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Research Article

Non Isothermal Association Thermodynamic Parameters (Conductometrically) for Bulk and Nano Nickel Sulfate in Mixed EtOH–H_2O Solvents

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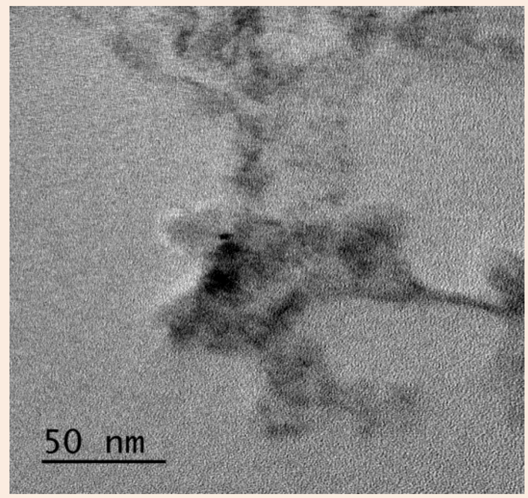
Abstract
The molar conductance for bulk and nano nickel sulfate ($NiSO_4$) in different percentages of ethanol (EtOH) and water were measured non- isothermally, at 298.15, 303.15, 308.15 and 313.15K temperatures. From the molar conductance for both bulk and nano $NiSO_4$, the solvation parameters like, activity coefficient, association constant, free energy of association, enthalpy of association and entropy of association were estimated. All these solvation parameters were discussed.



Keywords: Thermodynamics, molar conductance, nano nickel sulfate and bulk nickel sulfate, free energy, enthalpy, entropy of association, mixed EtOH – H_2O solvents

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Introduction

Nickel mineral is found in several foods including nuts , dried beans and peas soya beans , grains and chocolate .The body needs nickel ,but in very small amounts Nickel is a common trace element in multiple vitamins .Nickel is used for increasing iron absorption , preventing iron-poor blood (anemia) and treating weak bones (osteoporosis) [1,2]. Sulfate is one of the world`s most widely uses commodities. Nickel is used for nickel alloys, electroplating, batteries, coins , industrial, plumbing, park plugs, machinery parts, stainless steel, nickel –chrome resistance wires[3-8]. Our purpose is to give data to facilitate the estimation of different bulk and nano nickel sulfates in solutions.

Experimental
Materials

$NiSO_4.6H_2O$ from Al Nasr chemicals Co. was used without purification.
Absolute ethanol of the type Adwic was used.

Preparation of nano $NiSO_4$

$NiSO_4$ of the type Adwic was milled by ball - mill. The ball – mill was a Retsch MM2000 swing mill with 10cm^3 stainless steel, double-walled tube. Two stainless steel balls of 12 mm diameter and 7 gm weight for each were used.

Ball-milling was performed at 20225 Hz for half an hour at room temperature (without circulating liquid and the temperature did not rise above 30^{o}C).

Results and Discussion

X-ray diffraction

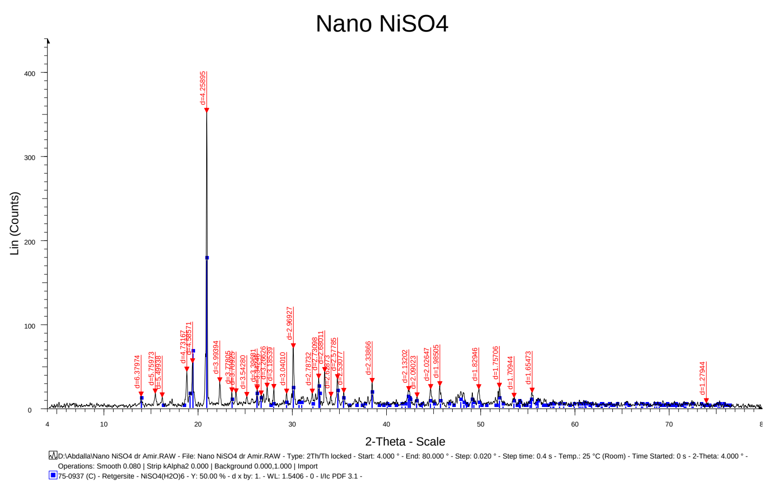

Figure 1 X-ray diffraction of nano nickel sulfate

The X-ray diffraction of nano cobalt sulfate in Fig. (1), shows that it has about the structure is $NiSO_4.6H_2O$, the same as mineral Retgresite. The axial ratio of a: c is 1: 2.695.

The crystal system is Tetragonal-Trpezohedrall. The forms are (0 1 1) (1 1 2) (110)(012)(001). The cleavage is {0 0 1} perfect. The density is 2.07 and the color is greenish white.

Table 1 The crystal size of nano nickel sulfate

Position	Area	Cry Size L(nm)	Microstrain	RMS Strain (%)
13.8525	2.6875	56.6	0.1	0.1
15.3668	4.1705	48.8	0.1	0.1
18.7068	8.3627	76.6	0.1	0.1
19.3219	13.1585	56.8	0.1	0.1
20.8316	48.9143	170.4	0.1	0.1
22.2308	5.1976	107.7	0.1	0.1
23.4996	2.5675	106.6	0.1	0.1
23.9412	2.8252	111	0.1	0.1
26.0638	19.6132	4	0.1	0.1
27.2577	4.0863	80.5	0.1	0.1
27.9642	2.1701	211.4	0.1	0.1
29.3202	1.9599	158	0.1	0.1
30.0422	11.5945	138.2	0.1	0.1

Conductometric Measurments

5 ml of the $NiSO_4$ solution (1.0 x 10^{-3} M) was placed in the titration cell, thermostated at the preset temperature and the conductance of the solution was measured after the solution reached thermal equilibrium. Then, a known amount of solvent was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition until the desired constant reading was achieved. The specific conductance values were recorded using conductivity bridge JENCO – 3175 COND.(USA) with a cell constant equal to 1. The conductometer was conducted with a stirring water bath of the type Artec , Elecsys 2010. The temperature was adjusted at 298.15, 303.15, 308.15 and 313.15K.

TEM Imagies

Figure (**2**) in all images measured by using JEOL HRTEM – JEM 2100 (JAPAN) show that TEM of $NiSO_4$ obtained in water are diffused dishes like clouds. The diameters are in the range of 9.9 – 28.69 nm.The small sizes in the range between 9 to 20 nm are collected to give bigger sizes till 101.93 nm. These different sizes were proved also by x- ray diffraction which gave average crystal size of 101.93nm.The non homogeneity in sizes for nano nickel sulfate need controlling during the primary preparation of the samples .The image (D) in Fig.(2) shows that nano $NiSO_4$ is in the crystalline form with the ration r_1 to r_2 equal 0.555 and r_2 to r_1 equal 1.8.

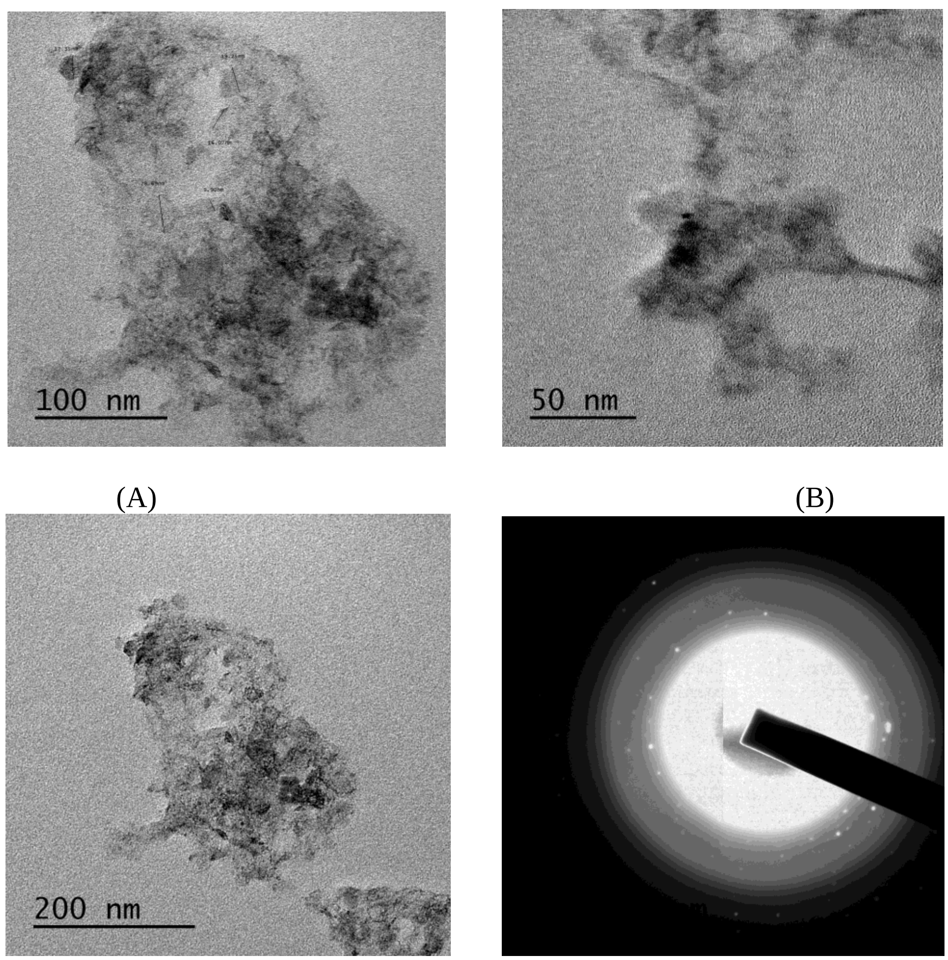

Figure 2 TEM for nano nickel sulfate

Association and triple ion association constants:

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

The molar conductance (Λ_m) values were calculated using equation (1) [9-26]:

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \qquad (1)$$

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 $NiSO_4$ solution.

By drawing the relation between molar conductance ($/\backslash_m$) and $C^{1/2}$, straight lines were obtained from which we extrapolate the line to zero salt concentration to evaluate the limiting equivalent conductance.

The association constant K_A was calculated by using equation (2). The experimental data for conductance measurements were analyzed using Fuoss-Shedlovsky extrapolation techniques which follows equation: -

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

Where $S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \ldots\ etc.$ ....*(3)*

And $$Z \quad \frac{S(\Lambda_m C)^{1/2}}{\Lambda_o^{3/2}} \qquad \text{.......(4)}$$

The value of (Λ_o) was used to calculate the Onsager slope ***(S)*** from the equation (3)

$$S = a\Lambda_o + b \qquad \text{......(5)}$$

$$\text{Where} \quad a = 8.2 \times 10^5 /(\varepsilon T)^{3/2} \qquad \text{......(6)}$$

$$b = 82.4/\eta((\varepsilon T)^{1/2} \qquad \text{...... (7)}$$

Where (ε) is the dielectric constant 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:

$$(\alpha) = \frac{\Lambda_m S(Z)}{\Lambda_o} \qquad \text{.........(8)}$$

Using these (α) and (ε) values, the mean activity coefficients ($\gamma_\pm$) were evaluated by means of equation ***(9)***

And $$\log \gamma_{\pm} = -\frac{Z_+ Z_- A\sqrt{I}}{I + Br^o\sqrt{I}} \qquad \text{.........(9)}$$

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

$$A = 1.824 \times 10^6\ (\varepsilon T)^{-3/2} \ ; \ B = 50.29 \times 10^8\ (\varepsilon T)^{-1/2}$$

And (r^o) is the solvated radius. Using the values of association constant (K_A), the values of the dissociation constant (K_D) were easily calculated by means of the following equation:

$$K_D = 1/K_A \qquad \text{......... (10)}$$

The values of the triple ion association constant (K_3) were calculated by using the equation (***11***)

$$\frac{\Lambda_m C^{1/2}}{(1-\frac{\Lambda_m}{\Lambda_o})^{1/2}} = \frac{\Lambda_o}{(K_A)^{1/2}} + \frac{\lambda_3^o C}{K_3 (K_A)^{1/2}} (1-\frac{\Lambda_m}{\Lambda_o}) \quad \text{......... (11)}$$

Equation (***11***) was derived by Fuoss and using Walden product ($\Lambda_o = 3\lambda_o$). The values of ($\eta_o, \Lambda_o, \Lambda_m$, C, S, Z, S(Z), $\gamma_\pm$, K_A, K_D, α and K_3 for the solutions of 10^{-3} M concentration were calculated and are reported in Tables (1-8) for nano nickel and bulk sulfate in mixed EtOH-H_2O solvents at different temperatures.

Table 1 The values of viscosity (η_o), limiting molar conductance (Λ_o), molar conductance (Λ_m), Fuoss-Shedlovsky parameters (S, Z and S(z)), activity coefficient ($\gamma_\pm$), association constant (K_A), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for nano $NiSO_4$ in (EtOH-H_2O mixture) at 298.15K

VOL.% OF EtOH	X_S (mole fraction of ethanol)	102 η_o (poise)	Λ_o	Λ_m	S	Z	S(z)	$\gamma_\pm$	K_A	$10^3 K_D$	α	$10^5 K_3$	ΔG_A (k.J/mole)
20%	0.0717	0.9042	145.85	98.6764	95.3848	0.01658	1.0167	0.8821	892.3262	1.1206	0.6878	4.0804	-16.8437
40%	0.1708	0.9209	85.04	50.4839	82.3247	0.02299	1.0232	0.8820	1439.442	0.6947	0.6074	6.3554	-18.0292
60%	0.3166	0.9455	28.55	18.4128	69.4607	0.060222	1.0620	0.8613	952.5961	1.0497	0.6849	5.3147	-17.0058
80%	0.5527	0.9853	18.67	8.3475	70.97955	0.078353	1.0814	0.8503	3215.198	0.3110	0.4835	12.8895	-20.0217
100%	1	1.0607	5.86	2.7947	99.05908	0.359813	1.4303	0.4998	2878.231	0.3474	0.6821	10.6954	-19.7472

Table 2 The values of viscosity (η_o), limiting molar conductance (Λ_o), molar conductance (Λ_m), Fuoss-Shedlovsky parameters (S, Z and S(z)), activity coefficient ($\gamma_\pm$), association constant (K_A), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for nano $NiSO_4$ in (EtOH-H_2O mixture) at 303.15K

VOL.% OF EtOH	X_S (mole fraction of ethanol)	$10^2 \eta_o$ (poise)	Λ_o	Λ_m	S	Z	S(z)	$\gamma_\pm$	K_A	$10^3 K_D$	α	$10^5 K_3$	ΔG_A (k.J/mole)
20%	0.0717	0.8082	158.57	100.827	106.4480	0.0164	1.0166	0.8840	1139.641	0.8774	0.6464	5.089667	-17.7429
40%	0.1708	0.8193	81.05	51.3345	89.4335	0.0270	1.0274	0.8765	1129.948	0.8849	0.6507	5.243202	-17.7213
60%	0.3166	0.8358	29.77	17.8911	78.3025	0.0628	1.06485	0.8639	1239.890	0.8065	0.6399	6.644065	-17.9554

80%	0.5527	0.8625	18.33	9.34691	80.4474	0.0965	1.1013	0.8375	2085.612	0.4794	0.8613	-1199.17	-19.2663
100%	1	0.9133	5.51	2.58497	114.2152	0.4376	1.5437	0.4821	2381.235	0.4199	0.7242	0	-1.5325

Table 3 The values of viscosity (η_o), limiting molar conductance (Λ_o), molar conductance (Λ_m), Fuoss-Shedlovsky parameters (S, Z and S(z)), activity coefficient ($\gamma_\pm$), association constant (K_A), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for nano $NiSO_4$ in ($EtOH-H_2O$ mixture) at 308.15K

VOL.% OF EtOH	**X_S (mole fraction of ethanol)**	$10^2 \eta_o$ (poise)	Λ_o	Λ_m	**S**	**Z**	**S(z)**	$\gamma_\pm$	**K_A**	**$10^3 K_D$**	α	**$10^5 K_3$**	**ΔG_A (k.J/mole)**
20%	0.0717	0.6363	164.95	106.6752	128.4491	0.01930	1.0194	0.8796	1066.262	0.9378	0.6593	4.8139	-18.1549
40%	0.1708	0.6537	78.20	50.5396	107.0608	0.0338	1.0344	0.8726	1035.522	0.9656	0.6668	5.0152	-18.0787
60%	0.3166	0.6724	33.25	18.1440	97.1425	0.0665	1.0687	0.8668	1716.608	0.5825	0.5832	8.6307	-19.3949
80%	0.5527	0.6862	13.13	10.3560	103.5028	0.0872	1.0910	0.8393	2913.072	0.3432	0.5042	12.1529	-20.7720
100%	1	0.7117	6.61	3.4608	150.0878	0.5064	1.6506	0.4237	1066.023	0.9380	0.8642	16.6489	-18.1543

Table 4 The values of viscosity (η_o), limiting molar conductance (Λ_o), molar conductance (Λ_m), Fuoss-Shedlovsky parameters (S, Z and S(z)), activity coefficient ($\gamma_\pm$), association constant (K_A), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for nano $NiSO_4$ in ($EtOH-H_2O$ mixture) at 313.15K

VOL.% OF EtOH	**X_S (mole fraction of ethanol)**	$10^2 \eta_o$ (poise)	Λ_o	Λ_m	**S**	**Z**	**S(z)**	$\gamma_\pm$	**K_A**	**$10^3 K_D$**	α	**$10^5 K_3$**	**ΔG_A (k.J/mole)**
20%	0.0717	0.9042	142.38	96.77012	94.5547	0.0168	1.0170	0.8818	874.8067	1.14311	0.69121	8.970595	-16.7946
40%	0.1708	0.9209	78.95	52.2900	80.7710	0.0251	1.0254	0.8781	991.1794	1.0088	0.6791	4.3060	-17.1042
60%	0.3166	0.9455	37.10	19.03825	71.9024	0.0427	1.0437	0.8763	2219.202	0.4506	0.5355	9.4794	-19.1025
80%	0.5527	0.9853	10.08	6.10038	67.8103	0.1578	1.1707	0.8253	937.6994	1.0664	0.7083	7.9038	-16.9667
100%	1	1.0607	5.08	2.3447	97.0976	0.4004	1.4885	0.5071	2709.736	0.3690	0.6872	13.0004	-19.9263

Table 6 The values of viscosity (η_o), limiting molar conductance (Λ_o), molar conductance (Λ_m), Walden product ($\Lambda_o \eta_o$), fluidity ratio (R_x), Fuoss-Shedlovsky parameters (S, Z and S(z)), activity coefficient ($\gamma_\pm$), association constant (K_A), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for bulk $NiSO_4$ in (EtOH-H_2O mixture) at 303.15K

VOL.% OF EtOH	X_S (mole fraction of ethanol)	$10^2 \eta_o$ (poise)	Λ_o	Λ_m	S	Z	S(z)	$\gamma_\pm$	K_A	$10^3 K_D$	α	$10^5 K_3$	ΔG_A (k.J/mole)
20%	0.0717	0.8082	155.75	99.792	105.7638	0.0167	1.0168	0.8836	1106.709	0.9035	0.6515	4.9636	-17.669
40%	0.1708	0.8193	84.32	53.7659	90.2798	0.0263	1.0267	0.8761	1104.854	0.9050	0.6546	5.1175	-17.6647
60%	0.3166	0.8358	32.93	18.606	79.2183	0.0557	1.0573	0.8682	1575.836	0.6345	0.5973	7.7249	-18.5598
80%	0.5527	0.8625	18.62	6.66517	80.5546	0.0798	1.0830	0.8630	5754.557	0.1737	0.3877	-2020.34	-21.8248
100%	1	0.9133	4.09	1.62801	112.2881	0.5337	1.6949	0.4945	3077.992	0.3248	0.6745	22.5941	-20.2475

Table 7 The values of viscosity (η_o), limiting molar conductance (Λ_o), molar conductance (Λ_m), Walden product ($\Lambda_o \eta_o$), fluidity ratio (R_x), Fuoss-Shedlovsky parameters (S, Z and S(z)), activity coefficient ($\gamma_\pm$), association constant (K_A), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for bulk $NiSO_4$ in (EtOH-H_2O mixture) at 308.15K

VOL.% OF EtOH	X_S (mole fraction of ethanol)	$10^2 \eta_o$ (poise)	Λ_o	Λ_m	S	Z	S(z)	$\gamma_\pm$	KA	$10^3 K_D$	α	$10^5 K_3$	ΔG_A (k.J/mole)
20%	0.0717	0.7329	160.96	102.6495	114.8662	0.0175	1.0177	0.8823	1126.467	0.8877	0.6490	5.0417	-18.0057
40%	0.1708	0.7478	83.54	53.9595	97.3057	0.0288	1.0292	0.8735	1046.22	0.9558	0.6647	4.9190	-17.8164
60%	0.3166	0.7697	33.43	18.3225	85.8496	0.0585	1.0603	0.8681	1732.273	0.5772	0.5811	8.3819	-19.1085
80%	0.5527	0.8054	20.12	8.0115	87.2453	0.0844	1.0880	0.8520	4368.498	0.2289	0.4332	15.9047	-21.4787
100%	1	0.8735	5.78	2.05215	121.1021	0.3848	1.4659	0.5264	6718.924	0.1488	0.5205	16.7389	-22.5818

Table 8 The values of viscosity (η_o), limiting molar conductance (Λ_o), molar conductance (Λ_m), Walden product ($\Lambda_o \eta_o$), fluidity ratio (R_x), Fuoss-Shedlovsky parameters (S, Z and S(z)), activity coefficient ($\gamma_\pm$), association constant (K_A), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for bulk $NiSO_4$ in (EtOH-H_2O mixture) at 313.15K

VOL.% OF EtOH	X_S (mole fraction of ethanol)	$10^2 \eta_o$ (poise)	Λ_o	Λ_m	S	Z	S(z)	$\gamma_\pm$	K_A	$10^3 K_D$	α	$10^5 K_3$	ΔG_A (k.J/mole)
20%	0.0717	0.6363	157.19	106.8569	126.507	0.02040	1.0206	0.8766	870.9178	1.1482	0.6593	4.0181	-17.6279
40%	0.1708	0.6537	81.71	52.4445	107.9877	0.0326	1.0331	0.8730	1058.045	0.9451	0.6631	5.0721	-18.1347
60%	0.3166	0.6724	31.09	17.2040	96.5016	0.0711	1.0737	0.8656	1614.18	0.6195	0.5942	8.4375	-19.2346
80%	0.5527	0.6862	28.57	10.4527	104.9472	0.0685	1.0709	0.8567	5667.226	0.1764	0.3918	17.4810	-22.5049
100%	1	0.7117	5.26	1.9243	148.1185	0.5243	1.6796	0.4848	4583.346	0.2181	0.6140	21.6167	-21.9522

Association thermodynamic parameters of the nano and bulk nickel sulfate solutions:

The Gibbs of free energy change of association (ΔG_A) of different concentration of the metal salt solutions in mixed EtOH-H_2O were calculated [27-50] from the association constant (K_A) by using equation ***(3).***

$$\Delta G_A = -2.303\ RT \log K_A \qquad \text{......... (12)}$$

Where R is the gas constant and T is the absolute temperature. The enthalpy changes of association (ΔH_A) for the metal salts were calculated for each type from the association constants by using Van't Hoff equation [62-71]:

$$\frac{d\ln K}{dT} = \frac{\Delta H_A^o}{RT^2} \qquad \text{...... (13)}$$

By drawing the relation between log K_A and 1/T giving straight line with slope ($-\Delta H_A/2.303R$) as shown in Figures (3 and 4) for bulk and nano $NiSO_4$.

The entropies of association (ΔS_A) for the electrolytes were calculated by the use of Gibbs-Helmohltz equation (***14***) [63-79] **.**

$$\Delta G_A = \Delta H_A - T\Delta S_A \qquad \text{...... (14)}$$

The calculated values of (ΔH_A) and (ΔS_A) for the metal salts are presented in Tables (9-12) for nano NiSO4 and Tables (13-14) for bulk $NiSO_4$ nonisothermally.

The limiting equivalent conductance (Λ_o) increase as the temperature increased and dissociation degree decrease and then increase as the temperature increased indicating higher solvation process.

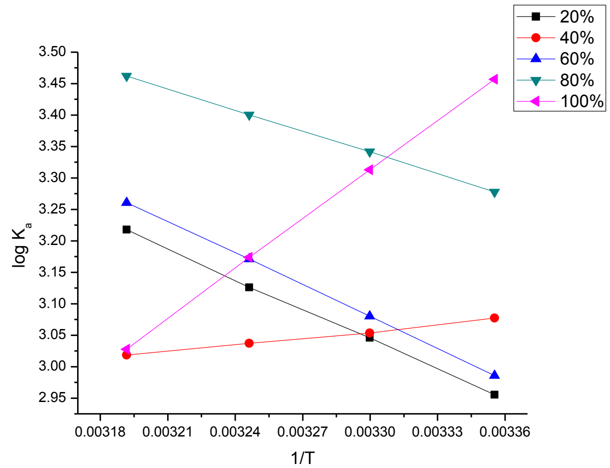

Figure 3 Relation between log K_A versus 1/T for nano $NiSO_4$ at different percentage of ethanol-water mixtures

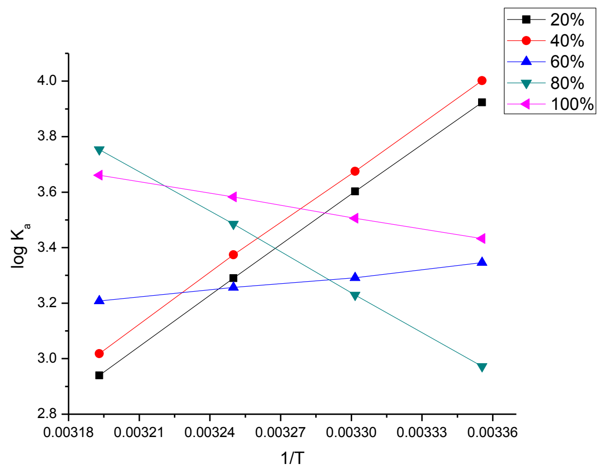

Figure 4 Relation between log K_A versus 1/T for bulk $NiSO_4$ at different percentage of ethanol-water mixtures

Table 9 Enthalpy of association (ΔH_A), ($T\Delta S_A$) and entropies (ΔS_A) for nano $NiSO_4$ in ($EtOH-H_2O$ mixture) at 298.15K

X_S	ΔH_A kJ.mol^{-1}	$T\Delta S_A$ kJ.mol^{-1}	ΔS_A J.mol^{-1}
0.0717	30.8728	47.7165	160.0421
0.1708	-6.3974	11.6318	39.01327
0.3166	32.5718	49.5776	166.2841
0.5527	22.6287	42.6503	143.0500
1	-51.1654	-31.4182	-105.3770

Table 10 Enthalpy of association (ΔH_A), ($T\Delta S_A$) and entropies (ΔS_A) for nano $NiSO_4$ in (EtOH-H_2O mixture) at 303.15K

X_S	ΔH_A kJ.mol^{-1}	$T\Delta S_A$ kJ.mol^{-1}	ΔS_A J.mol^{-1}
0.0717	30.8728	48.6157	160.3685
0.1708	-6.3974	11.3239	37.3541
0.3166	32.5718	50.5272	166.6741
0.5527	22.6287	41.8950	138.1991
1	-51.1654	-49.6328	-163.7240

Table 11 Enthalpy of association (ΔH_A), ($T\Delta S_A$) and entropies (ΔS_A) for nano $NiSO_4$ in (EtOH-H_2O mixture) at 308.15K

X_S	ΔH_A kJ.mol^{-1}	$T\Delta S_A$ kJ.mol^{-1}	ΔS_A J.mol^{-1}
0.0717	30.8728	49.3026	159.9956
0.1708	-6.3974	11.5502	37.4825
0.3166	32.57186	51.2979	166.4706
0.5527	22.6287	42.9673	139.4364
1	-51.1654	-30.9292	-100.3710

Table 12 Enthalpy of association (ΔH_A), ($T\Delta S_A$) and entropies (ΔS_A) for nano $NiSO_4$ in (EtOH-H_2O mixture) at 313.15K

X_S	ΔH_A kJ.mol^{-1}	$T\Delta S_A$ kJ.mol^{-1}	ΔS_A J.mol^{-1}
0.0717	30.8728	49.0276	156.5629
0.1708	-6.3974	11.6812	37.3023

0.3166	32.5718	51.9667	165.9480
0.5527	22.6287	43.4007	138.5940
1	-51.1654	-33.0111	-105.4160

Table 13 Enthalpy of association (ΔH_A), ($T\Delta S_A$) and entropies (ΔS_A) for bulk $NiSO_4$ in (EtOH-H_2O mixture) at 298.15K

X_S	ΔH_A kJ.mol^{-1}	$T\Delta S_A$ kJ.mol^{-1}	ΔS_A J.mol^{-1}
0.0717	-115.3040	-98.5098	-330.4030
0.1708	-118.2590	-101.155	-339.2740
0.3166	-16.0324	3.07006	10.2970
0.5527	92.6531	109.6198	367.6668
1	27.0804	47.0067	155.0609

Table 14 Enthalpy of association (ΔH_A), ($T\Delta S_A$) and entropies (ΔS_A) for bulk $NiSO_4$ in (EtOH-H_2O mixture) at 30:3.15K

X_S	ΔH_A kJ.mol^{-1}	$T\Delta S_A$ kJ.mol^{-1}	ΔS_A J.mol^{-1}
0.0717	-115.304	-97.6354	-322.0700
0.1708	-118.259	-100.5940	-331.8300
0.3166	-16.0324	2.5273	8.33703
0.5527	92.6531	114.478	377.6282
1	27.0804	47.3279	156.1206

Table 15 Enthalpy of association (ΔH_A), ($T\Delta S_A$) and entropies (ΔS_A) for bulk $NiSO_4$ in (EtOH-H_2O mixture) at 308.15K

X_S	ΔH_A kJ.mol^{-1}	$T\Delta S_A$ kJ.mol^{-1}	ΔS_A J.mol^{-1}
0.0717	-115.3040	-97.2986	-315.7510
0.1708	-118.2590	-100.4430	-325.9530
0.3166	-16.0324	3.0760	9.98220
0.5527	92.6531	114.1318	370.3775
1	27.0804	49.6622	161.1626

Table 16 Enthalpy of association (ΔH_A), ($T\Delta S_A$) and entropies (ΔS_A) for bulk $NiSO_4$ in (EtOH-H_2O mixture) at 313.15K

X_S	ΔH_A kJ.mol^{-1}	$T\Delta S_A$ kJ.mol^{-1}	ΔS_A J.mol^{-1}
0.0717	-115.3040	-97.6765	-311.9160
0.1708	-118.2590	-100.1240	-319.7320
0.3166	-16.0324	3.2022	10.2258
0.5527	92.6531	115.1581	367.7410
1	27.0804	49.0326	156.5788

It was seen in TEM images diffusion of the particles forming cloud shape indicating association and also favoring that nano $NiSO_4$ has stronger association parameters than that of bulk one (normal, without milling).Both nano and normal $NiSO_4$ have small triple ion association values .The activity coefficients have big values indicating the ion – ion interaction in the form of association .The entropies of association for nano $NiSO_4$ (Tables 9-12) have positive values indicating the spontaneous character and ease of solvation in the mixed EtOH-water solvent .Some entropy values for solvation for normal $NiSO_4$ (Tables 13-16) have negative values indicating its hard solvation. In mixed solvents the association parameters are greater than that of pure solvents due to both ion solvent and solvent – solvents interactions resulting to the formation of more ions than that produced in pure solvents.

Conclusion

This research focused on the study of conductance measurements for nano $NiSO_4$. The stability constants of association were measured by applying the conductometric method at different temperatures. Based on the results, the association constants decrease with increase in percentage of ethanol and increase with increasing temperatures. indicating increase in association on adding EtOH in solution and decrease by raising temperature due to the increase in the kinetic energy.

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