



Utilizing Fe(III)/(II)-EDTA Couple for Estimation of Transition Metal Ion Mixture Over Platinum Electrode

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(Received: 24 May 2012;

Accepted: 6 March 2013)

AJC-13069

The work describes an indirect estimation of some transition metal ions and their binary mixture over platinum electrode by generating Fe(III)/(II)-EDTA redox couple in solution. This approach offers easy estimation and can allow replacement of costly and delicate ion selective electrodes with simple platinum electrode within the limits of concentration and tolerable margin of error.

Key Words: Platinum electrode, Iron(III)-iron(II), EDTA, Redox couple.

INTRODUCTION

Potentiometry is a simple and wide spread electro-analytical technique used in monitoring of industrial, pharmaceutical, biological and environmental samples¹. In a potentiometric titration, the analyte is an electro active species which participates in the reaction of the galvanic cell formed in the titration set up. Platinum as redox electrode has many desirable features like good surface characteristics, quick equilibration, well Nernstian behaviour, easy storage and longer life. However being inert it can only sense species that generate a redox couple in solution². Many metals with single stable oxidation state Zn(II), Cu(II) and Ni(II) cannot be estimated directly over platinum electrode and require costly ion selective electrodes for estimation³.

Complexometric titration of metal ions involving direct or back EDTA titrations have been thoroughly investigated⁴ and many instrumental methods have been used for end point detection of such titrations^{4,5}. Potentiometric estimation of metal ions with EDTA is generally done over mercury electrode⁶ posing risk of mercury toxicity; further selective analysis of binary metal ion mixtures is not possible over mercury electrode. We therefore report a direct potentiometric method for estimation of Ni(II), Zn(II) and their binary mixtures over platinum electrode using [FeEDTA]²⁻/[FeEDTA]⁻ redox couple. This approach allows replacement of hazardous, costly and delicate ion selective electrodes with simple platinum electrode and also allows simultaneous estimation of the binary metal ion mixtures (not possible with ion selective electrodes) within the limits of concentration and tolerable margin of error.

EXPERIMENTAL

All solutions were prepared in double distilled water from analytical grade chemicals. A 100 mL solution of each reagent was prepared using 1.9607 g ammonium ferrous sulphate hexahydrate for 5×10^{-2} M, iron(II) solution, 3.7223 g EDTA disodium salt dihydrate to give 1×10^{-1} M EDTA stock solution, 2.41125 g ammonium ferric sulphate dodecahydrate for 5×10^{-2} M, iron(III) solution.

General procedure: Four 25 mL volumetric flasks labeled 1, 2, 3 and 4 were taken and three sets of experiments were performed. In each set 4.0 mL of 1×10^{-1} M EDTA, 1.0 mL of 5×10^{-2} M iron(II), were initially added to which in first set {1.0, 1.5, 2.0, 2.5 mL} of 1×10^{-1} M zinc(II) and in second set {1.0, 1.5, 2.0, 2.5 mL} of 1×10^{-1} M nickel(II) and in third set {0.5, 1.0, 1.5, 2.0 mL} of 1×10^{-1} M zinc(II) and {2.0, 1.5, 1.0, 0.5 mL} 1×10^{-1} M nickel(II) were added. The volume in flask was raised to 25 mL with 2 M acetate buffer of pH 4.2. After an initial development time of 15 min, 20 mL aliquot were taken for titration with 5×10^{-2} M iron(III). Potentiometric titrations were performed manually using a platinum indicator and calomel reference electrode over a potentiometer (Systronics India Model 318) at 25 ± 2 °C. A Siskin Julabo thermostat was used to maintain a constant temperature within ± 2 °C. The titration vessel consisted of a self designed six necked vessel (for micro burette, platinum, calomel electrodes, temperature probe, inlet and outlet of nitrogen gas)⁷. All potential measurements were carried out in triplicate within a margin of error less than 3 %.

RESULTS AND DISCUSSION

Ferri-Ferro-EDTA $\{[\text{FeEDTA}]/[\text{FeEDTA}]^{2-}\}$ redox couple was used for estimation of transition metal ions and their binary mixture over platinum. Based on the relative stabilities of $\{[\text{Fe(III)EDTA}]^{-}$ complex and the other metal ion EDTA complexes, The studied metal ions can be categorized into following classes:

Metals which did not exchange bound EDTA with iron(III) and gave single equivalence point corresponding to free EDTA only (Fig. 1).

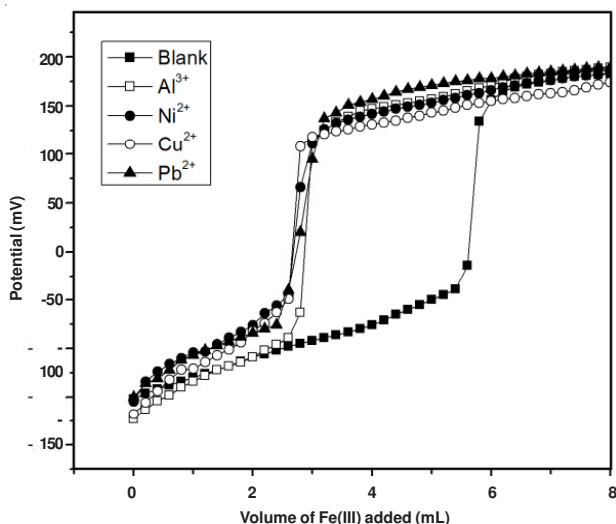


Fig. 1. Potentiometric titration of 20 mL samples containing (2.0 mL of 8.0×10^{-2} M Al(III), Ni(II), Cu(II) and Pb(II) With (5.0×10^{-2}) M iron(III) in presence of (4.0 mL 8×10^{-2} M EDTA and (1.0 mL of 4.0×10^{-2} M iron(II)

Metals which exchanged bound EDTA with iron(III) and gave two equivalence points corresponding to free EDTA and the total exchange of EDTA between metal ion and iron(III) (Fig. 2).

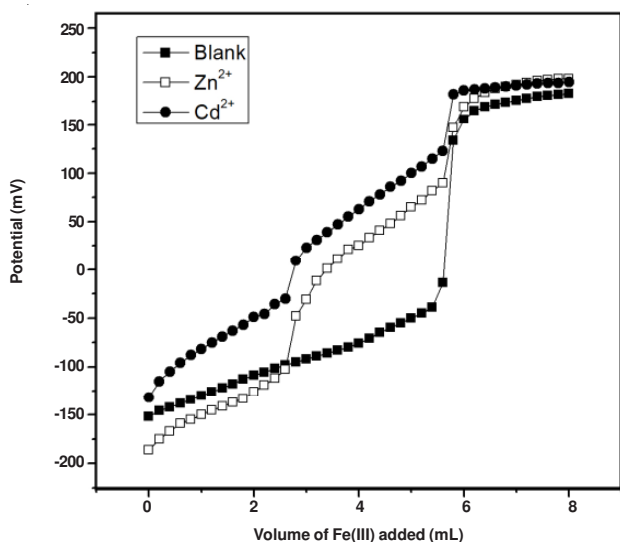


Fig. 2. Potentiometric titration of 20 mL samples containing (2.0 mL of 8.0×10^{-2} M Zn(II) and Cd(II) with (5.0×10^{-2}) M iron(III) in presence of (4.0 mL of 8×10^{-2} M EDTA and (1.0 mL of 4.0×10^{-2} M iron(II)

Metals which very weakly bind EDTA and gave a single prominent and stoichiometric equivalence corresponding to the total EDTA initially added (Fig 3).

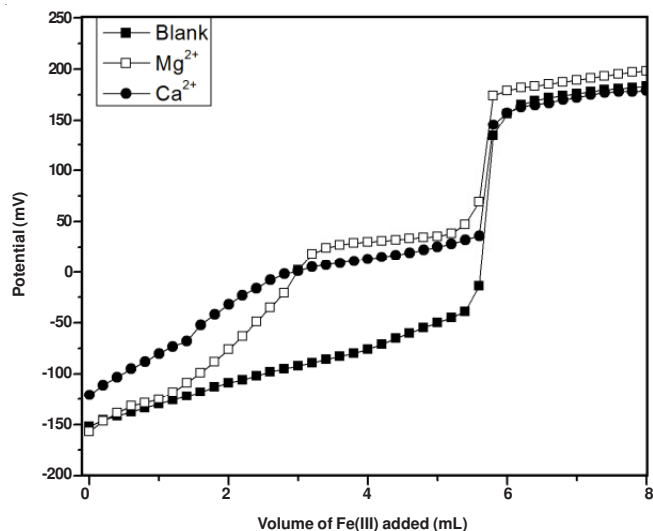


Fig. 3. Potentiometric titration of 20 mL samples containing (2.5 mL of 8.0×10^{-2} M Ca(II) and Mg(II) with (5.0×10^{-2}) M iron(III) in presence of (4.0 mL of 8×10^{-2} M EDTA and (1.0 mL of (4.0×10^{-2}) M iron(II)

Bimetallic mixture of metals in which one exchanged and other did not exchange the bound EDTA to iron(III) giving two equivalence points corresponding to free EDTA and to the total exchange of EDTA between metal ion and iron(III) (Fig. 4).

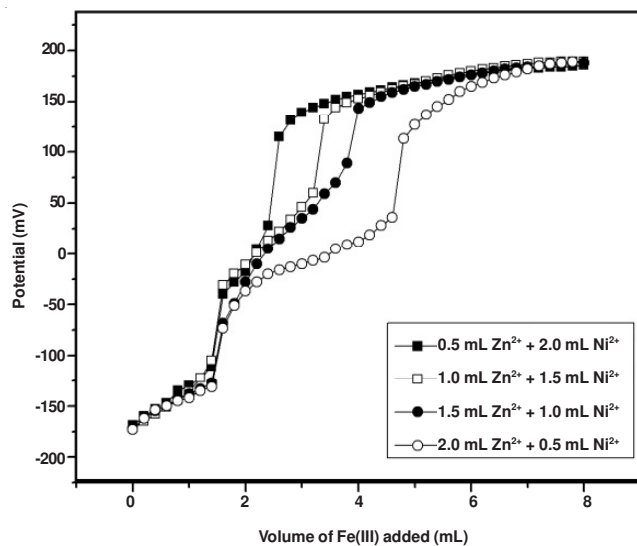


Fig. 4. Potentiometric titration of 20 mL samples containing (0.5-2.0 mL of 8.0×10^{-2} M Zn(II) and (2.0-0.5 mL of 8.0×10^{-2} M Ni(II) with (5.0×10^{-2}) M iron(III) in presence of (4.0 mL of 8×10^{-2} M EDTA and (1.0 mL of 4.0×10^{-2}

The behaviour of different classes of metal ions summarized in Table-1. A theoretical consideration of stability constants predict an exchange of EDTA from Ni(II) to Fe(III) as $\{\log \beta[\text{Ni(II)EDTA}]^{2-} \text{ and } [\text{Fe(III)EDTA}]^{-} = 18.62 \text{ and } 25.1\}$ ⁸. However a single equivalence point corresponding to free EDTA in solution was experimentally obtained. Thermodyna-

TABLE-1
 PROBABLE REASONS FOR DIFFERENT BEHAVIOUR OF METAL IONS

Metal class	Metal ion	Observation	Inference	Reason
A	Al ³⁺ , Cu ²⁺ , Ni ²⁺ , Pb ²⁺	A single distinct potential jump corresponding to free EDTA in solution	At titration pH 4.2 the binding of EDTA to these metals is strong, which gives the sharp jump at equivalence point	Due to kinetic reasons and the improper pH these metals do not exchange the bound EDTA to Fe(III).
B	Zn ²⁺ and Cd ²⁺	Two potential jumps corresponding to free EDTA and exchanged EDTA between Zn(II), Cd(II) and Fe(III) respectively.	Fe(III) first binds to free EDTA giving first equivalence point and then exchange bound EDTA from Zn(II) and Cd(II)	The lower formation constant of Zn(II), Cd(II) EDTA complexes compared to Fe(III) EDTA at the titration pH 4.2
C	Mg ²⁺ and Ca ²⁺	No distinctive jump corresponding to free EDTA but a potential jump corresponding to available EDTA	At titration pH 4.2 the binding of EDTA to Mg(II) and Ca(II) is weak and hence no sharp potential jump is seen.	The formation constants of Mg and Ca(II) EDTA complexes are low and their appropriate EDTA binding pH is around 10 and 8.
D	Zn ²⁺ and Ni ²⁺ mixture	Two distinctive potential jumps corresponding to free EDTA and the exchanged EDTA between Zn(II) and Fe(III) respectively	Fe(III) first binds to free EDTA giving first inflection and then exchanges Zinc bound EDTA giving second inflection point.	Due to kinetic reasons and the improper pH Nickel does not exchange the bound EDTA to Fe(III) and only zinc exchanges.

mically EDTA exchange from Ni(II) to Fe(III) is possible ($\log \beta > 10^6$) but the reaction is kinetically unfavorable and too slow on potentiometric time scale at 30 °C. This point is further validated through spectrophotometry in which the absorbance at λ_{\max} 590 nm corresponding to $[\text{Ni(II)EDTA}]^{2-}$ remains constant during the addition of iron(III), however in presence of excess of iron(III) the λ_{\max} shifts to 560 nm due to the formation of soluble iron hydroxides $[\text{Fe(OH)}_n]^{(3-n)-}$. A binary mixtures of two metal ions Zn(II) and Ni(II) from class a {kinetically inert to exchange bound EDTA to iron(III)} and from class b {which exchange EDTA to iron(III)} were titrated for simultaneous estimation of two metal ions. The relative amounts of both the metal ions were varied, keeping the total amount constant. This gave no change in the amounts of free EDTA present and hence the first equivalence point, however there was shifting in the second equivalence point in proportion to the concentration of class B metal ion Fig. 4. The potentiometric titration of metal ions with iron(III) in presence of EDTA was carried out in the range of 10^{-3} - 10^{-1} M with analytical results of individual metals ions and their binary mixtures corresponding well with amounts taken for analysis under good reproducibility. The titration procedure was optimized for pH and iron(II) amounts initially added. While as pH had a strong effect on titration the amount of iron(II) initially added had no profound influence on titration, in our work we observed that 1 mL of iron(II) initially added and pH 4.2 as optimum for analytical estimations. The best possible pH for the titration was found to be 4.2 maintained by 2 M acetate buffer as it represented a working compromise between the different parameters differently influencing titration through pH.

The potential measured by platinum electrode in this titration is given by Nernst equation:

$$E_{\text{Pt}} = E^0_{\left\{ \begin{array}{l} \text{FeY}^{2-} \\ \text{FeY}^- \end{array} \right\}} - \frac{RT}{nF} \ln \frac{[\text{FeY}^{2-}]}{[\text{FeY}^-]}$$

$$E^0_{\left\{ \begin{array}{l} \text{FeY}^{2-} \\ \text{FeY}^- \end{array} \right\}} = E^0_{\left\{ \begin{array}{l} [\text{Fe(OH)}_6]^{3+} \\ [\text{Fe(OH)}_6]^{2+} \end{array} \right\}} - 0.59 \frac{\beta(\text{III})}{\beta(\text{II})}$$

where $\beta(\text{III})$ and $\beta(\text{II})$ are the formation constant of iron(III) EDTA and iron(II) EDTA, respectively⁷, on substituting values for two iron EDTA formation constants, free (aqua state) iron redox potential and other constants at 25 °C we get the final equation as:

$$E_{\text{Pt}} = 0.13 - 0.059 \log \frac{[\text{FeY}^{2-}]}{[\text{FeY}^-]}$$

Conclusion

This work extends use of a platinum redox electrode in estimation of non-redox transition metal ions and their mixtures with the object of replacement of costly and delicate ion selective electrodes with simple platinum electrode. This method also allows simultaneous estimation of the binary metal ion mixtures not possible with ion selective electrodes.

ACKNOWLEDGEMENTS

One of the authors (Masood Ahmad Rizvi) acknowledged the financial support by UGC (GOI) in the form of minor research project. The authors are also thankful to Prof. Khaliq Zaman Khan, Head Department of Chemistry, University of Kashmir for the facilities, support and valuable guidance.

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