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Full Paper

Ionic association and thermodynamic functions for solvation interaction of nano copper sulfate (NCS) with methyl red (MR) in mixed methanol (MeOH) –Water solvents

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Abstract

Specific conductivities for nano copper sulfate (NCS) have been measured in binary mixed solvent-solvent with methyl alcohol (MeOH) mass fraction 0%, 20% and 40% (W/W) (MeOH-H_2O) at different temperatures: 298.15, 303.15 ,308.15 and 313.15 K (with a step of 5 K) and in the presence of methyl red indicator (MR) as chelating agent. The experimental data have been analyzed by the use of Fuoss-Shedlovsky conductivity model (FSH) equation. Molar conductance (Λ_m), limiting molar conductance (Λ_0) , Walden product ($\Lambda_0 \eta_0$), ion-pair association constant (K_A) and the standard thermodynamic parameters for the association ($\Delta G°_A$, $\Delta H°_A$ and $\Delta S°_A$) were estimated and discussed in absence and in presence of methyl red (MR). All the thermodynamic parameters were evaluated for the interaction of nano copper sulfate (NCS) with methyl red (MR).The ion pair association constant (K_A) and the different thermodynamic functions were increased by increasing the percentage of methanol by molar mass and increase of temperature favoring more ion - solvent interactions between nano copper sulfate (NCS) and methyl red (MR). The effect of formation of hydrogen bond (FHB) in solution also has been studied. The obtained results show that the association constant (K_A) was increased as the relative bulk permittivity of the solvent decreased while the molar conductance (Λ_m) and the limiting molar conductivities (Λ_0) were decreased. Furthermore, as the temperature increased, the association constant (K_A) values were increased indicating the association process is endothermic.

Keywords: Molar conductance (Λ_m), ion-pair association constant (K_A), Binary mixed solvents. Permittivity of the solvent , Thermodynamic parameters, Fuoss-Shedlovsky model (FSH), Methyl red (MR).

1. Introduction

Nanoparticles are valuable for medicine industry and environment, because of their increased specific behaviors. The increasing in the physical properties of nanomaterials (NM) are due to their high surface area (SA) and small volume (V), makes them very reactive, catalytic and able to pass through cell membranes and tissues. Copper sulphate is used in the treatment of some bacteria, algae, fungus and some fish parasites such as Itch. It can also be used to kill snails, accidentally or on purpose. The disadvantage of copper sulphate is that it is toxic in water and slightly alkaline solutions [1, 2]. Studies of the association phenomena through the use of conductivity technique (CT) can result in investigation the factors affecting the thermodynamic and kinetic stability of the used salt. Thus in this study, it was attempted to obtain good information about the association at different temperatures (298.15, 303.15, 308.15 and 313.15K) using conductometric measure-ments. The limiting molar conductance (Λ_o) and association constants of nano copper sulfate (NCS) in mixed solutions were driven by analyzing conductivity data through Fuoss- Shedlovsky (FSH) model equation [3-10]. Thermodynamic functions (ΔH^o,ΔG^o, ΔS^o) were calculated and compared based on the interaction of solvent at the used specific temperature. The nature of the association process is complicated by strong hydration of the free ions and Fuoss–Shedlovsky (FSH) conductivity method has been successfully used for discussing this property.

2. Experimental

Chemicals

Bidistilled water was used in the preparation of mixed solvent with a specific conductivity of 0.09 μS cm^{-1} at 298.15 K. (MeOH 99.9%), copper sulfate ($CuSO_4.5H_2O$) pentahydrate (99.9%) from El Nasr Company, methyl red (MR) from Riedel-de Haën Company (Germany) were used without further purification. Nano $CuSO_4$ (NCuS) was prepared by balling using Retsch MM 2000 swing mill with 10 cm^3 stainless steel double walled tube. Two balls stainless steel with diameter of 12 mm were used. Ball milling was performed at 20225Hz and shaking was done for one hour not rise in temperature was allowed. Methyl Red (MR):Structure and calculated using theoretical quantum calculation by Gaussian 09 programmed in gases state and the counter lines of its structure are given below Fig.1 and its properties given in Table 1.

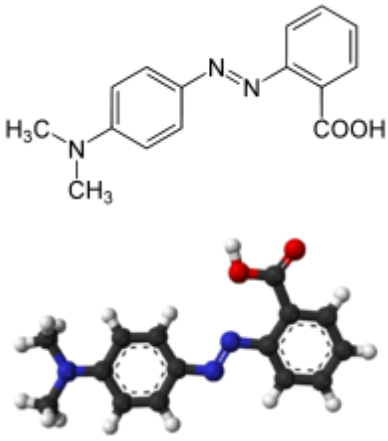

Fig. 1 Structure of Methyl red (MR)

Table 1 Properties of Methyl red (MR)

IUPAC name	2-{[4 (Dimethyl amino)phenyl]diazenyl}benzoic acid
Chemical formula	$C_{15}H_{15}N_3O_2$
Molar mass	269.30 g·mol^{-1}
Density	0.791 g/cm^3

Table 2 Theoretical quantum calculations of Methyl red (MR)

Calculation Type	SP
Calculation Method	RB3LYP
Basis Set	6-311G
Charge	0
Spin	Singlet
Total Energy	-895.04009626 a. u.
RMS Gradient Norm	-0.00000000 a. u.
Dipole Moment	4.0316 Debye

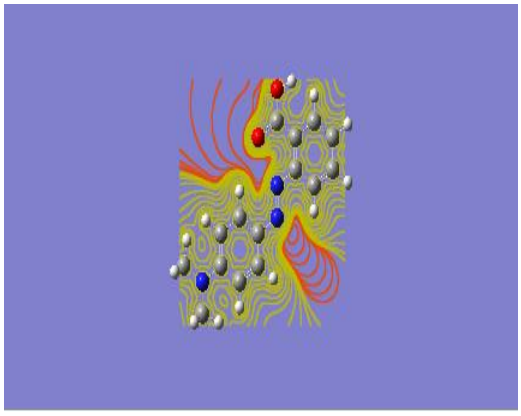

Fig. 2 Gaussian 09 calculated properties of methyl red (MR).

Conductivity measurements of mixed solvents

The binary mixed solvents of (MeOH-H_2O) with the methanol mass fractions of 20%, and 40% were chosen to be the solvent media for the present study and were prepared by mixing required volume of methanol (MeOH) and water (with error ± 0.02%) by applying equation (1).

The physical properties, relative bulk permittivity (ε), absolute density (ρ) and absolute viscosity (η^o) of (MeOH - water) with the MeOH mass fractions of 0 %, 20%, and 40% at temperatures from 298.15 to 313.15 K were obtained from previous literature data [11-13]. 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. The solutions of nano copper sulfate (NCS) and methyl red (MR) were prepared by mass (Mettler AE 200 balance with a sensitivity of ± 0.0001 g) with a concentration range (1 x 10^{-3} – 7.1 x 10^{-4} mol.dm^{-3}) and (1 x 10^{-4} –8.3 x10^{-5} mol.dm^{-3}) respectively, which were prepared by taking certain volume of the salt standard solution and diluted to the required volume for the measurements by using a (JENCO – 3173 COND) bridge (USA) with a cell constant value 1 cm^{-1} of ±0.12 S cm^{-1}. (Accuracy ± 0.01%) of a cell constant value 1±10% cm^{-1}. The cell constant was determined with potassium chloride solutions. MLW 3230 (Germany) ultra-thermostat was connected to the Conductivity Bridge.

3. Results and discussion

3.1 TEM Images for nano $CuSO_4$

The photogram from transmission electron microscope (TEM) is presented for nano $CuSO_4$ salt (NCS). The image in Fig. 3 showed that the nano $CuSO_4$ (NCS) is in the form of irregular spheres or deformed spheres; the image shows also crystalline form. The boundaries were hardly seen due to its dissolution and the size ranging from 20-40 nm.

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

Where d_1 and d_2 are the densities of methanol (MeOH) and water respectively. V_1 is the volume of methanol which will be added to the volume V_2 of water to get the mixture of the required percentage.

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

Solvent	T/K	ε	ρ/g cm^{-3}	η/mPa s
0% (MeOH-H_2O)	298.15	78.3	0.9970	0.8904
	303.15	76.51	0.9942	0.7975
	308.15	74.76	0.9912	0.7194
	313.15	73.05	0.9880	0.6529
20% (MeOH-H_2O)	298.15	73.74	0.9761	0.8556
	303.15	71.84	0.9732	0.7688
	308.15	69.94	0.9700	0.6641
	313.15	68.05	0.9680	0.5715
40% (MeOH-H_2O)	298.15	67.88	0.9492	0.8086
	303.15	66.09	0.9461	0.7286
	308.15	64.33	0.9428	0.6334
	313.15	62.57	0.9380	0.5476

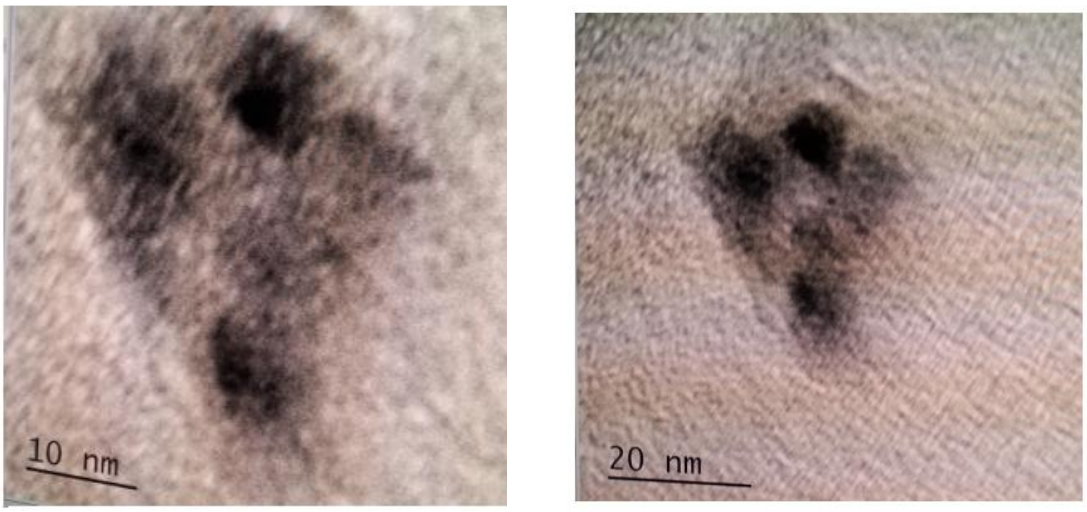

Fig. 3 : Tem images of nano CuSO4 (NCS)

3.2 Estimation the limiting molar conductance

The specific conductance (Ks, μS cm^{-1}) of prepared solutions of the salt in binary mixed solvents of (MeOH – H_2O) with methanol mass fractions of 0%, 20%, and 40% at different temperatures was measured in absence and in presence of methyl red (MR). The molar conductance (Λ_m) for $CuSO_4$ solutions in binary mixed solvents at different temperatures was calculated by applying the use of Eq. (2) and tabulated in Table 4. The experimental conductance data (ED) were analyzed by using Fuoss- Shedlovsky Conductivity model equation (FSH) for $CuSO_4$ in absence and in presence of methyl red (MR) and the limiting molar conductance (Λ_o) were estimated in (MeOH-H_2O) mixed solvents at different temperatures by extrapolating the linear Onsager plot [14] between (Λ_m) and $(C)^{½}$ as shown in Fig. 4 at 298.15 K as example . Applying equations 3-12 the association constant,dissociation degrees (α) and other Fuoss – Shedlovsky (FSH) parameters Z, S(Z) were evaluated and presented in Tables 4 and 5.

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

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.

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

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

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

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

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

$$a = 82 \times 10^4 / (\varepsilon T)^{3/2} \quad (7)$$

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

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 evaluated and 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:

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

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

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

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

$$A = 1.824 \text{ X } 10^{6} (\varepsilon T)^{-3/2} \quad (11)$$

$$B = 50.29 \text{ X } 10^{8} (\varepsilon T)^{-1/2} \quad (12)$$

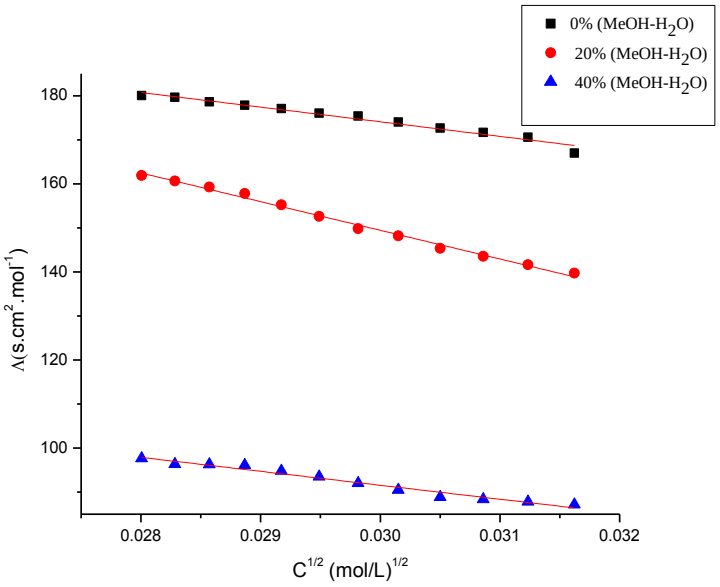

Fig. 4 The plot of (Λ) versus ($C^{1/2}$) at 298.15 K in mixed (MeOH–H_2O) solvents for nano copper sulphate (NCS).

Table 4 The limiting molar conductance (Λ_o, ±0.20%, S cm^2 mol^{-1}) and Fuoss–Shedlovsky parameters of nano copper sulphate (NCS) in the used mixture solvents at the used different temperatures.

Solvent	T/K	Λ_o	S	Z	S(Z)	A	γ±	α
0% (MeOH-H_2O)	298.15	265	123.362	0.0111	1.0111	0.5113	0.8895	0.6170
	303.15	326	143.787	0.0100	1.0100	0.5184	0.8966	0.5223
	308.15	380	167.747	0.0093	1.0093	0.5265	0.9020	0.4514
	313.15	355	93.177	0.0050	1.0050	0.5347	0.9011	0.4465
20% (MeOH-H_2O)	298.15	344	151.680	0.0088	1.0088	0.5595	0.9010	0.4087
	303.15	352	162.715	0.0092	1.0093	0.5677	0.8997	0.4081
	308.15	379	182.793	0.0094	1.0094	0.5766	0.9008	0.3869
	313.15	383	101.049	0.0051	1.0052	0.5863	0.8989	0.3894
40% (MeOH-H_2O)	298.15	186	124.769	0.0144	1.0145	0.6333	0.8807	0.4740
	303.15	194	136.260	0.0151	1.0152	0.6437	0.8787	0.4751
	308.15	214	155.454	0.0150	1.0151	0.6539	0.8818	0.4355
	313.15	216	64.7784	0.0063	1.0063	0.6650	0.8776	0.4538

Table 5: The limiting molar conductance (Λ_o, ±0.20%, S cm^2 mol^{-1}) and Fuoss–Shedlovsky parameters of nano copper sulphate (NCS) in presence of ligand (Methyl red) in the used different mixture solvents at the used different temperatures.

Solvent	T/K	Λ_o	S	Z	S(Z)	A	γ±	α
0% (MeOH-H_2O)	298.15	550	187.001	0.0038	1.0038	0.5113	0.9482	0.5196
	303.15	598	207.250	0.0039	1.0039	0.5184	0.9470	0.5284
	308.15	625	225.879	0.0039	1.0039	0.5265	0.948	0.5249
	313.15	702	168.944	0.0025	1.0025	0.5347	0.97	0.4939
20% (MeOH-H_2O)	298.15	450	178.175	0.0043	1.0044	0.5595	0.9443	0.5356
	303.15	459	189.902	0.0047	1.0047	0.5677	0.9420	0.5638
	308.15	504	215.334	0.0040	1.0047	0.5766	0.9422	0.5435
	313.15	597	157.456	0.0027	1.0027	0.5863	0.9453	0.4682
40% (MeOH-H_2O)	298.15	293	155.261	0.0058	1.0058	0.6333	0.937	0.5312
	303.15	317	171.921	0.0059	1.0059	0.6437	0.9369	0.5224
	308.15	341	192.953	0.0063	1.0063	0.6539	0.9340	0.5547
	313.15	437	130.848	0.0030	1.0030	0.6650	0.9401	0.4399

It is evident from Table 4 and 5 that the values of Λ_o increase regularly with increase in temperature for nano copper sulphate (NCS), indicating higher mobility of the ions in all solvent systems studied. This is due to the fact that the increased thermal energy (TE) results in greater bond breaking (BB) and also variation in vibrational, rotational and translational energy of molecules giving higher frequency and higher mobility of ions. With the rise of temperature the viscosity of the solvent also decreases which makes the ions to move freely towards the electrode [15].

3.3 Ion-pair association constant

The values of the ion-pair association constant (KA) were represented in Table 6. It is clear that the association constant (KA) values increase with an increase in temperature which indicates an endo-thermic association process. Also this temperature dependence of the association process of ions can be explained on the basis of the interplay between dehydration and association of ions .Whereas the temperature increases, the dehydration and/or desolvation process of ions take place, then the ions will have short distance of contact, therefore the association of ions increases [16-18] . It was found through conductometric data analysis that copper sulfate showed more association or ion pair formation increase as the proportions of organic solvent increase in the mixtures, the mobility of ions are decreased, giving a chance for ions for association. This increasing in association constant values may interpret on the basis of the interplay between association constant and strength of the ion solvation in different solvents, whereas the solvation of the ions is sronge the association between cations

and anions is weak. The values of ion-pair association constant (K_A) for nano copper sulphate (NCS) in presence of methyl red (MR) was found to be higher than values of ion-pair association constant (K_A) for nano copper sulfate (NCS) in absence of MR and this give indication about favoring more interaction between nano copper sulfate (NCS) and methyl red due to the complex formation. Also, the presence of methyl red (MR) in solution make hindrance to copper sulfate ions, reduce its mobility in solution and give chance for the association. This explanation was confirmed by theoretical calculation for methyl red, which has a high dipole moment (4.0316 Debye).

3.4 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 7 and 8.

$$\Delta G^\circ_A = - RT \ln K_A \qquad (13)$$

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) as in Fig. 5, 6 and 7, 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. (14).

$$\Delta G^\circ_A = \Delta H^\circ_A - T\Delta S^\circ_A \qquad (14)$$

The thermodynamic parameters of association values showed the effect of temperature from increasing in the negative values (-ve) of the associating free energy (ΔG°_A) as the temperature rise from 298.15 to 313.15 K. It was found that the association processes in all studied systems are spontaneous processes and the associating free energy becomes more negative by increasing temperature. This indicates that ion-pair association is favored with lowering of dielectric constant (ε) of the medium. By comparing the associating free energy in absence and in presence of methyl red, we found the associating free energy in presence of methyl red (MR) has greater values than in case of absence of methyl red (MR) and this indicating the interaction occurs between methyl red and nano copper sulfate (NCS).

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 disorder and the positive (ΔH°_A) and (ΔS°_A) values are in a good agreement with several theories in many solvents [19- 22].

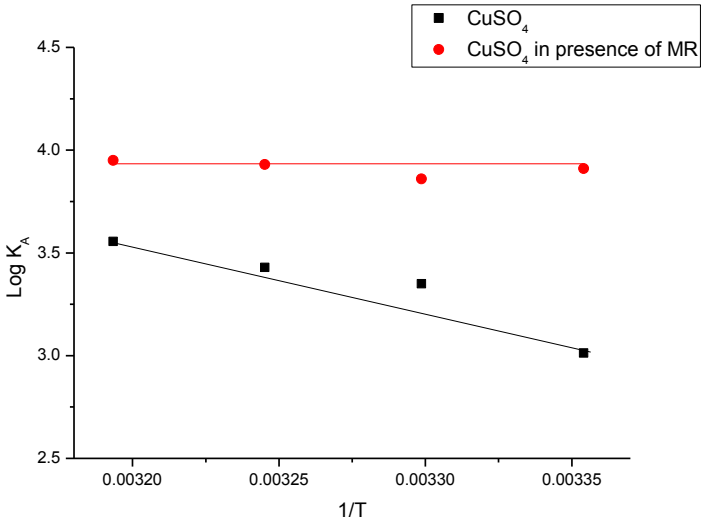

Fig. 5 Relation of (log k_A) vs. (1/T) in water for nano copper sulfate (NCS) in absence and in presence of MR.

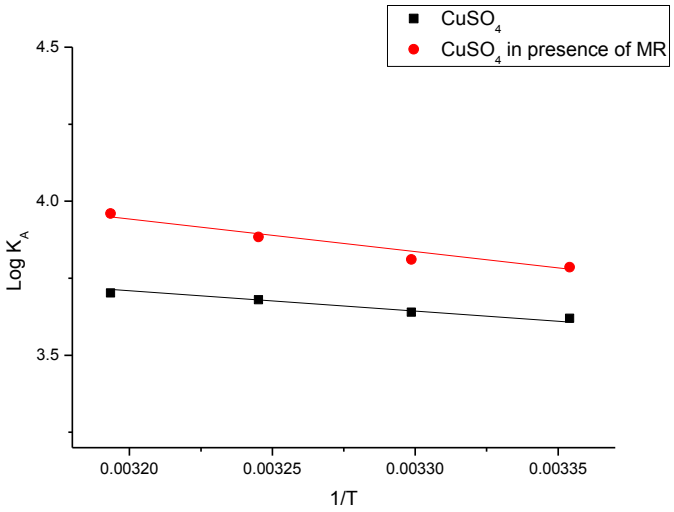

Fig. 6 Relation of (log k_A) vs. (1/T) in 20% (MeOH-H_2O) for nano copper sulfate (NCS) in absence and in presence of MR.

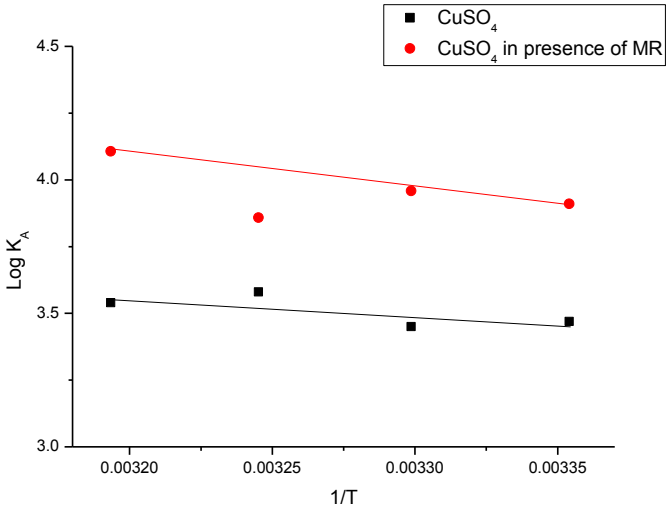

Fig. 7 Relation of (log k_A) vs. (1/T) in 40% (MeOH-H_2O) for nano copper sulfate (NCS) in absence and in presence of MR.

Table 7: The thermodynamic parameters of association (ΔG°_{A}, ±0.33%), (ΔH°_{A} ±0.22%) and (ΔS°_{A} ±7.42%) for nano copper sulfate (NCS) in used solvents at different temperatures.

Solvent	T/K	ΔH°_{A}	ΔG°_{A}	ΔS°_{A}
		(KJ.mol^{-1})	(KJ.mol^{-1})	(J.mol^{-1})
0% (MeOH-H_2O)	298.15	61.7970	-17.7200	266.701
	303.15		-19.3757	267.764
	308.15		-20.7654	267.929
	313.15		-21.1875	264.999
20% (MeOH-H_2O)	298.15	8.4126	-20.7757	97.8970
	303.15		-21.1422	97.4923
	308.15		-21.8484	98.2024
	313.15		-22.1696	97.6599
40% (MeOH-H_2O)	298.15	9.8889	-19.8646	99.7938
	303.15		-20.1918	99.227
	308.15		-21.1382	100.688
	313.15		-21.2063	99.2981

Table 8: The thermodynamic parameters of association (ΔG°_{A}, ±0.33%), (ΔH°_{A} ±0.22%) and (ΔS°_{A} ±7.42%) for nano copper sulphate (NCS) in presence of ligand (Methyl red) in used solvents at different temperatures.

Solvent	T/K	ΔH°_{A}	ΔG°_{A}	ΔS°_{A}
		(KJ.mol^{-1})	(KJ.mol^{-1})	(J.mol^{-1})
0% (MeOH-H_2O)	298.15	10.9952	-22.3016	111.6782
	303.15		-22.5511	110.6593
	308.15		-23.1241	110.7231
	313.15		-23.97688	111.678
20% (MeOH-H_2O)	298.15	20.2166	-22.2389	142.3964
	303.15		-22.2073	139.9437
	308.15		-22.8745	139.8382
	313.15		-24.40325	142.487
40% (MeOH-H_2O)	298.15	22.3475	-22.3397	149.8818
	303.15		-22.8479	149.0862
	308.15		-22.7509	146.3525
	313.15		-24.89119	150.8500

4. Conclusions

In this paper, it was concluded that the association constant for nano copper sulfate(NCS) in presence of methyl red (MR) has greater values than that in case of absence of methyl red (MR) in all mixed solvents used and in all temperatures indicating and favoring more interaction between nano copper sulfate (NCS) and methyl red (MR). The presence of methyl red in solution facilitates the association of ions due to its high value of dipole moment. The conductivity data have been analyzed using Fuoss-Shedlovsky (FSH) model equation. The association degrees for nano coppers sulfate decreased on adding methyl red to the mixed solvents indicating less dissociation of the salt in presence of the ligand favoring more complexation ability. The increase in association constants for nano copper sulfate with adding methyl red are due to the complex reaction between the two in mixed used solvents. 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}) indicates that the association process is endothermic.

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