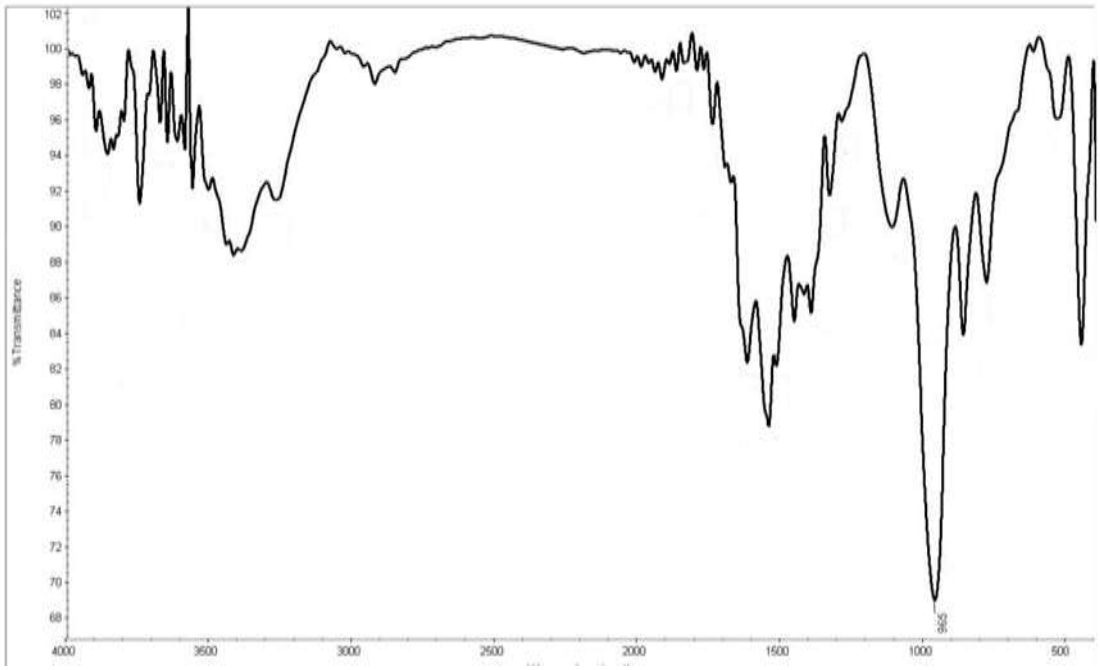


Fig (11): IR spectrum of [VO(Hβ-A)$_2$] complex.

The most important infrared bands of $H_2\beta$-A and its metal complexes are listed in table (7,8) and represented graphically in figures (10,11). The IR spectrum of $H_2\beta$-A display three bands at 1639, 3095 and 3420 assigned to $\upsilon(COO^-)$, $\upsilon(NH_3)^+$, and υ(OH) respectively.

In [VO(β-A)$_2$], complexe β-A acts as mononegative bidentate coordinating via carbonyl oxygen (COO^-) and (NH_3^+) This mode of chelation is based on change of β-Alanine (amino acid) to Zwitter ion as follow

$NH_2\text{-}CH_2\text{-}CH_2\text{-}COOH \leftrightarrow {}_3HN^+\text{-}CH_2\text{-}CH_2\text{-}COO^-$

Which show vibration of $\upsilon(NH_3^+)$to lower value in complexes of $[VO(H\beta\text{-}A)_2]$, vibration to lower wave length (2926) . Moreover, the IR spectra of all isolated complexes show new bands in the range of (419-482) cm^{-1} regions which may be attributed to υ(M-O) and υ(M-N) respectively.

Electronic spectra and magnetic moment of $H_2\beta$-A metal complexes

The ligand field parameters, electronic spectral bands and magnetic moments of metal complexes and described graphically in figure (12-13) .

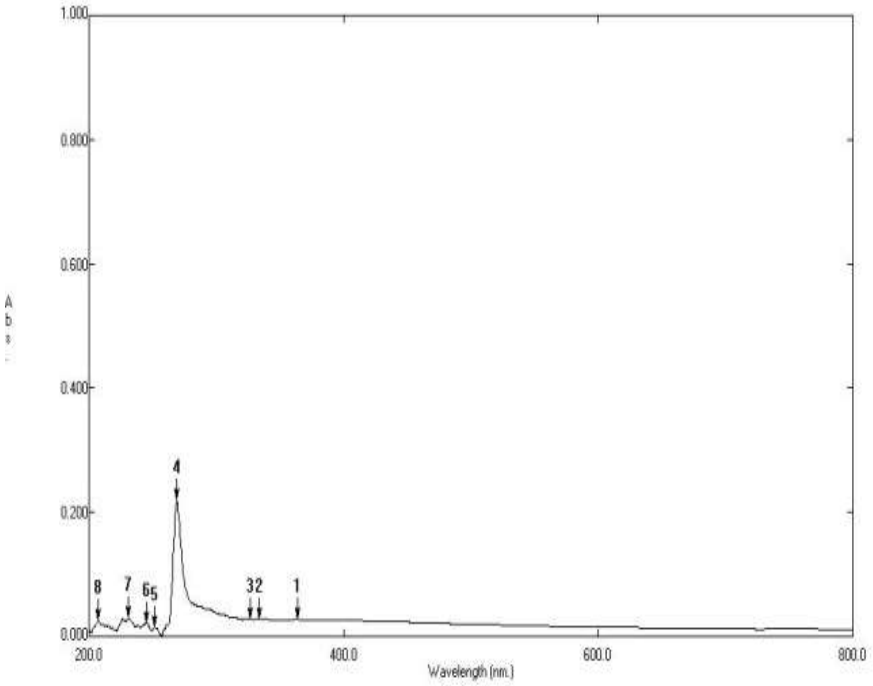


Fig. (12) UV-Vis of $H_2\beta$-A ligand

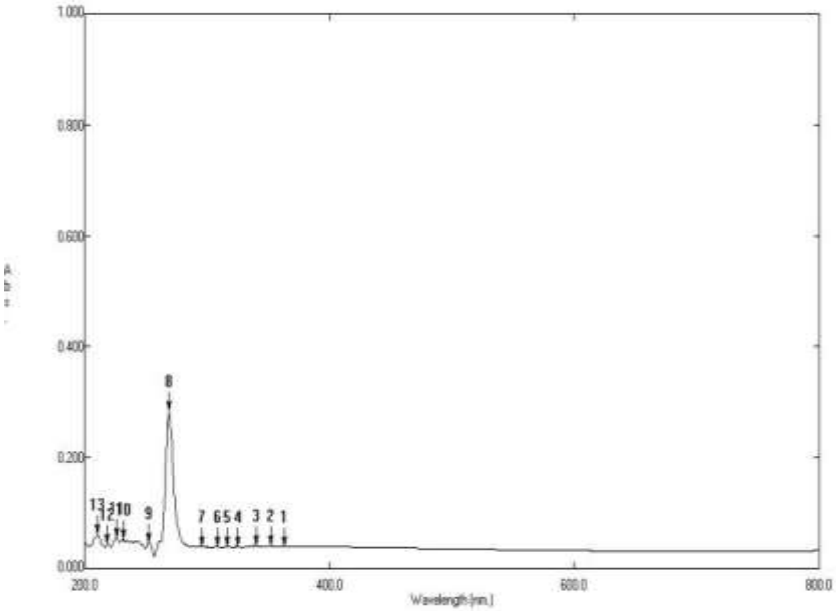


Fig. (13) UV-Vis of $[VO(H\beta\text{-}A)_2]$

The magnetic moment value of VO(II) complex (2.1 BM), indicates the presence of VO(II) ion. The electronic spectrum of $[VO(H\beta\text{-}A)_2]$ complex show a broad band at

16777cm^{-1} with shoulder at 14285 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively.in a tetragonally distorted octahedral configuration[25-27]

4 Conclusions:

The association parameters for Beta-alanine amino acid with nano $VOSO_4$ are great values in all the pure and mixed ($EtOH-H_2O$) solvents used. This is because these values contain the association and favor complex formation. All calculated thermodynamic parameters for nano $VOSO_4$ mainly association constants and Gibbs association energy, have great values and increase with an increase of the temperature due to the increase of mobility of ions in solutions. Similarly, the association values increase by more increasing ethanol percentage due to more solvation. The triple ion for association constants is very small in nano $VOSO_4$ measurements.

Furthermore the activity coefficients values increase by increasing temperatures indicating more ion-ion interactions, which support the increase in association parameters. The decrease in enthalpy of association ΔH_A for nano $VOSO_4$ by increasing temperature indicates easier solvation at higher temperatures. The present study traces the development of VO (II) complexes containing biologically significant ligands. In conjunction with data on the stability constants of such amino acid complexes.

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