

CHAPER III

EXPERIMENTAL

3.1 Chemicals and Instruments

3.1.1 Chemicals and Materials

1. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: Merck, Analytical grade
2. titrisol NaOH : 5.0 moldm^{-3} , Merck
3. titrisol NaOH : 0.1 moldm^{-3} , Merck
4. titrisol HNO_3 : 0.1 moldm^{-3} , Merck
5. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: Merck, Analytical grade
6. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: Baker, Analytical grade
7. $\text{Na}_2\text{SO}_4(\text{anhydrous})$: Merck, Analytical grade
8. $\text{NaNO}_3(\text{anhydrous})$: Merck, Analytical grade
9. Degassed Doubly Distilled Water (dddw)
10. Nitrogen gas : 99.99%

3.1.2 Instruments

1. Mettler Toledo DL 55 Titrator
2. Thermostat bath
3. Metrohm 744 pH meter

3.2 Preparation of Solutions

1. **0.500, 0.100, 0.010, 0.005, and 0.001 M NaNO₃ solutions.** Accurate amounts of NaNO₃ were dissolved in dddw.
2. **0.010 M Cu(NO₃)₂ solutions.** 0.250±0.001 g of Cu(NO₃)₂·3H₂O were dissolved in 0.500, 0.100, 0.010, 0.005, and 0.001 M NaNO₃ solutions.
3. **0.010 M Zn(NO₃)₂ solutions.** 0.295±0.001 g of Zn(NO₃)₂·6H₂O were dissolved in 0.500, 0.100, 0.010, 0.005, and 0.001 M NaNO₃ solutions.
4. **Stock solution of 0.1 M HNO₃** 1 L of 0.1 M HNO₃ solution was made from accurate volume of titrisol HNO₃ solution in dddw.
5. **0.01 M HNO₃ solutions.** Stock solution of 0.1 M HNO₃ were diluted volumetrically to give 0.01 M HNO₃ in 0.500, 0.100, 0.010, 0.005, and 0.001 M NaNO₃ solutions.
6. **2.5 M NaOH solutions.** Accurate volume of titrisol 5.0 M NaOH were diluted in dddw.
7. **Stock solutions of 0.1 M NaOH** 1 L of 0.1 M NaOH was made from accurate volume of titrisol NaOH solution in dddw.
8. **0.01 M NaOH solutions.** Stock solution of 0.1 M NaOH were diluted volumetrically to give 0.01 M NaOH in 0.500, 0.100, 0.010, 0.005, and 0.001 M NaNO₃ solutions.
9. **0.01 M Na₂SO₄ solutions.** 0.071±0.001 g of Na₂SO₄ were dissolved in 0.500, 0.100, 0.010, 0.005, and 0.001 M NaNO₃ solutions.

3.3 Synthesis and Characterization of Goethite

Goethite was synthesized according to Atkinson's method [31] by adding 400.0 cm³ of 2.5 M NaOH dropwisely to approximate 100g of Fe(NO₃)₃ · 9H₂O in 1.65 L of degassed doubly distilled water. The yellowish-brown precipitate was initially formed at pH about 12. The suspension was then heated(aged) for 24 hrs at 60 °C. The goethite suspension was washed several times until the pH was about 7-8 to remove excess Na⁺, NO₃⁻, and OH⁻. The suspension was stored in a polyethylene bottle under nitrogen atmosphere.

The prepared goethite was structurally characterized by X-ray powder diffraction technique and the surface area determined by the BET nitrogen adsorption method (Appendix A).

The total concentration of active sites on the surface of goethite, $[\equiv\text{FeOH}]_{\text{tot}}$, was determined by adding an excess of 0.01 M HNO₃ into 5.00 cm³ of goethite suspension in 25.00 cm³ * of 0.10 M NaNO₃ until the initial pH was 2.5. The titration was then carried out with 0.01 M NaOH within the pH range of 2.5-3.0 whereby the goethite surface was assumed to be completely protonated. In this range, the $[\equiv\text{FeOH}]_{\text{tot}}$ was calculated by subtracting free proton concentration (at the equivalent point) from the total concentration of proton initially added.

* Standard B-grade 25-cm³ bulb pipette with tolerance of about ± 0.06 cm³ was used

3.4 Determination of Dried weight per Volume of Goethite Suspensions

Goethite suspensions of 1.00, 2.00, 3.00, and 5.00 cm³ were pipeted* into each of the 8 previously weighed 50 cm³ Erlenmeyer flasks. They were then heated at 110 °C for 6 hrs, after which the dried material were reweighed. The same procedure was repeated to obtain the second set of weights. Combining these sets of data, the average dried weight per volume of goethite suspension was obtained.

3.5 Potentiometric Titrations

The potentiometric titrations were performed with the Mettler Toledo DL 55 automatic titrator using Mettler glass calomel pH electrode. The reaction vessels were thermostated at 25.0 ± 0.1 °C. The titration procedure was the EQP mode (equivalent point titration) and the 0.01 M NaOH solution was used as a titrant. The criteria for potential measurement were appropriately set. The titrations were studied within the pH range 3.5 to 9.5. The ratios of total concentrations of goethite / H⁺, goethite/ H⁺ / Cu²⁺(Zn²⁺), and goethite / H⁺ / Cu²⁺(Zn²⁺) / SO₄²⁻ = 1. The data of potential vs. volume of titrant (61 data points) and the titration curve (E-V curve) were obtained. The example of titration curves for each system was shown in Appendix B.

* Standard B-grade 1-cm³ and 5-cm³ bulb pipettes with tolerance of about ± 0.01 cm³ were used. The 2-cm³ and 3-cm³ samples were made by twice and three-time deliveries of 1 cm³ of the suspension.

3.5.1 Calibration of Electrode

Thirty cm^3 of 0.500 M NaNO_3 and 2.00 cm^3 of 0.01 M HNO_3 were pipeted into the reaction vessel. The criteria for the titration procedure and the potential measurement were set as : $\Delta E = 0.10 \text{ mV}$, $\Delta t = 30 \text{ s}$, $t_{\min} = 30 \text{ s}$, $t_{\max} = 60 \text{ s}$, $\Delta V = 0.08 \text{ cm}^3$, and $V = 4.0 \text{ cm}^3$. The same procedures were repeated in 0.1, 0.01, 0.005 and 0.001 M NaNO_3 .

(* ΔE = the measured potential change within a defined time Δt . Δt = the wait up time to the next incremental titrant addition, also depends on the minimum time (t_{\min}) and maximum time (t_{\max}). t_{\min} = the earliest time a termination can take place, it depends on the minimum consumption of titrant within the defined time range. t_{\max} = the latest time that a termination can take place. ΔV = a constant volume increment for the addition. V = the maximum volume of titrant added in the vessel.)

3.5.2 The System of Goethite($\equiv\text{FeOH}$)- H^+

Twenty-five cm^3 of 0.500 M NaNO_3 , 5.00 cm^3 of goethite suspension and 1.00 cm^3 of 0.01 M HNO_3 were pipeted into the reaction vessel. Nitrogen gas was passed through the solution about 10 minute prior to the titration. The solution system was allowed to attain equilibrium for 3 hrs in the thermostat bath until a drift in the reading potential was smaller than 0.6 mV/hr before starting the titration. The criteria for potential measurement were set as: $\Delta E = 0.02 \text{ mV}$, $\Delta t = 120 \text{ s}$, $t_{\min} = 120 \text{ s}$, $t_{\max} = 300 \text{ s}$, $\Delta V = 0.09 \text{ cm}^3$, and $V = 4.5 \text{ cm}^3$. The titrations were carried out

with additions of 0.01 M NaOH solution. The same procedures were repeated in 0.100, 0.010, 0.005 and 0.001 M NaNO₃.

3.5.3 The System of Goethite($\equiv\text{FeOH}$) - H^+ - Cu^{2+} and

Goethite($\equiv\text{FeOH}$) - H^+ - Zn^{2+}

Twenty-five cm³ of 0.500 M NaNO₃, 5.00 cm³ of goethite suspension, 1.00 cm³ of 0.01 M HNO₃, and 1.00 cm³ of 0.01 M Cu(NO₃)₂ or Zn(NO₃)₂ were pipeted into the reaction vessel. The titrations were performed in the same manner as in section 3.5.2 except for the following values for the criteria : $t_{\text{max}} = 480$ s., $\Delta V = 0.075$ cm³, and $V = 4.5$ cm³.

3.5.4 The System of Goethite($\equiv\text{FeOH}$)- H^+ - Cu^{2+} - SO_4^{2-} and

Goethite($\equiv\text{FeOH}$) - H^+ - Zn^{2+} - SO_4^{2-}

The procedure was the same as in section 3.5.3 but with 1.00 cm³ of 0.01 M Na₂SO₄ added into the reaction vessel.