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Extraction of Chromium(III) and Manganese(II) with N, N^{I}-ethylenebis(salicylimine)(H_2EBSI) in Acid Medium: Determination of Stability Constant and Thermodynamic Parameters of the Extracted Species

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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.

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ABSTRACT

In this study, the solvent extraction of chromium(III) and manganese(II) with N, N^{1}-ethylenebis(salicylimine) were carried out from different concentrations of various mineral acids (HCl, HNO_3, H_2SO_4, and $HClO_4$). 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 $HClO_4$ 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

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Mn(II) = 5.88). Also, the extraction system suggests a chelating mechanism where mononuclear ion pair chromium(III) H_2EBSI complex and dinuclear ion pair manganese(II) H_2EBSI complex are formed.

Keywords: Chromium(III); manganese(II); stability constant; N; N^1-ethylenebis(salicylimine); liquid-liquid extraction.

1. INTRODUCTION

N,N^1-ethylenebis(salicylimine) a tetradentate 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^I-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^I-ethylenebis(salicylimine) metal complexes have been reported [9]. Also mononuclear and dinuclear-complexes of Cr and Mn - N, N^I-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^I-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^I-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^I-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^I-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 HNO_3, H_2SO_4, HCl, $HClO_4$, $Cr(NO_3)_3.9H_2O$, $Mn(CH_3COO)_2.4H_2O$, NaCl, salicylaldehyde, ethylenediamine, chloroform, carbontetrachloride, sodium carbonate and absolute ethanol. Distilled deionized water was used through the experimental process. N,N^1- ethylenebis (salicylimine) was prepared by the method described by Nworie et al. [13] by mixing ethylenediamine and salicyladehyde 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 100mL of absolute ethanol. 1 mg/mL metal ion solutions were prepared by dissolving requisite amount of $Cr(NO_3)_3$. $9H_20$ and $Mn(CH_3COO)_2$. $4H_20$ in distilled deionized water. 2M solution of the acids (HCl, HNO_3, H_2SO_4 and $HClO_4$) 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-photometrically 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

$$D = \frac{[MLn](\mathrm{org})}{[M^{n+}](\mathrm{aq})} \qquad (1)$$

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 ΔG^O , ΔH^O and ΔS^O 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

$$\Delta \mathrm{G}_\mathrm{n}^\mathrm{o} = -2.303\mathrm{RT}\beta\mathrm{n} \qquad (2)$$

Where T is absolute temperature R is universal gas constant and logβ is stability constant of the complex. The values of ΔH^O were calculated from the relation.

$$\frac{\mathrm{dIn}\beta}{\mathrm{dT}} = -\frac{\Delta \mathrm{H}_\mathrm{n}^\mathrm{O}}{\mathrm{RT}} \qquad (3)$$

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

$$\Delta \mathrm{G}_\mathrm{n}^\mathrm{o} = \Delta \mathrm{H}_\mathrm{n}^\mathrm{O} - \mathrm{T}\Delta \mathrm{S}_\mathrm{n}^\mathrm{o} \qquad (4)$$

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 ∝ is represented by

$$\propto = \frac{\mathrm{So}-\mathrm{Smax}}{\mathrm{So}} = 1 - \frac{\mathrm{Smax}}{\mathrm{So}}. \qquad (5)$$

Smax = 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.

$$\mathrm{M}^{\mathrm{n}+} + n\mathrm{HAorg} \rightleftarrows \mathrm{MAnorg} + \mathrm{nH}^+ \qquad (6)$$

n represents the number of moles of the chelating agent
The kex for the extraction then becomes

$$\mathrm{Kex} = \frac{[MAn]_{org} \cdot [H^+]^n}{[M^{n+}][HA]_{org}^n} \qquad (7)$$

$$Kex = \frac{D[H^+]^n}{[HA]_{org}^n} \qquad (8)$$

The distribution ratio D is

$$\log D = \log kex + n \log[HA] + n\mathrm{p}^\mathrm{H} \qquad (9)$$

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

$$\mathrm{M}^{\mathrm{n}+} + \mathrm{mH_3B}^+ + \mathrm{nX}^- \overset{\mathrm{kex}}{\rightleftharpoons} \mathrm{M(H_2B)}_\mathrm{M}^{\mathrm{n}+}\,\mathrm{nX}^- + \mathrm{mH}^+ \qquad (10)$$

$$\mathrm{kex} = \frac{[\mathrm{M\,(H_2B)}_\mathrm{M}^{\mathrm{n}+} \cdot \mathrm{nX}^-][\mathrm{H}^+]^\mathrm{m}}{[\mathrm{M}^{\mathrm{n}+}][\mathrm{H_3B}^+]^\mathrm{M}[\mathrm{X}^-]^\mathrm{n}} \qquad (11)$$

Consequently, the distribution ratio is

$$\log \mathrm{D} = \mathrm{m} \log[\mathrm{H_2B}] + \mathrm{n} \log[\mathrm{X}^-] + \mathrm{m} \log \mathrm{K}_1 + \log \mathrm{kex} \qquad (12)$$

Where x^- represents the acid radicals Cl^-, ClO_4^-, NO_3^-, or HSO_4^-

$$\text{and} \quad \log \mathrm{K}_1 = \log[\mathrm{H}_3 EBSI^+] - \log[H_2 EBSI] + \mathrm{p}^\mathrm{H} \qquad (13)$$

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 H_2EBSI 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 $HClO_4$ where the distribution ratio is 2.68. The distribution ratio for the extraction of Cr(III) in 10^{-4}M HNO_3 and H_2SO_4 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}HCl (D = 198) and lowest in 10^{-4} $HClO_4$ (D = 6). The distribution ratio for the extraction of Mn(II) in 10^{-4} HNO_3 and H_2SO_4 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 (H_2EBSI) fig. 3, a chelating mechanism is proposed.

$$\mathrm{Cr}^{3+} + \mathrm{H_2EBSI} \overset{\mathrm{kex}}{\rightleftharpoons} \mathrm{Cr}\ (HEBSI)^{2+} + \mathrm{H}^{+} \ldots\ldots\ldots. \qquad (14)$$

$$\mathrm{Mn}^{2+} + 2\mathrm{H_2EBSI} \overset{\mathrm{kex}}{\rightleftharpoons} \mathrm{Mn}(HEBSI)_2 + 2\mathrm{H}^{+}\ldots.. \ (15)$$

Mononuclear and dinuclear H_2EBSI 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

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

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) – H_2EBSI 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 $\Delta G_n^o = -2.303\mathrm{RT\,PKa}$ for the complexes are also shown in the table to be 7.76 and 7.69 for Cr(III) and Mn(II) respectively.

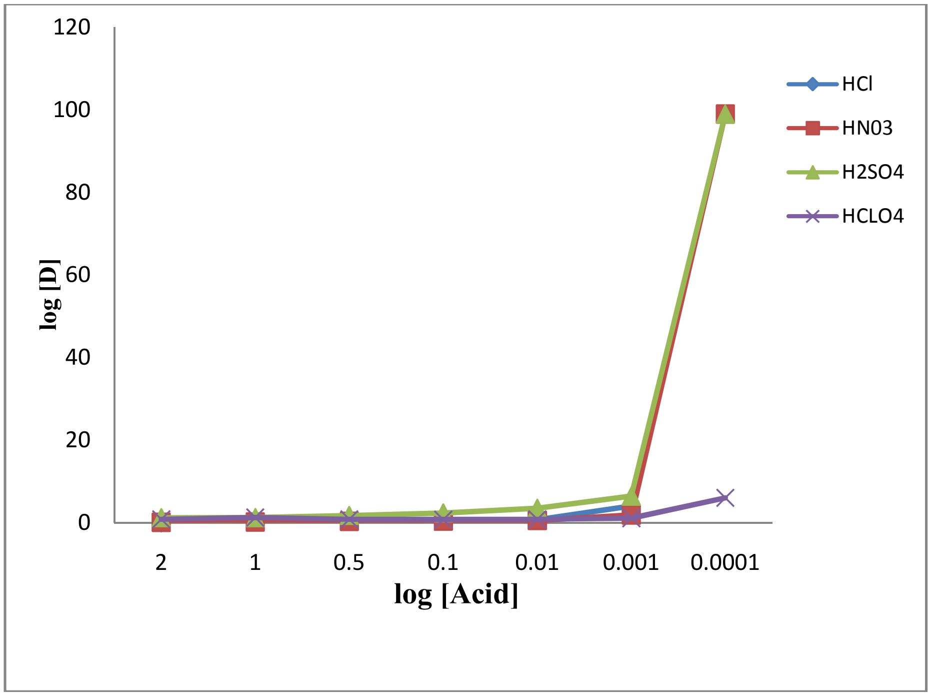

Fig. 1. Plot of logDVs log[Acid] for Mn(II)withH2EBSI

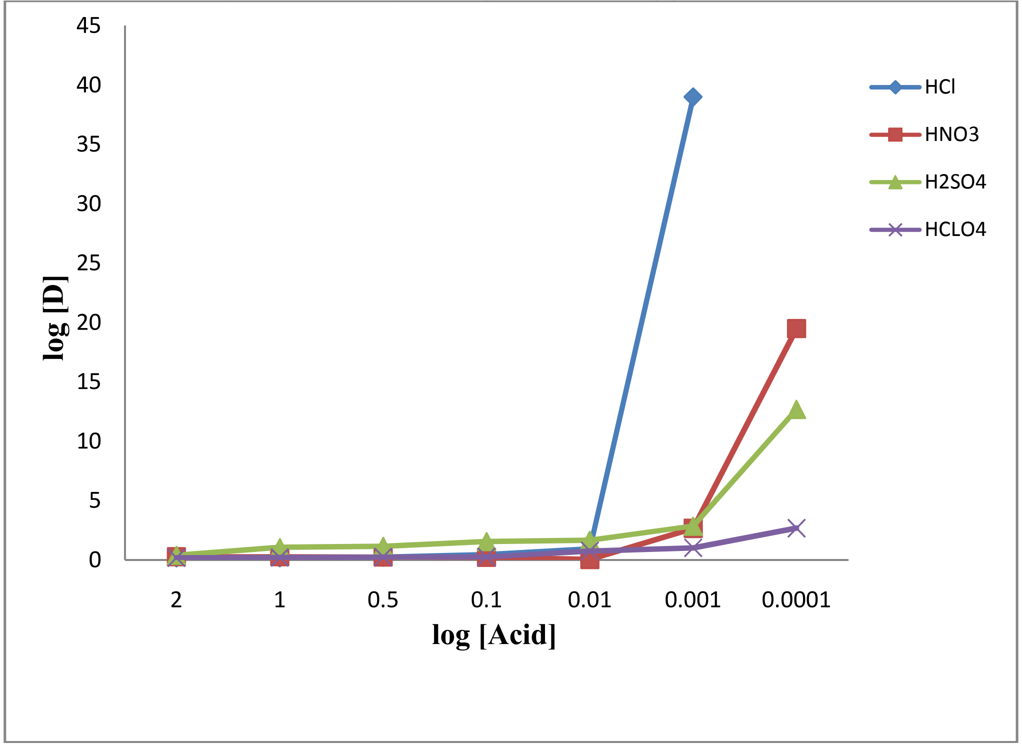

Fig. 2. Plot of logDVs log[Acid] for Cr(III)withH2EBSI

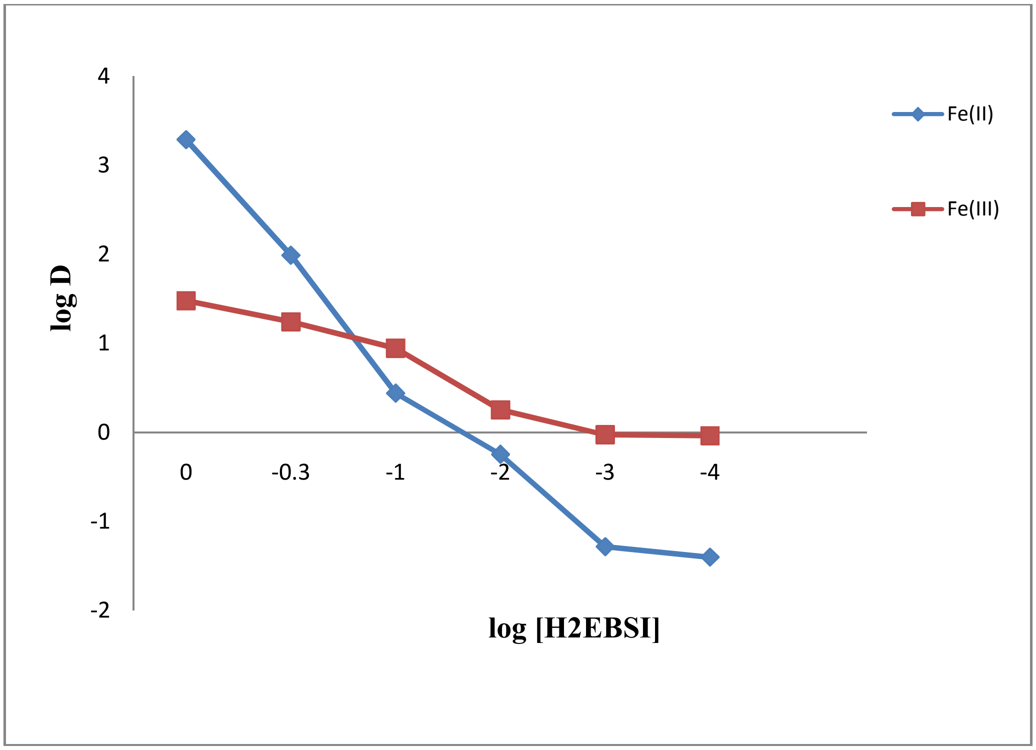

Fig. 3. Plot of logD vs log[H2EBSI] for Mn(II) and Cr(III) with H2EBSI

Table 1. Stability constants and thermodynamic parameters of Cr(III)and Mn(II) H_2EBSI complexes

Parameters	Cr(III)	Mn(II)
Thermodynamic Stability Constant	5.98	5.88
ΔG^0 (KJ/mol)	-43.99	-43.58
ΔH^0 (KJ/mol	-148.59	-146.11
ΔS^0 (KJ/mol)	-0.351	-0.344
Pka	7.76	7.69

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

(1) The negative value of ΔS^o shows that the complex formation involves a solvation process [19,21].
(2) The negative value of ΔG^o suggests that the complexation process is spontaneous [19,21].
(3) The negative value of ΔH^o 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) H_2EBSI- 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 H_2EBSI are dinuclear and mononuclear respectively. Results from stability constant and thermodynamic parameters suggest that Cr-H_2EBSI is more stable than Mn-H_2EBSI.
(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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