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Association thermodynamic parameters for nano Cu(NO$_3$)$_2$·2.5H$_2$O with ligands at different temperatures

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Association thermodynamic parameters are important because they give information about the nature of ion–ion interaction in solution, the dielectric constant of the medium and the intermolecular hydrogen bonding between the solvent molecules. The different association thermodynamic parameters for nano copper(II) nitrate hemi pentahydrate in the presence of 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol as ligands were calculated. Conductance measurements were used in different concentrations of binary mixed solvents (DMF and water) at different temperatures, 293.15, 303.15, 313.15 and 323.15 K. A comparison between association thermodynamic parameter data such as association constants (K_A), degree of dissociation (α), free energies of association (ΔG_A), enthalpies of association (ΔH_A) and entropies of association (ΔS_A) in the case of using the two ligands was done. Different calculated thermodynamic parameters indicate that the association is more favorable with 4,6-diacetylresorcinol as a ligand than 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol due to the large size of 6-bis(1-hydrazonoethyl)benzene-1,3-diol.

1. Introduction

The study of thermodynamic parameters is very important to know information about the intermolecular interactions and geometrical effects in the systems, thermo-physical and bulk properties of solutions. Also, study of thermodynamic parameters is necessary in theoretical and applied areas of research and very useful in many other fields of industry.[1] In addition, thermodynamics parameters have been utilized to get vital information about spontaneity of a given process at a particular temperature.[2,3]

Studying information about transport properties such as association, conductance and ionic mobility of electrolytes in aqueous and partially aqueous media tells us all about ion–ion and ion–solvent interactions in these solutions.[4–9] Fuoss–Shedlovsky equation is one of the mathematic equations of conductivity theories, which have been used successfully to investigate many electrolytes in solutions. The physical properties of the binary mixed solvents can be varied over a wide range making them a favorite solvent system for the study of ion association and ion mobility.[10–13]

Research on ions and ionic interactions in solution has become a leading scientific direction. Fundamental studies on ionic species in the liquid phase promote new conceptual development of ionic drugs. Application of ionic liquids in

pharmacy and biochemistry is a rapidly developing multidisciplinary area.[14]

Copper(II) salts have many uses in organic synthesis as catalysts, mediators or oxidants. Compared with some noble metals such as rhodium, gold or palladium, copper(II) reagents have emerged as efficient and competitive promoters.[15–19]

Copper(II) nitrate hemi pentahydrate is one of the most common copper(II) salts. It presents as a blue crystalline solid, with features such as low toxicity, inexpensiveness, commercial availability and operational easiness. Copper(II) nitrate hemi pentahydrate has five different hydrates structures and the most common one is trihydrate form.[20–22]

Copper(II) nitrate hemi pentahydrate has a variety of important applications, the main one being its conversion to copper(II) oxide, which is used as catalyst in many reactions in organic chemistry. Copper(II) nitrate hemi pentahydrate solution is used in textiles and polishing agents for other metals. It is also found in some pyrotechnics. It is often used in school laboratories to demonstrate chemical voltaic cell reactions. Finally, it is a component in some ceramic glazes and metal patinas.[23–26]

4,6-Diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol (Schemes 1 and 2) have been used as bis(bidentate) ligands towards transition metal ions (VO(IV),[27] Co(II),[28] Ni(II),[29] Cu(II)[28,29] and Ru(II)[30]), alkaline earth metal ions (Mg(II), Ca(II), Sr(II) and Ba(II)[31]) in addition to Ce(III) and UO$_2$(VI) ions.[27] In addition, these organic compounds have been used to synthesize different polydentate ligands including ON, ONN and ONS-donor ligands, which used to obtain solid polynuclear

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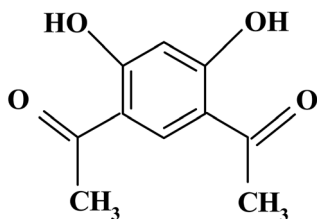
Scheme 1 Molecular structure of the ligand; 4,6-diacetylresorcinol.
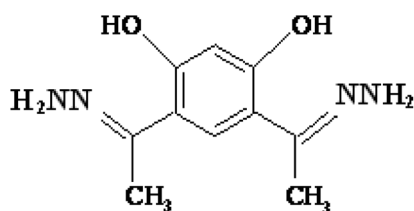
Scheme 2 Molecular structure of the ligand; 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol.

complexes.[32–47] These complexes showed structure versatility with various modes of bonding and potential biological applications.[32–34,36,38,39,46] However, literature survey showed that no previous papers studied the interactions (association) of nano copper(II) nitrate hemi pentahydrate with 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol as ligands using the temperatures and ratios of DMF, which used in the current study.

In previous work, authors have studied the complexation thermodynamic parameters of nano $Cu(NO_3)_2 \cdot 2.5H_2O$ with 4,6-diacetylresorcinol in mixed DMF-water solvents. To provide a complete study of all thermodynamic parameters, the current study was presented on the association parameters of nano copper nitrate hemi pentahydrate with different ligands in the same mixed solvents and temperature of the pervious published paper.[48]

The aim of the present work is to investigate the effect of association thermodynamic parameters on the interactions of nano copper(II) nitrate hemi pentahydrate with different ligands; 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl) benzene-1,3-diol in a binary mixed solvents using conductometric measurements. Also, study the effect of concentration of organic solvent in mixture and the effect of temperature on the interaction of nano salt with ligands in solutions.

2. Experimental

2.1. Materials

The salt used is copper(II) nitrate hemi pentahydrate $(Cu(NO_3)_2 \cdot 2.5H_2O)$ which obtained from Merck company (with purity 99.5%). The ligands; 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol were synthesized according to the literature methods[48] and,[29] respectively as follows:

2.1.1 4,6-Diacetylresorcinol. In a round-bottom flask 5 g; 36.7 mmol of anhydrous zinc(II) chloride and 2.5 g resorcinol; 22.75 mmol, 4.64 g of acetic anhydride; 45.5 mmol was added drop by drop with continuous stirring. The mixture was heated to reflux at ~140–150 °C in a paraffin oil bath for ~1 h. After cooling, the mixture was slowly poured onto 50% dil. HCl (~75 mL) where an orange-red precipitate was obtained, which was then filtered, washed with bidistilled water till the color of the filtrate is approximately colorless. Ethanol is used in crystallization and the obtained crystals were kept in a desiccator until used. % yield = 78% and m.p. 179 °C.

2.1.2 4,6-Bis(1-hydrazonoethyl)benzene-1,3-diol. To a hot solution of 4,6-diacetylresorcinol (4.85 g, 25 mmol) in methanol, a solution of hydrazine hydrate (2.5 mL, 50 mmol) in methanol (~30 mL) was added dropwise. The mixture was heated to reflux on a water bath for ~4 h where a bright-yellow crystalline precipitate was formed, which was washed with methanol and dried in a desiccator. % yield = 80% and m.p. >300 °C.

2.2. Preparation of nano copper(II) nitrate hemi pentahydrate

The bulk salt of copper(II) nitrate hemi pentahydrate $(Cu(NO_3)_2 \cdot 2.5H_2O)$ was milled using ball mill instrument of type Retsch MM 2000 swing mill with two balls of stainless steel with diameter of 12 mm to obtain copper(II) nitrate hemi pentahydrate in nano form. Ball milling was performed at 20 225 Hz and room temperature. The temperature was kept lower than 293 K.

2.3. Preparation of solutions and conductance measurements

Four solutions of $(1 \times 10^{-4}$ M) nano copper(II) nitrate hemi pentahydrate were prepared in different molar ratios of DMF and water (70%, 80%, 90% and 100% DMF). Four solutions of $(1 \times 10^{-3}$ M) of each ligand were prepared also in the same previous molar ratios of mixed solvents DMF-water. Each solution of nano copper(II) nitrate hemi pentahydrate was placed in a titration cell at a certain temperature. Then the solution of the ligand; 4,6-diacetylresorcinol was added to the copper(II) nitrate hemi pentahydrate solution step by step and the conductivity was measured after each addition of the ligand.[49–55] The pervious steps are repeated for each molar ratio of DMF-water mixed solvents at 293.15, 303.15, 313.15 and 323.15 K. The same method was used in case of another ligand; 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol. The specific conductance (K_s) of solutions was measured by using a conductivity bridge of type (JENCO – 3173 COND), which has cell constant equal to one.

3. Results and discussion

3.1. Calculations of molar and limiting molar conductance

The molar and limiting molar conductance of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol as ligands were

Table 1 Molar conductance (Λ_m), limiting molar conductance (Λ_0) and degree of dissociation (α) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol at different temperatures

T (K)	Mole fraction of DMF	Λ_m (Scm^2 mol^{-1})	Λ_0 (Scm^2 mol^{-1})	α
293.15	0.3528	246.42	521.71	0.4723
	0.4831	281.17	619.85	0.4536
	0.6774	313.82	711.85	0.4409
	1.0000	359.11	839.37	0.4278
303.15	0.3528	278.01	610.92	0.4551
	0.4831	313.82	711.85	0.4409
	0.6774	333.82	768.39	0.4344
	1.0000	398.06	949.75	0.4191
313.15	0.3528	334.88	771.53	0.4340
	0.4831	382.27	905.16	0.4223
	0.6774	422.28	1018.15	0.4148
	1.0000	462.30	1131.11	0.4087
323.15	0.3528	419.12	1009.22	0.4153
	0.4831	455.98	1113.27	0.4096
	0.6774	491.79	1214.11	0.4051
	1.0000	531.80	1327.06	0.4007

calculated in different concentrations of binary mixed solvents (DMF and water) at different temperatures, 293.15, 303.15, 313.15 and 323.15 K.

The molar conductance Λ_m values were calculated using eqn (1):[56,57]

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

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 solution. The limiting molar conductances (Λ_0) at infinite dilutions were estimated at different temperatures by extrapolating the relation between Λ_m

Table 2 Molar conductance (Λ_m), limiting molar conductance (Λ_0) and degree of dissociation (α) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at different temperatures

T (K)	Mole fraction of DMF	Λ_m (Scm^2 mol^{-1})	Λ_0 (Scm^2 mol^{-1})	α
293.15	0.3528	273.80	598.99	0.4571
	0.4831	213.77	429.46	0.4978
	0.6774	148.48	245.12	0.6057
	1.0000	207.46	411.63	0.5040
303.15	0.3528	310.66	702.93	0.4420
	0.4831	251.68	536.52	0.4691
	0.6774	184.29	346.30	0.5322
	1.0000	244.31	515.70	0.4737
313.15	0.3528	379.11	896.23	0.4230
	0.4831	341.20	789.37	0.4322
	0.6774	264.32	572.21	0.4619
	1.0000	307.50	694.01	0.4431
323.15	0.3528	461.25	1128.10	0.4089
	0.4831	350.67	816.12	0.4297
	0.6774	281.17	619.85	0.4536
	1.0000	336.98	777.31	0.4335

and $C^{1/2}$ to zero.[58–60] The values of molar and limiting molar conductance of nano copper(II) nitrate hemi pentahydrate in presence of ligands are listed in Tables 1 and 2.
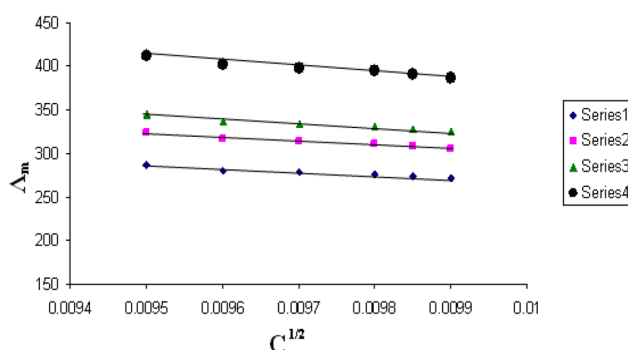
The molar conductances and limiting molar conductances for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol have higher values than those in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol due to the large size of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol as a ligand, which decrease the conductance.[61] The degree of dissociation (α) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol and in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol decreased with the increase of the temperature and this support that molar conductances and limiting molar conductances were increased with the increase of temperature.[62]

3.2. Relation between Λ_m and $C^{1/2}$ in presence of ligands

The relations between Λ_m and $C^{1/2}$ of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at different temperatures are shown in Fig. 1–4 and 5–8, respectively. Series 1: 70% DMF – 30% water, series 2: 80% DMF – 20% water, series 3: 90% DMF – 10% water and series 4: 100% DMF – 0% water. The correlation coefficients for the lines in Fig. 1–4 and 5–8 are in the range 0.992 to 0.999, which means very strong reversible relation between Λ_m and $C^{1/2}$.
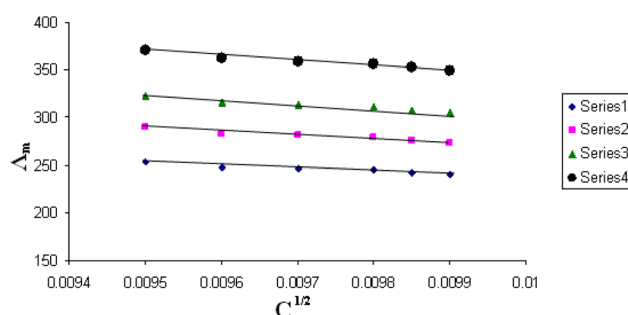
Fig. 1 Relation between Λ_m and $C^{1/2}$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol at 293.15 K.

Fig. 2 Relation between Λ_m and $C^{1/2}$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol at 303.15 K.

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Fig. 3 Relation between Λ_m and $C^{1/2}$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol at 313.15 K.
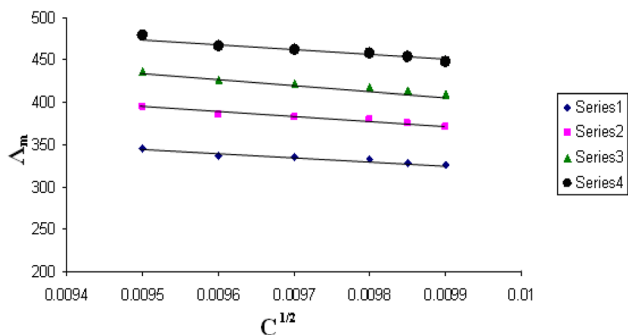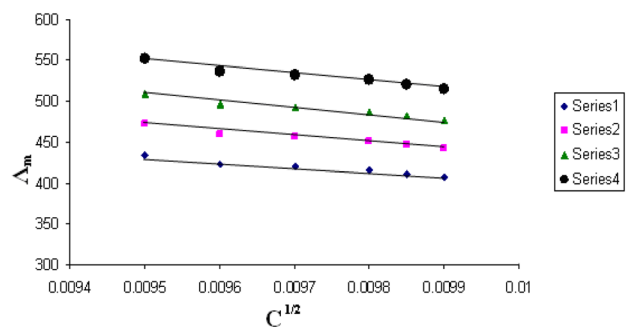

Fig. 4 Relation between Λ_m and $C^{1/2}$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol at 323.15 K.
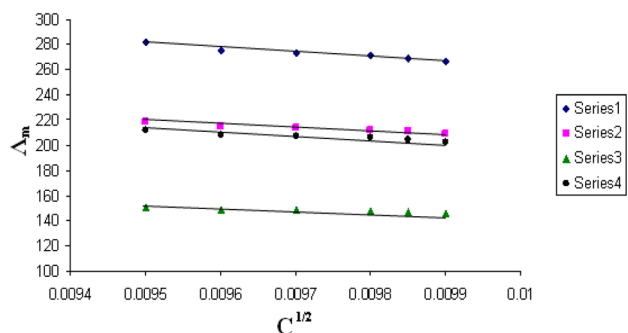

Fig. 5 Relation between Λ_m and $C^{1/2}$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at 293.15 K.

Fig. 6 Relation between Λ_m and $C^{1/2}$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at 303.15 K.

Fig. 7 Relation between Λ_m and $C^{1/2}$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at 313.15 K.

Fig. 8 Relation between Λ_m and $C^{1/2}$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at 323.15 K.
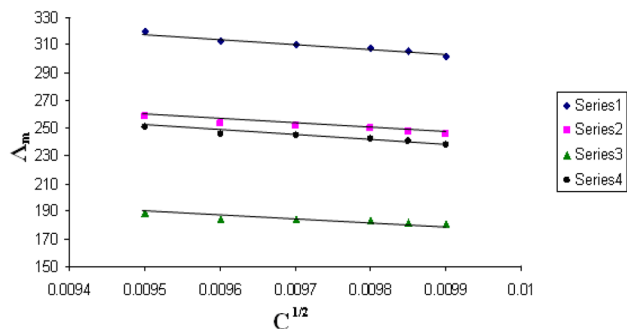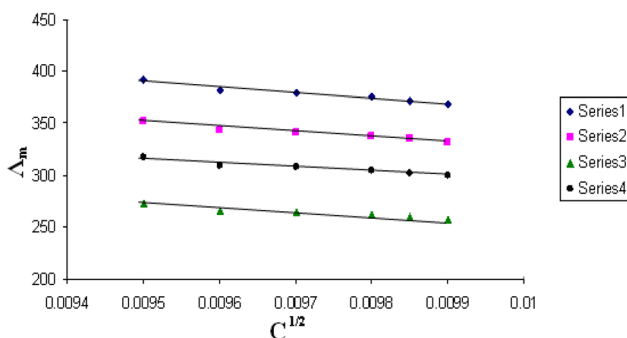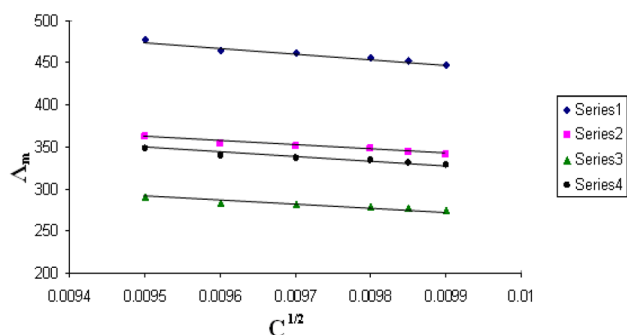
All figures show straight lines in relation between molar conductance and square root of concentration due to strong electrolytes.

3.3. Association thermodynamic parameters

The association thermodynamic parameters; association constants (K_A), free energies of association (ΔG_A), enthalpies of association (ΔH_A) and entropies of association (ΔS_A) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol

are listed Tables 3 and 4, respectively. The data are obtained in different concentrations of binary mixed solvents (DMF-water) at different temperatures; 293.15, 303.15, 313.15 and 323.15 K.

The association constants were calculated by using eqn (2):[63–66]

$$K_A = \frac{\Lambda_0(\Lambda_0 - S(Z)\Lambda_m)}{C_m \Lambda_m^2 S(Z)^2 \gamma \pm^2} \tag{2}$$

Table 3 Association constants (K_A), free energies of association (ΔG_A), enthalpies of association (ΔH_A) and entropies of association (ΔS_A) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol at different temperatures

T (K)	X_s of DMF	K_A	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	$T\Delta S$	ΔS (kJ mol^{-1} K)
293.15	0.3528	2.5481×10^4	−24.7276	11.0288	35.7564	0.1220
	0.4831	2.8608×10^4	−25.0096	9.8416	34.8512	0.1189
	0.6774	3.0995×10^4	−25.2051	10.5501	35.7552	0.1220
	1.0000	3.3678×10^4	−25.4073	5.6676	31.0749	0.1060
303.15	0.3528	2.8349×10^4	−25.8398	11.0288	36.8686	0.1216
	0.4831	3.0995×10^4	−26.0649	9.8416	35.9065	0.1184
	0.6774	3.2282×10^4	−26.1674	10.5501	36.7175	0.1211
	1.0000	3.5625×10^4	−26.4157	5.6676	32.0833	0.1058
313.15	0.3528	3.2363×10^4	−27.0371	11.0288	38.0659	0.1216
	0.4831	3.4893×10^4	−27.2329	9.8416	37.0745	0.1184
	0.6774	3.6653×10^4	−27.3610	10.5501	37.9111	0.1211
	1.0000	3.8133×10^4	−27.4641	5.6676	33.1317	0.1058
323.15	0.3528	3.6524×10^4	−28.2253	11.0288	39.2541	0.1215
	0.4831	3.7915×10^4	−28.3258	9.8416	38.1674	0.1181
	0.6774	3.9063×10^4	−28.4059	10.5501	38.9560	0.1206
	1.0000	4.0202×10^4	−28.4833	5.6676	34.1509	0.1057

Table 4 Association constants (K_A), free energies of association (ΔG_A), enthalpies of association (ΔH_A) and entropies of association (ΔS_A) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at different temperatures

T (K)	X_s of DMF	K_A	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	$T\Delta S$	ΔS (kJ mol^{-1} K)
293.15	0.3528	2.7992×10^4	−24.9566	10.0625	35.0191	0.1195
	0.4831	2.1837×10^4	−24.3515	11.5296	35.8811	0.1224
	0.6774	1.1576×10^4	−22.8045	23.6852	46.4897	0.1586
	1.0000	2.1036×10^4	−24.2604	21.5841	45.8445	0.1564
303.15	0.3528	3.0780×10^4	−26.0473	10.0625	36.1098	0.1191
	0.4831	2.5992×10^4	−25.6211	11.5296	37.1507	0.1225
	0.6774	1.7796×10^4	−24.6664	23.6852	48.3516	0.1595
	1.0000	2.5261×10^4	−25.5492	21.5841	47.1333	0.1555
313.15	0.3528	3.4739×10^4	−27.2215	10.0625	37.2840	0.1191
	0.4831	3.2738×10^4	−27.0670	11.5296	38.5966	0.1233
	0.6774	2.7166×10^4	−26.5814	23.6852	50.2666	0.1605
	1.0000	3.0562×10^4	−26.8880	21.5841	48.4721	0.1548
323.15	0.3528	3.8093×10^4	−28.3384	10.0625	38.4009	0.1188
	0.4831	3.3279×10^4	−27.9755	11.5296	39.5051	0.1223
	0.6774	2.8608×10^4	−27.5691	23.6852	51.2543	0.1586
	1.0000	3.2472×10^4	−27.9095	21.5841	49.4936	0.1532

where (Λ_m, Λ_0) are the molar and limiting molar conductance of nano copper(II) nitrate hemi pentahydrate in presence of ligands, respectively, C_m is the molar concentration of copper(II) nitrate hemi pentahydrate, $S(Z)$ is Fouss–Shedlovsky factor, equal with unity for strong electrolytes and $\gamma\pm$ is the mean activity coefficient.

Gibbs free energies of association ΔG_A of nano copper(II) nitrate hemi pentahydrate in presence of ligands were calculated by using eqn (3).[67–72]

$$\Delta G_A = 2.303RT pK_a \quad (3)$$

From the linear plots of log K_{sp} vs. $1/T$, the enthalpies were calculated from the slopes (slopes = $-\Delta H/2.303R$)[73] and their values are given in Tables 3 and 4. The entropies of solvation were calculated by use of Gibbs–Helmholtz eqn (4):[74–80]

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad (4)$$

Association constants of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol have higher values than those in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol. Negative free energies mean that all interaction processes are spontaneous at all temperatures and mole fractions of DMF used for two ligands.

3.4. Relations between log K_A and $1/T$

The relations between log K_A and $1/T$ for different concentrations of DMF and water (mixed solvents) by volumes for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol are shown in Fig. 9 and 10, respectively. Straight lines
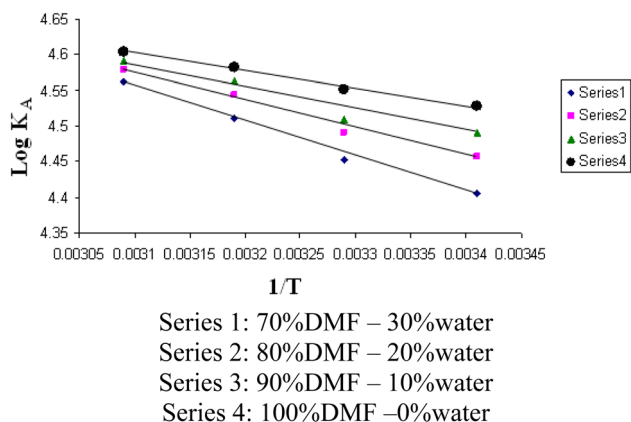
Series 1: 70%DMF – 30%water
Series 2: 80%DMF – 20%water
Series 3: 90%DMF – 10%water
Series 4: 100%DMF –0%water

Fig. 9 Relation between log K_A and $1/T$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol.
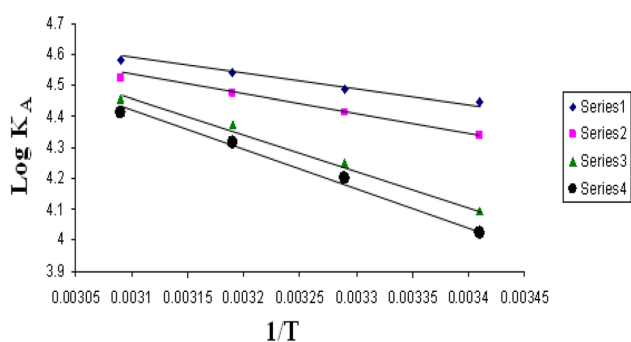

Fig. 10 Relation between log K_A and $1/T$ for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol.

relations at all of the used DMF percentages are obtained. The correlation coefficients for the lines in Fig. 9 and 10 are in the range 0.989 to 0.997, which means very strong reversible relation between log K_A and $1/T$.

The relation between log K_A and $1/T$ is inversely proportional which means endothermic processes so, enthalpy is positive.

4. Conclusion

The most values of molar conductance and limiting molar conductance for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol have higher values than those in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol due to the large size of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol as a ligand, which decrease the conductance. The molar and limiting molar conductance in presence of each ligand increase with increasing temperature. The effect of organic solvent in the mixture on conductivity differs from ligand to another where the molar and limiting molar conductance in presence of 4,6-diacetylresorcinol increases with increasing the concentration of DMF while in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol, the molar and limiting molar conductance decrease with increasing the concentration of DMF. The association constants in case of 4,6-diacetylresorcinol have higher values

than those in case of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at all temperatures, which indicates that the interactions of nano copper(II) nitrate hemi pentahydrate is more favourable with 4,6-diacetylresorcinol. The free energies of association of nano copper(II) nitrate hemi pentahydrate with 4,6-diacetylresorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol are of negative values, which means that the association process is spontaneously at all temperature and ratios of DMF used. The free energies in case of 4,6-diacetylresorcinol are more negative and this is the second parameter which indicates that the association is more favorable with 4,6-diacetylresorcinol as a ligand. The interaction process of nano copper(II) nitrate hemi pentahydrate with the two ligands is endothermic due to positive enthalpies but small positive values of enthalpies in case of 4,6-diacetylresorcinol is the third parameters which indicates that the interaction with 4,6-diacetylresorcinol is more favourable. Positive values of entropies in case of two ligands mean that the interactions are spontaneously. These data provide an opportunity for researchers to study the interactions in binary solvents solutions at different temperatures. In future work, authors will study different thermodynamic parameters for other heavy metals.

Conflicts of interest

There are no conflicts to declare.

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