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The redox titration of Fe (II) ions with $K_2Cr_2O_7$ using a potentiometry method the effect of EDTA and SCN^- ligands

Herlina*[1], Muhammad Razali[2]
[1]Institut Kesehatan Medistra Lubuk Pakam,
Jl. Sudirman No.38 Lubuk Pakam, Deli Serdang, Sumatera Utara, Indonesia
[2]Universitas Pembinaan Masyarakat Indonesia,
Jl. Teladan No.15, Teladan Bar., Kec. Medan Kota, Kota Medan, Sumatera Utara, Indonesia

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ABSTRACT

Complexometric titration is often used for determining the metal content, either through direct titration or back titration. This study aimed to investigate redox titration between Mohr salt solutions and potassium dichromate in an acidic atmosphere in the pH range 2. The results showed that the reaction proceeded effectively at pH 2, with Mohr's salt solution acting as titrant. Furthermore, experiments were conducted to compare the effectiveness of EDTA ligands and SCN^- ligands in improving the sharpness of the Fe^{2+}/ $Cr_2O_7^{2-}$ redox titration curve at pH 2. Results show that EDTA ligands are more effective than SCN- ligands in improving the sharpness of the titration curve. However, it should be noted that the addition of EDTA ligands can shift the equivalent point volume earlier, so adjustments need to be made in redox titration analysis. The use of EDTA and SCN^- ligands in the redox titration of Fe(II) ions with $K_2Cr_2O_7$ using a potentiometric method help in forming stable and detectable complexes with Fe(II), leading to clear and reliable potentiometric measurements. Research has also shown that adding excess moles of EDTA to total Fe (II) ions can decrease redox potential in Fe^{2+}/ $Cr_2O_7^{2-}$ systems. Based on the volume at the equivalence point, the Fe^{2+} ion in Mohr salt is 14.30%. with an average titration error of less than 0.30%. These results highlight the role of EDTA ligands in redox titration analysis and their impact on redox potential changes. The use of EDTA and SCN- ligands in the redox titration of Fe(II) ions with K2Cr2O7 using a potentiometric method help in forming stable and detectable complexes with Fe(II), leading to clear and reliable potentiometric measurements.

Keywords: complexation, EDTA, ligands, redox potential, pH

Corresponding author:
Herlina
Institut Kesehatan Medistra Lubuk Pakam
Jl. Sudirman No.38 Lubuk Pakam, Deli Serdang, Sumatera Utara, Indonesia
Email: herlina@medistra.ac.id

INTRODUCTION

Redox titration serves as a fundamental analytical technique in chemistry, allowing precise determination of the target concentration of analytes by measuring the titrant volume required to reach a specific endpoint. In the context of quantitative analysis, redox titration of Fe^{2+} ions using potassium dichromate ($K_2Cr_2O_7$) as a titrant has been widely used. This classical titration, often used to quantify iron content in various samples, is essential in educational and industrial laboratories (Barrera-Díaz et al., 2012; El Jamal, 2008). The Fe^{2+}/Fe^{3+} redox pair is known for its sensitivity to various environmental factors, especially pH and the presence of ligands. These variables can significantly impact the accuracy and precision of titration results, so it is essential to understand their effects. In this study, we explored the effect of pH and the role of ligands in redox titration of Fe^{2+} ions in Mohr salts ($FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$) with $K_2Cr_2O_7$ (Kabdaşlı & Tünay, 2023).

The redox system $Fe^{2+}/ Cr_2O_7^{2-}$ is the research focus due to its significant impact on chemical analysis and waste treatment. This reaction can only occur in an acidic environment due to modification of the redox potential by the pH of the solution. However, an increased pH can result in an unspontaneous reaction, so further research is needed to understand and address the problem (Kang et al., 2022). Using ligands, such as Tiron, 1,10–phenanthroline, and EDTA, became a strategy to increase the spontaneity of redox reactions by modifying the reduction potential. This is important because of the complexity of interactions between ligands and metal ions in forming complex compounds, which is also affected by the pH of the solution (Bashir et al., 2018).

The determination of metal ion concentrations is often conducted using UV/Vis absorption spectrometric titration with special ligands. Electrochemical measurements using selective electrodes to measure metal ion concentrations also require specific treatment to prepare the membrane to be active, and any defects can affect their response. Anodic stripping voltammetry and cyclic voltammetry have been widely utilized for the determination of various metals, as has amperometric titration using a dropping mercury electrode, though it requires special treatment. In this study, we propose a method that is relatively easy to use and does not require special preparation before use (El Jamal & Hammud, 2007).

Potentiometric titration techniques are relevant in this context because they are simple, easy, inexpensive, and environmentally friendly. However, special attention is needed to the pH range when performing redox titration of $Fe^{2+}/ Cr_2O_7^{2-}$ with ligands because it can affect the formation of deposits and the stability of complex compounds (Sukekava et al., 2024). Many studies in analytical chemistry have highlighted the significance of pH in redox titrations, as changes in pH levels can substantially upset the balance between Fe^{2+} and $K_2Cr_2O_7$. In addition, the presence of ligands in the sample matrix can lead to the formation of complex ions with Fe^{2+}, potentially complicating the stoichiometry of redox reactions. Therefore, this study aims to uncover the nuances of these critical factors and their collective influence on accuracy and reliability in Fe^{2+} determination via $K_2Cr_2O_7$ titration (Das et al., 2014).

Understanding how changes in pH levels affect the titration process is essential because it can significantly affect the redox balance between Fe^{2+} and $K_2Cr_2O_7$. In addition, ligands in the sample can form complex ions with Fe^{2+}, altering the stoichiometry of redox reactions. As a result, this study aims to provide a deeper understanding of these influential factors to improve accuracy and reliability in Fe^{2+} determination through $K_2Cr_2O_7$ titration. Potentiometric titration is a suitable electroanalytical technique for applying ligand influence concepts in redox systems due to its simplicity, ease of use, cost-effectiveness, and environmental friendliness. While this method is less commonly employed, it is crucial for evaluating samples in industries, pharmaceuticals, and environmental settings. The method has been used in iron speciation in drug samples and lake water, utilizing the concept of redox potential modification by the ligand 1,10-phenanthroline in Fe(II)-Co(II) redox systems (Rizvi et al., 2016).

EDTA and SCN^- are recognized for their ability to form stable complexes with metal ions such as Fe(II). In our study, these ligands interact with Fe(II) ions during the redox titration process. EDTA acts as a strong chelating agent, binding tightly to metal ions and preventing their precipitation, which is essential for achieving accurate titration results. The presence of EDTA and SCN^- influences the redox chemistry of Fe(II) ions. EDTA stabilizes Fe(II) ions in solution, thereby preventing premature oxidation or reduction during titration. SCN^-, on the other hand, forms complexes with Fe(II) that can modify the redox potential, thereby impacting the titration endpoint.

The determination of metal ion concentrations is often conducted using UV/Vis absorption spectrometric titration with special ligands. Electrochemical measurements using selective electrodes to measure metal ion concentrations also require specific treatment to prepare the membrane to be active, and any defects can affect their response. Anodic stripping voltammetry and cyclic voltammetry have been widely utilized for the determination of various metals, as has amperometric titration using a dropping mercury electrode, though it requires special treatment. In this study, we propose a method that is relatively easy to use and does not require special preparation before use.

By investigating the interaction between pH, ligands, and Fe^{2+} ion redox titration, we hope to develop a more comprehensive understanding of this analytical technique, which can ultimately lead to more precise and reproducible results in various practical applications.

MATERIALS AND METHOD

This research was conducted on the potentiometric titration method for the Redox reaction Fe^{2+}/ $Cr_2O_7^{2-}$. This redox reaction involves Fe^{2+} ions of Mohr Salt as a reducing agent (titrate) with potassium dichromate as an oxidizing agent (titrant). The cell potential measurement results are used to create a titration curve to determine the effect of ligands and pH on Fe^{2+}/ $Cr_2O_7^{2-}$ redox titration. Compounds used as ligands for this study include EDTA and SCN^- ligands.

Manufacture and characterization of Ag/AgCl comparator electrodes

The Ag/AgCl reference electrode is made by electrodeposition of AgCl on Ag wire in 0.1 M NaCl solution for 1 minute with a current source of 2.20 V until a blackish-gray AgCl precipitate is formed that coats the Ag wire. The Ag/AgCl electrode was placed into the electrode body filled with a 3.0 M NaCl saturated solution. The Ag/AgCl reference electrode that had been made was then characterized voltammetrically in a solution of $K_3[Fe(CN)_6]$ 0.01 M and $K_4[Fe(CN)_6]$ 0.01 M in a solution of 0.1 M NaCl supporting electrolyte using cyclic voltammetry techniques in the potential range of -200 mV to 800 mV with a scan rate of 100 mV/s. Cyclic voltammogram measurement results from artificial Ag/AgCl reference electrodes compared to commercial Ag/AgCl (BAS) electrodes. In addition, the artificial Ag/AgCl electrode is also potentiometrically characterized using Ag/AgCl as a working electrode. Measurement of electrode potentials in NaCl solutions of various concentrations is carried out in stages from low concentration to high concentration, respectively are 5×10^{-5}; 10^{-4}; 5×10^{-4}; 10^{-3}; 5×10^{-3}; $10^{-2;}$ 5×10^{-2} and 10^{-1} M.

Potentiometric titration in redox reactions Fe^{2+}/ $Cr_2O_7^{2-}$

Potentiometric titration uses a Pt wire working electrode as the cathode and an artificial Ag/AgCl reference electrode as the anode, and both are connected to the potentiometer. Cell potential measurements are carried out at room temperature.

Titration of 0.1 M Mohr salt solution by $K_2Cr_2O_7$ 0.0277 M with variation in H_2SO_4 concentration

A solution of 0.1 M Mohr salt in 0.05 M sulfuric acid, as much as 10 mL, is pipetted and put into a beaker, and 25 mL of 1 M sulfuric acid solution is added. The analyte solution is then titrated with 0.028 M potassium dichromate solution and stirred slowly until the solution is homogeneous. The cell potential in the solution is measured and recorded with every addition of 1 mL of titrant. The same procedure is repeated for variations of sulfuric acid with a concentration of 0.30; 0.08; and 0.02 M each. The repetition of each titration is carried out three times.

Titration of 0.01 M Fe(II) and Fe(III) mixed solution by 0.5 M NaOH with EDTA variation

A mixed solution of Mohr salt and $FeCl_3.6H_2O$ 0.01 M in 0.5 M sulfuric acid, as much as 5 mL, was put into a beaker and added with 2 mL of 0.03 M EDTA solution. Next, the solution was diluted with aqua DM to 50 mL and titrated slowly with 0.5 M NaOH. pH and cell potential measurements were carried out after adding NaOH solution. The same working procedure is repeated with variations in the volume of EDTA solution by 4 and 6 mL. In addition, titration of mixed solutions of Fe(II) and Fe(III) without adding EDTA ligands is carried out with the same working procedure. Each titration is carried out triplo.

Titration of 0.02 M Mohr salt solution by $K_2Cr_2O_7$ 0.007 M with EDTA concentration variation

A 0.02 M Mohr salt solution in 0.02 M sulfuric acid of 10 mL is put into a beaker, added with 25 mL of EDTA solution, and titrated with 0.007 M potassium dichromate solution slowly and stirred until the solution is homogeneous. Cell potential measurements were recorded with every addition of 1 mL of potassium dichromate solution. The work procedure was repeated for adding different EDTA concentrations, namely 0.008 M, 0.009 M, and 0.01 M. The redox titration curve Fe^{2+}/ $Cr_2O_7^{2-}$ with variations in EDTA concentration is then compared with the titration curve without EDTA ligands. Redox titration of Mohr salt solution with potassium dichromate without EDTA ligands was performed by replacing EDTA solution with aqua DM as much as 25 mL. Each of these redox titrations is performed triplo.

Titration of 0.02 M Mohr salt solution by $K_2Cr_2O_7$ 0.007 M with the addition of SCN- ligands

A 0.02 M Mohr salt solution in 0.02 M sulfuric acid, as much as 10 mL, was pipetted and put into a beaker, then added with a 25 mL SCN- solution and titrated slowly with 0.007 M potassium dichromate solution. Triple cell potential measurements are performed per mL titrant, and the results are recorded. The results of the possible measurement of the cell are then compared with the redox titration curve Fe^{2+}/ $Cr_2O_7^{2-}$ with the addition of EDTA ligands that have been performed.

RESULT AND DISCUSSION

Characterization of Ag/AgCl reference electrode

The reference electrode is essential in monitoring the working electrode in potentiometric titration. The characterization of Ag/AgCl reference electrodes is carried out by two methods, namely voltammetry and potentiometry. Voltammetry involves the ratio of artificial to commercial Ag/AgCl (BAS) electrodes in a mixed solution of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$. This solution was chosen because of its rapid and electrochemically reversible electron transfer reaction. NaCl solution acts as a supporting electrolyte to minimize the rate of ion migration from the analyte. Furthermore, the Cyclic Voltammetry method characterized the Ag/AgCl reference electrode in the potential range of -200 to +800 mV with a scan rate of 100 mV/s. The results show voltammogram similarity between the artificial Ag/AgCl electrode and BAS, as seen in Figure 1. The voltammogram profile allows the measurement of cathodic and anodic peak potentials and currents from mixed solutions of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ 0.01 M. The ratio of anodic peak (Ip_a) and cathodic (Ip_c) currents is close to 1, indicating a reversible redox process. The peak potential difference (ΔEp) between the anodic and cathodic peaks for artificial Ag/AgCl and BAS electrodes is 0.112 V, while the theoretical value is 0.059 V. The higher ΔEp in the experiment showed uncompensated electrical resistance, leading to slower electron transfer rates and higher separation between anodic and cathodic peaks (Brownson & Banks, 2014).

A paired t-test determines the difference between an artificial Ag/AgCl voltammogram and a BAS. The results of the t-test obtained a calculated t value (1.359) < t table (2.78), which means that there is no significant difference between the voltammogram of artificial Ag/AgCl electrodes and BAS. In addition, the voltammogram difference between the two electrodes can also be observed from the formal potential values. The formal potential of the two electrodes has the same value of 0.210 V, so there is no difference between them. These parameters indicate that the artificial Ag/AgCl electrode performs well with BAS.

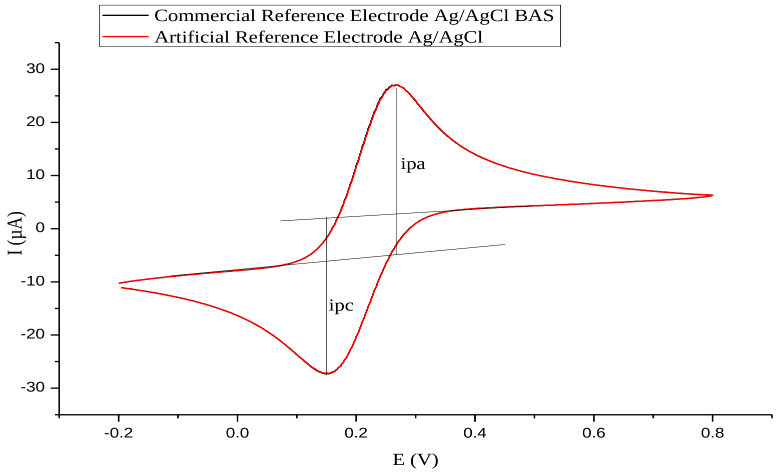

Figure 1. Cyclic voltammogram of commercial Ag/AgCl reference electrode (BAS) with artificial in a mixed solution of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ 0.01 M in 0.1 M NaCl solution

Potentiometric characterization of electrodes is carried out by measuring NaCl solutions in the concentration range of 5 x 10^{-5} - 10^{-1} M using Ag/AgCl wire as the working electrode. A deficient concentration of NaCl solution can dissolve the AgCl layer (K_{sp} = 1.8 x $10^{-10)}$ on the working electrode so that the lowest limit for measuring NaCl solution is 5 x 10^{-5} M. The results of measuring electrode potential in NaCl solution have theoretical compatibility; namely, the cell potential is directly proportional to pCl (-log Cl- ion concentration).

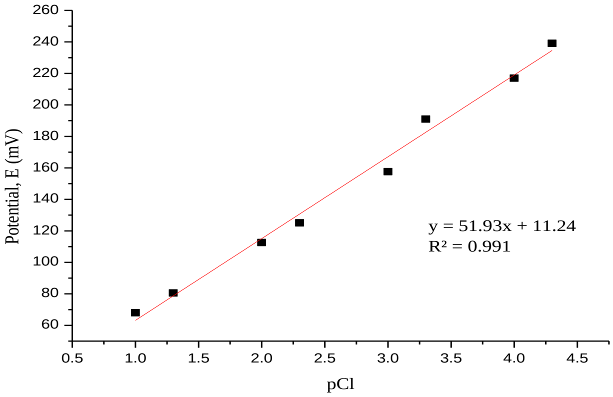

Figure 2. Cell potential curve to pCl of a homemade Ag/AgCl reference electrode with an Ag/AgCl wire working electrode

The Nernst factor is a commonly used parameter to determine electrode performance through the slope value of the relationship curve between potential to –-log analyte concentration. The test results of the artificial Ag / AgCl reference electrode in Figure 2 obtained a straight-line equation of E = 11.24 – 51.93 log[Cl^-], which is subject to the Nernst equation. The experimental Nernst factor value of 51.93 mV/decade is *Under-Nerstian* smaller than the theoretical value of 59.2 mV/decade at 25 °C. The difference in the value of the experimental Nernst factor with the theoretical value is influenced by temperature, the character of the AgCl precipitate on the Ag wire (purity and homogeneity), ion activity in the solution, the purity of the analyte solution, the solution in the reference, the connecting fluid potential, the cleanliness of the electrodes, and the membrane composition of the electrodes. However, the correlation factor value of 0.991, close to one, indicates that the system of working and comparator electrodes responded well to a slight increase in chloride ion concentration.

The results of overall electrode characterization by voltammetry and potentiometry methods show that the artificial Ag/AgCl reference electrode has good performance, so it is suitable for further potentiometric titration measurements. The things that need to be considered in making Ag / AgCl electrodes are the potential used during the electrolysis process and the selection of solutions in the reference electrode. The potential applied for the electrolysis process must be greater than the standard potential of the Ag/AgCl electrode due to the reduction of the potential by the *Ohmic potential*.

Effect of H_2SO_4 concentration on redox titration of mohr salt solution with $K_2Cr_2O_7$

Variations in sulfuric acid concentration were carried out to determine the effect of H^+ ion concentration on redox titration between Mohr salt solution and potassium dichromate. This can be known through the titration curve by channeling the relationship between the cell potential of the measurement results and the titrant volume. The cell potential measurement is carried out by potentiometric titration method using Pt wire as the working electrode and an artificial Ag/AgCl reference electrode that has been characterized. Mohr salts are a source of Fe^{2+} ions acting as analytes in titration. The use of sulfuric acid in making Fe (II) solution is to give an acidic atmosphere to the solution to slow down the rate of oxidation of Fe^{2+} ions to Fe^{3+} by dissolved oxygen (dissolve oxygen*) and prevent the formation of* hydrolyzed Fe^{2+} ion species that are easily oxidized. In addition, sulfuric acid is also used to vary the concentration of H^+ ions in redox titration of Mohr salt solution with potassium dichromate. Sulfuric acid is one of the appropriate acids used for titration because sulfate ions are not involved in the reaction and can meet the needs of H^+ ions for the redox reaction (Rizvi et al., 2016). Potentiometric titration between Mohr salt solution and potassium dichromate was performed in the acidic pH range to prevent the transformation of dichromate ions to chromate at pH > 6 and prevent an increase in the oxidation rate of Fe^{2+} ions by dissolved oxygen at pH > 4. Theoretically, the redox reaction between Mohr salt solution and potassium dichromate can be spontaneous up to pH 4. However, titration between 0.1 M Mohr salt solution and 0.03 M potassium dichromate was experimentally stopped to a pH of less than three due to the formation of brownish-yellow deposits derived from $Fe(OH)_3$ (Tian et al., 2024). The chemical reaction between a solution of Mohr salt and potassium dichromate in an acidic atmosphere is shown in Equation 3.

$$\text{Anode: } 6Fe^{2+}_{(aq)} \rightleftharpoons 6Fe^{3+}_{(aq)} + 6e^- \quad \ldots\ldots\ldots\ldots (1)$$

$$\text{Cathode: } Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} \quad \ldots\ldots\ldots\ldots (2)$$

Hence the equation of the chemical reaction that occurs:

$$Cr_2O_7^{2-}{}_{(aq)} + 6Fe^{2+}_{(aq)} + 14H^+_{(aq)} \rightleftharpoons 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O(l) \ldots\ldots\ldots (3)$$

The standard reduction potential () of the redox system Cr(VI)/Cr(III) is greater than that of the redox system Fe(III)/Fe(II) so that dichromate ions tend to be reduced while Fe^{2+} ions undergo oxidation. The redox titration curve between Mohr salt solution and potassium dichromate with variations in H^+ ion concentration is shown in Figure 3. The cell potential in the state before titration yields a positive value. This shows that there is already a Fe species^{3+} derived from the oxidation of Fe^{2+} by dissolved oxygen. The cell potential in the pre-titration state approaches the theoretical value for the Fe(III)/Fe(II) redox system in H_2SO_4 1.0 M is 0.460 V against the Ag/AgCl reference electrode so that the number of Fe^{3+} species that is present in solution in tiny amounts and can be ignored. states that redox potential without titrant addition cannot be calculated since the exact sum of Fe^{3+} ion concentrations, which is present in the solution, cannot be determined. If Fe^{3+} ions are not in solution or Fe^{3+} ion concentration is zero, the resulting redox potential becomes infinite.

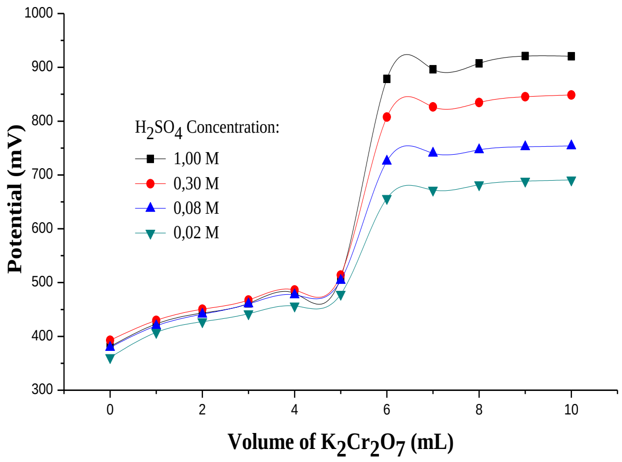

Figure 3a. Redox titration curve of 10 mL Mohr salt solution 0.1 M with $K_2Cr_2O_7$ 0.03 M with concentration variation H_2SO_4

Figure 3a. shows that a decrease in sulfuric acid concentration can decrease redox potential values in regions after the equivalence point. In that state, the redox potential value depends on the half-reaction Cr(VI)/Cr(III) in Equation (3) (El Jamal, 2008). H^+ ions as electroactive species are involved in the Cr(VI)/Cr(III) reduction reaction, so the sulfuric acid concentration directly affects the redox potential (Gao & Liu, 2017; Kabdaşlı & Tünay, 2023). The results of measuring cell potential in redox titration Fe^{2+}/ $Cr_2O_7^{2-}$ with variations in sulfuric acid concentration at that state are in theory that cell potential is directly proportional to the concentration of H^+ ions and inversely proportional to the pH of the solution. The relationship of cell potential to solution pH for Cr(VI)/Cr(III) reduction systems can be proved by the Nernst equation in Equation 4.

$$E = E^0_{Cr^{6+}/Cr^{3+}} - \frac{RT}{nF} \ln - 0.138 \text{ pH } \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}]} \text{ ....(4)}$$

The sulfuric acid concentration does not affect the redox potential found in the area before the equivalence point. In this situation, the amount of analyte in reduced and oxidized form is present in significant quantities in solution so that the cell potential value is influenced by half the reaction of the Fe(III)/Fe(II) system in Equation (1). Fe(III)/Fe(II) reduction reactions do not involve H ions$^+$, so the sulfuric acid concentration does not directly affect redox potential. However, the pH of a solution plays a role in determining the rate of oxidation of Fe ions^{2+} by dissolved oxygen. The oxidation rate of Fe ions^{2+} becomes Fe^{3+} by dissolved oxygen in the acidic state (pH <4) proceeds very slowly while in the alkaline state (pH 4-8) proceeds very quickly (El Jamal & Hammud, 2007). Redox potential at the state before the equivalence point for $Fe^{2+}/Cr_2O_7^{2-}$ redox can be determined by Equation (5).

$$E = E^0_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF} \text{ Log } \frac{[Fe^{2+}]}{[Fe^{3+}]} \text{ ....(5)}$$

Redox titration between Mohr salt solution and potassium dichromate does not use visual indicators so that the volume of the titration endpoint cannot be determined through colour changes in solution. The analyte solution changes colour to greenish-yellow as the volume of titrant increases. The volume of the equivalence point of such redox titration is determined based on the first derived curve in Figure 4. In the redox titration curve $Fe^{2+}/Cr_2O_7^{2-}$ it is seen that variations in sulfuric acid concentration do not shift the volume of the equivalent point. However, the variation in sulfuric acid concentration causes a change in the cell potential in the equivalence point region and can be calculated theoretically through Equation (6). Based on the volume of the equivalent point, it can be calculated that the Fe^{2+} ion content in Mohr salt is 14.30 %. The potentiometric titration method in the redox reaction $Fe^{2+}/Cr_2O_7^{2-}$ has a fairly good accuracy with an average titration error percentage of less than 0.30%.

$$E = -\,0.0591\ V \log \frac{m \times E^0_{Fe^{3+}/Fe^{2+}} + n \times E^0_{Cr^{6+}/Cr^{3+}}}{m[Fe^{3+}]/[Fe^{2+}] + n\,[Cr^{6+}]/[Cr^{3+}]} \frac{2.[Cr^{3+}]}{[H^+]^{14}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (6)$$

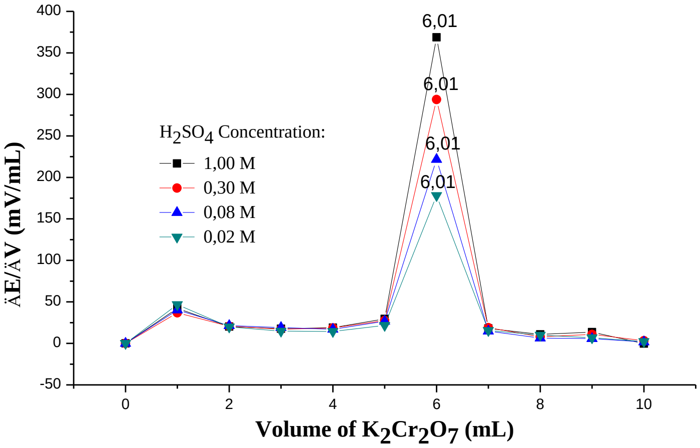

Figure 3b. First derived curve of redox titration of Mohr salt 0.1 M with $K_2Cr_2O_7$ 0.03 M with concentration variation H_2SO_4

The increase in sulfuric acid concentration in Figure 3b increases the equivalence point potential so that the resulting curve is sharper. The sharper the redox titration curve, the easier it is to determine the equivalent point volume on redox titration $Fe^{2+}/ Cr_2O_7^{2-}$. Based on Figure 3, the potential fracture is very large on the redox titration curve $Fe^{2+}/ Cr_2O_7^{2-}$ found at a very acidic pH i.e. at the addition of sulfuric acid 1 M. The potential fault on the titration curve shows a difference *E* between analytes and titrants. The greater the difference *E*, then the greater the equilibrium constant produced so that the equilibrium reaction progresses in the direction of the product. Therefore, redox titration $Fe^{2+}/ Cr_2O_7^{2-}$ in highly acidic atmospheres is preferred. Based on the results of the experiment as a whole, it can be concluded that the concentration of sulfuric acid can modify the cell potential of the redox system $Fe^{2+}/ Cr_2O_7^{2-}$ (Gao et al., 2022; Kang et al., 2022).

Effect of ligands on redox titration $Fe^{2+}/ Cr_2O_7^{2-}$

The effect of ligands on redox titration between Mohr salt solution and potassium dichromate was carried out at an initial pH of 2. The pH range of the solution is determined based on the results of previous studies that redox titration $Fe^{2+}/ Cr_2O_7^{2-}$ can last up to pH 2 without precipitate formation. However, potential jumps in the $Fe^{2+}/ Cr_2O_7^{2-}$ redox titration curve at that pH were found to be very low. The higher the cell potential jump produced by the titration curve, the easier it is to determine the equivalent point volume. The addition of appropriate ligands is expected to increase the sharpness of the $Fe^{2+}/ Cr_2O_7^{2-}$ redox titration curve at pH 2. Compounds used as ligands for such redox systems include EDTA and SCN- (Bashir et al., 2020; Rizvi et al., 2016; Sukekava et al., 2024). $Fe^{2+}/ Cr_2O_7^{2-}$ titration with variations in EDTA ligand concentration at pH 2 is performed to determine the optimum conditions for redox titration in the presence of ligands. An E-pH diagram for the Fe(III)/Fe(II) system with EDTA ligands was experimentally created to determine the effect of pH on the stability of the $[Fe\text{-}EDTA]^-/[Fe\text{-}EDTA]^{2-}$ complex. In redox systems Cr(VI)/Cr(III), E-pH diagrams in the presence of EDTA ligands are not investigated because the rate of complex formation of Cr(III) with ligands is so slow that measurement results are inaccurate. The results of cell potential measurements for Fe(III)/Fe(II) systems with variations in EDTA ligand volume can be seen in the E-pH diagram for the redox system is shown in Figure 5.

Figure 4 shows that the E-pH diagram of the Fe(III)/Fe(II) system without the presence of EDTA ligands is close to theoretical values and is not affected by the pH of the solution. The standard reduction potential Fe(III)/Fe(II) in H_2SO_4 1 M is theoretically 460 mV against the Ag/AgCl reference electrode due to the formation of the $[FeSO_4]^+$/[FeSO4] complex. At the addition of 2 mL EDTA to 0.03 M, the cell potential decreases compared to the absence of ligands and is constant to changes in the pH of the solution. The decrease in cell potential occurs due to the formation of complexes between EDTA ligands and the redox system Fe(III)/Fe(II) in Equation 7. At pH below 3, the EDTA (Y4-) species that predominate in solution are in the form of H_3Y-. Thus, the most likely reaction formed between Fe(III)/Fe(II) ions and EDTA ligands at pH is shown by Equation 7.

$$[FeH_3Y]^{2+}\,(aq) + e^- \rightleftharpoons [FeH_3Y]^+\,(aq)\ldots\ldots\ldots\ldots\ldots(7)$$

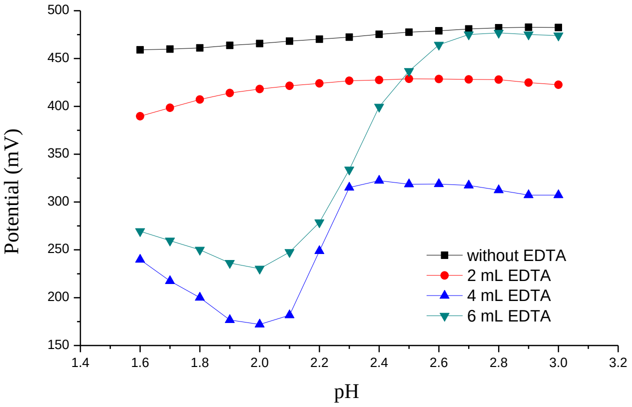

Figure 4. E-pH diagram of 5 mL mixture of Fe(III) and Fe(II) 0.01 M with EDTA mole variation of 0.03 M

A significant decrease in cell potential due to complexation occurs in the addition of 4 and 6 mL EDTA 0.03 M. At solution pH below 3, the cell potential value changes significantly with changes in solution pH. The inconstant cell potential value indicates that the formation of complex compounds between EDTA ligands and Fe(III)/Fe(II) ions is influenced by the pH of the solution. The complex [Fe-EDTA]^2- is unstable at very low pH due to the low value of the conditional constant, but the complex formation constant [Fe-EDTA]- is so large that it causes a decrease in the reduction potential of its free ionic state (Bashir et al., 2020). The experimental results of the E-pH diagram for the Fe(III)/Fe(II) system with the presence of EDTA ligands as a whole can be concluded that Fe(II) ions do not complex completely with ligands in very acidic atmospheres. In addition, the number of moles of EDTA also affects the formation of complexes $[FeH_3Y]^{2+}$/$[FeH_3Y]^+$. A comparable number of moles of EDTA and an excess of the total metal ions can significantly lower the cell potential. The lower the reduction potential, the greater the amount of $[FeH_3Y]^{2+}$/$[FeH_3Y]^+$ formed. Next, the determination of the complex formula of the EDTA ligand in the redox system Fe^{2+}/ $Cr_2O_7^{2-}$ at pH 2. The effect of EDTA ligand concentration on the redox system can be observed in Figure 5.

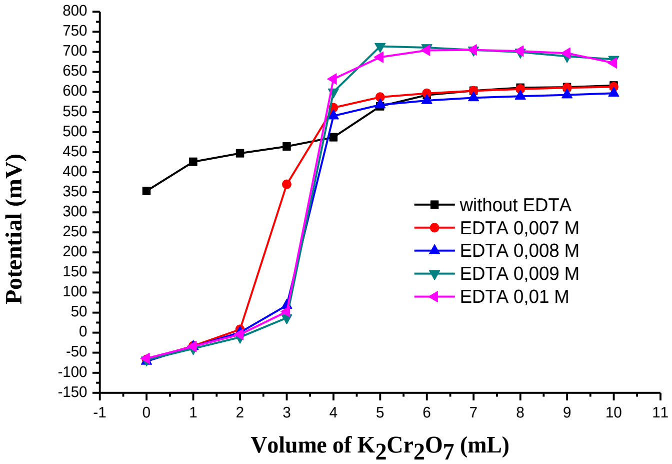

Figure 5. Redox titration curve of 10 mL 0.02 M Mohr salt solution with $K_2Cr_2O_7$ 0.0067 M with 25 mL EDTA at pH 2

Figure 6 shows a significant decrease in redox potential in the region before the equivalence point compared to without the presence of ligands. The decrease in redox potential occurs due to the formation of complexes $[FeH_{3Y}]^{2+}/[FeH_3Y]^{+}$ which is reinforced by the results of the E-pH diagram in Figure 5. The experimental results are in accordance with the theory that the complex formation constant between EDTA ligands and Fe(III) ($\beta=10^{25,1}$) greater than Fe(II) ($\beta=10^{25,1}$) so that the reduction potential decreases from the state of the free metal ion. In the state after the equivalence point, the addition of EDTA ligands does not significantly change the redox potential compared to the absence of EDTA ligands. Although metal ions are Cr(VI)/Cr(III) in significant quantities, the kinetics of complex formation with EDTA ligands are very slow at room temperature. In this situation, the redox potential value is influenced by the pH of the solution. The addition of EDTA ligands can maintain the pH of the solution in redox titrations $Fe^{2+}/\ Cr_2O_7^{2-}$ compared to the absence of ligands. Therefore, the redox potential with the addition of excess EDTA ligands is higher than without the presence of ligands in the state after the equivalence point (Bashir et al., 2018; El Jamal & Hammud, 2007; Morgan & Lahav, 2007; Rizvi et al., 2013).

The equivalent point volume in the redox system $Fe^{2+}/\ Cr_2O_7^{2-}$ at pH 2 with variations in EDTA concentration can be determined by the first derived curve in Figure 7. The volume of the equivalent point shows the ratio of moles between the total complex Fe(II) ions and EDTA ligands to the dichromate ions. The volume of the equivalent point in the presence of the EDTA ligand experimentally shifts earlier than the theoretical equivalent point volume. This happens because there is a small part of Fe(II) species that do not complex completely with EDTA ligands, resulting in a decrease in total moles of complex between Fe(II) ions and EDTA ligands. This condition is caused by the pH of the solution which affects the stability of complex formation. Furthermore, the effect of EDTA ligand concentration on equivalence point cell potential in the $Fe^{2+}/\ Cr_2O_7^{2-}$ redox system can also be observed in Figure 7. In the state of excess EDTA ligands of metal ions, the equivalence point cell potential increases. Thus, it can be concluded that in excess EDTA conditions it is effective to increase the equivalence point potential in redox titration $Fe^{2+}/\ Cr_2O_7^{2-}$(Bashir et al., 2020; Rizvi et al., 2013, 2016; Sukekava et al., 2024).

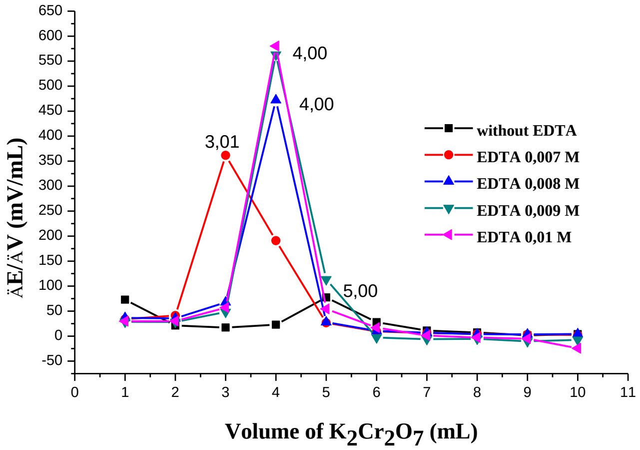

Figure 6. First derived curve of redox titration of Mohr salt solutions 0.02 M to $K_2Cr_2O_7$ 0.0067 M with variations in EDTA concentration at pH 2

The effect of EDTA and SCN- ligands on Fe^{2+}/ $Cr_2O_7^{2-}$ redox titration at pH 2 can be compared in Figure 8 which shows that EDTA ligands are effective enough to improve the sharpness of the Fe^{2+}/ $Cr_2O_7^{2-}$ redox titration curve compared to the presence of SCN^- ligands. The reaction that mention Equation 8

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$........................(8)

The reaction between (Fe^{2+}) and EDTA forms a stable complex, typically written as $Fe(EDTA)^{2-}$. When titrated with $K_2Cr_2O_7$, the $Cr_2O_7^{2-}$ ion acts as an oxidizing agent, converting Fe^{2+} to Fe^{3+} while itself being reduced to Cr^{3+}.

Fe reacts with SCN^- to form the reddish complex ion $Fe(SCN)^{2+}$, which is often used as an indicator for the presence of Fe^{3+}. $Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+\cdot}$ When titrated with $K_2Cr_2O_7$, Fe^{2+} is oxidized to Fe^{3+} by the $Cr_2O_7^{2}$ which is reduced to Cr^{3+} similarly to the above reaction (El Jamal & Hammud, 2007; Najib & Hayder, 2011).

The complex formation constant between SCN^- ligands and Fe(II) ions is so small that the possibility of forming complex compounds is very low. Therefore, the addition of SCN^- ligands does not affect the redox potential Fe^{2+}/ $Cr_2O_7^{2-}$ at the state before the equivalence point.

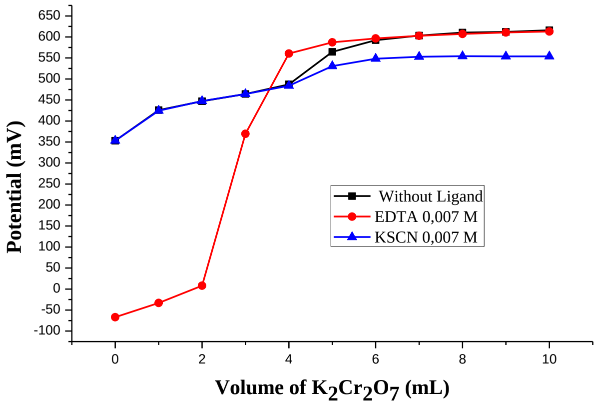

Figure 7. Reference of redox titration curve of 10 mL Mohr 0.02 M salt solution to $K_2Cr_2O_7$ 0.0067 M with 25 mL of EDTA ligand or SCN- at pH 2

CONCLUSION

Redox titration between Mohr salt solution and potassium dichromate can take place well in acidic atmospheres up to pH 2. EDTA ligands are quite effectively used to improve the sharpness of the Fe^{2+}/ $Cr_2O_7^{2-}$ redox titration curve at pH 2 compared to SCN- ligands. However, the addition of EDTA ligands can shift the volume of the equivalent point earlier. Adding excess moles of EDTA to total Fe(II) ions can decrease the redox potential Fe^{2+}/ $Cr_2O_7^{2-}$. Based on the volume at the equivalence point, the Fe^{2+} ion in Mohr salt is 14.30%. with an average titration error of less than 0.30%. Potentiometric titration is a suitable electroanalytical technique for applying ligand influence concepts in redox systems due to its simplicity, ease of use, cost-effectiveness, environmental friendliness and their impact on redox potential changes.

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