Potentiometric and Thermodynamic Studies of Some Azosulfoxine Derivatives and Their Metal Complexes

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Abstract: The proton-ligand dissociation constants of some azosulfoxine derivatives and metal-ligand stability constants of their complexes with the metal ions (Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$) have been determined potentiometrically in 0.1 M KCl and 50% (by volume) DMF-water mixture at (298, 308 and 318) K. The stability constants of the formed complexes increases in the order Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$. The effect of temperature was studied and the corresponding thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$) were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavourable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favourable.

Keywords: Azosulfoxines, potentiometry, stability constants and thermodynamics.

INTRODUCTION

There has been a growing interest in studying azo compounds especially heterocyclic compounds and their transition metal complexes, because of their wide importance in both academic and industrial fields [1-6]. These compounds and their metal complexes are interesting for various reasons. For example the presence of donor atoms such as N, S and O in the compound backbone contributes greatly to their thermal and environmental stability [7]. Other important features include the nature of metal–oxygen bonding interaction and the biological activity of these materials [8]. The presence of –N=N– group can lead to increase the solubility of low valent metal oxidation states due to its $\pi$ acidity and presence of low lying azo centered $\pi^*$ molecular orbitals [2, 3]. The azo compounds are used in dying processes; some of them are used in analytical separation of many metal ions in a mixture [4], redox active, pH-sensitive and their complexes act as a molecular switch [5]. In continuation of our earlier work [9-13], we report here the dissociation constant of 4-Methoxyphenylazo-5-sulfo-8-hydroxyquinoline (L$_1$), 4-phenylazo-5-sulfo-8-hydroxyquinoline (L$_2$) and 4-nitrophenylazo-5-sulfo-8-hydroxyquinoline (L$_3$) were prepared [14] from aniline or its p-substituted derivatives (10 mmol) which dissolved in hydrochloric acid (20 mmol/25 mL distilled water). The hydrochloric compounds were diazotized below -5 °C with a solution of sodium nitrite (0.8 gm, 10 mmol, 30 ml distilled water). The diazonium chloride was coupled with an alkaline solution of sulfoxine (10 mmol) in 20 mL of ethanol containing KOH (10 mmol). The crude dyes were collected by filtration and crystallized from dimethylformamide (DMF), then dried in a vacuum desiccator over anhydrous CaCl$_2$.

EXPERIMENTAL

All compounds and solvents used are pure grade chemicals from BDH Alderich or Sigma.

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A ligand solution (0.001 M) was prepared by dissolving an accurately weighed amount of the solid in DMF (Analar). Metal ion solutions (0.0001 M) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA [15]. Solutions of 0.001 M HCl and 1 M KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 50% (by volume) DMF-water mixture was used as titrant and standardized against oxalic acid (Analar).

The apparatus, general conditions and methods of calculation were the same as in previous work [9-11].
The following mixtures (i) – (iii) were prepared and titrated potentiometrically at 298 K against standard 0.002 M NaOH in a 50 % (by volume) DMF –water mixture:

i) $5 \text{ cm}^3 0.001 \text{ M } \text{HCl} + 5 \text{ cm}^3 1 \text{ M } \text{KCl} + 5 \text{ cm}^3 \text{ DMF}$

ii) $5 \text{ cm}^3 0.001 \text{ M } \text{HCl} + 5 \text{ cm}^3 1 \text{ M } \text{KCl} + 5 \text{ cm}^3 0.001 \text{ M ligand}.$

iii) $5 \text{ cm}^3 0.001 \text{ M } \text{HCl} + 5 \text{ cm}^3 1 \text{ M } \text{KCl} + 5 \text{ cm}^3 0.001 \text{ M ligand} + 10 \text{ cm}^3 0.0001 \text{ M metal chloride}.$

For each mixture, the volume was made up to 50 cm$^3$ with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K. The temperature was controlled to within ± 0.05 K by circulating thermostated water (Neslab 2 RTE 220) through the outer jacket of the vessel. The pH measurements were carried out using VWR Scientific Instruments Model 8000 pH-meter accurate to ± 0.01 units. The pH-meter readings in the non–aqueous medium were corrected [16]. The electrode system was calibrated according to the method of Irving et al. [17]. All titrations have been carried out between pH 4.0 – 11.0 and under nitrogen atmosphere.

**RESULTS AND DISCUSSION**

The average number of the protons associated with ligands (L$_1$, L$_2$ and L$_3$) at different pH values, $\bar{n}_A$, was calculated from the titration curves of the acid in the absence and presence of ligands (L$_1$, L$_2$ and L$_3$).

Applying eq. 1:

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^o + E^o)}{(V^o + V_1)TC_L^o}$$

where Y is the number of available protons in ligands (L$_1$, L$_2$ and L$_3$) (Y=2) and $V_1$ and $V_2$ are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, $V^o$ is the initial volume (50 cm$^3$) of the mixture, $TC_L^o$ is the total concentration of the reagent, $N^o$ is the normality of sodium hydroxide solution and $E^o$ is the initial concentration of the free acid. Thus, the formation curves ($\bar{n}_A$ vs. pH) for the proton-ligand systems were constructed and found to extend between 0 and 2 in the $\bar{n}_A$ scale. This means that ligands (L$_1$, L$_2$ and L$_3$) has two ionizable protons (the enolized hydrogen ion of the phenolic OH group, $pK_1^H$ and the enolized hydrogen ion of the –SO$_3$H, $pK_2^H$).

Different computational methods [18] were applied to evaluate the dissociation constants. Three replicate titrations were performed. The average values obtained are listed in Table 1. The completely protonated form of the ligands (L$_1$, L$_2$ and L$_3$) has two dissociable protons, that dissociates in the measurable pH range. The deprotonation of the phenolic hydroxy group most probably results in the formation of stable intramolecular H–bonding with the nitrogen of the azo group. Such an interaction decreases the dissociation process of ligands (L$_1$, L$_2$ and L$_3$), i.e. increases the $pK^H$ value [19, 20].

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}_A$) vs. the free ligands exponent (pL), according to Irving and

**Table 1: Thermodynamic Functions for the Dissociation Constants of Ligands in 50% (by Volume) DMF-Water Mixture and 0.1 M KCl at Different Temperatures**

| Compound | T/K | Dissociation Constant | Gibbs energy kJ.mol$^{-1}$ | Enthalpy kJ.mol$^{-1}$ | Entropy J.mol$^{-1}$.K$^{-1}$ |
|----------|-----|-----------------------|-----------------------------|-------------------------|-------------------------------|
|          |     | $pK_1^H$ | $pK_2^H$ | $\Delta G_1$ | $\Delta G_2$ | $\Delta H_1$ | $\Delta H_2$ | $\Delta S_1$ | $\Delta S_2$ |
| L1       | 298 | 9.95     | 5.61    | 56.77       | 32.00       | 36.99          | 27.21         | 66.37         | 16.07         |
|          | 308 | 9.76     | 5.46    | 57.55       | 32.19       | 66.57          | 16.16         | 66.32         | 16.16         |
|          | 318 | 9.56     | 5.30    | 58.08       | 32.32       | 66.57          | 16.16         | 66.32         | 16.06         |
| L2       | 298 | 9.62     | 5.48    | 54.89       | 31.26       | 54.53          | 18.90         | 51.94         | 19.05         |
|          | 308 | 9.40     | 5.31    | 55.43       | 31.31       | 54.51          | 18.53         | 51.94         | 19.05         |
|          | 318 | 9.06     | 5.20    | 55.16       | 31.66       | 51.94          | 19.05         |                |               |
| L3       | 298 | 8.56     | 5.42    | 48.84       | 30.92       | 45.03          | 23.45         | 46.49         | 23.89         |
|          | 308 | 8.34     | 5.29    | 49.18       | 31.19       | 44.67          | 23.57         |                |               |
|          | 318 | 8.17     | 5.18    | 49.74       | 31.53       | 46.49          | 23.89         |                |               |
Rossotti [21]. The average number of the reagent molecules attached per metal ion, $\bar{n}$, and free ligands exponent, $p_L$, can be calculated using eqs. 2 and 3:

$$n = \frac{(V_2 - V_3)(N^0 + E^0)}{(V^0 + V_2)\pi A T C_M^0}$$  \hspace{1cm} (2)

and

$$p_L = \log_{10}\left(\frac{\sum_{n=0}^{n-1} \beta_n \frac{1}{\text{anti } \log \text{pH}}}{T C_{L}^0 - n T C_{M}^0} \right) \cdot \frac{V^0 + V^3}{V^0}$$  \hspace{1cm} (3)

where $T C_M^0$ is the total concentration of the metal ion present in the solution, $\beta_n^H$ is the overall proton-reagent stability constant. $V_1$, $V_2$, and $V_3$ are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand and complex, respectively. These curves were analyzed and the successive metal-ligand stability constants were determined using different computational methods [22, 23]. The values of the stability constants ($\log K_1$ and $\log K_2$) are given in Table 2. The following general remarks can be pointed out:

(i) The maximum value of $\bar{n}$ was $\sim 1$ indicating the formation of 1:2 (metal : ligand) complexes only [24].

(ii) The metal ion solution used in the present study was very dilute ($2 \times 10^{-5}$ M), hence there was no possibility of formation of polynuclear complexes [25, 26].

(iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves point to the formation of strong metal complexes [27, 28].

(iv) For the same ligand at constant temperature, the stability of the chelates increases in the order $\text{Mn}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$ and $\text{Cu}^{2+}$ [29, 30]. This order largely reflects that the stability of $\text{Cu}^{2+}$ complexes are considerably larger than those of other metals of the 3d series. Under the influence of both the polarizing ability of the metal ion and the ligand field [31], $\text{Cu}^{2+}$ will receive some extra stabilization due to tetragonal distortion of octahedral symmetry in its complexes. The greater stability of $\text{Cu}^{2+}$ complexes is produced by the well known Jahn–Teller effect [32].

The dissociation constant ($pK^{H}$) for ligands (L1, L2 and L3), as well as the stability constants of its complexes with $\text{Mn}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$ and $\text{Cu}^{2+}$ have been evaluated at 298 K, 308 K, and 318 K, and are given in Tables 1 and 2, respectively. The enthalpy ($\Delta H$) for the dissociation and complexation process was calculated from the slope of the plot $pK^{H}$ or $\log K$ vs.

| Compound | $\text{M}^{n+}$ | 298K | 308K | 318K |
|----------|-----------------|------|------|------|
|          | $\log K_1$ | $\log K_2$ | $\log K_1$ | $\log K_2$ | $\log K_1$ | $\log K_2$ |
| L1       | $\text{Mn}^{2+}$ | 7.41 | 6.34 | 7.56 | 6.48 | 7.71 | 6.62 |
|          | $\text{Co}^{2+}$ | 7.59 | 6.51 | 7.75 | 6.65 | 7.89 | 6.80 |
|          | $\text{Ni}^{2+}$ | 7.72 | 6.63 | 7.88 | 6.77 | 8.02 | 6.91 |
|          | $\text{Cu}^{2+}$ | 7.95 | 6.87 | 8.12 | 7.03 | 8.25 | 7.20 |
| L2       | $\text{Mn}^{2+}$ | 7.29 | 6.22 | 7.44 | 6.36 | 7.60 | 6.60 |
|          | $\text{Co}^{2+}$ | 7.47 | 6.39 | 7.62 | 6.54 | 7.76 | 6.70 |
|          | $\text{Ni}^{2+}$ | 7.60 | 6.52 | 7.74 | 6.66 | 7.89 | 6.80 |
|          | $\text{Cu}^{2+}$ | 7.84 | 6.77 | 7.98 | 6.92 | 8.15 | 7.08 |
| L3       | $\text{Mn}^{2+}$ | 7.12 | 6.06 | 7.25 | 6.20 | 7.39 | 6.34 |
|          | $\text{Co}^{2+}$ | 7.28 | 6.22 | 7.42 | 6.36 | 7.36 | 6.60 |
|          | $\text{Ni}^{2+}$ | 7.40 | 6.34 | 7.54 | 6.48 | 7.70 | 6.62 |
|          | $\text{Cu}^{2+}$ | 7.66 | 6.60 | 7.81 | 6.75 | 7.96 | 6.89 |
\[ \Delta G = -2.303 \, RT \log K = \Delta H - T \Delta S \]  

or

\[ \log K = (\Delta H / 2.303 \, R)(1/T) + (\Delta S / 2.303 \, R) \]

From the \( \Delta G \) and \( \Delta H \) values one can deduce the entropy \( \Delta S \) using the well known relationships 4 and 6:

\[ \Delta S = (\Delta H - \Delta G) / T \]

All thermodynamic parameters of the dissociation process of ligands (L1, L2 and L3) are recorded in Table 1. From these results the following conclusions can be made:

(i) The pK\textsuperscript{H} values decrease with increasing temperature, i.e. the acidity of the ligand increases [9].

(ii) A positive value of \( \Delta H \) indicates that the process is endothermic.

(iii) A large positive value of \( \Delta G \) indicates that the dissociation process is not spontaneous [33].

(iv) A negative value of \( \Delta S \) is obtained due to the increased order as a result of the solvation process.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species [23] and the obtained values of \( \Delta H \) and \( \Delta S \) can then be considered as the sum of two contributions: (a) release of H\textsubscript{2}O molecules, and (b) metal-ligand bond formation. Examination of these values shows that:

(i) The stability constants (log \( K_1 \) and log \( K_3 \)) for ligands (L1, L2 and L3) complexes increase with increasing temperature, i.e. its stability constants increase with increasing temperature [34].

(ii) The negative value of \( \Delta G \) for the complexation process suggests the spontaneous nature of such processes [35].

(iii) The \( \Delta H \) values are positive, meaning that these processes are endothermic and favourable at higher temperature.

(iv) The \( \Delta S \) values for the ligand complexes are positive, confirming that the complex formation is entropically favourable [11].

An inspection of the results in Table 1 reveals that the pK\textsuperscript{H} values of \( L_2 \) and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. The \( p \)\textsubscript{OCH\textsubscript{3}} derivatives (L1) have a lower acidic character (higher pK\textsuperscript{H} values) than the \( p \)\textsubscript{NO\textsubscript{2}} (L3). This is quite reasonable because the

| Compound | \( Mn^2+ \) | Gibbs energy/kJ.mol\textsuperscript{-1} | Enthalpy/kJ.mol\textsuperscript{-1} | Entropy/J.mol\textsuperscript{-1}.K\textsuperscript{-1} |
|----------|-------------|----------------------------------------|----------------------------------|---------------------------------|
|          | \( \Delta G_1 \) | \( \Delta G_2 \) | \( \Delta H_1 \) | \( \Delta H_2 \) | \( \Delta S_1 \) | \( \Delta S_2 \) |
| L1       | Mn\textsuperscript{2+} | 42.28 | 36.17 | 27.21 | 25.39 | 233.18 | 206.57 |
|          | Co\textsuperscript{2+} | 43.30 | 37.41 | 27.23 | 26.29 | 236.67 | 212.85 |
|          | Ni\textsuperscript{2+} | 49.75 | 37.82 | 27.23 | 25.39 | 258.32 | 212.11 |
|          | Cu\textsuperscript{2+} | 51.06 | 39.19 | 27.25 | 29.92 | 262.78 | 231.91 |
| L2       | Mn\textsuperscript{2+} | 41.59 | 35.49 | 28.11 | 34.37 | 233.89 | 234.42 |
|          | Co\textsuperscript{2+} | 42.62 | 36.46 | 26.31 | 28.11 | 250.43 | 216.67 |
|          | Ni\textsuperscript{2+} | 43.36 | 37.20 | 26.29 | 25.39 | 233.72 | 210.03 |
|          | Cu\textsuperscript{2+} | 44.73 | 38.60 | 28.09 | 28.11 | 244.36 | 233.85 |
| L3       | Mn\textsuperscript{2+} | 40.62 | 34.57 | 24.84 | 25.39 | 219.66 | 201.20 |
|          | Co\textsuperscript{2+} | 41.53 | 35.49 | 25.39 | 25.39 | 224.56 | 234.42 |
|          | Ni\textsuperscript{2+} | 42.22 | 36.17 | 27.19 | 25.39 | 232.91 | 206.57 |
|          | Cu\textsuperscript{2+} | 43.70 | 37.65 | 27.21 | 26.31 | 237.95 | 214.63 |
presence of \(p\)-OCH\(_3\) group (i.e. an electron-donating effect) will enhance the electron density by their high positive inductive or mesomeric effect, whereby a stronger O—H bond is formed. The presence of \(p\)-NO\(_2\) group (i.e. an electron-withdrawing effect) will lead to the opposite effect. The para substituent in the phenyl moiety have a direct influence on the pK\(_a\) values of the investigation compounds, revealing the coplanarity of the molecule and thus affording a maximum resonance via delocalization of its \(\pi\)-system.

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