ABSTRACT

The association constant, formation constants and Gibbs free energies are calculated from the conductometric titration curves of CuCl2 with 4-phenyl-2-diacetyl monoxime-3-thiosemicarbazone (BMPTS) in absolute ethanol at different temperatures (293.15 K, 298.15 K, 303.15 and 308.15 K). On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines are obtained indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometric complexes. The formation constants of different complexes in absolute ethanol follow the order: Kf (2:1) > Kf (1:1) > Kf (1:2) for (M: L). As the temperature increases, the formation constants and association constants of different complexes increase. The enthalpy and entropy of formation and association of CuCl2 with (BMPTS) were also estimated and their values were also discussed.

INTRODUCTION

Transition metal ions have a strong role in bio-inorganic chemistry and redox enzyme systems and may provide the basis of models for active sites of biological systems. Cu(II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents. The hydrazones and their metal complexes have many important applications in analytical chemistry and pharmacology. Schiff bases hydrazone derivatives and their metal complexes have been studied for their interesting and important properties, e.g., antibacterial, antifungal, antioxidant, anticancer and catalytic activity in oxidation of cyclohexene. Moreover, Schiff bases hydrazone derivatives are versatile ligands and they offer the possibility of different modes of coordination towards transition metal ions. Also, some of these derivatives have been applied as iron chelator drugs in therapy of anemia and treatment of neuropathic pain, and in analysis of salts in bodies and environnement.

This work deals with the Determination of solvation free energies (ΔG) and the entropy of solvation (ΔS) from conductometric technique. Thus, thermodynamic studies of complexation reactions of this Schiff base with transition metal ions is important on the thermodynamics of complexation reaction, but also lead to a better understanding of the high selectivity of this ligand towards different metal cations.

The aim of this work is the evaluation the non-covalent behavior of CuCl2 with (BMPTS) in absolute ethanol solutions at 294.15 K. These non-covalent interactions can help us for analysis of salts in bodies and environnement.

EXPERIMENTAL

Materials and Methods

All manipulations were performed under aerobic conditions. The cupper chloride and the used reagents were Merck pure.
Preparation of PDMSC

4-phenyl-1-diacylmonoxime-3-thiosemicarbazone (BMPTS) was prepared by boiling an EtOH solution of 4-phenylthiosemicarbazone (1.7g, 1mmole) with an EtOH solution of diacetylmonoxime(1g, 1mmole) under reflux for two hours. The solution was then concentrated to one half of its volume and cooled. Yellowish white needles separated which were recrystallized from hot absolute EtOH. (M.p: 192°C; yield 80%). The purity of the compound was checked by TLC.

![Scheme 1: The outline of the synthesis of 4-phenyl-2-diacyl monoxime-3-thiosemicarbazone (BMPTS)](image)

**Conductance measurement**

The conductometric titration of the CuCl₂ (1x10⁻⁴ mole/L) against the ligand (1x10⁻⁵ mole/L) in absolute ethanol was performed with 0.2 ml interval additions from (BMPTS) solution. The specific conductance values were recorded using conductivity bridge AdWa, AD 3000 with a cell constant equal to 1 cm⁻¹. The temperature was adjusted at 293.15 K, 298.15 K, 303.15 K and 308.15 K.

**RESULTS AND DISCUSSION**

The specific conductance values (κₖ) of different concentrations of CuCl₂ in absolute ethanol were measured experimentally in absence and in the presence of ligand at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

The molar conductance (Λₘ) values were calculated [16] using equation:

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

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 CuCl₂ solutions.

The limiting molar conductances (Λₘ) at infinite dilutions were estimated for CuCl₂ in absolute ethanol alone at different temperatures by extrapolating the relation between \(\Lambda_m\) and \(C^{-1/2}\) to zero concentration as shown in Figure 1.
Figure 1: The relation between molar conductance ($\Lambda_m$) and ($C_m^{1/2}$) of CuCl$_2$ alone in absolute ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

The limiting molar conductances ($\Lambda_0$) at infinite dilutions were estimated for CuCl$_2$ in the presence of the ligand (BMPTS) by extrapolating the relation between $\Lambda_m$ and $C_m^{1/2}$ to zero concentration Figure 2.

Figure 2: The relation between molar conductance ($\Lambda_m$) and ($C_m^{1/2}$) of CuCl$_2$ in presence of BMPTS at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K).

By drawing the relation between molar conductance ($\Lambda_m$) and the molar ratio of metal to ligand (M:L) concentrations (Figure 3,4,5,6), different lines are obtained with sharp breaks indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometric complexes.
The experimental data of \( \frac{1}{\lambda_m} \) and \( \frac{1}{\lambda_o} \) were analyzed for the determination of association and formation constants for each type of the stoichiometric complexes.

The association constants of \( \text{CuCl}_2 \) in the presence of ligand (BMPTS) in absolute ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K) for 2:1, 1:1 and 1:2 (M:L) were calculated by using equation \(^{[17,18]}\):

\[
K_a = \frac{\Lambda_o^2(\Lambda_o - \Lambda_m)}{4C_m^2 \gamma^2 \Lambda_m S(Z)}
\]
The obtained values (K$_1$) for CuCl$_2$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M: L) [21, 22] by using equation:

$$K_f = \frac{\Lambda_{ML} - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]}$$  \hspace{1cm} (4)

Where $\Lambda_{ML}$ is the limiting molar conductance of the CuCl$_2$ alone, $\Lambda_{obs}$ is the molar conductance of solution during titration and $\Lambda_{ML}$ is the molar conductance of the complex.

The obtained values (K$_1$) for CuCl$_2$-ligand stoichiometric complexes are presented in Table 3.
The calculated \( \Delta G_f \) values are presented in Table 4.

**Table 3:** Formation constants for 1:2, 1:1 and 2:1 (M/L) complexes in 80%V ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

<table>
<thead>
<tr>
<th></th>
<th>( K_f )</th>
<th>( \Delta G_f ) (k J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 1:2 ) (M/L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 1:1 ) (M/L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 2:1 ) (M/L)</td>
<td></td>
</tr>
<tr>
<td>( Cm ) 298.15 K</td>
<td>2.94E+05</td>
<td>7.20E+06</td>
</tr>
<tr>
<td>9.09E-05</td>
<td>1.51E+06</td>
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<tr>
<td>8.98E-05</td>
<td>4.78E+05</td>
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</tr>
<tr>
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<td>8.77E-05</td>
<td>1.39E+05</td>
<td>1.51E+05</td>
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<tr>
<td>8.67E-05</td>
<td>9.99E+04</td>
<td>1.07E+05</td>
</tr>
<tr>
<td>( Cm ) 298.15 K</td>
<td>2.94E+05</td>
<td>7.20E+06</td>
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<td>9.82E+05</td>
</tr>
<tr>
<td>9.26E-05</td>
<td>3.56E+05</td>
<td>3.87E+05</td>
</tr>
<tr>
<td>( Cm ) 298.15 K</td>
<td>2.94E+05</td>
<td>7.20E+06</td>
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<tr>
<td>9.09E-05</td>
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<td>2.92E+06</td>
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<tr>
<td>9.26E-05</td>
<td>3.56E+05</td>
<td>3.87E+05</td>
</tr>
</tbody>
</table>

The Gibbs free energies of formation for each stoichiometric complexes were calculated by using the equation:

\[
\Delta G_f = - R T \ln K_f \tag{5}
\]

The enthalpy (\( \Delta H \)) for \( \text{CuCl}_2 \) complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) by using van ’t Hoff equation \([23,24]\):

\[
\frac{d \ln K}{dT} = \frac{\Delta H^\Theta}{RT^2} \tag{6}
\]
Where $R$ is the gas constant (8.341 J) and $T$ is the absolute temperature. By drawing the relation between log $K_A$ and $1/T$, different lines are obtained indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometric complexes Table 7.

By drawing the relation between log $K_A$ and $1/T$, different lines are obtained indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometric complexes.

![Figure 7: The relation between (log $K_A$) and (1/T).](image)

From the relation between log $K_A$ and $1/T$, $\Delta H_A$ can be calculated for each type of complexes from the slope of each line ($-\Delta H/2.303R$). The entropy ($\Delta S_A$) for CuCl$_2$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) by using equation:

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

Where $S$ is the entropy of system.

The calculated values of ($\Delta H_A$) and ($\Delta S_A$) for CuCl$_2$-ligand stoichiometric complexes are presented in Table 5:

**Table 5: The enthalpies and entropies of association of complexes at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).**

<table>
<thead>
<tr>
<th>M:L</th>
<th>Temp</th>
<th>(ΔS$_A$)kJ/mol.K</th>
<th>(ΔH$_A$)kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293.15 K</td>
<td>298.15 K</td>
<td>303.15 K</td>
</tr>
<tr>
<td>1:2</td>
<td>0.2752</td>
<td>0.2752</td>
<td>0.2754</td>
</tr>
<tr>
<td>1:1</td>
<td>0.2956</td>
<td>0.2960</td>
<td>0.2962</td>
</tr>
<tr>
<td>2:1</td>
<td>0.3033</td>
<td>0.3036</td>
<td>0.3039</td>
</tr>
</tbody>
</table>

By drawing the relation between log $K_f$ and $1/T$, different lines are obtained indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometric complexes Figure 8.

The enthalpy $(\Delta H_f)$ for CuCl$_2$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) by using Van’t Hoff equation.

The calculated values of ($\Delta H_f$) and ($\Delta S_f$) for CuCl$_2$-ligand stoichiometric complexes are presented in Table 6:

**Table 6: The enthalpies and entropies of formation of complexes at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).**

<table>
<thead>
<tr>
<th>M:L</th>
<th>Temp</th>
<th>(ΔS$_f$)kJ/mol.K</th>
<th>(ΔH$_f$)kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293.15 k</td>
<td>298.15 K</td>
<td>303.15 K</td>
</tr>
<tr>
<td>1:2</td>
<td>0.4385</td>
<td>0.4356</td>
<td>0.4366</td>
</tr>
<tr>
<td>1:1</td>
<td>0.5311</td>
<td>0.5314</td>
<td>0.5296</td>
</tr>
<tr>
<td>2:1</td>
<td>0.5499</td>
<td>0.5532</td>
<td>0.5493</td>
</tr>
</tbody>
</table>
Since the conductance of an ion depends mainly on its mobility, it is quite reasonable to treat the rate process taking place with the change of temperature on the basis of equation (8):

$$/\omega = A e^{\frac{E_a}{RT}}$$

(8)

where A is the frequency factor, R is the gas constant and Ea is the Arrhenius activation energy of the transfer process. Consequently, from the plot of $\log /\omega$ vs. $1/T$, the Ea values can be evaluated as shown in Fig (9), giving high activation energy value due to solvation behavior.

**Figure 8: The relation between $(\log K_f)$ and $(1/T)$.**

**Figure 9: The relation between $\log /\omega$ and $1/T$. $E_a = 20.7985 \text{ kJ/mol}$**

**CONCLUSION**

The stability constants for the complexation of copper(II) ion with (BMPTS) were determined conductometrically at different temperatures. Thermodynamic parameters of complexation were determined from the temperature dependence of the formation constant. The negative values of $\Delta G$ show the ability of the studied ligand to form stable complexes and the process trend to proceed spontaneously. However, the obtained positive values of $\Delta H$ means that enthalpy is not the driving force for the formation of the complexes. Furthermore, the positive values of $\Delta S$ indicate that entropy is responsible for the complexing process. The formation constants and Gibbs free energies of different complexes follow that order: $K_f (2:1) > K_f (1:1) > K_f (1:2)$ for (M:L), and $\Delta G_r (2:1) > \Delta G_r (1:1) > \Delta G_r (1:2)$ for (M:L)
REFERENCES


