Chemometrics of Solvent Extraction of Mn(II) and Fe(III) Bis(salicylidene) Ethylenediamine Complexes in Acid Medium

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Abstract

In this study, the preparation and solvent extraction parameters of Mn(II) and Fe(III) -bis(salicylidene) ethylenediamine (H2SAL) was modeled with classical statistical analyses processed using SPSS19.0 software. The linear correlation coefficients for Mn(II) was between 59.5 to 1.0 % whereas for Fe(III), it was between 48-1.0%. The F-values, a measure of the significance of the models indicated that all the factors are needed though at differing degrees for the preparation and extraction of the metal complexes. The significance level for each model was lower than 5% and as such the relationship can be generalized to the whole process. The experiments indicated that the solvent extraction combined with modeling method was accurate, efficient, and reproducible and can be applied in industrial scale production.

Keywords: Modeling; H2SAL; Solvent Extraction; Metal Ions; SPSS.

1. Introduction

Manganese and iron, the twelfth and the fourth most abundant element in the earth crust has concentrations of $9.50 \times 10^{2}$ and $5.63 \times 10^{4}$ respectively [1-2]. Rustamov and Abbasova (2014) [2] have shown that manganese is present in water, sediment, soil and biological samples due to its cumulative nature and as such affect adversely the central nervous system. Iron on the other hand, has been shown to be important in many biological and biochemical processes but in excess, toxicity and eventual death of organisms have been implicated [3].

The determination of manganese with complexones from various samples using various analytical methods have been reported ranging from the use of toluidine [4], mordant brown 33 [5], phenoxazine [6], eosin [7], pyrazolone [8], 0-nitrobenzolazosalicylic acid [2] to Schiff bases like bis(salicylidene)ethylenediamine [9].

Similarly, the determination of iron using complexones such as Leucoxylenecyanol, 1,2-dihydroxy-3,4-diketocyclobutene(squaric acid), 1,2- methyl1-3-hydroxy-4-one, Thiocyanate, 9-(4-carboxyphenyl)-2,3,7-trihydroxy1-6-Flurone, 2′,3,4′,5,7-Pentahydroxyflavone has been described [10, 11].

In the determination, solvent extraction where the complexone and the extractant reacts with the metal ions in aqueous phase to generate a complex compound which could be retained as aqueous raffinate or transferred into the organic medium is routinely used. Kandil et al. (2012) and Ogwuegbu & Chileshe (2000) [12, 13] have shown that this

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method leads to favourable issues such as simplicity, selectivity, preconcentration, high speed, high range of determination, accuracy, ease of operation, precision, wide pH or acidity range, thermal stability and ease of manipulation.

Bis(salicylidene)ethylenediamine -metal complexes have been implicated to be useful in variety of biological, industrial, photochemical, catalytic and other miscellaneous applications [14, 15]. The preparation has always followed the organic synthetic pathways as described by Cozzi [16] without much attention to the solvent extraction method. Similarly, determinations of metal ions in spectrophotometry mainly end in evaluating the spectrophotometric properties such as molar absorptivity, detection limit, quantification limit without attention to the contributions of the various variables and their level of participation and relevance in complex formation and extraction.

This work models the preparation and extraction conditions of the complexes of Mn(II) and Fe(III) with a Schiff bis base H$_2$SAL with a view to determining the relevance of the variables and modeling their field applicability.

**2. Materials and Methods**

Analar grade reagents were used.

**Measurement and Characterization**

All measurement and characterizations involving FTIR, NMR, UV-Vis and melting point have been previously reported [19]. Rotary shaker (RF-12 Remi equipment) was used for all equilibrations and shakings. The concentration of the metal ions were determined spectrophotometrically as described elsewhere [18]. The contributions of the various parameters to preparation and extraction of the metal complexes was done using SPSS19.0 software.

**Solution preparation**

Solution of hydrochloric acid, H$_2$SAL, Mn(II) and Fe(II) were prepared according to literature [19].

**Synthesis of H$_2$SAL**

Synthesis, characterization and nature of H$_2$SAL have been reported previously [18, 19].

**Metal Extraction Analyses**

Preliminary investigation showed highest percentage extraction to be obtained at acid concentration of 10$^{-4}$M, 0.5% H$_2$SAL solution, temperature of 30°C and shaking time of 15 min. Solution of metal ions (10 cm$^3$) was added with 10 cm$^3$ of 10$^{-4}$M HCl solution, 5cm$^3$ of H$_2$SAL solution and 25 cm$^3$ of chloroform in a beaker. The mixture was stirred in a magnetic stirrer for 10 min and thereafter shaken for 15 min in a rotary shaker at 300 rpm and 30°C. The solution was then allowed to stand for 10 min in a separatory funnel and the phases separated. The amount of Mn(II) and Fe(III) ions unreacted and in the aqueous phase was determined spectrophotometrically[18]. The quantity of Mn(II) and Fe(III) ions, (b) and extraction efficiency, (%) indicating the quantity of metal ions complexed with H$_2$SAL is as shown in Equations 1 and 2.

\[
b = (x_o - x_e) \frac{Y}{Z}
\]

**Extraction efficiency (%)** = \(100 \times \frac{x_o - x_e}{x_e}
\)

where; \(x_o\) = initial amount of Mn(II) and Fe(III) ions, \(x_e\) = the equilibrium amount of Mn(II) and Fe(III) ions (mg/mL), \(Y\) and \(Z\) represents quantity of metal solution and mass of H$_2$SAL.

**3. Results and Discussions**

**Characterization of H$_2$SAL**

Data on the preparation and characterization of the ligand H$_2$SAL (Figure 1) has been previously reported [18-21].

![Figure 1. Synthesis of the Schiff base H$_2$EBNMD](image)
**Statistical Consideration**

The experimental conditions for the preparation and extraction of Mn(II) and Fe(III) H$_2$SAL complexes which include time, acid concentration, ligand concentration, temperature and metal concentration was modeled to ascertain the relevance, contribution and significance of the factors in the process. The results are presented in Tables 1 to 10 as analyzed using statistical and inferential method.

In Table 1, the coefficient of correlation between the amount extracted and time, temperature, metal concentration, acid concentration and ligand concentration has multiple $R^2$ of 0.612, 0.830, 1.000, 0.595 and 0.979 respectively indicating 51.2, 59.5 and 97.9% variance of the amount extracted to be accurate to time, acid concentration and ligand concentration.

An examination of Table 2 shows that the F values are significant with ligand concentration having the strongest significant value of 92.158. The F - values show that all the variables, listed have impact on the amount of complex extracted.

| Variable     | Model | Sum of squares | Df | Mean square | F     | Sig.  |
|--------------|-------|----------------|----|-------------|-------|-------|
| Time         | 1     | Regression 0.000 | 1  | 0.000       | 0.118 |
|              | 2     | Residual 0.000  | 3  | 0.000       | 4.724 | 0.118 |
|              | 3     | Total 0.000    | 4  |             |       |       |
| Temperature  | 2     | Regression 0.10  | 1  | 0.010       | 19.487| 0.12  |
|              | 3     | Residual 0.002  | 4  | 0.001       |       |       |
|              | 4     | Total 0.012    | 5  |             |       |       |
| Metal conc   | 3     | Regression 0.108 | 1  | 0.108       |       |       |
|              | 4     | Residual 0.000  | 2  | 0.00        | 6.606E 3 | 0.000 |
| Acid conc    | 4     | Total 946.026  | 1  | 946.026     |       |       |
|              | 5     | Regression     | 1  | 0.006       | 92.158| 0.011 |
|              | 6     | residual 0.000  | 2  | 0.00        |       |       |
| Ligand conc  | 5     | 0.006          | 3  | 0.006       |       |       |

An examination of Table 3 shows that the coefficient of determination ($R^2$) for all the variables are significant and explain the variation in the amount of complex extracted.

| Model        | Coefficient | Std err | t     | sig  |
|--------------|-------------|---------|-------|------|
| 1a constant  | 0.066       | 0.003   | 24.533| 0.000|
| Time         | 0.01        | 0.000   | 2.174 | 0.118|
| 1c Constant  | 0.710       | 0.032   | -4.414| 0.012|
| Temperature  | -0.005      | 0.001   | -4.414| 0.012|
| 1e Constant  | 0.008       | 0.005   | 81.2768| 0.000|
| Metal conc   | 0.029       | 0.000   | 81.2768| 0.000|
| 1d. Constant | 81.320      | 5.334   | -2.712 | 0.042|
| Acid conc    | 016.80      | 6.154   | -2.712 | 0.042|
| 1e Constant  | 0.630       | 0.001   | -9.600 | 0.011|
| Ligand conc  | 0.005       | 0.001   |       |      |
From Table 5, the coefficient of correlation between the variables, time, temperature, metal concentration, acid concentration and ligand concentration and indicates a strong and direct relationship among the variables with significance level for each lower than 5%.

| Variable  | Model | R   | R²   | Adj R² | Std Error of the estimate | R²change | F Charge | Df₁ | Df₂ | Sig f change |
|-----------|-------|-----|------|--------|---------------------------|----------|----------|-----|-----|-------------|
| Temperature| 1     | 0.817 | 0.668 | 0.585  | 0.10565                   | 0.668    | 8.045    | 1   | 4   | 0.047       |
| Metal conc| 1     | 1.000 | 1.000 | 1.000  | 0.00063                   | 1.000    | 2.492ES  | 1   | 2   | 0.00        |
| Time      | 1     | 0.754 | 0.569 | 0.426  | 0.01289                   | 0.569    | 3.963    | 1   | 3   | 0.141       |
| ligand conc| 1    | 0.782 | 0.612 | 0.534  | 15.58787                  | 0.612    | 7.885    | 1   | 5   | 0.038       |
| Acid conc | 1     | 0.840 | 0.706 | 0.633  | 0.13050                   | 0.706    | 9.608    | 1   | 4   | 0.036       |
| Time and acid conc| 1 | 0.693 | 0.480 | 0.350  | 1.85794                  | 0.480    | 3.695    | 2   | 8   | 0.073       |

**Statistical and Inferential Analysis on the Extraction of Fe (III) H₂SAL Complex**

An examination of Table 6 shows that the values are significant with acid concentration having the strong F-values of 9.608. Based on this, it is assumed that the variables, temperature, metal concentration, time, acid concentration and ligand concentration have an impact on the amount of complex prepared and extracted. The regression analysis for generating the possible combination of factors for the preparation and extraction of the complex is shown in Tables 7 and 8.
Table 6. Results of ANOVA Test for preparation and extraction of Fe(III) H$_2$SAL Complex

| Source of variation | Model    | SS      | Df | Ms    | F      | Sig   |
|---------------------|----------|---------|----|-------|--------|-------|
| Temperature         | 1. Regression | 0.090   | 1  | 0.090 | 8.045  | 0.047 |
|                     | Residual  | 0.045   | 4  | 0.011 |        |       |
|                     | Total     | 0.134   | 5  | 0.027 |        |       |
| Metal conc          | 2. Regression | 0.100   | 1  | 0.100 | 2.492  | 0.00  |
|                     | Residual  | 0.00    | 2  | 0.00  |        |       |
|                     | Total     | 0.100   | 3  | 0.033 |        |       |
| Time                | 3. Regression | 0.000   | 1  | 0.000 | 1.899  | 0.24  |
|                     | Residual  | 0.000   | 4  | 0.000 |        |       |
|                     | Total     | 0.000   | 5  | 0.000 |        |       |
| Acid conc           | 4. Regression | 0.164   | 1  | 0.164 | 9.608  | 0.036 |
|                     | Residual  | 0.068   | 4  | 0.17  |        |       |
|                     | Total     | 0.22    | 5  | 0.044 |        |       |
| Ligand conc         | 5. Regression | 1915.824 | 1 | 1915.824 | 7.885 | 0.038 |
|                     | Residual  | 1214.909 | 5 | 242.982 |      |       |
|                     | Total     | 3130.733 | 6 |       |        |       |
| Time and acid conc. | 6. Regression | 25.508  | 2  | 12.754 | 3.695  | 0.073 |
|                     | Residual  | 27.616  | 8  | 3.452 |        |       |
|                     | Total     | 53.124  | 10 |       |        |       |

Table 7. The results of regression analysis for the preparation of Fe(III) H$_2$SAL complex

| Model                    | Coefficient | Std error | T     | Sig   |
|--------------------------|-------------|-----------|-------|-------|
| a (constant) temperature | 0.845       | 0.145     | 5.811 | 0.004 |
| b (constant) metal conc. | -0.002      | 0.001     | -2.582| 0.123 |
| c (constant) Time        | 0.597       | 0.010     | 1.430 | 0.000 |
| D (constant) Acid        | 0.141       | 0.085     | 1.659 | 0.172 |
| e. (Constant ) ligand conc | -23.751   | 8.458     | -2.808| 0.38  |
|                         |             |           |       |       |

Table 8. The results of regression analysis for the preparation of Fe(III) H$_2$SAL complex with metal concentration constant

| Model                    | Coefficient | Std error | t     | Sig   |
|--------------------------|-------------|-----------|-------|-------|
| 1 (constant) Acid conc   | 0.832       | 1.154     | 0.721 | 0.492 |
| Acid conc                | 80.542      | 32.721    | 2.461 | 0.039 |
| Time                     | 0.000       | 0.000     | 0.586 | 0.574 |

The main model (Equation 4) for extraction of the complex formed from dependent, independent and control variables is a regression model which follows the fixed effect method (Equation 3).

Yit = b + β it + Eit

The model is of the form Y = f(x$_1$, x$_2$) where:

Y = Dependent variable = yit

X$_1$ = First independent variable = acid concentration.

X$_2$ = Second independent variable = time of extraction.

Y = 0.832 + 80.532 x$_1$, i(t$_i$) + 0.000x$_2$, i(t$_i$)

From Table 9, the relationship among the variables is strong, positive and direct. Also, the significance level for each is lower than 5%, and as such the relation can be generalized to the whole process.
Table 9. Result of Pearson correlation for extraction of Fe(III) H$_2$SAL complex

| Parameters       | Pearson correlation | Amount extracted | Temperature |
|------------------|---------------------|------------------|-------------|
| Amount extracted | Pearson correlation | 1.000            | -0.817      |
|                  | Sig (1-tailed)      | 6                | 0.024       |
|                  | N                   | 6                |             |
|                  | Pearson correlation | -0.817           | 1.000       |
|                  | Sig (1-tailed)      | 0.024            |             |
|                  | N                   | 6                | 6           |
| Amount extracted | Pearson correlation | 1.000            | 1.000       |
|                  | Sig (1-tailed)      | 0.000            |             |
|                  | N                   | 4                | 4           |
| Metal concentrative | Pearson correlation | 1.000            | -0.567      |
|                  | Sig (1-tailed)      | 0.120            |             |
|                  | N                   | 6                | 6           |
| Time             | Pearson correlation | -0.567           | 1.000       |
|                  | Sig (1-tailed)      | 0.120            |             |
|                  | N                   | 6                | 6           |
| Amount extracted | Pearson correlation | 1.000            | 0.840       |
|                  | Sig (1-tailed)      | 0.018            |             |
|                  | N                   | 6                | 6           |
| Acid conc        | Pearson correlation | 0.840            | 1.000       |
|                  | Sig (1-tailed)      | 0.018            |             |
|                  | N                   | C                | 6           |
| Amount extracted | Pearson correlation | 1.000            | -0.782      |
|                  | Sig (1-tailed)      | 0.019            |             |
|                  | N                   | 7                | 7           |
| Ligand conc      | Pearson correlation | 0.782            | 1.000       |
|                  | Sig (1-tailed)      | 0.019            |             |
|                  | N                   | 7                | 7           |

In Table 9, the relationship is strong and positive for acid concentration whereas for time, it is weak. This was also observed in the extraction process where the extraction process is mainly acid concentration dependent and some complexes at certain acid concentration showed insignificant variation in time of extraction.

4. Conclusion

The preparation and solvent extraction qualities of a bis Schiff base have been and modeled. The factors of time, acid concentration, temperature, metal ion concentration and ligand concentration are noted to be significant in complex formation and extraction. Acid concentration of 0.0001M, shaking time of 15 minutes, temperature of 30°C and ligand concentration of 0.5% were suitable for the complexation and extraction. The relationship among these variables was observed to be strong, positive and direct with the significance level for each lower than 5%, and as such the relation can be generalized to the whole process.

5. Declarations

5.1. Data Availability Statement

The data presented in this study are available in article.

5.2. Funding

The author received no financial support for the research, authorship, and/or publication of this article.

5.3. Declaration of Competing Interest

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the author.
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