Thermodynamic studies on metal complexes of Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ with 8-hydroxy 5-quinolinesulfonic acid in water, methanol and water-methanol binary solvent systems at 303.15 K, 313.15 K and 323.15 K by conductometric method

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ABSTRACT
Stability constants are measured for complexes of Cd$^{2+}$, Cu$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ with 8-Hydroxy 5-Quinolinesulfonic acid [HQS] in water, methanol and water-methanol binary solvent systems at 303.15 K, 313.15 K and 323.15 K by conductometric method. The results show that the stoichiometry of the complexes HQS with Co$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ metals in all binary mixed solvents is 1:2. The log $K_f$ values of HQS-M$^{2+}$ complexes in H$_2$O-MeOH binary mixtures increases with increasing % of MeOH and temperature. The $\Delta H^0$ and $\Delta S^0$ of the complexation reaction in the different H$_2$O-MeOH binary mixtures were evaluated by the temperature dependence of the formation constants using a linear least square analysis according to van’t Hoff equation.

Keywords: 8-Hydroxy 5-QuinolineSulfonic acid; stability constants; complexation; thermodynamic parameters

INTRODUCTION
Metal complex study is well established area of research work. To study the formation constant of ligand with metal ions in solution conductometric method is widely used because of its various advantages such as low cost, eco-friendly, less time consuming, proper thermodynamic calculation with different parameters and most important easy to operate [1-3]. Using conductometric method, researcher can calculate all thermodynamic parameters for specific reactions and also investigate stability constant. By using conductometric method, basic research on thermodynamic studies like enthalpy, entropy, Gibbs free energy can also be determined [3-5]. The factors responsible for the stability of complexes are charge and size of the metal ion, type of the metal ion, counter ion, nature of the ligand, temperature and physical properties of solvents. From conductometric method, the value of stability constant (log $K_f$) can be evaluated by GENPLOT computer program. The enthalpy change ($\Delta H$) and entropy change ($\Delta S$) of the complexation reactions in the different binary mixtures can be calculated by temperature dependence of the formation constant using a linear least square analysis according to van’t Hoff equation. Quinoline and its derivatives are used in medical science viz. in the treatment of cancer and malaria [6-7]. In this paper we have reported the stability constants of HQS with Cd$^{2+}$, Cu$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ in water, methanol and water-methanol binary solvents at 303.15 K, 313.15 K and 323.15 K. This study is useful to understand the effect of ionic size, solvent composition, temperature and the nature of the complexing agent.

MATERIALS AND METHOD
The reagents used were of analytical reagent grade and used without further purification. nickel nitrate (Ni(NO$_3$)$_2$ .6H$_2$O), cobalt nitrate (Co(NO$_3$)$_2$ .6H$_2$O) and potassium chloride (KCl) were purchased from Merck limited Mumbai, cupric nitrate (Cu(NO$_3$)$_2$ .3H$_2$O), cadmium nitrate (Cd(NO$_3$)$_2$ .4H$_2$O) were purchased from ACS chemicals Ahmedabad and 8-Hydroxy 5-Quinoline Sulfonic acid hydrate was purchased from Sigma Aldrich, Germany. Methanol extra pure was purchased from Finar Chemicals Limited Ahmedabad. Conductivity water with conductivity less than 2.0 x 10$^{-6}$ was used for preparation of all the solutions. Glassware used were thoroughly cleaned with freshly prepared aqua - regia and rinsed thoroughly with deionized water.

The conductance measurements were performed using model EQ-665, a digital Equiptronics conductivity apparatus, at a constant temperature maintained within ±0.3 °C using WENSAR thermostat, model WMS 300. The conductance of the solutions was measured using a conductivity cell consisting of two platinum electrodes with a cell constant of 1.02 cm$^{-1}$ throughout the studies. The cell constant was determined using 0.1N and 0.01 N analytical grade KCl in deionized water and the mean value was
used. The specific conductance of this solution at various temperatures has been reported in the literature [1].

**MEASUREMENT OF CONDUCTANCE AND EVALUATION OF STABILITY CONSTANT (Kf)**

The change in conductance is measured when a metal salt solution to which ligand solution is added, this provide valuable information about metal ligand interactions. Conductance measurement gives information about the affinity of the ligand and the stoichiometry of the complexation reaction. The measurement of conductance is generally carried out by titrating the metal salt solution with ligand solution in a suitable solvent system. The titration may give rise to two different conductometric effects. In the case when ligand titrated to the metal salt solution in which the metal salt is not fully dissociated, the opposite conductometric effect is observed. In the case when the metal salt is completely dissociated in the solvent, the complexation by a ligand leads to a large cationic complex of the metal ion and the ligand. In this case the complex has less mobility in the solution than the uncomplexed metal cation, resulting in the diminished capacity of charge transfer and hence the conductivity of the solution decreases. Since the ligand coordinates to the metal ion, leaving the anion undisturbed, dissociation of the metal salt increases and hence the conductivity of the solution increased [1].

In some cases, in spite of increase in the ligand concentration the change in conductance is negligible; consequently, determination of the formation constant by conductometric method becomes difficult.

There are two factors responsible for a very small change in conductance in spite of an increase in the concentration of ligand: (1) when there is no complexation occurs between metal ion and ligand and (2) mobilities of a resulting metal-ligand complex and the corresponding metal ion are both equal at the same concentration. The first factor is responsible in the most of the cases. When the dielectric constant of the solvent is very high and concentration is very low, the conductometric effects. In the case when ligand titrated to the metal salt solution in which the metal salt is not fully dissociated, the opposite conductometric effect is observed. In the case when the metal salt is completely dissociated in the solvent, the complexation by a ligand leads to a large cationic complex of the metal ion and the ligand. In this case the complex has less mobility in the solution than the uncomplexed metal cation, resulting in the diminished capacity of charge transfer and hence the conductivity of the solution increased [1].

The dilute conditions used make it possible to neglect ion aggregation and corrections for viscosity changes. The molar conductivities Λ can be calculated by using the following equation,

\[ \Lambda = \frac{1000 \kappa}{[M]_t} \]  \hspace{1cm} \(7\)

where \(\kappa\) is the conductivity of the test solution in Siemens·cm⁻¹. On the other hand, \(\Lambda\) can be related to \(\alpha\) by the following equation,

\[ \Lambda = \alpha \Lambda_{M+} + (1 - \alpha) \Lambda_{ML} \]  \hspace{1cm} \(8\)

where, \(\Lambda_{M+}\) and \(\Lambda_{ML}\) represent the molar conductivities of the ligand free metal salt solution and the complexed cation solution at the same concentration, respectively.

Rearranging Equation [8] gives an expression for \(\alpha\) as;

\[ \alpha = \frac{\Lambda - \Lambda_{ML}}{\Lambda_{M+} - \Lambda_{ML}} \]  \hspace{1cm} \(9\)

Substituting Equations [8] and [9] into Equation [7] gives the following equation:

\[ K_{ML^+} = (1 - \alpha)/\alpha \Lambda [L] \]  \hspace{1cm} \(10\)

Substituting the value of \(\alpha\) from Equation [9] in [10]:

\[ K_{ML^+} = \frac{\Lambda_{M+} - \Lambda}{\Lambda - \Lambda_{ML}} \]  \hspace{1cm} \(11\)

Further, substitution of Equation [9] into Equation [6] gives

\[ [L] = [L]_t - \left( \frac{\Lambda_{M+} - \Lambda}{\Lambda - \Lambda_{ML}} \right) [M]_t \]  \hspace{1cm} \(12\)

Substitution of Equation [12] into Equation [11] gives the expression for \(K_{ML^+}\):

\[ K_{ML^+} = \frac{\Lambda_{M+} - \Lambda}{\Lambda - \Lambda_{ML} - \left( \frac{\Lambda_{M+} - \Lambda}{\Lambda - \Lambda_{ML}} \right) [M]_t} \]  \hspace{1cm} \(13\)

The above equation can be simplified as

\[ K_{ML^+} = \frac{a_1 a_2}{a_1 [L]_t} \]  \hspace{1cm} \(14\)

where, \(a_1 = \Lambda_{ML} - \Lambda\), \(a_2 = \Lambda_{M+} - \Lambda_{ML}\), \(a_3 = \Lambda - \Lambda_{ML}\).

Here, Equation [18] can be rearranged to form a quadratic equation in terms of \(\Lambda\) as:

\[ a\Lambda^2 + b\Lambda + c = 0 \]  \hspace{1cm} \(15\)

where

\[ a = K_{ML^+} [M]_t \]

\[ b = (K_{ML^+} [L]_t + 1) \cdot [M]_t \cdot K_{ML^+} (\Lambda + \Lambda_{ML}) \]

\[ c = [M]_t \cdot K_{ML^+} \Lambda \Lambda_{ML} - a2([L]_t \cdot K_{ML^+} \Lambda + \Lambda_{ML}) \].
RESULT AND DISCUSSION

The variation of molar conductance (\(\Lambda\)) versus the ligand [L]/cation [M] molar ratio ([L]/[M]) for complexation of HQS with Cd\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\) and Ni\(^{2+}\) in water, methanol and water-methanol binary solvents were studied at various temperatures.

Typical series of molar conductance values as a function of [L]/[M] mole ratios in pure H\(_2\)O, pure MeOH and H\(_2\)O-MeOH (v/v % MeOH = 20/40/60) binary systems are shown in Figure 1-4. From figure 1-4, it is observed that, addition of HQS to metal ions (Cd\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\) and Ni\(^{2+}\)) in pure H\(_2\)O, pure MeOH and H\(_2\)O-MeOH (v/v % MeOH = 20/40/60) binary solvent systems at different temperatures resulted in an increase in molar conductance by increasing the ligand concentration. It is observed that addition of HQS to cadmium ion solution at different temperatures results in an increase in molar conductance. This indicates that (Cd\(^{2+}\) - HQS) complexes is more mobile than free solvated cadmium cations. Similar behavior were observed for Cu\(^{2+}\), Co\(^{2+}\) and Ni\(^{2+}\) cations in various solvent systems.

Figure 1 Molar conductance (ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\)) vs. HQS/[Cd\(^{2+}\)] plots in pure H\(_2\)O, pure MeOH and H\(_2\)O-MeOH binary mixture at various temperatures. v/v % of MeOH in the binary mixture is: (A) 0% (B) 20% (C) 40%, (D) 60% and (E) 100%.
Figure 2 Molar conductance (ohm$^{-1}$ cm$^2$ mol$^{-1}$) vs. HQS / [Cu$^{2+}$] plots in pure H$_2$O, pure MeOH and H$_2$O–MeOH binary mixture at various temperatures. v/v % of MeOH in the binary mixture is: (A) 0% (B) 20 % (C) 40%, (D) 60% and (E) 100%.

Figure 3 Molar conductance (ohm$^{-1}$ cm$^2$ mol$^{-1}$) vs. HQS / [Co$^{2+}$] plots in pure H$_2$O, pure MeOH and H$_2$O–MeOH binary mixture at various temperatures. v/v % of MeOH in the binary mixture is: (A) 0% (B) 20 % (C) 40%, (D) 60% and (E) 100%.
Figure 4 Molar conductance (ohm-1 cm2 mol-1) vs. HQS/[Ni2+] plots in pure H2O, pure MeOH and H2O–MeOH binary mixture at various temperatures. v/v % of MeOH in the binary mixture is: (A) 0% (B) 20 % (C) 40%, (D) 60% and (E) 100%.

The stability constant of the HQS at each temperature were calculated from the variation of the molar conductance as a function of [L]/[M] mole ratios using GENPLOT computer programme. The values of the stability constant [Log K_f] for the HQS-M^{2+} (M^{2+} = Cd^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+}) complexes in various solvent systems are listed in Table-1.

Table 1 Log K_f values of HQS-M^{2+} complex in pure H2O, pure MeOH and H2O-MeOH binary mixtures at different temperatures.

| Complex     | Solvent Medium               | Log K_f ± SD     |
|-------------|------------------------------|------------------|
| HQS-Cd^{2+} | Pure H2O                     | 303.15 K         |
|             | 80% H2O-20% MeOH             | 4.061±0.03       |
|             |                              | 313.15 K         |
|             |                              | 4.102±0.05       |
|             |                              | 323.15 K         |
|             |                              | 4.152±0.07       |
|             | 80% H2O-20% MeOH             | 4.086±0.06       |
|             |                              | 4.159±0.04       |
|             |                              | 4.243±0.05       |
| Solvent System | HQS-Cu²⁺ | HQS-Co²⁺ | HQS-Ni²⁺ |
|----------------|-----------|-----------|-----------|
| 60% H₂O - 40% MeOH | 4.151±0.05 | 4.096±0.04 | 4.064±0.06 |
| 40% H₂O - 60% MeOH | 4.185±0.04 | 4.051±0.05 | 3.983±0.03 |
| Pure MeOH | 4.240±0.03 | 4.164±0.06 | 4.018±0.07 |

It is evident that the stability constant values increase with increases in temperature. This indicates that the complexation reaction for HQS and metal ions (Cd²⁺, Cu²⁺, Co²⁺, and Ni²⁺) in pure H₂O, pure MeOH and H₂O-MeOH solvent system is endothermic.

**VAN'T HOFF Plot for Complexation**

For better understanding of the thermodynamics of complexation reactions of Cd²⁺, Cu²⁺, Co²⁺, and Ni²⁺ ions with HQS, it is useful to investigate the enthalpic and entropic contributions in these reactions. The ΔH° and ΔS° of the complexation reactions in different H₂O-MeOH mixtures were evaluated by the temperature dependence of the formation constants using a linear least squares method according to the van’t Hoff equation [7].

![Figure 5 Ln Kf vs. 1000/T plots for the complexation of Cd²⁺, Cu²⁺, Co²⁺, and Ni²⁺ ions with HQS in different solvent mixtures systems: (A = Pure MeOH, B = 60% MeOH, C = 40% MeOH, D = 20% MeOH, E = Pure H₂O)](image-url)
Comparison of the stability constant values given in the Table-1 provides information that the stability constant increase by increase in the concentration of MeOH with smaller Gutmann donor number (DN: MeOH=19.0) in binary solvents. However the stability constant decreases with increasing H$_2$O concentration with relatively equal donor number (Dn: H$_2$O $\geq$ 19.0) which is in accordance with the reverse order of the solvating ability according to Gutmann donor number. As donor number of MeOH (19.0) and H$_2$O ($\geq$ 19.0) are approximately equal and if we ignore very small difference in donor number of solvents it seems to dielectric constant ($\varepsilon$) of solvents play an important role in the formation of complexes.

The result which are summarized in Table-2 show that in all the cases, the complexation reactions between HQS and the studied metal cations in H$_2$O–MeOH binary solutions are entropy stabilized and enthalpy destabilized. According to the data in the table indicates that the thermodynamic quantities are very sensitive to the composition and the nature of the mixed solvent and non-monotonic behavior is observed for the variation of enthalpy and entropy changes versus the composition of the water-methanol binary solvent systems [8].

Table 2 Thermodynamic parameters for HQS-M$^{2+}$ complexes in H$_2$O–MeOH binary systems at 30°C

| Complex | Solvent Medium | $\Delta G^0 \pm$ SD (kJ.mol$^{-1}$) | $\Delta H^0 \pm$ SD (kJ.mol$^{-1}$) | $\Delta S^0 \pm$ SD (J.mol$^{-1}$K$^{-1}$) |
|---------|----------------|--------------------------------------|--------------------------------------|--------------------------------------|
| HQS- Cd$^{2+}$ | Pure H$_2$O | -23.56±0.08 | 8.54 ±0.09 | 105.96±3 |
| | 80% H$_2$O - 20% MeOH | -23.70±0.09 | 14.65±0.1 | 126.60±5 |
| | 60% H$_2$O - 40% MeOH | -24.08±0.1 | 15.21±0.09 | 129.68±3 |
| | 40% H$_2$O - 60% MeOH | -24.27±0.09 | 20.28±0.11 | 147.07±6 |
| | Pure MeOH | -24.60±0.1 | 24.87±0.08 | 163.27±4 |
|HQS- Cu$^{2+}$ | Pure H$_2$O | -22.09±0.09 | 17.88±0.08 | 131.95±5 |
| | 80% H$_2$O - 20% MeOH | -23.66±0.1 | 9.16 ±0.1 | 105.03±7 |
| | 60% H$_2$O - 40% MeOH | -23.50±0.09 | 7.10 ±0.09 | 101.04±6 |
| | 40% H$_2$O - 60% MeOH | -23.76±0.08 | 13.2 ±0.1 | 122.17±7 |
| | Pure MeOH | -24.16±0.1 | 13.9 ±0.15 | 125.93±4 |
|HQS- Co$^{2+}$ | Pure H$_2$O | -21.89±0.08 | 13.55±0.1 | 116.98±2 |
| | 80% H$_2$O - 20% MeOH | -22.41±0.09 | 10.31±0.12 | 108.00±5 |
| | 60% H$_2$O - 40% MeOH | -22.87±0.06 | 15.09±0.09 | 125.31±4 |
| | 40% H$_2$O - 60% MeOH | -23.31±0.07 | 12.91±0.08 | 119.57±3 |
| | Pure MeOH | -23.91±0.06 | 11.19±0.1 | 115.85±4 |
|HQS-Ni$^{2+}$ | Pure H$_2$O | -21.52±0.1 | 15.17±0.09 | 121.11±3 |
| | 80% H$_2$O - 20% MeOH | -21.99±0.09 | 16.48±0.1 | 126.99±4 |
| | 60% H$_2$O - 40% MeOH | -22.62±0.08 | 12.52±0.09 | 115.99±3 |
| | 40% H$_2$O - 60% MeOH | -23.10±0.1 | 11.00±0.1 | 112.58±2 |
| | Pure MeOH | -23.56±0.07 | 11.84±0.1 | 116.86±4 |

SD: standard deviation
From Figure 6, the changes of the stability constant (log $K_f$) of HQS–Cd$^{2+}$, HQS–Cu$^{2+}$, HQS–Cu$^{2+}$ and HQS–Ni$^{2+}$ complexes versus the composition of H$_2$O–MeOH binary system at various temperatures were observed. It is interesting to note that the formation constants of HQS–M$^{2+}$ (M = Cd, Cu, Co, Ni) complexes increase with increase in the methanol percent in H$_2$O–MeOH binary solvent systems.

**Effect of Ionic Size on Complexation**

The variation of log $K_f$ for formation of HQS-Cd$^{2+}$, HQS-Cu$^{2+}$, HQS-Co$^{2+}$ and HQS-Ni$^{2+}$ complexes versus the ionic radius in H$_2$O–MeOH binary solvent systems are shown in Figure 7. It is evident from these Figures that, the order of selectivity of these complexes at 30 °C, 40 °C and 50 °C is HQS-Cd$^{2+}$ > HQS-Cu$^{2+}$ > HQS-Co$^{2+}$ > HQS-Ni$^{2+}$. Similar selectivity order was observed in all compositions of the binary solvent systems.
CONCLUSION

According to the results obtained in the present work, complexes formed between the ligand and the metal cation, it indicates the probability of changes in the stabilities and stoichiometry of the complexes due to the composition of the solvent systems. In most of the cases HQS formed 1:2 complexes but in the case of Ni⁺², HQS formed 1:1 complex. The results obtained in our studies suggest that stability of the complexes of HQS with the metal cations in solutions undergoes the chemical and physical properties of each solvent molecule such as donor number and polarity and with increasing methanol percent when mixed one another and therefore changing their solvating ability towards the ligand, metal cation and the resulting complex . The negative values of ∆G shows the ability of the studied ligand to form stable complexes and process trends to be spontaneously. However, the obtained positive value of ∆H indicates that the enthalpy is not driving force for the formation of the complexes. Furthermore, the positive value of ∆S indicates that entropy is a driving force for the complexation reaction.

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