

PARAMETERS FOR THE CONDUCTOMETRIC ASSOCIATION FOR LUMP AND NANO $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ IN THE PRESENCE AND ABSENCE OF FUCHSIN ACID IN WATER AT DIFFERENT TEMPERATURE

Mohamed Fathi¹, Esam A. Gomaa², Shereen E. Salem², Hamada M. Killa¹, Ayman A. Gouda^{1*} and Abdel Hamid Farouk¹

¹Chemistry Department, Faculty of Science, Zagazig University, 44519, Zagazig, Egypt

²Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

(Received November 8, 2022; Revised January 6, 2023; Accepted January 10, 2023)

ABSTRACT. For lump and nanocobalt sulfate (CoSO_4) in pure water, the affiliation and thermodynamic association characteristics were measured at 298.15, 303.15, 308.15, and 313.15 K. Based on the bulk and nano CoSO_4 molar conductance, estimates were made for the parameters of the solvation, such as the activity coefficient, free energy of association, enthalpy of association, association constant, and entropy of association. We discussed about each of these solvation parameters. Two stoichiometric complexes were formed by the interaction of bulk and nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ with fuchsin acid: 1:1 and 1:2. In the case of 1:1 ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ /fuchsin acid) compared to 1:2 (fuchsin acid in pure water as solvent), the complex K_f and ΔG_f are higher, indicating simpler complex formation. The temperature increase resulted in a drop in the formation constants. The complexation's negative ΔG_f values demonstrate that the process of complex synthesis was spontaneous and that the temperature improved the spontaneity.

KEY WORDS: Molar conductance, Association constants, Fuchsin acid, Nano cobalt sulfate salt, Formation constant

INTRODUCTION

An electrolyte solution's conductivity is an indication of how well it conducts electricity. Siemens per meter (S/m) is the SI unit for conductivity [1, 2]. The quantity of ions in a solution may be quickly, cheaply, and accurately determined using conductivity measurements in various industrial and environmental applications [3-6]. For instance, one common technique for monitoring changes in the effectiveness of water purification systems over time is the measurement of product conductivity. One of the most precise physical methods for evaluating the electrolyte of solutions is conductance measurement. Measurements of conductivity are commonly utilized in industry. Water treatment is one of the most crucial applications since untreated water from a lake, river, or the pipe is usually ineffective for industrial usage. If the contaminants in the water are not removed, they will cause corrosion and scale in the plant's machinery, especially in the boilers, cooling towers, and heat exchangers. There are numerous methods for treating water, and each one has a unique purpose. Demineralization, or the elimination of all or almost all contaminants, is frequently the intended outcome. In some instances, the intention is to eliminate only a certain contaminant, such as hardness ions (calcium and magnesium). Since conductivity measures the entire ion concentration [7, 8], analyzing complexation processes in different solvent systems and interpreting them in terms of the solute being solvated preferentially by one of the solvent components [9-11].

Water can demonstrate a broad range of relative permittivity (ϵ), viscosity (η), and a strong hydrogen bonding effect at various temperatures. The measurement of conductivity can be used to investigate the various interactions between lump and nano cobalt sulphate alone and in combination with fuchsin acid in water as a solvent at various temperatures [12]. One physico-chemical method for analysing complexation processes is conductance measurement among metal ions and ligands in solutions [13].

*Corresponding author. E-mail: aymangouda77@gmail.com; mohamed.fathi257@yahoo.com
This work is licensed under the Creative Commons Attribution 4.0 International License

In this work, calculations of conductivity were done utilizing lump and nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in H_2O in the lack and in the presence of fuchsin acid. Cobalt compounds have received a lot of attention lately because they perform a big part in a lot of biochemical processes and are used in so many various industries including industrial and medicinal chemistry [13, 14].

Antibiotics, often known as antibacterial, are antimicrobial drugs that are used to treat and prevent bacterial infections. These compounds may kill or inhibit bacteria. Only a few antibiotics have antiprotozoal activity [16]. Acid fuchsin is a mixture of basic fuchsin homologues with sulfonic groups attached. Fuchsin was first created in 1856 by Jakub Natanson using aniline and 1,2-dichloroethane. Additionally, it can be utilized to find bacteria that are multiplying.

One of the most well-liked research areas is the study of metal complexes. There has been a lot of interest in complex formation. Some of the physicochemical methods that are applicable for researching these complexation reactions include conductometry, calorimetry, cyclic voltammetry, NMR spectrometry, and potentiometry. It is also possible to determine basic thermodynamic characteristics such as enthalpy, entropy, and Gibbs free energy [17-19].

On the molar conductance (m) and the limiting molar conductance (Λ_0), the effects of metal salt concentrations and temperature were investigated. Additionally, it was discussed how each of the aforementioned variables affected the values of the dissociation degree (α), Walden product ($\Lambda_0\eta_0$), association, triple-ion association constants (K_D , K_A , and K_3) and Gibbs free energies of association (G_A) and transfer (G_t), as well as other thermodynamic parameters.

By conductometrically titrating Co^{2+} solution with fuchsin acid solution in pure deionized water at various temperatures, the complexation's formation constants and thermodynamic characteristics were identified.

EXPERIMENTAL

Chemicals

At 298.15 K, improved water with a specified conductivity of $6 \mu\text{S}\cdot\text{cm}^{-1}$ has been used. Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) was obtained from Sigma-Aldrich that was used directly with no further purifying. Fuchsin acid (benzene sulfonic acid, 2-amino-5-((4-amino-3-sulphophenyl)(4-imino-3-sulfo-2,5-cyclohexadien-1-ylidene)methyl)-3-methyl-, disodium salt) ($\text{C}_{20}\text{H}_{17}\text{N}_3\text{Na}_2\text{O}_9\text{S}_3$, M.W. 585.533 $\text{g}\cdot\text{mol}^{-1}$) was obtained from Oxford Laboratory and it was used without purification.

Solutions

Distilled water was selected as the study's solvent medium. The physical properties, density (ρ), relative permittivity (ϵ) and viscosity (η_0) of water at temperatures 298.15, 303.15, 308.15 and 313.15 K were recorded in Table 1 [20]. By using the associations of these properties at the accessible temperatures extracted from the cited references, the unknown quantities of the (ϵ), (η_0), and (ρ) were determined.

Table 1. The dielectric constant (ϵ), and viscosity (mPa.s) at various temperatures of the utilized pure water solvent.

Salt type	T (K)	Dielectric constant (ϵ)	Viscosity (η)/mPa.s
Bulk CoSO_4	298.15	78.304	0.8903
	303.15	76.546	0.7975
	308.15	74.828	0.7195
	313.15	73.151	0.6532
Nano CoSO_4	298.15	78.304	0.8903
	303.15	76.546	0.7975
	308.15	74.828	0.7195
	313.15	73.151	0.6532

Preparation of nano materials

Ball milling, a process for reducing material particle size, was used to create nano cobalt sulfate (NCS). Bulk cobalt sulfate was ball milled to get nano cobalt sulfate. For two days, a ball-milling device of the Retsch MM2000 swing mill was used to shatter bulk cobalt sulfate. Three stainless steel balls with a diameter of 12 mm were used in the ball milling process along with stainless steel tubes with a volume equal to 10 cm^3 . After a 20225 Hz at room temperature ball milling procedure, the particles reach a nano size that requires examination with a transmission electron microscope (TEM).

Transmission electron microscope (TEM)

To investigate nanoparticle size and morphology, TEM is a useful instrument. A high quality down to a nano scale range was provided by TEM. With the help of JEOL-JAPAN2100, 200 kV, 1.5X.

TEM Images of nano salt

The part particle sizes of nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ are between 20 and 35 nm seen in Figure 1.

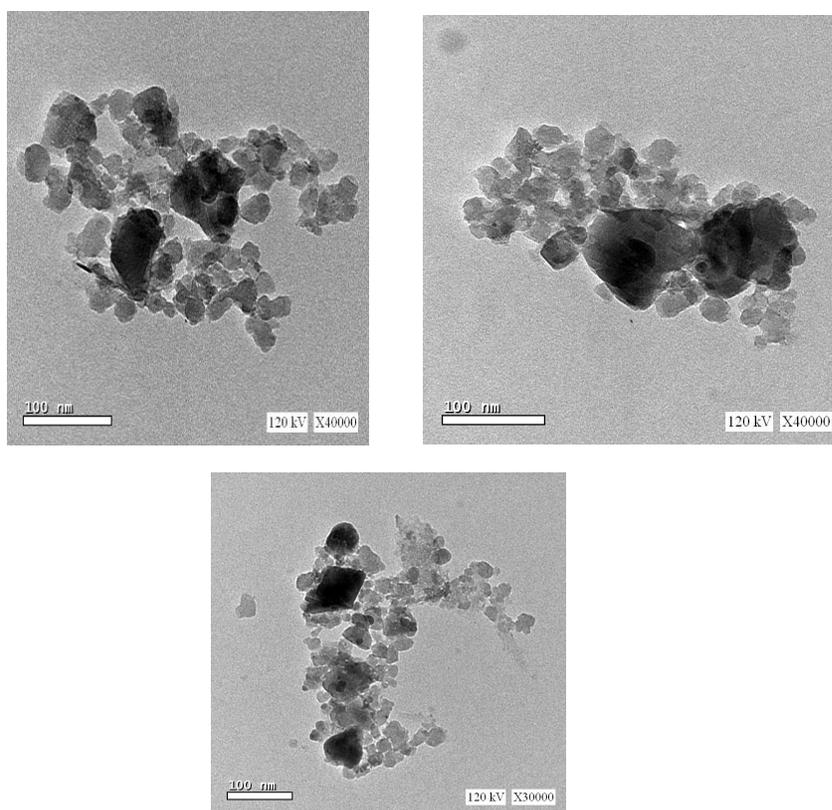


Figure 1. TEM image of nano cobalt sulfate.

Conductivity measurement

Vision plus EC3175 conductance from JENCO For measuring the conductivity of sample solution, a meter with a cell constant of 1.03 cm^{-1} and a deviation of $(0.1 \text{ ohm}^{-1} \cdot \text{cm}^{-1})$ was connected to an ultra-thermostat of type Kottermann 4130 (to maintain the temperature constant at the appropriate value with a departure of $0.006 \text{ }^\circ\text{C}$). Potassium chloride solutions were utilized to calibrate the cell.

RESULTS AND DISSCUTION*Limiting molar conductance estimation*

Experimental measurements of the specific conductance values (K_s) of solutions of various concentrations of bulk and nano CoSO_4 solution in water were made in both the lack and presence of ligands at various temperatures (298.15, 303.15, 308.15 and 313.15 K). Eq. 2 was used to get the molar conductance (Λ_m) values [21-26].

$$\Lambda_m = \frac{(K_s - K_{\text{solvent}}) \cdot K_{\text{cell}} \cdot 1000}{C} \quad (2)$$

where K_s and K_{solvent} are the particular conductance of the solution and the solvent, respectively, and K_{cell} is the cell constant. C is the molar concentration of the metal salt solution.

Walden products of CoSO_4 solutions

The Walden product ($\Lambda_o \eta_o$) values were computed using solutions of CoSO_4 in water at various concentrations. From the perspective of ion-solvent interactions, the Walden product values obtained from the limiting molar conductance values (Λ_o), might be useful. The ratios of fluidity were also calculated by using equation (3)

$$R_x = \frac{\Lambda_o \eta_o (\text{organic solvent})}{\Lambda_o \eta_w (\text{in water})} \quad (3)$$

The limiting molar conductance (Λ_o) were estimated for bulk and nano CoSO_4 in water solvent in the absence and in the presence of the ligand fuchsin acid by extending the linear Onsager plot between Λ_m and $(C_m)^{1/2}$ at various temperatures [23, 25] as shown in Figure 2 (a) and (b).

Association thermodynamic parameters of bulk and nano CoSO_4 in water solvent

A series of conductometric measurements was carried out using CoSO_4 in H_2O in the absence and in the presence of the ligand. The effects of metal salt concentrations, type of solvent used and the temperature on the molar conductance (Λ_m) and hence the limiting molar conductance (Λ_o) were also studied. Moreover, the influences of all the above-mentioned factors on the values of Walden product ($\Lambda_o \eta_o$); degree of dissociation (α); dissociation, association, triple-ion association constants (K_D , K_A and K_3); Gibbs free energies of association (ΔG_A) and transfer (ΔG_T) were discussed.

In absence and in the presence of fuchsin acid

Fuoss-Shedlovsky [22] extrapolation techniques were used to examine the experimental conductance measurement data and arrive at the following equations:

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

where $S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \dots$ etc. (5)

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

The Onsager slope (S) was calculated from the equation (6) using the value of (Λ_o):

$$S = a\Lambda_o + b \quad (7)$$

where $a = 8.2 \times 10^5 / (\epsilon T)^{3/2}$ (8)

$$b = 82.4 / \eta / (\epsilon T)^{1/2} \quad (9)$$

where the solvent's dielectric constant is (ϵ), its viscosity is (η_o), and the temperature is (T). The value of (S) was easily approximated using the values of (ϵ) and (η_o). The values of the degree of dissociation (α) were determined using the data of (Λ_m), S(z), and ($\Lambda_o \eta_o$), using the equation:

$$(\alpha) = \frac{\Lambda_m S(Z)}{\Lambda_o} \quad (10)$$

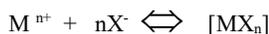
Using these (α) and (ϵ) values, the mean activity coefficients (γ_{\pm}) were evaluated by means of equation (11):

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

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

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

and (r°) is the solvated radius. The association constant (K_A) for the reaction of the type



Is given by equation (12)

$$K_A = \frac{C_{[MX_n]} \cdot \gamma_{[MX_n]}}{C_{M^{n+}} \cdot \gamma_{M^{n+}} \cdot C_{X^-}^n \cdot \gamma_{X^-}^n} \quad (12)$$

The values of the dissociation constant (K_D) were quickly computed using the values of the association constant (K_A), using the following equation:

$$K_D = 1 / K_A \quad (13)$$

The values of the triple ion association constant (K_3) were calculated by using the equation (14)

$$\frac{\Lambda_m C^{1/2}}{(1 - \frac{\Lambda_m}{\Lambda_o})^{1/2}} = \frac{\Lambda_o}{(K_A)^{1/2}} + \frac{\lambda_2 C}{K_3 (K_A)^{1/2}} (1 - \frac{\Lambda_m}{\Lambda_o}) \quad (14)$$

The values of (η_o , Λ_o , Λ_m , C , S , Z , $S(Z)$, γ_{\pm} , K_A , K_D , α and K_3 for the solutions of 10^{-3} M concentration were calculated and are reported in Table 2 for bulk and nano CoSO_4 in water solvent in absence and in the present of ligand fuchsin acid.

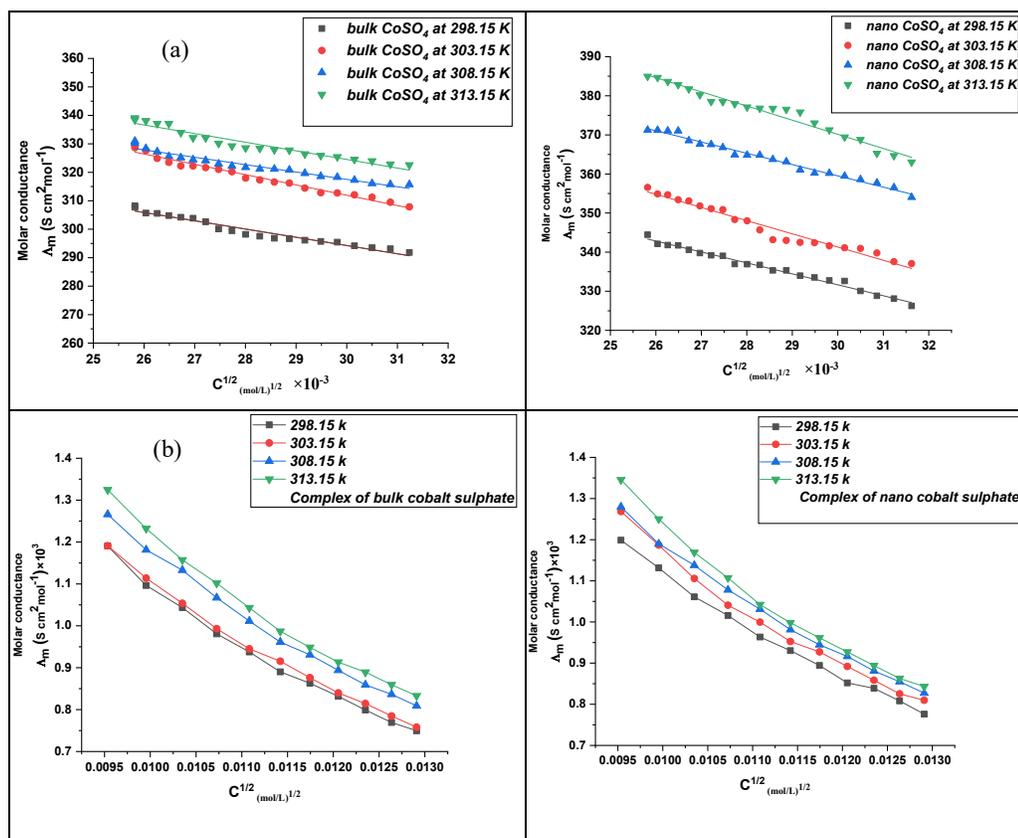


Figure 2. The relation between (Λ_m) and $C^{1/2}$ for lump and nano CoSO_4 in water at various temperatures 298.15, 303.15, 308.15, 313.15 K (a) in lack of fuchsin acid and (b) in presence of fuchsin acid.

Table 2. Various solvation parameters: K_A, K_D and K₃ for bulk and nanoCoSO₄ in water solvent in the absence and presence of ligand (fuchsin acid) at various temperatures 298.15, 303.15, 308.15, 313.15 K.

T (K)	Salt type	10 ² η _o (poise)	Λ _o	Λ _m	Λ _o η _o	S	Z	S(z)	α	γ _±	K _A	10 ³ K _D	10 ⁵ K ₃
In absence of fuchsin acid													
298.15	Bulk	0.890	379.08	291.83	3.374	147.71	0.0108	1.0108	0.7782	0.876	476.27	2.09	2.30
	Nano	0.890	415.60	326.23	3.700	156.10	0.0105	1.0105	0.7932	0.875	428.29	2.33	2.04
303.15	Bulk	0.797	420.75	307.86	3.355	168.46	0.0108	1.0108	0.7396	0.875	620.26	1.61	2.99
	Nano	0.797	442.57	337.08	3.529	173.65	0.0108	1.0108	0.7699	0.873	508.59	1.96	2.43
308.15	Bulk	0.719	395.33	315.71	2.844	167.96	0.0120	1.0120	0.8082	0.872	385.55	2.59	1.83
	Nano	0.719	446.07	354.02	3.209	179.83	0.0113	1.0114	0.8027	0.872	401.81	2.48	1.90
313.15	Bulk	0.653	415.43	322.59	2.713	178.63	0.0119	1.0120	0.7858	0.875	452.00	2.21	2.19
	Nano	0.653	478.83	363.01	3.127	193.28	0.0111	1.0111	0.7666	0.877	516.09	1.93	2.50
In presence of fuchsin acid													
298.15	Bulk	0.8903	3169.84	1190.57	28.221	789.23	0.00145	1.00145	0.3761	0.9728	51250.58	0.0195	1.729
	Nano	0.8903	2084.70	1198.65	18.560	539.78	0.00187	1.00187	0.5760	0.9664	15044.29	0.0664	0.722
303.15	Bulk	0.7975	3216.34	1191.036	25.650	813.94	0.00146	1.00146	0.3708	0.9727	53175.86	0.0188	1.767
	Nano	0.7975	2174.57	1268.421	17.342	572.27	0.00191	1.00191	0.5844	0.9659	14344.77	0.0697	0.694
308.15	Bulk	0.7195	3424.78	1265.88	24.641	877.18	0.00148	1.00148	0.3701	0.9725	53453.04	1.870	1.771
	Nano	0.7195	2239.29	1279.74	16.111	599.648	0.00193	1.00193	0.5725	0.9659	15366.95	6.507	0.734
313.15	Bulk	0.6532	3582.43	1324.78	23.400	930.63	0.00150	1.0015	0.3703	0.9722	53415.21	1.872	1.769
	Nano	0.6532	2349.68	1345.57	15.348	639.077	0.00196	1.00196	0.5737	0.9656	15272.59	6.547	0.729

*Λ_o in (S cm².mol⁻¹), Λ_m in (S.cm².mol⁻¹) and ΔG_A in (kJ.mol⁻¹).

When fuchsin acid and bulk and nano CoSO₄ interact in water solvent, the K_A decreases as the temperature rises due to more complexation. We notice that temperature is inversely proportional to K_A but directly proportional to K_D for bulk and nano CoSO₄. Also K_A data in presence of ligand fuchsin acid is higher than K_A data in absence of ligand fuchsin acid due to more complexation reaction. With rising temperature association constant for bulk CoSO₄ with fuchsin acid is higher than association constant for nanoCoSO₄ with fuchsin acid but dissociation constant for bulk and nanoCoSO₄ increase with increasing temperature. Data of K_A for bulk CoSO₄ with ligand fuchsin acid is higher than K_A for nano CoSO₄ with the same ligand. Also data of K_D for bulk and nano CoSO₄ with ligand increase with rising temperature leading to accepted complexation process.

The dissociation constant for bulk and nano CoSO₄ increase with rise in temperature due to the increase in the dissociation degrees and more solvation but association and triple ion constants decrease with rise in temperature due to the migration of ions outside the association field.

Association thermodynamic parameters of bulk and nanoCoSO₄ in water in absence of fuchsin acid

The Gibbs of free energy change of association (ΔG_A) of different concentrations of bulk and nano in water were calculated [27] from the association constant (K_A) by using equation (15):

$$\Delta G_A = - 2.303 RT \log K_A \quad (15)$$

where R is the gas constant, T is the absolute temperature. The free energies change of transfer (ΔG_t) were calculated from (ΔG_A) values, from water (w) as a reference solvent using eqn. (16):

$$\Delta G_t = \Delta G_{A(s)} - \Delta G_{A(w)} \quad (16)$$

where $\Delta G_{A(s)}$ and $\Delta G_{A(w)}$ are the free energies of association in mixed solvents and in water, respectively.

The enthalpy change of association (ΔH_A) for bulk and nanoCoSO₄ was calculated for each type from the association constants by using Van't Hoff equation (17)

$$\frac{d \ln K}{dT} = \frac{\Delta H_A^\circ}{RT^2} \quad (17)$$

where R is the gas constant (8.314 J.mol⁻¹.K⁻¹) and T is the absolute temperature. By drawing the relation between log K_A and 1/T giving straight line with slope ($-\Delta H_A/2.303R$) as shown in (Figure 3(a)) for bulk and nano CoSO₄ in water solvent in absence of fuchsin acid.

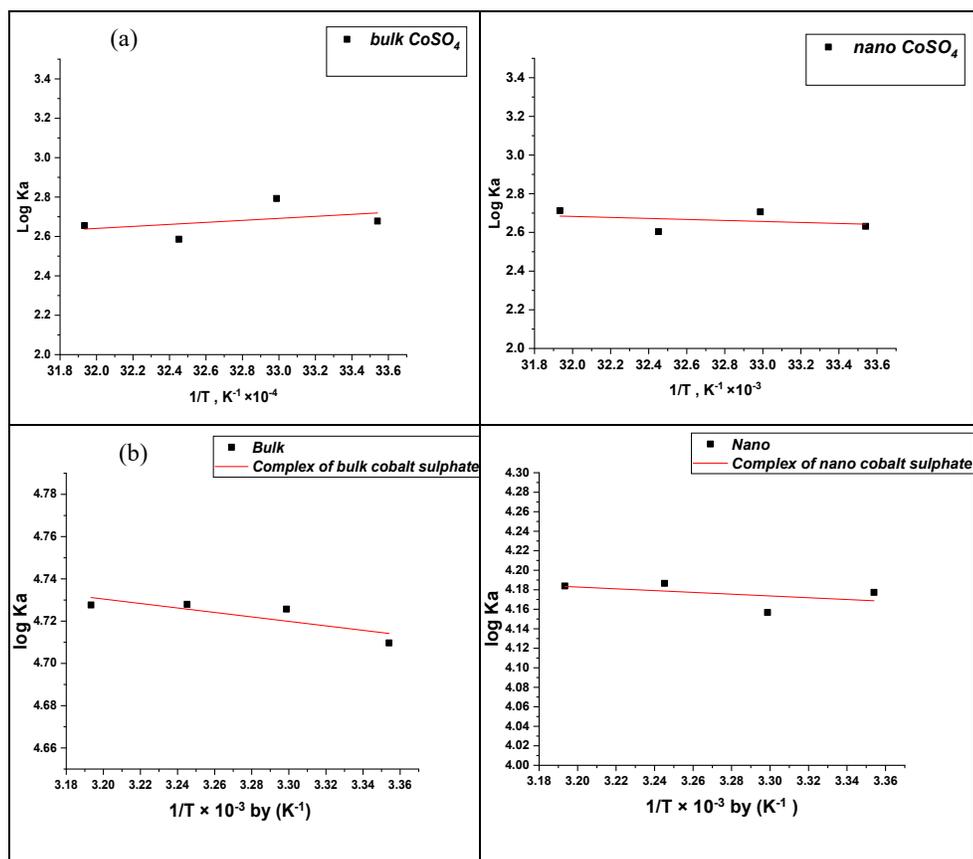


Figure 3. The relationship between Log K_A versus 1/T by kelven for bulk and nanoCoSO₄ in pure water solvent 9a) in lack of ligand fuchsin acid and (b) in the presence of fuchsin acid as a ligand.

When fuchsin acid and bulk and nano CoSO₄ interact in water solvent, the K_A decreases as the temperature rises due to more complexation. We notice that temperature is inversely proportional to K_A but directly proportional to K_D for bulk and nano CoSO₄. Also K_A data in presence of ligand fuchsin acid is higher than K_A data in absence of ligand fuchsin acid due to

more complexation reaction. With rising temperature association constant for bulk CoSO₄ with fuchsin acid is higher than association constant for nanoCoSO₄ with fuchsin acid but dissociation constant for bulk and nanoCoSO₄ increase with increasing temperature. Data of K_A for bulk CoSO₄ with ligand fuchsin acid is higher than K_A for nano CoSO₄ with the same ligand. Also data of K_D for bulk and nano CoSO₄ with ligand increase with rising temperature leading to accepted complexation process.

From Table 2 the association constant values for CoSO₄ in absence of fuchsin acid are decreasing with the rise of temperature giving more solvation but in the presence of fuchsin acid, the association constant K_A values for bulk CoSO₄ is greater than nano CoSO₄.

The entropies of association (ΔS_A) for the electrolytes were calculated by the use of Gibbs-Helmholtz equation (18)

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad (18)$$

The calculated values of (ΔG_A , E_a , ΔH_A and ΔS_A) are given in Table 3 for bulk and nano in water solvent in absence and in presence of fuchsin acid.

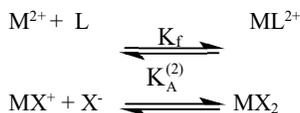
Table 3. Association thermodynamic parameters of bulk and nanoCoSO₄ in water solvent in absence and in presence of fuchsin acid.

T (K)	Salt type	ΔG_A (kJ.mol ⁻¹)	E_a (kJ.mol ⁻¹)	ΔH_A (kJ.mol ⁻¹)	$T\Delta S_A$ (kJ.mol ⁻¹ K)	ΔS_A (kJ.mol ⁻¹)
In absence of fuchsin acid						
298.15	Bulk	-15.287	3.325	-9.760	5.526	0.0185
	Nano	-15.023	0.407	4.978	20.002	0.0670
303.15	Bulk	-16.209	3.325	-9.760	6.448	0.0216
	Nano	-15.709	0.407	4.978	20.687	0.0693
308.15	Bulk	-15.258	3.325	-9.760	5.497	0.0178
	Nano	-15.364	0.407	4.978	20.342	0.0660
313.15	Bulk	-15.920	3.325	-9.760	6.159	0.0193
	Nano	-16.265	0.407	4.978	21.243	0.0667
In presence of fuchsin acid						
298.15	Bulk	-26.886	0	2.026	28.912	0.0969
	Nano	-23.847	0	1.7485	25.595	0.0858
303.15	Bulk	-27.430	0	2.0265	29.456	0.0971
	Nano	-24.127	0	1.748	25.875	0.0853
308.15	Bulk	-27.895	0	2.026	29.922	0.0971
	Nano	-24.701	0	1.748	26.450	0.0858
313.15	Bulk	-28.346	0	2.026	30.373	0.0969
	Nano	-25.086	0	1.748	26.834	0.0856

The activation energy of bulk CoSO₄ is less than activation energy of nano CoSO₄ so the complexation is favor in the case of nano CoSO₄ increase of temperature is followed by increasing in the Gibbs free energies of association ΔG_A for bulk and nano CoSO₄ alone giving good solvation process with decreasing entropies of that reaction since temperature is inversely proportional to entropy of the reaction.

The chelation of CoSO₄ with fuchsin acid, the formation constant and thermodynamic variables

The experimental data of (Λ_m) and (Λ_o) were analyzed for the determination of formation constants for each type of the stoichiometric complexes. The formation constants (K_f) for CoSO₄ complexes were calculated for each type of complexes (1:2) and (1:1) (M:L) [28, 29] by using the equations:



$$K_f = \frac{[\text{ML}]}{[\text{M}][\text{L}]} = \frac{\Lambda_{\text{M}} - \Lambda_{\text{obs}}}{(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]} \quad (19)$$

$$[\text{L}] = C_{\text{L}} - \left\{ C_{\text{M}} * \frac{\Lambda_{\text{M}} - \Lambda_{\text{obs}}}{(\Lambda_{\text{M}} - \Lambda_{\text{ML}})} \right\} \quad (20)$$

where Λ_{M} is the limiting molar conductance of the metal salt alone, Λ_{obs} is the molar conductance of solution during titration and Λ_{ML} is the molar conductance of the complex. The obtained values $\text{Log}(K_f)$ for the metal salt-ligand stoichiometric complexes are presented in Table 4 for bulk and nanoCoSO₄ in water solvent.

The relationship among Λ_{m} and the $[\text{M}]/[\text{L}]$ molar ratio for bulk and nano CoSO₄ in presence of fuchsin acid in H₂O solvent as shown in (Figure 4(a) and (b)).

Increasing temperature is followed by rise in the molar conductance and limiting conductance for both bulk and nano salt. All the molar conductances for bulk salt are greater than that of nano salt due to the thermodynamic mechanism which increases by increase the size of the molecules. The molar conductance for 1:2 complexes are greater than 1:1 complexes for bulk and nano salts at all the used temperatures.

The Gibbs free energies of formation for 1:1 and 1:2 (M:L) stoichiometry complex (ΔG_f) were calculated [30-35] by using the equation (21)

$$\Delta G_f = - 2.303 RT \log K_f \quad (21)$$

The enthalpy (ΔH_f) for the metal salt complexes were estimated for each type of complexes, (1:2) and (1:1) (M:L) by using van't Hoff equation:

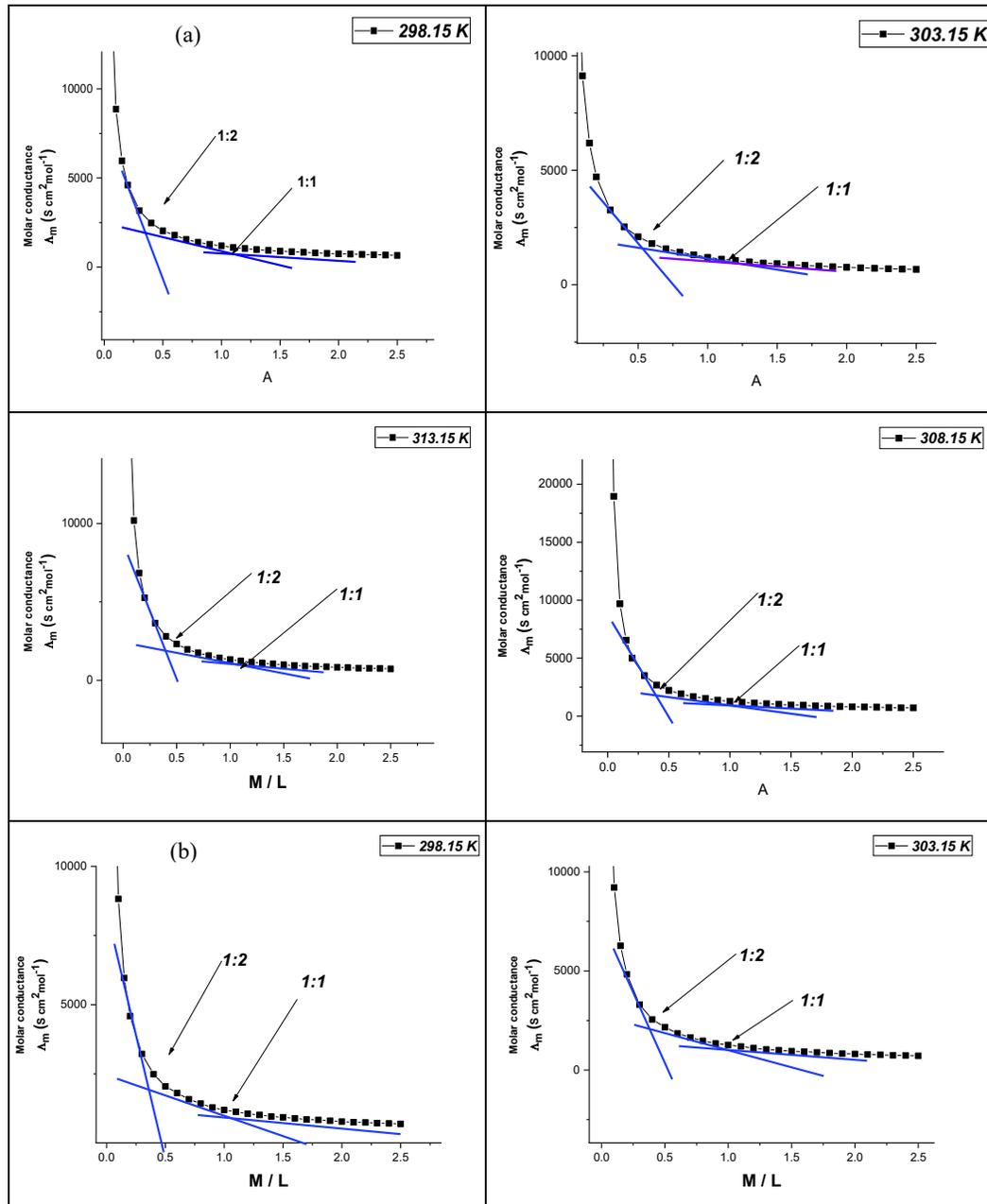
$$\frac{d \ln K_f}{dT} = \frac{\Delta H_f^0}{RT^2} \quad (22)$$

where R is the gas constant and T is the absolute temperature. By drawing the relationship among $\log K_f$ and $1/T$, various lines are obtained for the formation of 1:2 and 1:1 (M:L) stoichiometric complexes for CoSO₄ with fuchsin acid as shown in (Figure 5).

The slope of each line ($-\Delta H_f/2.303R$) can be used to determine H_f to every type of complex based on the relationship among $\log K_f$ and $1/T$. Using the formula:

$$\Delta G_f = \Delta H_f - T\Delta S_f \quad (23)$$

here (S) is the entropy of the solution, the entropy (S_f) for complexes was estimated to every type of complex (1:2) and (1:1) (M:L). And formation thermodynamic parameters (ΔS_f , ΔG_f , $T\Delta S_f$, ΔH_f) have been arranged in Table 5.



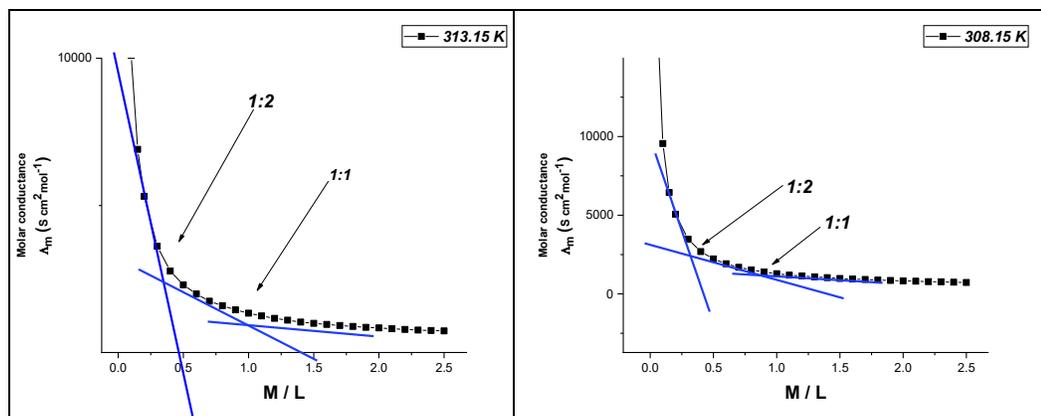


Figure 4. The relationship among Λ_m and the $[M]/[L]$ molar ratio for (a) bulk and (b) nano CoSO_4 in the presence of fuchsin acid in water solvent at various temperature 298.15, 303.15, 308.15, 313.15 K.

Table 4. Limiting molar conductance (Λ_0), formation constant (K_f), for bulk and nano CoSO_4 -fuchsin acid complex formation in water solvent at various temperatures.

T (K)	Salt type	M:L	$[L]_i \times 10^5$	$[M]_i \times 10^5$	Λ_m ($\text{S.cm}^2.\text{mol}^{-1}$)	Λ_{obs} ($\text{S.cm}^2.\text{mol}^{-1}$)	Log K_F
298.15	Bulk	1:2	9.52381	4.7619	3171.679	2034.774	4.265
		1:1	9.09091	9.09091	2034.774	1190.574	4.964
	Nano	1:2	9.52381	4.7619	3218.544	2050.209	4.289
		1:1	9.09091	9.09091	2050.209	1198.659	4.969
303.15	Bulk	1:2	9.52381	4.7619	3259.641	2095.191	4.259
		1:1	9.09091	9.09091	2095.191	1191.036	5.158
	Nano	1:2	9.52381	4.7619	3306.506	2163.546	4.203
		1:1	9.09091	9.09091	2163.546	1268.421	4.952
308.15	Bulk	1:2	9.52381	4.7619	3500.455	2216.025	4.309
		1:1	9.09091	9.09091	2216.025	1265.88	5.122
	Nano	1:2	9.52381	4.7619	3475.22	2224.845	4.272
		1:1	9.09091	9.09091	2224.845	1279.740	5.074
313.15	Bulk	1:2	9.52381	4.7619	3644.655	2317.455	4.294
		1:1	9.09091	9.09091	2317.455	1324.785	5.117
	Nano	1:2	9.52381	4.7619	3615.815	2306.430	4.284
		1:1	9.09091	9.09091	2306.43	1345.575	4.982

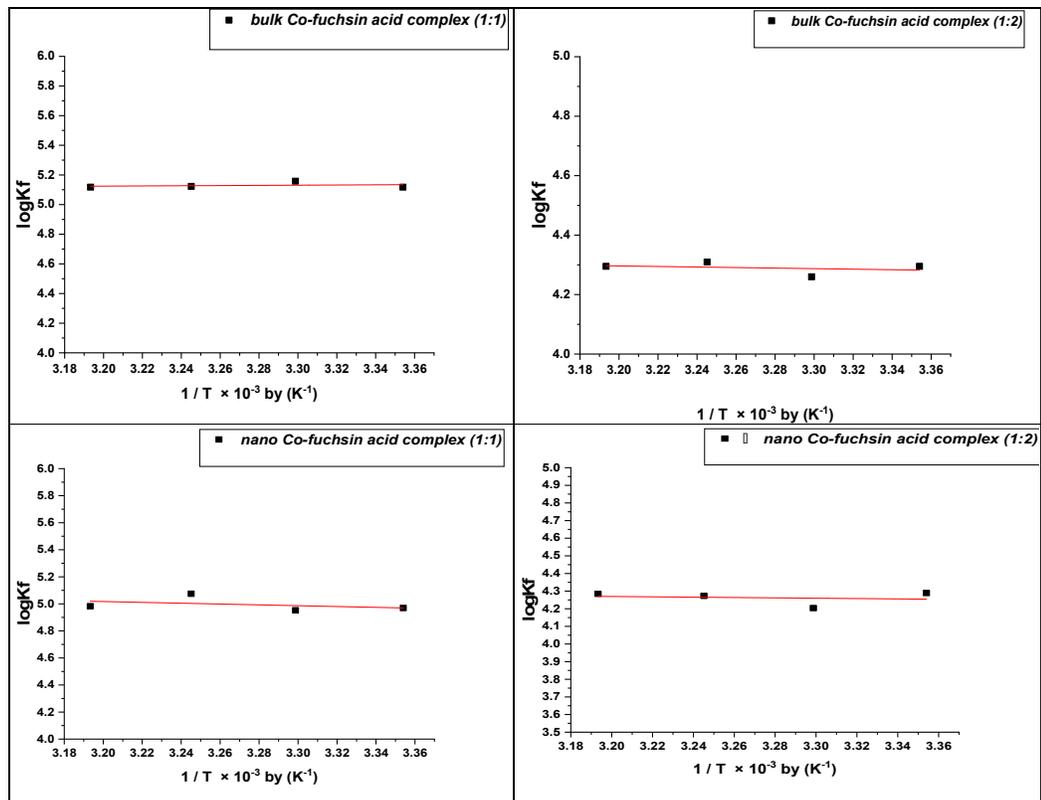


Figure 5. $\log K_f$ vs $1/T$ for bulk and nano Co-fuchsin acid complexes (1:1) and (1:2), respectively.

Table 5. Formation thermodynamic parameters for bulk and nano CoSO₄-fuchsin acid complex formation in H₂O solvent at various temperatures.

T (°K)	Salt type	M:L	ΔG_f (kJ.mol ⁻¹)	ΔH_f (kJ.mol ⁻¹)	T ΔS_f (kJ.mol ⁻¹)	ΔS_f (kJ.mol ⁻¹ .K ⁻¹)
298.15	Bulk	1:2	-24.353	1.741	26.094	0.0875
		1:1	-28.340	-1.205	27.135	0.0910
	Nano	1:2	-24.484	1.878	26.363	0.0884
		1:1	-28.368	5.888	34.257	0.1148
303.15	Bulk	1:2	-24.726	1.741	26.467	0.0873
		1:1	-29.940	-1.205	28.734	0.0947
	Nano	1:2	-24.399	1.878	26.278	0.0866
		1:1	-28.746	5.888	34.634	0.1142
308.15	Bulk	1:2	-25.425	1.741	27.167	0.0881
		1:1	-30.226	-1.205	29.020	0.0941
	Nano	1:2	-25.209	1.878	27.088	0.0879
		1:1	-29.942	5.888	35.831	0.1162
313.15	Bulk	1:2	-25.751	1.741	27.493	0.0877
		1:1	-30.685	-1.205	29.480	0.0941
	Nano	1:2	-25.689	1.878	27.568	0.0880
		1:1	-29.875	5.888	35.764	0.1142

All the complex formation data are larger in forming 1:1 complexes are greater than that of 1:2 indicating the case of formation of the first. All complex formation data increase with rise of temperature because of the increase in the kinetic energy. Also Gibbs free energy of complex formation for both lump and nano CoSO₄ with fuchsin acid increase with rising temperature leading to decreasing in entropy of that interaction and good complexation. All the entropy and enthalpy data reveal that the interaction depend on the enthalpy and entropy changes.

CONCLUSION

The conductance measurement method in water solvent was also used to determine complex thermodynamic parameters for bulk and nano-scale associations of CoSO₄ in the presence of fuchsin acid. From the conductometric data, it was observed that two stoichiometric complexes were obtained: 1:1 and 1:2 (CoSO₄:fuchsin acid) from the interaction of CoSO₄ with fuchsin acid. In the case of 1:1 as compared to 1:2, the complex thermodynamic formation parameters K_f and G_f are larger. (CoSO₄/fuchsin acid) complexes in water solvent for bulk and nano.

REFERENCES

1. Kelly, C.P.; Cramer, C.J.; Truhlar, D.G. A density functional theory continuum solvation model for calculating aqueous solvation free energies of neutrals, ions, and solute-water clusters. *J. Chem. Theory Comput.* **2005**, *1*, 1133-1152.
2. Yaffe, D.; Cohen, Y.; Espinosa, G.; Arenas, A.; Giralt, F. A Fuzzy ARTMAP-based quantitative structure-property relationship (QSPR) for the Henry's law constant of organic compounds. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 85-112.
3. Sanad, S.G. Thermodynamic parameters of solvation and volumes of nano Cu(NO₃)₂·2.5 H₂O in different concentrations of DMF-water mixed solvents. *J. Mol. Liq.* **2022**, *359*, 119354.
4. Hakimi, M.; Nezhadali, A.; Naemi, A. Conductometric study of complex formation between Cu(II) ion and 4-amino-3-ethyl-1,2,4-triazol-5-thione in binary ethanol/water mixtures. *E-J. Chem.* **2008**, *5*, 551-556.
5. Nezhadali, A.; Taslimi, G. Thermodynamic study of complex formation between 3,5-diiodo-hydroxy quinoline and Zn²⁺, Ni²⁺ and Co²⁺ cations in some binary solvents using a conductometric method. *Alex. Eng. J.* **2013**, *52*, 797-800.
6. Ding, R.; Lu, G.; Yan, Z.; Wilson, M. Recent advances in the preparation and utilization of carbon nanotubes for hydrogen storage. *J. Nanosci. Nanotechnol.* **2001**, *1*, 7-29.
7. Schröer, W.; Weingärtner, H. Structure and criticality of ionic fluids. *Pure Appl. Chem.* **2004**, *76*, 19-27.
8. Gray, J.R. *Conductivity Analyzers and Their Application in Environmental Instrumentation and Analysis Handbook*, John Wiley and Sons, Inc.: New York; **2005**; pp. 491-510.
9. Fainerman-Melnikova, M.; Nezhadali, A.; Rounaghi, G.; McMurtrie, J. C.; Kim, J.; Gloe, K.; Langer, M.; Lee, S.S.; Lindoy, L.F.; Nishimura, T.; Park, K.-M.; Seo, J. Metal ion recognition via 'selective detuning'. The interaction of selected transition and post-transition metal ions with a mono-N-benzylated O2N3-donor macrocycle and its xylyl-bridged ring analogue. *Dalton Trans.* **2004**, *1*, 122-128.
10. Glasson, C.R.K.; Lindoy, L.F.; Meehan, G.V. Recent developments in the d-block metallo-supramolecular chemistry of polypyridyls. *Coord. Chem. Rev.* **2008**, *252*, 940-963.
11. Nezhadali, A.; Rabani, N. Competitive bulk liquid membrane transport of Co(II), Ni(II), Zn(II), Cd(II), Ag(I), Cu(II) and Mn(II), cations using 2,2'-dithio(bis)benzothiazole as carrier. *Chin. Chem. Lett.* **2011**, *22*, 88-92.
12. Sheela, A.; Vijayaraghavan, R. Synthesis, spectral characterization, and antidiabetic study of new furan-based vanadium(IV) complexes. *J. Coord. Chem.* **2011**, *64*, 511-524.

13. Wei, Y.; Chan, C.C.; Tian, J.; Jang, G.W.; Hsueh, K.F. Electrochemical polymerization of thiophenes in the presence of bithiophene or terthiophene: kinetics and mechanism of the polymerization. *Chem. Mater.* **1991**, *3*, 888-897.
14. Xie, M.; Gao, L.; Li, L.; Liu, W.; Yan, S. A new orally active antidiabetic vanadyl complex-bis (α -furancarboxylato) oxovanadium(IV). *J. Inorg. Biochem.* **2005**, *99*, 546-551.
15. Wang, J.; Sun, X. Understanding and recent development of carbon coating on LiFePO₄ cathode materials for lithium-ion batteries. *Energy Environ. Sci.* **2012**, *5*, 5163-5185.
16. Khedr, A.K.; Zaky, R.R.; Gomaa, E.A.; Abd El-Hady, M.N. Elucidation for coordination features of N-(benzothiazol-2-yl)-3-oxo-3-(2-(3-phenylallylidene)hydrazineyl) propanamide on Co²⁺, Ni²⁺ and Cu²⁺: Structural description, DFT geometry optimization, cyclic voltammetry and biological inspection. *J. Mol. Liq.*, **2022**, *368*, 120613.
17. Morsi, M.A.; Gomaa, E.A.; Nageeb, A.S. Thermodynamic data (voltammetrically) estimated for the interaction of nano cadmium chloride (Ncc) with isatin using glassy carbon electrode. *Asian J. Nano. Mater.* **2018**, *1*, 282-293.
18. Gomaa, E.A.; Killa, H.A.; Fathi, H.; Farouk, A. Solvation data for the redox interaction between nano cobalt sulfate (NCS) and fuchsin acid (FA) using doped nano composite+ multicarbon nanotubes glassy carbon electrode at different temperatures. *Res. Square Platform LLC* **2021**, 1-16.
19. Salem, S.E.; Gomaa, E.A.; El-Defrawy, M.M.; Ebrahim, N.M. Studies on the complexation of succinic hydrazide with copper chloride salt. *Eur. J. Adv. Chem. Res.* **2021**, *2*, 14-20.
20. Abou Elleef, E.M.; Abd El-Hady, M.N.; Gomaa, E.A.; Al-Harazie, A.G. Conductometric association parameters for CdBr₂ in the presence and absence of Ceftazidime in water and 30% ethanol-water mixtures. *J. Chem. Eng. Data* **2021**, *66*, 878-889.
21. Ibrahim, K.M.; Gomaa, E.A.; Zaki, R.R.; Abd. El-Hadi, M.N. The association and complex formation constants for CuSO₄, NiSO₄ stoichiometric complexes with (E)-N'-(2-hydroxy-3H-indol-3-ylidene)-3-oxo-3-(thiazol-2-ylamino) propanehydrazide in ethanol solutions at 294.15 K. *AASCIT Communications* **2016**, *3*, 194-201.
22. Gomaa, E.A.; Mousa, M.A.; Zaky, R.R.; Rashad R.T. Association thermodynamic parameters (conductometrically) for nano cobalt sulfate in mixed EtOH-H₂O solvents at different temperatures. *Int. J. Eng. Sci. Res. Technol.* **2014**, *3*, 333-343.
23. Gomaa, E.A.; El Askalany, A.H.; Ibrahim, K.M.; Galal, R.M.; Hamada, M.A. Thermodynamic interaction parameters for bulk and nano copper acetate, CuAc with (CPB)* in mixed acetone (Ac)-H₂O solvents. *Am. Assoc. Sci. Technol.* **2015**, *2*, 85-92.
24. Helmy, E.T.; Gomaa, E.A.; Abou Elleef, E.M. Complexation of 2-mercaptoimidazol with some barium salts conductometrically in various solvents at different temperatures. *Int. J. Mod. Chem.* **2015**, *7*, 141-155.
25. Helmy, E.T.; Gomaa, E.A.; Abou Elleef, E.M. Gibbs free energy and activation free energy of complexation of some divalent cations with ampicillin in methanol at different temperatures. *Am. J. Appl. Chem.* **2016**, *4*, 256-259.
26. Gomaa, E.A.; El Askalany, A.H.; Ibrahim, K.M.; Galal, R.M.; Hamada, M.A. Thermodynamic interaction parameters for bulk and nano calcium acetate (Cac) with N-bezylidene-4-chlorobenzo-hydrazide (LB) in mixed EtOH-H₂O solvents. *Am. J. Mater. Res.* **2015**, *2*, 1-11.
27. Gomaa, E.A.; Galal, R.M. Molar solubility, solvation and conductivity association parameters of sodium fluoride in mixed aqueous-ethanol solvents at different temperatures. *Basic Sci. Med.* **2012**, *1*, 1-5.
28. Gomaa, E.A. Molal solubility, dissociation, association and solvation parameters for saturated benzoic acid solutions in various solvents at 298.15 K. *Phys. Chem. Liq.* **2012**, *50*, 279-283.
29. Gomaa, E.A. Gibbs free energies, enthalpies and entropies of transfer for reference ions Ph₄As⁺ and Ph₄B⁺ in mixed DMFA-H₂O solvents at different temperatures. *Am. J. Environ. Eng.* **2012**, *2*, 54-57.

30. Gomaa, E.A.; Abou Elleef, E.M. Thermodynamics of the solvation of potassium thiocyanate in mixed EtOH-H₂O solvents at 301.15 K. *Sci. Technol.* **2013**, *3*, 118-122.
31. Gomaa, E.A.; Abou Elleef, E.M.; Abdel-Razek, M.G. Thermodynamics of the solvation of CaSO₄ in mixed DMF-H₂O at 301.15 K. *Int. Res. J. Pure Appl. Chem.* **2013**, *3*, 320-325.
32. Gomaa, E.A.; Al-Jahdali, B.A. Conductometric studies of calcium ions with kryptofix 221 in mixed MeOH-DMF solvents at different temperatures. *Education* **2012**, *2*, 37-40.
33. Gomaa, E.A. Molal solubility, dissociation, association and solvation parameters for saturated phenylalanine solutions in various solvents at 298.15 K. *Am. J. Biochem.* **2012**, *2*, 25-28.
34. Gomaa, E.A. Molal solubility, dissociation, association and solvation parameters for saturated O-chlorobenzoic acid solutions in various solvents at 298.15 K. *Food Public Health* **2012**, *2*, 65-68.
35. Gomaa, E.A. The macroscopic and microscopic free energies of solvation of silver chromate and silver phosphate in some organic solvents at 298.15 K. *Front. Sci.* **2012**, *2*, 24-28.