Extraction of Chromium(III) and Manganese(II) with N, N'-ethylenbis(salicylimine)(H₂EBSI) in Acid Medium: Determination of Stability Constant and Thermodynamic Parameters of the Extracted Species

F. S. Nworie¹*, F. I. Nwabue¹ and J. John¹

¹Department of Industrial Chemistry, Ebonyi State University, P.M.B. 053 Abakaliki, Ebonyi State, Nigeria.

Authors’ contributions

This work was carried out in collaboration between all authors. Author FIN designed the study. Author FSN performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors JJ and FSN managed the analyses of the study. Authors FIN, FSN and JJ managed the literature searches. All authors read and approved the final manuscript.

ABSTRACT

In this study, the solvent extraction of chromium(III) and manganese(II) with N, N'-ethylenbis(salicylimine) were carried out from different concentrations of various mineral acids (HCl, HNO₃, H₂SO₄, and HClO₄). In the range of analytical concentrations of the acids studied (0.0001-2M), it was discovered that the distribution ratio was highest in 0.0001M HCl and lowest in HClO₄ for chromium (III) and manganese (II). The stability constant of the extracted species suggest that chromium (III) specie is more stable than manganese(II) specie (Logβ Cr(III) = 5.98 and Logβ
Mn(II) = 5.88). Also, the extraction system suggests a chelating mechanism where mononuclear ion pair chromium(III) H₂EBSI complex and dinuclear ion pair manganese(II) H₂EBSI complex are formed.

Keywords: Chromium(III); manganese(II); stability constant; N; N'-ethylenebis(salicylimine); liquid-liquid extraction.

1. INTRODUCTION

N,N'-ethylenebis(salicylimine) a tetradeutate ligand prepared by the condensation of salicylaldehyde and ethylenediamine has been known to form complexes with most transition elements such as Mn, Cr, Co, V, Cu, Ti, Ru, Fe, Zn [1-2] and other metals such as beryllium [3].

The use of N, N'-ethylenebis(salicylimine) in the extraction, preconcentration and determination of metal ions from various matrices have been widely reported [4-8]. Distorted octahedral geometry of N, N'-ethylenebis(salicylimine) metal complexes have been reported [9]. Also mononuclear and dinuclear-complexes of Cr and Mn - N, N'-ethylenebis(salicylimine) respectively have been prepared and characterized [10-11].

Studies [1,12] have noted that the separation and concentration of metal ions in acidic regions using Schiff base ligands such as N, N'-ethylenebis(salicylimine) is limited as the ligands are easily decomposed at acidic regions. This suggests they easily undergo demetallation and ligand degradation. This calls for the need of studying the stability of this ligand and its metal complexes in acidic solutions. Complexes of N, N'-ethylenebis(salicylimine) have been widely applied as a catalyst in the formation of epoxy resins [11], and in spectrophotometric studies [13-15]. Not much work have been done on the solution chemistry of N, N'-ethylenebis(salicylimine) and its manganese (II) and chromium (III) ions hence the need for this research.

This study x-rayed the extraction, stability constant studies and thermodynamic parameter determination of species formed by the complexation of N, N'-ethylenebis(salicylimine) with Cr(III) and Mn(II) ions.

2. EXPERIMENTAL

2.1 MATERIALS AND METHODS

All the chemicals used in this study were of analytical grade from Merc, Germany and BDH and used without further purification unless otherwise stated. The chemicals include HNO₃, H₂SO₄, HCl, HClO₄, Cr(NO₃)₃.9H₂O, Mn(CH₃COO)₂.4H₂O, NaCl, salicylaldehyde, ethylenediamine, chloroform, carbon tetrachloride, sodium carbonate and absolute ethanol. Distilled deionized water was used through the experimental process. N,N'-ethylenebis(salicylimine) was prepared by the method described by Nworie et al. [13] by mixing ethylenediamine and salicylaldehyde in the ratio of 1:2. The solution was heated and the resulting compound recrystallized twice in carbon tetrachloride. The golden yellow crystal formed was dried according to the method of Boucher and Farrell [16]. 0.5% of the ligand solution was prepared by dissolving requisite amount in 100 mL of absolute ethanol. 1 mg/mL metal ion solutions were prepared by dissolving requisite amount of Cr(NO₃)₃.9H₂O and Mn(CH₃COO)₂.4H₂O in distilled deionized water. 2M solution of the acids (HCl, HNO₃, H₂SO₄ and HClO₄) were prepared and standardized against standard sodium carbonate solution, the exact concentration of the various acids were determined and employed in the calculations.

2.2 Extraction Procedure

The extraction was performed by pipetting 0.1 mL of 4 µg/mL solution of each metal ion into different extraction bottles. A solution of an acid was added into each of the extraction bottles containing the metal ion solution and distilled deionized water added such that on final dilution to 5.0 mL analytical concentration range of 0.0001 M to 2 M of the acid was formed. 0.1 mL of the ligand solution was added to each of the extraction bottles and predetermined time for colour development allowed (10 minutes for each metal). Equal volume (5.0 mL) of chloroform was added and the phases equilibrated for 10 minutes for chromium (III) and 15 minutes for Mn (II) as predetermined, the phases were allowed to separate and the unextracted metal ions in the aqueous raffinate determined spectro-photo metrically as described previously [13] at 415 nm and 405 nm for chromium(III) ions and Mn(II) respectively. The amount of Cr (III) and Mn(II)
were determined from the material balance as described by Nwabue and Okafor [17].

The distribution ratio (D) was calculated as

\[ D = \frac{[MLn]_{\text{org}}}{[M^{n+}]_{\text{aq}}} \]  

(1)

Where MLn (org) is concentration of the metal chelate in organic phase and M\(^{n+}\)(aq) is the concentration of the metal ion in the aqueous phase.

### 2.3 Determination of the Thermodynamic Parameters

The thermodynamic parameters \(\Delta G^0\), \(\Delta H^0\) and \(\Delta S^0\) were determined as described by Zumdal [18] for each of the metal complexes depending on their stability constants. It was noted by Zumdal [18] that the stability constant and free energy of formation of a complex is related by

\[ \Delta G_n^0 = -2.303RT\beta_n \]  

(2)

Where T is absolute temperature R is universal gas constant and \(\beta_n\) is stability constant of the complex. The values of \(\Delta H^0\) were calculated from the relation.

\[ \frac{d\ln \beta_n}{dT} = -\frac{\Delta H_n^0}{RT} \]  

(3)

This shows the quantitative dependence of enthalpy of formation on the stability constant. Also the quantitative dependence of stability constant on temperature as reported by Zumdal [18] can be shown as

\[ \Delta G_n^0 = \Delta H_n^0 - T\Delta S_n^0 \]  

(4)

### 2.4 Determination of Stability Constant

The Job’s continuous variation method was used for the determination of the stability constant of the complexes [18,19,20]. Absorbances of the complexes were plotted against the reagent molar fractions. The stoichiometric ratio of the complex g: m for the complexation of the ligand (g) with the metal ion m for chromium and manganese are 1:1 and 2:1 respectively.

Thus, the degree of complex dissociation \(\alpha\) is represented by

\[ \alpha = \frac{S_0 - S_{\text{max}}}{S_0} = 1 - \frac{S_{\text{max}}}{S_0}. \]  

(5)

S\(_{\text{max}}\) = Analytical signal maximum on the curve

So = Analytical signal evaluated theoretically under maximum complexation condition.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Extraction of the Metal Species

Equilibration of a metal ion M\(^{n+}\) and reagent HA forms a metal chelate MAn according to the equation.

\[ M^{n+} + n\text{HA} \rightarrow M\text{An} + n\text{H}^+ \]  

(6)

\(n\) represents the number of moles of the chelating agent.

The \(k_{\text{ex}}\) for the extraction then becomes

\[ K_{\text{ex}} = \frac{[M\text{An}]_{\text{org}}}{[M^{n+}]_{\text{HA}}^{n}_{\text{org}}} \]  

(7)

\[ K_{\text{ex}} = \frac{D[H^+]^n}{[\text{HA}]^{n}_{\text{org}}} \]  

(8)

The distribution ratio \(D\) is

\[ \log D = \log k_{\text{ex}} + n \log [\text{HA}] + n p^H \]  

(9)

But since the extraction is in the presence of an acid, the ligand is protonated and the reaction below was proposed previously [17].

\[ k_{\text{ex}}\]

\[ M^{n+} + nH_2B^+ + nX^- \Rightarrow M(H_2B)^n_+ nX^- \]

\[ + mH^+ \]  

(10)

\[ k_{\text{ex}} = \frac{[M(H_2B)^n_+ nX^-][H^+]^m}{[M^{n+}] [H_2B]^m [X^-]^n} \]  

(11)

Consequently, the distribution ratio is

\[ \log D = m \log [H_2B] + n \log [X^-] + m \log K_1 + \log k_{\text{ex}} \]  

(12)

Where X\(^-\) represents the acid radicals Cl\(^-\), ClO\(_3^-\), NO\(_2^-\), or HSO\(_4^-\)

\[ \text{and} \quad \log K_1 = \log[H_2EBSI^+] - \log[H_2EBSI] + p^H \]  

(13)

#### 3.3 Effect of Concentration of Acid on the Extraction of Metal ions
The effect of concentration of acid on the extraction of Mn(II) and Cr(III) using H₂EBSI is shown in Fig. 1 and Fig. 2 respectively. From the graph, Cr(III) is best extracted in 10⁻⁴ M HCl where the distribution ratio is 199 and least extracted in 10⁻⁴ M HClO₄ where the distribution ratio is 2.68. The distribution ratio for the extraction of Cr(III) in 10⁻⁴ M HNO₃ and H₂SO₄ are 19.5 and 12.7 respectively. The graph shows lower distribution ratio at higher acid concentrations suggesting lower extraction of the metal ion.

For Mn(II) ion extraction, the distribution ratio is highest at 10⁻⁴ M HCl (D = 198) and lowest in 10⁻⁴ M HClO₄ (D = 6). The distribution ratio for the extraction of Mn(II) in 10⁻⁴ M HNO₃ and H₂SO₄ are 99 each. The extraction profile shows quantitative extraction at lower acid concentrations whereas at higher concentration of acids, the extraction decreased monotonously as shown in the graphs.

3.2 Mechanism of Extraction of Metal ions

From the plot of log D of Cr(III) and Mn(II) versus the ligand concentration (H₂EBSI) fig. 3, a chelating mechanism is proposed.

\[
\begin{align*}
\text{Cr}^{3+} + \text{H}_2\text{EBSI} \xrightarrow{k_{\text{ex}}} \text{Cr(HEBSI)}^{2+} + \\
\text{H}^+ \quad \text{......} \quad (14)
\end{align*}
\]

Mononuclear and dinuclear H₂EBSI complexes of Chromium and Manganese have been reported by Zhang et al. and Lloret et al. [10,11]. The mechanism suggests ion pair complexes of the type

\[
[\text{Mn(EBSI)}^{2+}]X^- \quad \text{and} \quad [\text{Cr(EBSI)(OH)}_2]X^-
\]

Log kex calculated was 0.4 and -0.3 for Chromium and Manganese respectively. This suggests that chromium complex is more stable than manganese – H2EBSI complex.

3.4 Determination of Stability Constant and Thermodynamic Parameters

The stability constant and thermodynamic parameters of Cr(III) and Mn(II) – H₂EBSI complexes are presented in table 1. The stability constant for Cr(III) is 5.98 and Mn(II) 5.88 expressed as log β. This suggests that Cr(III) is more stable than Mn(II). The Pka expressed as \(\Delta G_0^\circ = -2.303RT \text{PKa} \) for the complexes are also shown in the table to be 7.76 and 7.69 for Cr(III) and Mn(II) respectively.
Fig. 1. Plot of logDVs log[Acid] for Mn(II) with H2EBSI

Fig. 2. Plot of logDVs log[Acid] for Cr(III) with H2EBSI
Table 1. Stability constants and thermodynamic parameters of Cr(III) and Mn(II) H2EBSI complexes

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cr(III)</th>
<th>Mn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermodynamic Stability Constant</td>
<td>5.98</td>
<td>5.88</td>
</tr>
<tr>
<td>$\Delta G^0$ (KJ/mol)</td>
<td>-43.99</td>
<td>-43.58</td>
</tr>
<tr>
<td>$\Delta H^0$ (KJ/mol)</td>
<td>-148.59</td>
<td>-146.11</td>
</tr>
<tr>
<td>$\Delta S^0$ (KJ/mol)</td>
<td>-0.351</td>
<td>-0.344</td>
</tr>
<tr>
<td>Pka</td>
<td>7.76</td>
<td>7.69</td>
</tr>
</tbody>
</table>

The thermodynamic parameters as presented in the table shows that $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ are all negatives and based on this, the following assumptions are made.

1. The negative value of $\Delta S^0$ shows that the complex formation involves a solvation process [19,21].
2. The negative value of $\Delta G^0$ suggests that the complexation process is spontaneous [19,21].
3. The negative value of $\Delta H^0$ suggests that the complexation process is exothermic and thermodynamically unfavourable at higher temperature.

4. CONCLUSION

The following conclusion can be drawn from the result of the study.

1. H2EBSI- complexes of Cr(III) and Mn(II) with acid solutions are extractable with chloroform at the optimized conditions.
2. The complexes of Mn(II) and Cr(III) with H2EBSI are dinuclear and mononuclear respectively. Results from stability constant and thermodynamic parameters suggest that Cr-H2EBSI is more stable than Mn-H2EBSI.
3. Extraction from the acids at different concentrations suggest that the metal ions are better extracted at $10^{-4}$ M HCl.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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