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Association Thermodynamic Parameters (Conductometrically) for Solvation of Vanadyl sulfate in (Ethanol-Water) Mixed Solvent at Different Temperatures

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Abstract The measurements of vanadyl sulfate conductance have happened in binary mixed solvent with ethanol in different mass fraction 0.0, 0.2 and 0.4 (W/W) ($EtOH-H_2O$) at four different temperatures from 298.15to 313.15K (with a step of 5K).The experimental data have been analyzed by using the Fuoss-Shedlovsky extrapolation technique. All thermodynamic parameters for association were calculated and discussed. This parameters such asmolar conductance (Λ_m), limiting molar conductance (Λ_0), Walden product ($\Lambda_0 \eta_0$), ion-pair association constant (K_A), the activation energy for the transport process (E_a) and also the standard thermodynamic parameters for association (ΔG^o_A, ΔH^o_A and ΔS^o_A).Although we studied the effect of hydrogen bond formation in solution. The results estimated show that the association constant was increased with increasing temperature while the molar conductance and the limiting molar conductance values were decreased. Furthermore, all the association constant values were increased indicating that the association process is endothermic.

Keywords Limiting molar conductance, Ion-pair association Constants, Binary Mixed solvents, Walden product, Association constant, Vanadyl sulfate

Introduction

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 [1-3]. 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 [3-9]. 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]. The physical properties of the binary mixed solvents like the viscosity and the relative permittivity can be varied over a wide range making them a favorite solvent system for the study of ion association and ion mobility. Recently, a study of the properties of vanadium compounds attracts tremendous attention due to its essential in many fields such as biochemistry, medicinal chemistry and in many industries [15-17]. It forms numerous inorganic compounds as vanadyl sulfate. Vanadium compounds exhibit antitumor or carcinogenic properties. Vanadium (IV) oxide sulfate is a known inorganic compound of vanadium, which has a high physiological and industrial importance [18-24]. One of the importance of vanadyl sulfate used in industry as vanadium battery, its efforts such as longer life, better stability, higher efficiency and easy operation. The present article show the effect of all parameters on the transport properties of vanadium oxide sulfate 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 298.15to 313.15K (with a step of 5K).By applying the Fuoss-Shedlovsky conductivity equation [25].

2. Experimental

2.1. Chemicals

Mixed solvent prepared by used bidistilled water with a specific conductivity of 0.07 μS cm^{-1} at 298.15°K. All chemical used are represented in Table 1

Table 1: Specification of chemical samples

Chemicals	Suppliers	Mass fraction purity	Purification method
EtOH	Sigma-Aldrich	99.5%	None
$VOSO_4$	Sigma-Aldrich	≥99.9%	None
KCl	Sigma-Aldrich	99.9%	None

2.2. Solutions

Binary mixed solvent of ethanol – water with the alcohol mass fractions of 0.0, 0.2, and 0.4were selected to be the solvent media for this study and were prepared by mixing required volume of ethanol and water (with error ± 0.01%) by applying the following equation:

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

Where d_1 and d_2 are the density of alcohol and water respectively. V_1 is the volume of alcohol which will be added to the volume V_2 of water to get the mixture of the required percentage. The physical properties, relative permittivity (ε), density (ρ) and viscosity (η^o) of (ethanol - water) with the alcohol mass fractions of 0.0, 0.2, and 0.4 at temperatures from 298.15 to 313.15K (with a step of 5K) were tabulated in Table 1 [26-29]. The unknown values of the (ρ), (η^o) and (ε) were evaluated by applying the empirical relations of these properties at the available temperatures taken from the referred references. Seventeen solutions of $VoSO_4$ were prepared by mass (Mettler AE 200 balance with a sensitivity of ± 0.0002 g) with a concentration range ($1 \times 10^{-3} – 7.1 \times 10^{-4}$ $mol.dm^{-3}$) in the previously prepared mixed solvents by taking a certain volume of the salt standard solution and diluted to the required volume.

Table 2 The relative permittivity (ε), density (ρ, $g.cm^{-3}$) and viscosity (η, mPa s) at different temperatures of the used solvents.at pressure p = 0.1 MPa

Solvent	T/K	ε	ρ/g cm^{-3}	η/mPa s
0.0 (EtOH-H_2O)	298.15	78.31[a]	0.9970[b]	0.8904[c]
	303.15	76.51[a]	0.9942[b]	0.7975[c]
	308.15	74.74[a]	0.9912[b]	0.7194[c]
	313.15	73.05[a]	0.9908[b]	0.6529[c]
0.2 (EtOH-H_2O)	298.15	76.21[a]	0.9820[b]	0.9118[c]
	303.15	74.26[a]	0.9713[b]	0.8132[c]
	308.15	70.60[a]	0.9697[b]	0.7397[c]
	313.15	69.58[a]	0.9643[b]	0.6547[c]
0.4 (EtOH-H_2O)	298.15	73.05[a]	0.9612[b]	0.9319[c]
	303.15	71.18[a]	0.9416[b]	0.8267[c]
	308.15	65.48[a]	0.9404[b]	0.7576[c]
	313.15	62.67[a]	0.9306[b]	0.6539[c]

The standard uncertainties u are u(p) = 0.05 p, u(T)=0.01(level of confidence = 0.95).

[a] From Ref.[26]

[b] From Ref.[27]

[c] From Ref.[28]

2.3. Density and Conductivity measurement

A JENCO, Vision plus EC3175 conductance Meter of cell constant equal (1.05 cm^{-1}) with a DC power supply and a deviation of (±0.1 $\mu S\ cm^{-1}$) connecting with ultra-thermostat of the type Kottermann4130 (to keep the temperature constant at the desired value with a deviation ±0.005 °C) were used for measuring the conductivity of prepared solutions. The cell was calibrated by potassium chloride solutions [30-33].

The prepared solutions densities were measured using an Anton Paar DMA 35 (Austria) digital densimeter with a deviation (±0.0001 $g.cm^{-3}$). The densimeter was calibrated by using bidistilled water and dried air.

3. Results and discussion

3.1. Calculation of limiting molar conductance

The specific conductance (Ks, $\mu S\ cm^{-1}$) of prepared solutions of the salt and solvent with a concentration range of ($1 \times 10^{-3} - 7.1 \times 10^{-4}$ $mol.dm^{-3}$) in binary mixed solvents of (ethanol – water) with the alcohol mass fractions of 0.0, 0.2 and 0.4 at different temperatures from 298.15to 313.15K (with a step of 5K) was obtained and tabulated in Table S1 and S2. The molar conductance (Λ_M) for $VOSO_4$ solutions in binary mixed solvents at different temperatures was calculated by applying Eq. (2) and calculated in Table 1.

$$\Lambda_m = \frac{(K_s - K_{solv})\ .\ K_{cell}\ \ .\ 1000}{C} \qquad (2)$$

Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively; K_{cell} is the cell constant and C is the molar concentration of the metal salt solution.

The experimental conductance data were analyzed by using Fuoss-Shedlovsky conductivity equations. The limiting molar conductance (Λ_o) were estimated for vanadium oxide sulfate solutions in H_2O and ($EtOH$-H_2O) mixed solvents at different temperatures by extrapolating the linear Onsager plot [34] between (Λ_m) and $(C)^{½}$ as shown in Fig. 1.

$$\frac{1}{\Lambda_m S(Z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda_m \gamma_\pm^2 S(Z)\right) \qquad (3)$$

$$S\ (Z) = 1 + Z + Z^2/2 + Z^3/8 + \ldots\ \text{etc.} \qquad (4)$$

$$Z = \frac{S(\Lambda_m C)^{1/2}}{\Lambda_o^{3/2}} \qquad (5)$$

The value of (Λ_o) was used to calculate the Onsager slope (S) from the Eq. (6)

$$S = a\Lambda_o + b \qquad (6)$$

$$a = 8.2 \times 10^5 / (\varepsilon T)^{3/2} \qquad (7)$$

$$b = 82.4/\ \eta((\varepsilon T)^{1/2} \qquad (8)$$

Where (ε) is the relative permittivity of the solvent, (η_o) is the viscosity of the solvent and (T) is the temperature. Using the values of (ε) and (η_o), the value of (S) were easily estimated. Using the data of (Λ_m), S (z) and (Λ_o), the values of degree of dissociation (α) were calculated by using the following equation:

$$(\alpha) = \frac{\Lambda_m\ S(Z)}{\Lambda_o} \qquad (9)$$

Using these (α) and (ε) values, the mean activity coefficients ($\gamma_\pm$) were evaluated by means of Eq. (10).

$$\log \gamma_\pm = -\frac{Z_+ Z_- A\sqrt{I}}{I + Br^o\sqrt{I}} \qquad (10)$$

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

$$A = 1.824 \times 10^6\ (\varepsilon T)^{-3/2} \qquad (11)$$

$$B = 50.29 \times 10^8\ (\varepsilon T)^{-1/2} \qquad (12)$$

Table 3: The molar conductance (Λ±0.07, S cm^2 mol^{-1}) for vanadyl sulfate in the used solvents at different temperatures at pressure p = 0.1 MPa

Solvent	**298.15**		**303.15**		**308.15**		**313.15**	
	C(mol. kg)x10^3	**Λ(S cm^{-2} mol^{-1})**	**C(mol. kg)x10^3**	**Λ(S cm^{-2} mol^{-1})**	**C(mol. kg)x10^3**	**Λ(S cm^{-2} mol^{-1})**	**C(mol. kg)x10^3**	**Λ(S cm^{-2} mol^{-1})**
0.0 (EtOH-H_2O)	1.00	163.00	1.00	167.00	1.01	174.00	1.01	179.00
	0.98	164.10	0.98	167.18	0.98	173.23	0.98	178.35
	0.95	171.89	0.96	168.63	0.96	175.35	0.96	180.60
	0.93	170.73	0.93	169.21	0.94	175.76	0.94	181.14
	0.91	170.39	0.91	170.50	0.92	176.11	0.92	181.61
	0.89	171.05	0.89	172.91	0.90	177.08	0.90	182.70
	0.87	171.79	0.87	173.42	0.88	178.37	0.88	184.12
	0.85	171.58	0.85	175.19	0.86	179.66	0.86	185.53
	0.83	173.43	0.84	176.88	0.00	180.60	0.84	186.60
	0.82	173.88	0.82	178.36	0.82	181.30	0.82	187.43
	0.8	174.20	0.80	178.88	0.81	183.13	0.81	189.38
	0.78	175.63	0.79	180.03	0.79	183.09	0.79	189.47
	0.77	177.10	0.77	181.22	0.78	184.86	0.78	191.36
	0.75	177.71	0.76	182.45	0.76	184.71	0.76	191.33
	0.74	177.82	0.75	183.06	0.75	185.22	0.75	191.97
	0.73	177.96	0.73	184.33	0.73	187.00	0.73	193.88
0.2 (EtOH-H_2O)	1.03	61.00	1.03	64.00	1.03	70.00	0.99	74.00
	1.01	62.53	1.00	65.70	1.00	71.85	0.97	75.85
	0.99	63.32	0.98	66.78	0.98	72.98	0.94	76.97
	0.96	64.29	0.96	67.73	0.96	74.07	0.92	78.26
	0.94	64.79	0.93	68.53	0.94	75.02	0.90	79.42
	0.92	65.48	0.91	69.53	0.92	75.94	0.88	80.66
	0.90	66.13	0.89	70.38	0.90	76.82	0.87	81.65
	0.88	66.86	0.88	71.32	0.88	77.67	0.85	82.72
	0.86	67.44	0.86	72.12	0.86	78.72	0.83	83.76
	0.85	68.11	0.84	72.89	0.84	79.63	0.82	84.65
	0.83	68.50	0.82	73.63	0.82	80.38	0.80	85.75
	0.81	68.85	0.81	74.33	0.81	81.09	0.79	86.70
	0.80	69.29	0.79	75.14	0.79	81.90	0.78	87.36
	0.78	69.83	0.78	75.79	0.78	83.21	0.76	88.51
	0.77	70.34	0.76	76.41	0.76	83.97	0.75	89.24
	0.75	71.09	0.75	77.00	0.75	84.84	0.74	90.06
0.4 (EtOH-H_2O)	1.07	43.00	1.06	46.00	1.06	49.00	1.00	53.00
	1.05	44.50	1.03	47.15	1.03	50.02	0.99	54.02
	1.02	44.79	1.01	47.99	1.01	51.03	0.97	55.13
	1.00	45.26	0.99	48.81	0.99	52.03	0.95	56.33
	0.97	45.80	0.96	49.72	0.96	52.91	0.93	57.42
	0.95	46.53	0.94	50.51	0.94	54.00	0.91	58.50
	0.93	47.25	0.92	51.41	0.92	54.97	0.89	59.57
	0.91	47.96	0.90	52.17	0.90	55.93	0.87	60.63

0.89	48.76	0.88	52.92	0.88	56.76	0.86	61.80
0.88	49.56	0.87	53.66	0.87	57.70	0.84	62.60
0.86	50.23	0.85	54.63	0.85	58.75	0.83	63.75
0.84	51.00	0.83	55.46	0.83	59.42	0.81	65.03
0.83	51.77	0.82	56.03	0.82	60.19	0.80	65.78
0.81	52.52	0.80	56.45	0.80	60.95	0.78	66.65
0.80	53.27	0.79	57.11	0.79	62.10	0.77	67.64
0.78	54.27	0.77	57.75	0.77	62.98	0.76	68.48

The standard uncertainties u are u(p) = 0.05 p, u(T)=0.01 and u(Λ)=0.9 (level of confidence = 0.95).

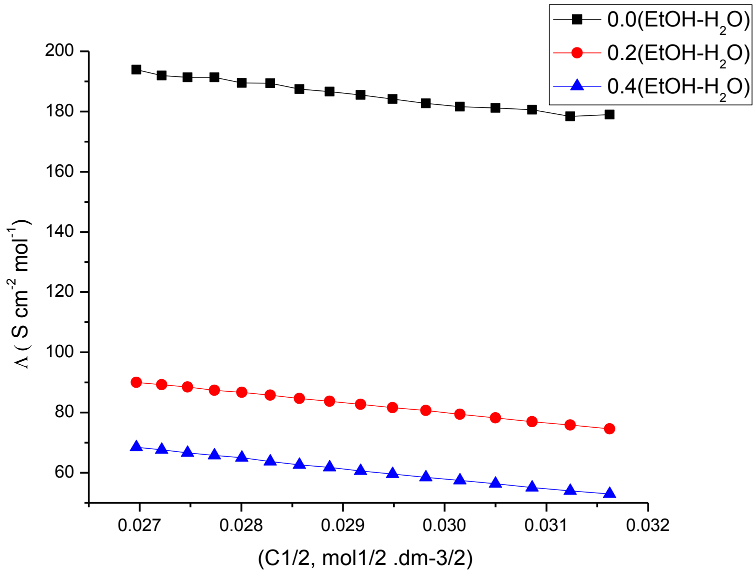

Figure 1: The plot of (Λ) versus ($C^{1/2}$, mol$^{1/2}$ .dm$^{-3/2}$) at 313.15K in mixed (EtOH–H_2O) solvents for vanadyl sulfate.

Table 4: The limiting molar conductances (Λ_o, ±0.25%, S cm^{2}mol^{-1}), (S, Z and S(Z) are Fuoss–Shedlovsky parameters, (A) Debye-Huckel constant, (Ɣ±) is the mean activity coefficient and the degree of dissociation (α) of vanadyl sulfate in the used solvents at different temperatures at pressure p = 0.1 MPa.

Solvent	T/K	Λ_o(S cm^2 mol^{-1})	S	Z	S(Z)	A	γ±	α
0.0 (EtOH-H_2O)	298.15	257.28	119.599	0.0112	1.0113	0.6744	0.9446	0.6744
	303.15	266.00	129.703	0.0117	1.0118	0.6733	0.9439	0.6733
	308.15	271.27	139.612	0.0123	1.0124	0.6657	0.9433	0.6657
	313.15	284.37	156.498	0.0131	1.0131	0.6559	0.9429	0.6559
0.2 (EtOH-H_2O)	298.15	123.32	88.299	0.0134	1.0135	0.5246	0.9497	0.5446
	303.15	148.55	101.776	0.0136	1.0137	0.5195	0.9422	0.4804
	308.15	164.48	113.286	0.0138	1.0139	0.5169	0.9419	0.4735
	313.15	179.48	124.958	0.0138	1.0139	0.5148	0.9401	0.4612
0.4 (EtOH-H_2O)	298.15	119.04	90.9985	0.0143	1.0144	0.5674	0.9519	0.4186
	303.15	125.83	101.018	0.0145	1.0146	0.5554	0.9509	0.4047
	308.15	143.70	118.683	0.0148	0.0149	0.5363	0.9475	0.3883
	313.15	159.72	129.347	0.0151	1.0152	0.5246	0.9469	0.3784

The standard uncertainties u areu(p) = 0.05p, u(T)=0.01and U(Λo)=0.91 (level of confidence = 0.95).

The results obtained for vanadium oxide sulfate Table 2 in a binary mixed solvent (EtOH-H_2O)at different temperatures is different than in case of water [35], AS the limiting molar conductance of vanadium oxide sulfate in (EtOH-H_2O) mixtures is less than in water because conductivity values decrease when mixed solvent increase so in decrease in case of 0.4 than 0.2than that in water and this due to formation of intermolecular and intramolecular hydrogen bonding which make hindrance to the ions mobility, in case of increasing content of ethanol in mixed solvent lead to reduce the solvation and dissociation of vanadyl sulfate molecules.

Also, the limiting molar conductance for vanadyl sulfate in all solvents used is increased with rise in temperature due to the increasing of kinetic energies of ions, this was supported by ionization degree (α) which is decreased by increasing the temperature.

Table 5: The mean ion pair association constant (K_A, ±0.3%, mol. dm^{-3}), Walden product ($\Lambda_o\eta$, S. mol^{-1} cm^2Pa.s) and the hydrodynamic radii (R_H) of vanadyl sulfate in the used solvents at different temperatures at pressure p = 0.1 MPa.

Solvent	T/K	K_A	$\Lambda_o\eta$	R_H
0.0 (EtOH-H_2O)	298.15	922.7565	227.5228	0.0036
	303.15	930.4575	212.8266	0.0038
	308.15	975.1020	195.9112	0.0042
	313.15	1034.4170	178.6279	0.0046
0.2 (EtOH-H_2O)	298.15	1957.5980	112.7741	0.0073
	303.15	2854.9410	107.1800	0.0076
	308.15	2978.7010	106.4690	0.0077
	313.15	3225.6160	103.6580	0.0079
0.4 (EtOH-H_2O)	298.15	4492.6180	84.0869	0.0097
	303.15	4325.6310	81.0724	0.0101
	308.15	5194.7470	74.1422	0.0110
	313.15	5565.8410	73.1018	0.0112

The standard uncertainties are u(p) = 0.05p,u(T)=0.01and U areU(K_A) =16.88 (level of confidence = 0.95).

3.2. Ion-pair association constant

The mean values of the ion-pair association constant (K_A) of all systems under study were represented in Table 3. It was seen that the association constant for vanadyl sulfate in the used solvents, increases with temperature increase which indicates an endothermic association process. This temperature dependence of the association process of ions can be explained from the relation between desolvation and association of ions whereas the temperature increases, the desolvation process of ions take place, the ions will be closer than before, therefore the association of ions increases [36,37].

For all studied systems the association constant increase as the proportions of organic solvent increase at the same temperature with an exception in the case of 0.2 (EtOH-H_2O). This increasing in association constant values may be related to decreasing in relative permittivity by increasing the proportions of organic solvent and decrease in ions mobility which giving chance for ions to associate. Also, this can be interpreted on the basis of the interplay between association constant and strength of the ion solvation in different solvents, whereas the stronger ion is solvated, the association between cations and anions are weaker.

The association constant values for vanadyl sulfate in 0.2 (EtOH-H_2O) is lower than values of association constant in water. This may be related to the interaction between ethanol and water at a low concentration from ethanol are affected by the formation of cage-like structures, commonly known as (icebergs) around the hydrophobic ends of the ethanol, which effect on the mobility of ions and decrease association constant [38].

3.3. Triple-ion association constant

From Fuoss equation [25], the triple ion association constant (K_3) for vanadyl sulfate was calculated. The triple ion formation can be neglected due to the small values of triple ion association.

3.4. Walden Product

The Walden product (Λ_0 η_0 or λ_0 η_0) is very important from the point of view of ion-solvent interaction [39, 40]. The Walden product (Λ_0 η_0) is expected to be constant for a given electrolyte in a series of solvent mixtures in which the ion–solvent interactions are uniform due to the Walden product is the product of the limiting molar conductance by the viscosity of the medium, should be independent of the nature of the solvent and the molar conductance at infinite dilution depending only on mobility of ions. Walden has written his rule in the form as in Eq. (13).

$$\Lambda_0\eta_0 = 0.82\left[\frac{1}{r_s^+}+\frac{1}{r_s^-}\right]. \qquad (13)$$

The factor ($\frac{1}{[1/r_s^+ + 1/r_s^-]}$) is a measure of the hydrodynamic radii (R_H) of the ions, r is the radius of a hypothetical sphere that diffuses with the same speed as the particle under study. In practice, the solute molecules in solution are solvated and dynamic. So, the radius calculated from the diffusion properties of the particle is indicative of the apparent size of the dynamic hydrated/solvated particle, and the hydrodynamic radius. This means that the hydrodynamic radius (R_H) includes both solvent (hydro) and shape (dynamic) effects. The values of Walden product and hydrodynamic radii for the salts and ions under study were calculated and listed in Table3 and represented in Fig.2. The inverse behavior of the hydrodynamic radii with Walden product was reported by many authors [38, 42].

The obtained value of Walden product decrease by increasing temperature. This may be related to the increase in the size of solvated ions in the mixtures as we raise the temperature which occur due to the variation of the proportion of the ethanol and H_2O molecules in the sheath of solvation with temperature. Walden product is affected by two factors, limiting molar conductance which is directly proportional to temperature, and viscosity which is inversely proportional to temperature. From this observation, we can conclude that the viscosity value is the most effective factor on the inverse proportional behavior of the Walden product with the temperature. The decrease in values of Walden product with increasing proportion of ethanol in the order: 0.0>0.2>0.4 can be explained from the point of view, increasing the content of organic solvent leads to a bigger size of solvation shells around cation and this reduces its mobility as well as Walden product [42].Many authors reported the change in Walden product with temperature, solvent composition and nature of electrolyte [4, 43 and 44].

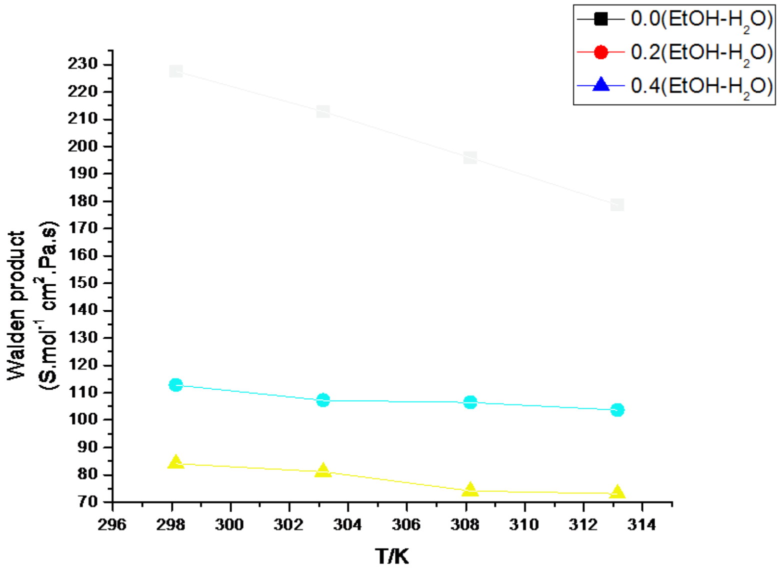

Figure 2: The plot of Walden product (Λ_0 η)vs. temperature (T/K) for vanadyl sulfate in the used solvents

3.5. Thermodynamics of association

The standard Gibbs free energy of association (ΔG°_{A}) was calculated by using Eq. (13) for all salts under study in all solvent mixtures at all temperatures and its values were tabulated in Table 4.

$$\Delta G^{\circ}_{A} = -RT\ln K_{A} \qquad (14)$$

Where R is the gas constant and equal (8.314 $J.mol^{-1}.K^{-1}$).The values of the standard enthalpy (ΔH°_{A}) and the standard entropy (ΔS°_{A}) of association process were obtained from van't Hoff equation$\left(\frac{d\ln K}{dT}\right) = \left(\frac{\Delta H^{\circ}_{A}}{RT^{2}}\right)$ by plotting (log K_A) versus (1/T), where the slope is equal the value of ($-\Delta H_A/2.303R$) while the entropies of association (ΔS°_{A}) were calculated by the use of Gibbs–Helmohltz equation Eq. (15).

$$\Delta G^{\circ}_{A} = \Delta H^{\circ}_{A} - T\Delta S^{\circ}_{A} \qquad (15)$$

The thermodynamic parameters of association values showed the effect of temperature from increasing in the negative values of the associating free energy (ΔG°_{A}) as the temperature rise from 298.15 to 313.15K. It was found that the association processes in all studied systems are spontaneous processes and the associating free energy becomes more negative with increase in temperatures. This indicates that ion-pair association is favored with lowering of dielectric constant of the medium [45].

The positive value of (ΔH°_{A}), indicates the ion association processes are endothermic in nature. A positive entropy values (ΔS°_{A}) can be explained on the assumption that iceberg structure around the cation is broken when association takes place leading to an increase in the degree of disorderliness and the positive (ΔH°_{A}) and (ΔS°_{A}) values are in a good agreement with several theories in many solvents [46].Positive values of (ΔH°_{A}) and (ΔS°_{A}) for association can be attributed to counterbalance of the enthalpy term by a favorable entropy change resulting from the short- and long-range desolvation of both ions. Positive (ΔS°_{A}) values attributed to desolvation of both ions are also supported by the positive enthalpy values indicating a lack of covalent bonds.

Table 6: The thermodynamic parameters of association (ΔG°_{A},±0.33%) Gibbs free energy of association, (ΔH°_{A}±0.22%) Enthalpy change of association and (ΔS°_{A}±7.42%) which is the entropy of association for vanadyl sulfate in used solvents at different temperatures and at pressure p = 0.1 MPa

Solvent	T/K	ΔG°_{A}	ΔH°_{A}	ΔS°_{A}
		($kJ.mol^{-1}$)	($kJ.mol^{-1}$)	($J.mol^{-1}$)
0.0 (EtOH-H_2O)	298.15	-16.9269	6.0219	76.6707
	303.15	-17.2317		76.7067
	308.15	-17.6360		76.7741
	313.15	-18.0759		76.9531
0.2 (EtOH-H_2O)	298.15	-18.7915	25.8308	149.6641
	303.15	-20.0579		151.3729
	308.15	-20.4974		150.3432
	313.15	-21.0374		149.6670
0.4 (EtOH-H_2O)	298.15	-20.8511	19.3482	134.8291
	303.15	-21.1053		133.4438
	308.15	-21.9225		133.9338
	313.15	-22.4579		133.5019

The standard uncertainties u(p) = 0.05p,u(T)=0.01 and the combined expanded uncertainties U are U(ΔG^{o}_{A})=0.12, U(ΔH^{o}_{A})=0.07 and U(ΔS^{o}_{A})=17.34 (level of confidence = 0.95).

3.6. Activation energy of the transfer process

Ion mobility is very effective in conductance study, so it is highly sensible to treat the rating process happening with a change of temperature on the basis of Eq. (16).

$$\Lambda_0 = Ae^{-E_a/RT} \qquad (16)$$

Where A is the frequency factor, R is the gas constant and E_a is the Arrhenius activation energy of the transfer process. The E_a values can be obtained from the plot of (log Λ_0) vs. (1/T)Fig.3.The values obtained of Arrhenius activation energy of the transfer process of the studied salts in all mixture solvents are tabulated in Table 5. The behavior of activation energy change is inverse that of Λ_0.The observed behavior of change in the activation energy of transfer was also reported by many authors [8, 9 and 36].

Table 7: The Activation energy (E_a/kJ.mol^{-1}) for vanadyl sulfate in all used solvents at pressure p = 0.1 MPa

Solvent	E_a (kJ.mol^{-1})
0.0 (EtOH-H_2O)	3.2868
0.2 (EtOH-H_2O)	3.4492
0.4 (EtOH-H_2O)	3.9246

The standard uncertainties U are U(E_a) = 0.16,u(T)=0.01 and u(p) = 0.05p (level of confidence = 0.95).

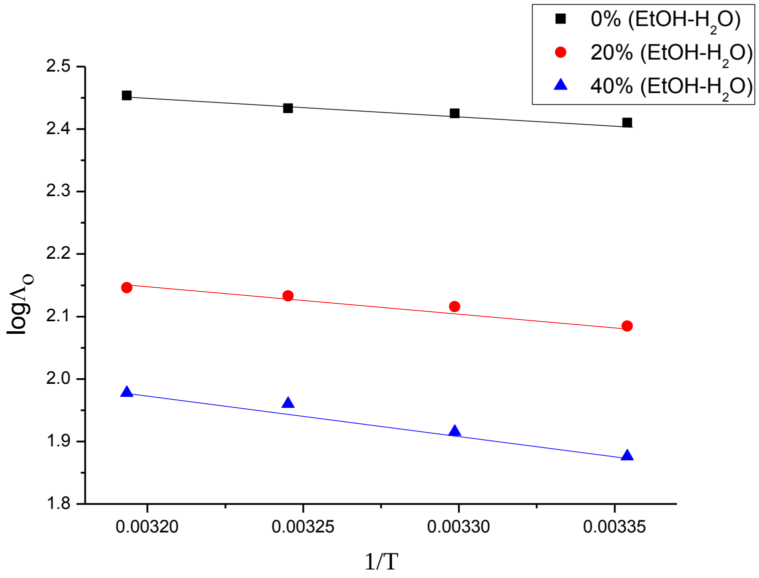

Figure 3: The plot of ($\log\Lambda_0$) vs. (1/T) for vanadyl sulfate in the used solvents.

4. Conclusions

In this paper, conductivity measurements for vanadium oxide sulfate in a binary mixed solvent with alcohol mass fraction of 0.0, 0.2, and 0.4 (EtOH-H_2O)at different temperatures from 298.15to 313.15K (with a step of 5K) have been reported. The conductivity data have been analyzed using Fuoss – Shedlovsky equation.

The extent of ion-pairing in vanadyl sulfate solutions under study depends on the nature of the (ion-solvent) and (solvent-solvent) interaction taking place in the solution. Furthermore, it depends on the relative permittivity and the properties of the medium. The association constant increases as the temperature increases and as the proportion of ethanol increases. Also the unusual behavior of 0.2 (EtOH-H_2O) mixed solvent have been studied. The values of Gibbs free energy of association (ΔG°_{A}) become more negative gives an indication of the association process is spontaneous in nature. The positive value of entropy change (ΔS°_{A}) is indicating that the entropy is the driving force for the association process. The positive value of the enthalpy change (ΔH°_{A}) is indicating that the association process is endothermic.

References

1. Zhang, S., Ma, P., Zhai, Y., Chen, W.: Determination of vanadyl sulfate ion-pair dissociation constant at 298.15 K by Fuoss method. Rare Met. 34 (2015) 873–876. doi:10.1007/s12598-014-0353-9

2. Shunquan, Z., Weirong, S., Qian, W., Haitao, Y., Baoguo, W.: Review of R&D status of vanadium redox battery. Chemical industry and engineering progress. 26 (2007)207.
3. Bo, T., Chuan-wei, Y., Qing, Q., Hua, L., Fu-hui, W.: Battery Bimonthly 4 (2003)023.

4. Haldar, P., Das, B.: Electrical conductances of sodium bromide and sodium tetraphenylborate in 2-ethoxyethanol+ water mixtures at 308.15, 313.15, 318.15 and 323.15 K. J. Mol. Liq. 130 (2007) 29–33. doi:10.1016/j.molliq.2006.04.003
5. Tsierkezos, N.G., Molinou, I.E.: Conductivity Studies of n-TetrabutylammoniumTetraphenylborate in 3-Pentanone in the Temperature Range from 283.15 to 329.15 K.J. Solution Chem. 36 (2007) 153–170. doi:10.1007/s10953-006-9103-4
6. El-Dossoki, F.I.: Effect of hydrogen bond, relative permittivity and temperature on the transport properties and the association behavior of some 1: 1 electrolytes in some binary mixed solvents. J. Mol. Liq. 151 (2010) 1–8. doi:10.1016/j.molliq.2009.10.007
7. Dash, U.N., Mahapatra, J.R., Lal, B.: Ion association and solvation of Co (III) complexes in water+ alcohol mixtures at different temperatures. J. Mol. Liq. 124 (2006) 13–18. doi:10.1016/j.molliq.2005.04.002
8. Roy, M.N., Gurung, B.B., Dakua, V.K.: Conductometric study of some metal halides in glycerol+ water mixtures. "International journal of thermo physics. 27 (2006) 1539-1550. doi: 10.1007/s10765-006-0096-4
9. Tsierkezos, N.G., Molinou, I.E.: Transport properties of 2: 2 symmetrical electrolytes in (water+ ethylene glycol) binary mixtures at T= 293.15 K. J. Chem. Thermodyn. 38 (2006) 1422–1431. doi:10.1016/j.jct.2006.01.011
10. Bešter-Rogač, M., Hauptman, N., Barthel, J.: Conductometric study of ion association of divalent symmetric electrolytes: II. $MgSO_4$ in water+ 1, 4-dioxane mixtures. J. Mol. Liq. 131–132 (2007) 29–35. doi:10.1016/j.molliq.2006.08.024
11. Gomaa, E. A., Tahoon, M. A.: Ion association and solvation behavior of copper sulfate in binary aqueous–methanol mixtures at different temperatures. J. Mol. Liq. 214 (2016) 19–23. doi:10.1016/j.molliq.2015.11.046
12. Gomaa, E. A., Tahoon, M. A, Shokr, A.: Ionic association and solvation study of $CoSO_4$ in aqueous-organic solvents at different temperatures. Chemical Data Collections, 3–4 (2016) 58–67. doi: 10.1016/j.cdc.2016.06.005
13. Klofutar, C., Šegatin, N.: Electrical conductivity studies of quinic acid and its sodium salt in aqueous solutions. J. Solution Chem. 36 (2007) 879–889. doi: 10.1007/s10953-007-9154-1
14. El-Dossoki, F.I.: Dissociation and kinetic of hydrochloric acid in mixed isomeric alcoholic-aqueous solvents-A conductance study. J. Mol. Liq. 158 (2011) 18–2. doi:10.1016/j.molliq.2010.09.009
15. El-Dossoki, F.I.: Conductometric and spectroscopic studies of the ion-pair association of sodium and potassium picrate in 2-butanone. J. Mol. Liq.160 (2011) 119–123. doi:10.1016/j.molliq.2011.03.006
16. Hoppe, E., Limberg, C.: Oxo vanadium (V) tetrathiacalix [4] arene complexes and their activity as oxidation catalysts. Chem. Eur. 13(2007) 7006.doi: 10.1002/chem.200700354
17. Xie, M., Gao, L., Li, L., Liu, W., Yan, S.: A new orally active antidiabetic vanadyl complex–bis (α-furancarboxylato) Oxo vanadium (IV). J. Inorg. Biochem. 99 (2005) 546-551. doi:10.1016/j.jinorgbio.2004.10.033
18. Sheela, A., Vijayaraghavan, R.: Synthesis, spectral characterization, and antidiabetic study of new furan-based vanadium (IV) complexes. J. Coord. Chem. 64 (2011) 511. doi: 10.1080/00958972.2010.550916
19. Seaborn, C. D., Mitchell, E. D., Stoecker, B. J.: Vanadium and ascorbate effects on 3-hydroxy-3-methylglutaryl coenzyme A reductase, cholesterol and tissue minerals in guinea pigs fed low-chromium diets. Magnes. Trace. Elem., 10(1991-1992) 327.
20. D'Cruz, O. J., Ghosh, P., Uckun, F. M.: Spermicidal activity of chelated complexes of bis (cyclopentadienyl) vanadium (IV). Mol. Hum. Reprod, 4 (1998) 683. doi: 10.1093/molehr/4.7.683

21. Molinuevo, M. S., Barrio, D. A., Cortizo, A. M., Etcheverry, S. B.: Anti tumoral properties of two new vanadyl (IV) complexes in osteoblasts in culture: role of apoptosis and oxidative stress. Cancer Chemother. Pharmacol. 53 (2004) 163. doi:10.1007/s00280-003-0708-7
22. Naso, L., Ferrer, E.G., Lezama, L., Rojo, T., Etcheverry, S.B., Williams, P.: Role of oxidative stress in the antitumoral action of a new vanadyl (IV) complex with the flavonoid chrysin in two osteoblast cell lines: relationship with the radical scavenger activity.J. Biol. Inorg. Chem. 15 (2010) 889. doi:10.1007/s00775-010-0652-z
23. Chohan, Z.H., Sumrra, S.H.: Some biologically active Oxo vanadium (IV) complexes of triazole derived Schiff bases: their synthesis, characterization and biological properties. J. Enz. Inhib. Med. Chem. 25 (2010) 599.doi: 10.3109/14756360903257884
24. Singh, S., Bharti, N., Mohapatra, P.P.: Chemistry and Biology of Synthetic and Naturally Occurring Antiamoebic Agents. Chem. Rev. 109 (2009) 1900. doi: 10.1021/cr068217k
25. Fuoss, R.M., Shedlovsky, T.: Extrapolation of conductance data for weak electrolytes. J. Am. Chem. Soc. 71 (1949) 1496–1498. doi: 10.1021/ja01172a507
26. Mohsen-Nia, M., Amiri, H., Jazi, B.: Dielectric constants of water, methanol, ethanol, butanol and acetone: measurement and computational study. J Solution Chem.39 (2010) 701–708. doi:10.1007/s10953-010-9538-5
27. Khattab, I.S., Bandarkar, F., Fakhree, M.A.A., Jouyban, A.: Density, viscosity, and surface tension of water+ ethanol mixtures from 293 to 323K. Korean J. Chem. Eng. 29 (2012) 812–817. doi: 10.1007/s11814-011-0239-6
28. Stokes, R.H. Mills, R. Viscosity of Electrolytes and Related Properties, 1st ed, Pergamon Press, London, 1965.
29. Afanas'jev, V.N., Yefremova, L.S., Volkova, T.V., Phiziko-khimicheskijesvoistvabinarnihrastvoritelei. Vodosoderzhashijesistemi (Physico-chemical Properties of Binary Solvents. Water-content Systems), P.I, II IHNR, Ivanovo, Russia, 1988 (412 pp. (in Russ.)).
30. Wypych-Stasiewicz, A., Szejgis, A., Chmielewska, A., Blad, A.: Conductance studies of $NaBPh_4$, NBu_4 I, NaI, NaCl, NaBr, $NaClO_4$ and the limiting ionic conductance in water+ propan-1-ol mixtures at 298.15 K. J. Mol. Liq.130 (2007) 34. doi:10.1016/j.molliq.2006.04.002
31. Gileadi, E., Kirowa-Eisner, E.: Electrolytic conductivity—the hopping mechanism of the proton and beyond. Electro. ChimicaActa51 (2006) 6003. doi:10.1016/j.electacta.2006.03.084
32. Rahimi-Nasrabadi, M., Ahmadi, F., Pourmortazavi, S.M., Ganjali, M.R., Alizadeh, K.: Conductometric study of complex formations between some substituted pyrimidines and some metal ions in acetonitrile and the determination of thermodynamic parameters. J. Mol. Liq. 144 (2009) 97–101. doi:10.1016/j.molliq.2008.10.012
33. Lind Jr., J.E., Zwolenik, J.J., Fuoss, R.M.: Calibration of Conductance Cells at 25° with Aqueous Solutions of Potassium Chloride1. J. Am. Chem. Soc.81 (1959) 1557. doi: 10.1021/ja01516a010
34. Onsager, L.: The theory of electrolytes. Z. Phys, 28 (1927) 277–298.
35. Singh, N. M.: Ion Association and Solvation Behaviour of Metal (II) Chlorides in Binary Mixtures of Methanol+ Water: A Conductance Method.Asian Journal of Chemistry, 28.4 (2016): 910.
36. Gomaa, E. A.: Single ion thermodynamics for Cl−, Br−, I−, Ph4B−, K+, Rb+, Cs+ and Ph4As+ in mixed hexa methyl phosphort. Thermo chimica acta, 91, (1985) 235-241. doi: 10.1016/0040-6031(85)85217-5
37. El-Dossoki, F. I.: Conductometric and thermodynamic studies on the ionic association of HCOONH 4, phCOONH 4, HCOONa and phCOONa in aqueous–organic solvents. J. Mol. Liq. 142 (2008) 72–77. doi:10.1016/j.molliq.2008.05.001
38. S.A. Baker, G.G. Birch, Food Chem. 67 (1999) 146–241.

39. Walden, P.: Über den Zusammenhang zwischen dem Grenzleitvermögen λ∞ der binären Elektrolyte in nichtwässerigen Lösungsmitteln und der Viskosität η∞ der letzteren λ∞· η∞= konst. Anorg. Allg. Chem. 113 (1) (1920) 85.
40. Walden, P.: Über Die Ionendurchmesser in Nichtwässerigen Lösungen. Anorg. Allg. Chem. 113(2/3) (1920) 125.
41. Rao, K.C., Subha, M.C.S., Rao, S.B.: Ion-Pair Association Constants of alkali and alkaline-earth metal formats in formic acid-acetonitrile mixtures at 30-degrees C-A conductance. Indian J. Chem. 28A (1989) 102–105.
42. Szejgis, A., Bald, A., Gregorowicz, J., Kinart, C.M.: Conductivity studies on LiBr, NaBr, KBr and CsBr solutions in binary mixtures of N, N+ dimethylformamide with water at 298.15 K. Phys. Chem. Liq. 34 (1997) 189.
43. Szejgis, A., Bald, A., Gregorowicz, J., Zurada, M.: Conductance studies in mixtures of water with DMF at 298.15 K. Part VI. Lithium and sodium nitrates, sodium perchlorate and propionate, potassium picrate and thiocyanate, and limiting ionic conductance. . Mol. Liq. 79 (1999) 123-136.
44. Ezz-Elarab, M.A.F., Shehata, H.A.: Conductivity and Viscosity of Ba $(NO_3)_2$ in Glycerol-H_2O Mixture at 25°C. J. Sci. Phys. Sci. 4 (1) (1992) 51–55.
45. E.A. Gomaa, R.M. Abu-Qarn, Ionic association and thermodynamic parameters for solvation of vanadyl sulfate in ethanol-water mixtures at different temperatures, J. Mol. Liq. 232 (2017). doi:10.1016/j.molliq.2017.02.085.
46. Nacollas, G.H.: Interactions in Electrolyte Solutions, 1st ed. Elsevier, Amsterdam, 1966.