Association thermodynamic parameters for nano Cu(NO₃)₂·2.5H₂O with ligands at different temperatures

Sameh G. Sanad and Magdy Shebl*

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-diacytlyeresorcinol 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 (Kₐ), degree of dissociation (α), free energies of association (ΔGₐ), enthalpies of association (ΔHₐ) and entropies of association (ΔSₐ) in the case of using the two ligands was done. Different calculated thermodynamic parameters indicate that the association is more favorable with 4,6-diacytlyeresorcinol 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. In addition, thermodynamics parameters have been utilized to get vital information about spontaneity of a given process at a particular temperature.

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. 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.

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.

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. 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.

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.

4,6-Diacyltresorcinol 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), Co(II), Ni(II), Cu(n), Cu(n) and Ru(n)), alkaline earth metal ions (Mg(n), Ca(n), Sr(n) and Ba(n)) in addition to Ce(n) and UO(IV) ions. In addition, these organic compounds have been used to synthesize different polydentate ligands including ON, ON and ONS-donor ligands, which used to obtain solid polynuclear...
complexes. These complexes showed structure versatility with various modes of bonding and potential biological applications. 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$_3$)$_2$·2.5H$_2$O 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 Cu(NO$_3$)$_2$·2.5H$_2$O with 4,6-diacetylresorcinol and 4,6-bis[1-hydrazonoethyl]benzene-1,3-diol as ligands using conductometric measurements. Also, study the effect of concentration of organic solvent in mixture and the effect of temperature on the molar and limiting molar conductance of nano Cu(NO$_3$)$_2$·2.5H$_2$O in presence of 4,6-diacetylresorcinol and 4,6-bis[1-hydrazonoethyl]benzene-1,3-diol as ligands were synthesized according to the literature methods and respectively as follows:

2.1. Materials

The salt used is copper(II) nitrate hemi pentahydrate [Cu(NO$_3$)$_2$·2.5H$_2$O] 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 and 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$_3$)$_2$·2.5H$_2$O] 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 × 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 × 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. The previous 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 (Ks) 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
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 \( A_m \) values were calculated using eqn (1):\(^{35,37}\)

\[
A_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C}
\]

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 \( (A_0) \) at infinite dilutions were estimated at different temperatures by extrapolating the relation between \( A_m \)

### Table 1: Molar conductance \( (A_m) \), limiting molar conductance \( (A_0) \) and degree of dissociation \( (\alpha) \) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacytiresorcinol at different temperatures

| \( T \) (K) | Mole fraction of DMF | \( A_m \) (Scm\(^2\) mol\(^{-1}\)) | \( A_0 \) (Scm\(^2\) mol\(^{-1}\)) | \( \alpha \) |
|---|---|---|---|---|
| 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 | 0.4511 |
| | 0.4831 | 313.82 | 711.85 | 0.4409 |
| | 0.6774 | 333.82 | 768.39 | 0.4344 |
| | 1.0000 | 398.06 | 947.75 | 0.4191 |
| 313.15 | 0.3528 | 334.88 | 771.53 | 0.4334 |
| | 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 | 1099.22 | 0.4153 |
| | 0.4831 | 455.98 | 1133.27 | 0.4096 |
| | 0.6774 | 491.79 | 1214.11 | 0.4051 |
| | 1.0000 | 531.80 | 1327.06 | 0.4007 |

### Table 2: Molar conductance \( (A_m) \), limiting molar conductance \( (A_0) \) and degree of dissociation \( (\alpha) \) 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 | \( A_m \) (Scm\(^2\) mol\(^{-1}\)) | \( A_0 \) (Scm\(^2\) mol\(^{-1}\)) | \( \alpha \) |
|---|---|---|---|---|
| 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 | 244.81 | 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.\(^{38-40}\) 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-diacytiresorcinol 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.\(^{41}\) The degree of dissociation \( (\alpha) \) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacytiresorcinol 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 \( A_m \) and \( C^{1/2} \) in presence of ligands

The relations between \( A_m \) and \( C^{1/2} \) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacytiresorcinol 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 \( A_m \) and \( C^{1/2} \).

![Fig. 1](image1.png)  
**Fig. 1** Relation between \( A_m \) and \( C^{1/2} \) for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacytiresorcinol at 293.15 K.

![Fig. 2](image2.png)  
**Fig. 2** Relation between \( A_m \) and \( C^{1/2} \) for nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacytiresorcinol at 303.15 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):\(^6\)

$$K_A = \frac{A_0(A_0 - S(Z)A_m)}{C_mA_mS(Z)^2γ^2}$$

**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.
Table 3 Association constants ($K_A$), free energies of association ($\Delta G_A$), enthalpies of association ($\Delta H_A$) and entropies of association ($\Delta S_A$) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacetylresorcinol at different temperatures

| $T$ (K) | $X_0$ of DMF | $K_A$ | $\Delta G$ (kJ mol$^{-1}$) | $\Delta H$ (kJ mol$^{-1}$) | $T\Delta S$ | $\Delta S$ (kJ mol$^{-1}$ K$^{-1}$) |
|-------|-------------|------|-----------------|-----------------|----------|----------------|
| 293.15 | 0.3528 | $2.5481 \times 10^4$ | $-24.7276$ | 11.0288 | 35.7564 | 0.1220 |
| 0.4831 | $2.8608 \times 10^4$ | $-25.0510$ | 9.8416 | 34.8512 | 0.1189 |
| 0.6774 | $3.0995 \times 10^4$ | $-25.4073$ | 5.6576 | 31.0749 | 0.1060 |
| 1.0000 | $3.3678 \times 10^4$ | $-25.8398$ | 11.0288 | 36.8686 | 0.1216 |
| 303.15 | 0.3528 | $2.8349 \times 10^4$ | $-26.0649$ | 9.8416 | 35.9065 | 0.1184 |
| 0.4831 | $3.2282 \times 10^4$ | $-26.1674$ | 10.5501 | 36.7175 | 0.1211 |
| 0.6774 | $3.5625 \times 10^4$ | $-26.4157$ | 5.6576 | 32.0833 | 0.1058 |
| 1.0000 | $3.8133 \times 10^4$ | $-26.7971$ | 11.0288 | 38.0659 | 0.1216 |
| 313.15 | 0.3528 | $3.2363 \times 10^4$ | $-27.1037$ | 11.0288 | 37.0745 | 0.1184 |
| 0.4831 | $3.6593 \times 10^4$ | $-27.2329$ | 9.8416 | 38.1674 | 0.1181 |
| 0.6774 | $3.6653 \times 10^4$ | $-27.3610$ | 10.5501 | 37.9111 | 0.1211 |
| 1.0000 | $3.8133 \times 10^4$ | $-27.4641$ | 5.6576 | 33.1317 | 0.1058 |
| 323.15 | 0.3528 | $3.6524 \times 10^4$ | $-28.2253$ | 11.0288 | 39.2341 | 0.1215 |
| 0.4831 | $3.7915 \times 10^4$ | $-28.3258$ | 9.8416 | 38.9560 | 0.1206 |
| 0.6774 | $3.9063 \times 10^4$ | $-28.4059$ | 10.5501 | 38.9560 | 0.1206 |
| 1.0000 | $4.0202 \times 10^4$ | $-28.4833$ | 5.6576 | 34.1509 | 0.1057 |

Table 4 Association constants ($K_A$), free energies of association ($\Delta G_A$), enthalpies of association ($\Delta H_A$) and entropies of association ($\Delta S_A$) of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at different temperatures

| $T$ (K) | $X_0$ of DMF | $K_A$ | $\Delta G$ (kJ mol$^{-1}$) | $\Delta H$ (kJ mol$^{-1}$) | $T\Delta S$ | $\Delta S$ (kJ mol$^{-1}$ K$^{-1}$) |
|-------|-------------|------|-----------------|-----------------|----------|----------------|
| 293.15 | 0.3528 | $2.7992 \times 10^4$ | $-24.9566$ | 10.0625 | 35.0191 | 0.1195 |
| 0.4831 | $2.1837 \times 10^4$ | $-24.3515$ | 11.5296 | 35.8811 | 0.1224 |
| 0.6774 | $2.1576 \times 10^4$ | $-22.8045$ | 23.6852 | 46.4987 | 0.1586 |
| 1.0000 | $2.1036 \times 10^4$ | $-22.6045$ | 21.5841 | 45.8445 | 0.1564 |
| 303.15 | 0.3528 | $3.0780 \times 10^4$ | $-26.0473$ | 10.0625 | 36.1998 | 0.1191 |
| 0.4831 | $2.5992 \times 10^4$ | $-25.6211$ | 11.5296 | 37.1507 | 0.1225 |
| 0.6774 | $1.7796 \times 10^4$ | $-24.6664$ | 23.6852 | 48.3516 | 0.1595 |
| 1.0000 | $2.5261 \times 10^4$ | $-25.5492$ | 21.5841 | 47.1333 | 0.1555 |
| 313.15 | 0.3528 | $3.4739 \times 10^4$ | $-27.2215$ | 10.0625 | 37.2840 | 0.1191 |
| 0.4831 | $3.2738 \times 10^4$ | $-27.0670$ | 11.5296 | 38.5966 | 0.1233 |
| 0.6774 | $2.7166 \times 10^4$ | $-26.5814$ | 23.6852 | 50.2666 | 0.1605 |
| 1.0000 | $3.0562 \times 10^4$ | $-26.8880$ | 21.5841 | 48.4721 | 0.1548 |
| 323.15 | 0.3528 | $3.8093 \times 10^4$ | $-28.3384$ | 10.0625 | 38.4009 | 0.1188 |
| 0.4831 | $3.3279 \times 10^4$ | $-27.9755$ | 11.5296 | 39.5052 | 0.1223 |
| 0.6774 | $2.8608 \times 10^4$ | $-27.5691$ | 23.6852 | 51.2543 | 0.1546 |
| 1.0000 | $3.2472 \times 10^4$ | $-27.9095$ | 21.5841 | 49.4936 | 0.1532 |

where ($A_m$, $A_s$) are the molar and limiting molar conductance of nano copper(II) nitrate hemi pentahydrate in presence of ligands, respectively, $C_{\text{m}}$ is the molar concentration of copper(II) nitrate hemi pentahydrate, $S(2)$ is Fouss–Shedlovsky factor, equal with unity for strong electrolytes and $\gamma \pm$ is the mean activity coefficient.

Gibbs free energies of association $\Delta G_A$ of nano copper(II) nitrate hemi pentahydrate in presence of ligands were calculated by using eqn (3).$^{67-72}$

$$\Delta G_A = 2.303RTpK_A$$

From the linear plots of $\log K_A$ vs. $1/T$, the enthalpies were calculated from the slopes ($\Delta H_A = -\Delta G_A / Tp$) and their values are given in Tables 3 and 4. The entropies of solvation were calculated by use of Gibbs–Helmholz eqn (4).$^{73-80}$

$$\Delta G_A = \Delta H_A - T\Delta S_A$$

Association constants of nano copper(II) nitrate hemi pentahydrate in presence of 4,6-diacyltelyrosorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol at different temperatures.

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-diacytelyrosorcinol and 4,6-bis(1-hydrazonoethyl)benzene-1,3-diol are shown in Fig. 9 and 10, respectively. Straight lines

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The 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 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 interaction with 4,6-diacetylresorcinol is more favourable. Positive values of entropies in case of 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 parameter which indicates that the interaction 4,6-diacetylresorcinol is more favourable. Positive values of entropies in case of 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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