Pseudo-indicator behaviour of platinum electrode explored for the potentiometric estimation of non-redox systems

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ABSTRACT

A pseudo-indicator electrode based potentiometric method for estimation of non-redox metal ions is presented. In the proposed method, nature and concentration specific impact of analyte over the redox potential of ideally polarisable Pt/pregenerated-redox-couple interface forms the basis of quantification. Utility of the method in estimation of six non-redox metal ions viz. Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+} in the concentration range of 10^{-1}–10^{-3} moldm^{-3}, individually and as binary mixtures is also presented. Three types of potentiometric behaviours, which we ascribe to the nature specific thermodynamic and kinetic aspects of metal-EDTA binding, were observed. While Cu^{2+}, Ni^{2+}, Pb^{2+} and Al^{3+} were found to bind EDTA efficiently, without exchanging Fe^{3+}; Zn^{2+} and Cd^{2+} were observed to replace Fe^{3+} from EDTA. In contrast, Ca^{2+} and Mg^{2+} were found to show no binding affinity to EDTA in the pH range employed in the present work. The proposed method was also used to explore the reversibility and the Nernstian behaviour of ferricyanide/ferrocyanide redox couple through spectroelectrochemical titration of Zn^{2+} with ferrocyanide. The presented method is presaged to be a reliable and low cost future replacement for costly and delicate ion selective electrodes (ISE) in the estimation of non-redox species like Zn^{2+}, Cu^{2+}, etc.

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1. Introduction

Potentiometric quantification of analyte concentration is based on the Nernstian type dependence of electromotive force (EMF) over the concentration of oxidised and reduced forms of analyte. Thus electron transfer is a prerequisite for such type of analysis [1,2]. This strategy has been explored for analytical monitoring of many industrial, pharmaceutical, biological and environmental samples [3–7]. In such methods, the electrode actually sensing the changes in the analyte concentration is regarded as indicator electrode and many a times, a simple redox electrode in the potentiometric setup acts as reliable and sensitive indicator electrode. Even after eighty years of its first reported use, platinum continues to be the most commonly used redox-indicator electrode, owing to its good surface characteristics, quick equilibration, well Nernstian behaviour, modest cost, easy storage and longer life [8–10]. However, there are a number of biologically [11,12] and environmentally [13,14] important species like Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, I^-, Cl^-, and Br^- which being non-redox fail to generate a redox couple in vicinity of platinum contact in potentiometric cells and hence cannot be sensed through use of this metal contact in redox electrode. It is in this context that a good quantum of analytical work in recent past has been devoted to the development of alternate methods for estimation of such ionic species which include chemosensor based ion selective electrodes (ISE) [15–22] spectroflorescent probes (SFP) [23–25] and coated wire electrodes (CWE) [26–28]. ISE consist of macrocyclic and porphyrin type Schiff base adducts adsorbed over polyvinyl chloride material, with an appropriate pore size to bind a specific metal ion. SEP are made up of florescent type ligands which show change in spectral or fluorescent properties on interaction with specific metal ions. CWE are the modified electrodes obtained by the electrodeposition of a chemosensor material over a bare platinum electrode. All these reported analytical techniques for the estimation of these important ionic species involve either a sophisticated instrumentation or costly ion selective electrodes. Moreover, poor shelf life and less chemical stability in various media associated to ISE have limited their general application in analytical chemistry. As of now to the best of our knowledge, there has been no attempt to make use of platinum electrode for the estimation of non-redox ions. The work presented in this report describes a novel indirect method for estimation of non-redox species like Zn^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+} over platinum by exploring their impact on redox potential of a pregenerated redox couple within the analyte solution. The non-redox cell reaction changes concentration of one of the two forms in the redox couple allowing potential to change and hence allows the quantitative monitoring of the

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analyte concentrations. Three redox couples *viz* I^-/I_2, $[Fe(CN)_6]^{-4}/[Fe(CN)_6]^{-3}$ and $[Fe(EDTA)]^{-1}/[Fe(EDTA)]^{-2}$ were used to estimate: I^- with Ag^{+1}, Zn^{+2} with $[Fe(CN)_6]^{-4}$ and Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Al^{3+} both individually and as binary mixtures with $[Fe(EDTA)]^{-1}$ over a platinum electrode. Use of such redox systems for indirect estimation of non-redox species through a non-redox reaction has been referred as the pseudo-indicator method. The presented method owes its speciality to sense changing the Nernstian ratio through precipitation or complexation without involvement of an actual electron transfer. In addition, the work presented describes validation of the Nernst equation and determination of standard electrode potential for $[Fe(CN)_6]^{-4}/[Fe(CN)_6]^{-3}$ redox couple in spectroelectrochmical titration of Zn^{2+} with ferrocyanide.

2. Experimental

2.1. Reagents

Metal ion salts, acetic acid, sulphuric acid, disodium ethylenediaaminetetraacetic acid (EDTA) were purchased from Merck India. Metal ion and EDTA solutions were standardized by appropriate chemical methods. Sodium acetate, potassium ferrocyanide, potassium ferricyanide, potassium iodide were also obtained from Merck India and used without further treatment. Solutions were prepared in triple distilled water. $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$, ferrocyanide and ferricyanide solutions were prepared in 10^{-4} moldm^{-3} H_2SO_4 solution.

2.2. Equipment

The potentiometric measurements were carried at 25 °C ($\pm$0.2 °C) over Eutech PC5500 ion analyser using a platinum electrode and saturated calomel electrode assembly over a thermostatic magnetic stirrer. Spectrophotometric measurements were done using UV–visible spectrophotometer (Schimadzu 1650PC). Supernatant liquid of Zn^{2+} ferrocyanide titration mixture was centrifuged using Eppendrof minispin centrifuge at 500 rpm prior to absorbance measurement. Data were analysed using Micocal Origin 8.5.

2.3. Procedure

I/I_2 redox couple was set by adding 2–3 drops of methanolic solution of I_2 to iodide solution before titration with Ag^{1+}. $[Fe(CN)_6]^{-4}/[Fe(CN)_6]^{-3}$ redox couple was generated by adding 2 ml of ferricyanide to ferrocyanide solution before titrating it with Zn^{2+}. $[Fe(EDTA)]^{-2}/[Fe(EDTA)]^{-1}$ redox couple was generated by adding 1 ml of $Fe^{2+}_{(aq)}$ to standardised EDTA solution prior to titration with $Fe^{3+}_{(aq)}$. The titrations were carried over concentration range of 10^{-1}–10^{-3} moldm^{-3}. Titrations involving $[Fe(EDTA)]^{-2}/[Fe(EDTA)]^{-1}$ redox couple were carried under controlled pH using acetate buffer. Titrations carried over a pH range, revealed pH=4.2 to be the optimum pH value for such titrations. Spectroelectrochemical titration was carried in eight 100 mL beakers, which virtually represented the different stages of a titration. A fixed number of millimoles of ferricyanide and ferrocyanide were taken and an increasing volume of $Zn^{2+}_{(aq)}$ was added sequentially. After an initial development time of 05 min, the potential of solution in each beaker was recorded followed by absorbance measurements of supernatant liquid from each titration stage.

3. Results and discussion

The proposed pseudo-indicator model enabled the analytical monitoring of non-redox systems through use of platinum as indicator electrode in a simple and low cost potentiometric assembly. Preliminary iodide estimation results (Table 1) obtained using the proposed model were found to be in good agreement with the actual analyte concentrations. These results served as a motivation to explore the workability of the proposed model for analytical monitoring of other non-redox systems.

3.1. Iodine–iodide system

The potentiometric titrations of iodide ions with Ag^+ (in presence of I_2) over platinum were carried over the range of 10^{-3}–10^{-1} moldm^{-3} iodide concentration. As depicted in Fig. 1, with gradual addition of Ag^+ the potential first increases slowly and then abruptly near the equivalence point and finally reaching a plateau region wherein the potential is insensitive to the addition of titrand. The analytical results summarised in Table 1 correspond well with the amounts taken for analysis.

The addition of Ag^+ ions to I^- solution results in precipitation of I^- as AgI, thereby decreasing the available I^- ions. As a consequence accordingly there is a rise in EMF of the system as predicted by the Nernst equation.

$$E_{Pt} = E_{I_2/2I^-} - \frac{RT}{2F}2.303\log\frac{[I^-]^2}{[I_2]}$$ (1)

Table 1
Potentiometric estimation of I^- over platinum in five lab made samples.

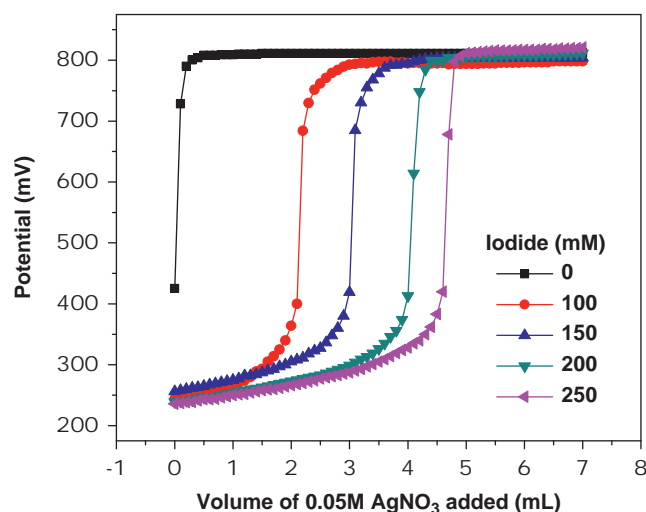| Sample no.	I^- in sample (mmol)	I^- estimated (mmol)
1	0	No pot. break
2	100	100 ± 0.50
3	150	150 ± 0.50
4	200	200 ± 0.50
5	250	250 ± 0.50

Fig. 1. Potentiometric estimation of five iodide solutions of different concentrations with Ag^+ in presence of iodine over platinum electrode.

3.2. Zinc-ferrocyanide system

The proposed pseudo-indicator model was also tested for the estimation of non-redox Zn^{2+} ions over platinum by employing $[Fe(CN)_6]^{-4}/[Fe(CN)_6]^{-3}$ redox couple. The couple was pregenerated in a titration beaker to which Zn^{2+} solution was added in small increments. Initially the EMF increases slowly and then abruptly near the equivalence point. On reversing the titration an exactly opposite trend was observed in variation of potential (Fig. 2), thus indicating that titration can be monitored potentiometrically by either adding Zn^{2+} to ferrocyanide or vice-versa. It is apposite to mention here that same stoichiometry was established under both the cases. The potentiometric titrations of Zn^{2+} ions with ferrocyanide in presence of ferricyanide over platinum electrode were carried over a range of 10^{-3}–10^{-1} moldm^{-3}. The amount of Zn^{2+} ions estimated was in good agreement with the amount taken for analysis.

It is reported that Zn^{2+} in neutral or slightly acidic medium reacts with ferrocyanide to form a white coloured complex $K_2Zn_3[Fe(CN)_6]_2$ [29]

$$3Zn^{2+}2K_4[Fe(CN)_6] \rightarrow K_2Zn_3[Fe(CN)_6]_2 + 6K^+$$
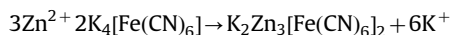
The gradual addition of Zn^{2+} causes the precipitation of ferrocyanide as Zn-ferrocyanide complex which results in decrease in available ferrocyanide with a concomitant increase in potential as predicted by Eq. (2).

$$E_{Pt} = E_{[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}} - \frac{RT}{nF}2.303 \log \frac{[Fe(CN)_6]^{4-}}{[Fe(CN)_6]^{3-}} \quad (2)$$

The Nernstian behaviour for $[Fe(CN)_6]^{-4}/[Fe(CN)_6]^{-3}$ redox couple over platinum electrode was verified by performing a spectroelectrochmical titration. The spectra of eight different stages of the titration are presented in Fig. 3. The concentrations of ferricyanide and ferrocyanide at each stage were calculated from their absorbance values at 442 nm and 312 nm corresponding to their λ_{max} respectively. As is evident from the figure, the absorbance corresponding to ferrocyanide ($\lambda = 312$ nm) decreases with addition of Zn^{2+}, which is due to complexation of former with later. On the other hand absorbance corresponding to ferricyanide ($\lambda = 442$ nm) remained constant initially and decreases abnormally near the equivalence point. The abnormal decrease was explained on the basis complexation of Zn^{2+} with ferricyanide after the entire ferrocyanide had complexed.
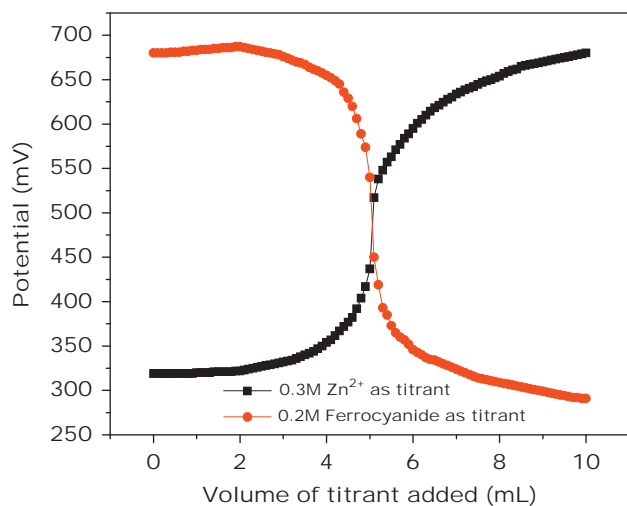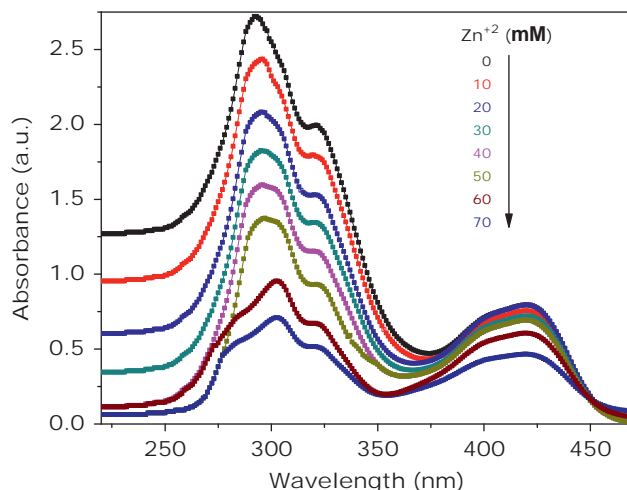

Fig.3. Absorbance spectra of supernatant liquid at various stages of Zn^{2+}–ferrocyanide titration.

Ferricyanide, ferrocyanide concentrations and corresponding EMF values corresponding to different stages of titration are presented in Table 2. The observed cell EMF vs. $\ln[Fe(CN)_6]^{-4}/[Fe(CN)_6]^{-3}$, follows a linear relation line (Fig. 4) with a regression coefficient of 0.98, with the slope $-RT/nF = 44.14$ and intercept $(E^\circ - E_{ref}) = 0.181$ V.Since the electrode assembly consists of saturated calomel as reference, a value of 0.242 V (E° calomel) was added to the intercept that leads to $E^\circ = 0.423$ V for $[Fe(CN)_6]^{-4}/[Fe(CN)_6]^{-3}$ redox couple. The calculated value is in good agreement with the reported value of 0.430 V [30] for the said couple. These results imply that above mentioned novel spectroelectrochemical titration can be used for evaluation standard electrode potential of similar redox systems.

3.3. Ferri-EDTA/ferro-EDTA system

The proposed model was further extended to the estimation of eight non-redox metal ions, both individually as well as binary mixtures. The estimation is based on the principle of monitoring potential changes with $[Fe(EDTA)]^{-2}/[Fe(EDTA)]^{-1}$ redox couple in presence of different analyte metal ions. The analysed metal ions exhibited three types of potentiometric behaviours as evident from Fig. 5. The nature of potentiometric profiles was correlated with complexing ability i.e. the value of binding constant with EDTA in comparison to Fe^{3+}. Erstwhile to the estimation experiments, the effect of pH, initial concentration of Fe^{2+} and concentration of analyte metal ion was also investigated.

3.3.1. Effect of pH

The effect of pH on the titration curves of $[Fe(EDTA)]^{-2}/[Fe(EDTA)]^{-1}$ redox couple was examined in the range of 3–5 (Fig. 6) The results reveal that the pH has a prominent effect on the shape of the titration curve, the potential measured, the height of inflection point and volume corresponding to equivalence. The dependence of potential profiles on pH is attributed to its impact on conditional formation constant of $[Fe(EDTA)]^{-2}$ and $[Fe(EDTA)]^{-1}$ complexes. Below pH 3.0 the stability constants are very low and above pH 6.0 Fe^{3+} hydrolyse to $[Fe(OH)_n]^{(3-n)-}$ even in presence of EDTA. Moreover, the conditional formation constant of $[M^{2+}EDTA]^{(n-4)-}$ also varies with pH. The estimation studies at pH 3.5, 4.2 and 5.0 imply pH of 4.2 as optimum for the estimation studies. This is further supported by the stability constant data for metal-EDTA complexes at changing pH [31].

Fig. 2. Potentiometric estimations of Zn^{2+} and ferrocyanide solutions in presence of ferricyanide over platinum electrode.

Table 2
Potential and absorbance at different stages of Zn^{2+}- ferrocyanide titration.

Zn(II) added ml	A_{max} Ferrocyanide	[Ferrocyanide] (mmol dm^{-3})	A_{max} Ferricyanide	[Ferricyanide] (mmol dm^{-3})	ln[ferro]/ [ferri]	EMF (mV)
0.0	2.72	0.60	0.80	0.10	1.79	104 ± 0.1
0.5	2.41	0.53	0.76	0.10	1.67	107 ± 0.1
1.0	2.06	0.46	0.80	0.10	1.57	110 ± 0.1
1.5	1.81	0.40	0.80	0.10	1.38	116 ± 0.1
2.0	1.57	0.35	0.70	0.09	1.34	122 ± 0.1
2.5	1.34	0.30	0.70	0.09	1.22	129 ± 0.1
3.0	0.82	0.18	0.70	0.09	0.73	149 ± 0.1
3.5	0.62	0.14	0.47	0.08	0.58	223 ± 0.1

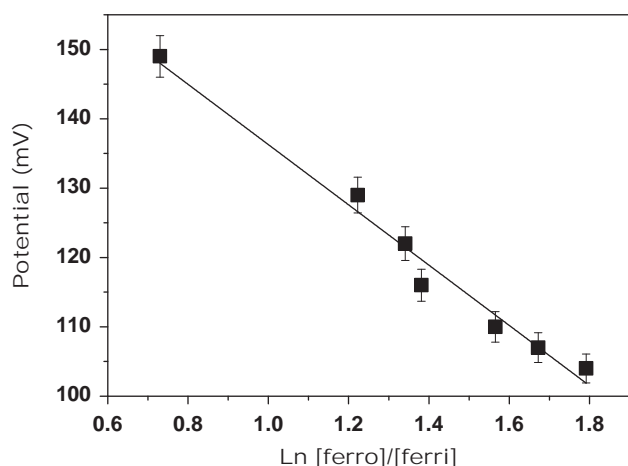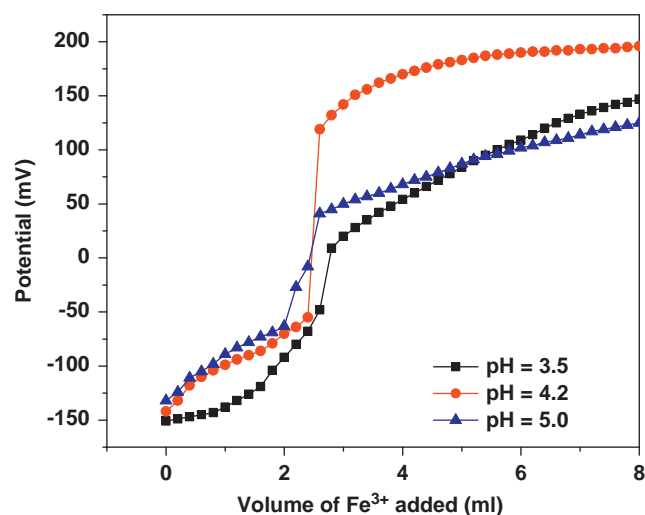**Fig. 4.** Plot of EMF vs. $\ln[Fe(CN)_6]^{-4}/[Fe(CN)_6]^{-3}$.

Fig. 6. Effect of solution pH on potentiometric behaviour of $Fe^{2+}EDTA/Fe^{3+}EDTA$ couple in presence of Ni^{2+} ions.
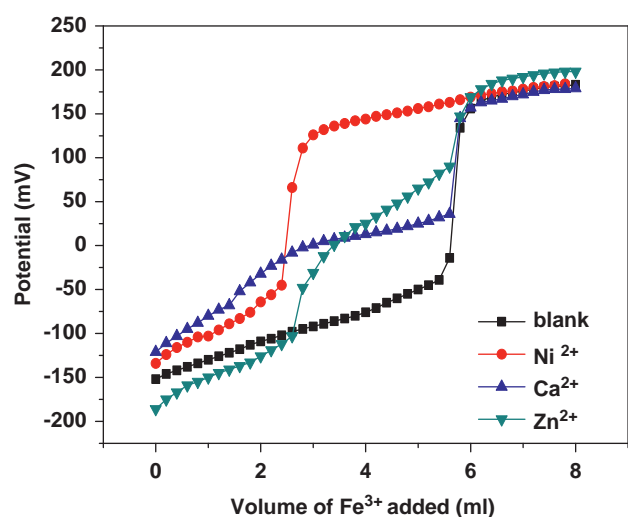

Fig. 5. Comparison potentiometric behaviours of Ni^{2+}, Ca^{2+} and Zn^{2+} metal ions.
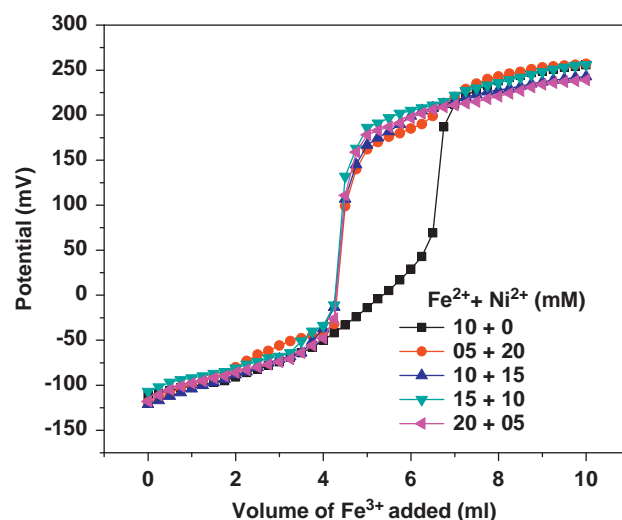

Fig. 7. Effect of change in initially added Fe^{2+} concentration on Potentiometric estimation of Ni^{2+} over platinum.

3.3.2. Effect of initial volume of Fe^{2+} $_{(aq)}$ and analyte concentration

Our observation for titration curves of Fe^{3+} with EDTA in presence of changing volumes of Fe^{2+} (Fig. 7) indicate that the initially added volume of Fe^{2+} to the titration mixture neither affects the shape of the titration curve nor the volume corresponding to the equivalence point (Fig. 7). We preferred to add 1 mL of 0.01 moldm^{-3} of Fe^{2+} solution for the other estimation experiments. Fig. 8 shows that observed and expected inflection points are at same position in a titration series with changing Ni^{2+} and Zn^{2+} concentrations without any significant change in the shape of the curve.

3.3.3. Potentiometric response

As mentioned earlier three types of potentiometric behaviours were observed during titration of investigated metal ions. Depending on the behaviour observed metal ions we categorise the metal ions into the following three groups (Fig. 9).

Group I: Includes metal ions Ni^{2+}, Cu^{2+}, Al^{3+} & Pb^{2+} which do not exchange bound EDTA with Fe^{3+} and show a single Potential break corresponding to free EDTA only.
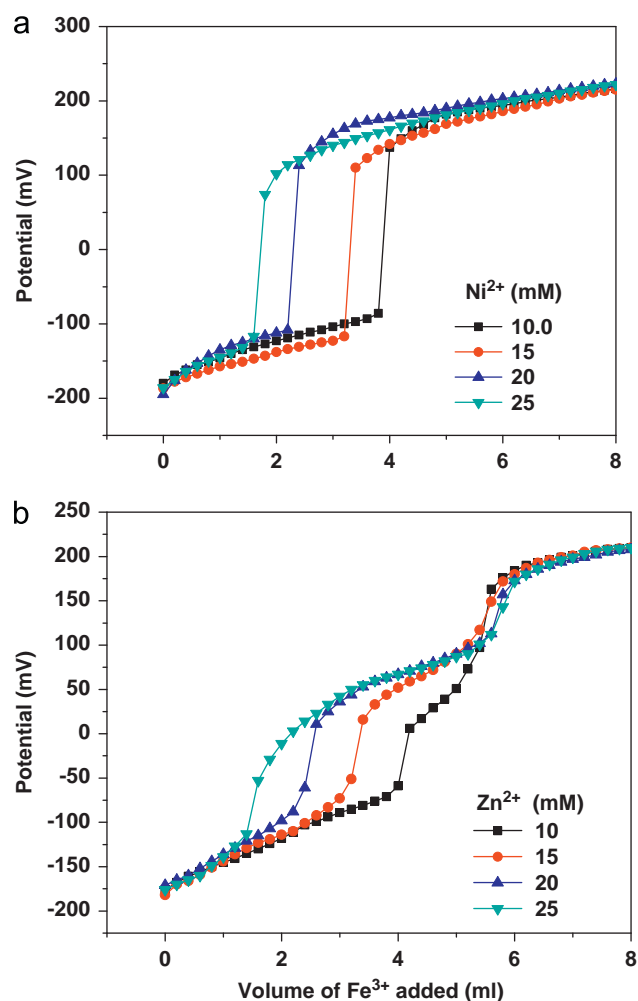
Fig. 8. Effect of concentration on potentiometric estimation over platinum (a) Ni^{2+} (b) Zn^{2+}.

Group II: Includes metal ions Zn^{2+} and Cd^{2+} which exchange bound EDTA with Fe^{3+} and show two Potential breaks, first corresponding to free EDTA and the second corresponding to total exchanged EDTA between metal ion and Fe^{3+}.

Group III: Includes metal ions Ca^{2+} and Mg^{2+} which do not bind EDTA and show a single potential break corresponding to the total EDTA initially added.

Titration of Fe^{3+} with EDTA in presence of Fe^{2+} develops $[Fe(EDTA)]^{-2}/[Fe(EDTA)]^{-1}$ redox couple in the solution. With the progress of titration the EMF of the solution increases and at the equivalence point there is a potential break. However, in presence of the analyte metal ion there is a decrease in free EDTA resulting in the shifting of inflection point of the titration curve to the left.

For Group I metal ions (Ni^{2+}, Cu^{2+}, Al^{3+} and Pb^{2+}), the potentiometric curve consists of a single inflection point shifted to left. This shift in equivalence point was proportional to the number of millimoles of metal ion present. Group1 metal ions have high EDTA binding constants with optimum complexation at pH used. As a result there was an efficient metal-EDTA binding, which decreases the free EDTA. Compared to the Group I metal ions, the metal ions from Group II have lower EDTA binding constant values but large enough to bind EDTA efficiently (Table 3). Stability constant data predict that both Group I and Group II metal ions should exchange EDTA to Fe^{3+} due to their very high EDTA binding constant (log K=25.1). However, it was
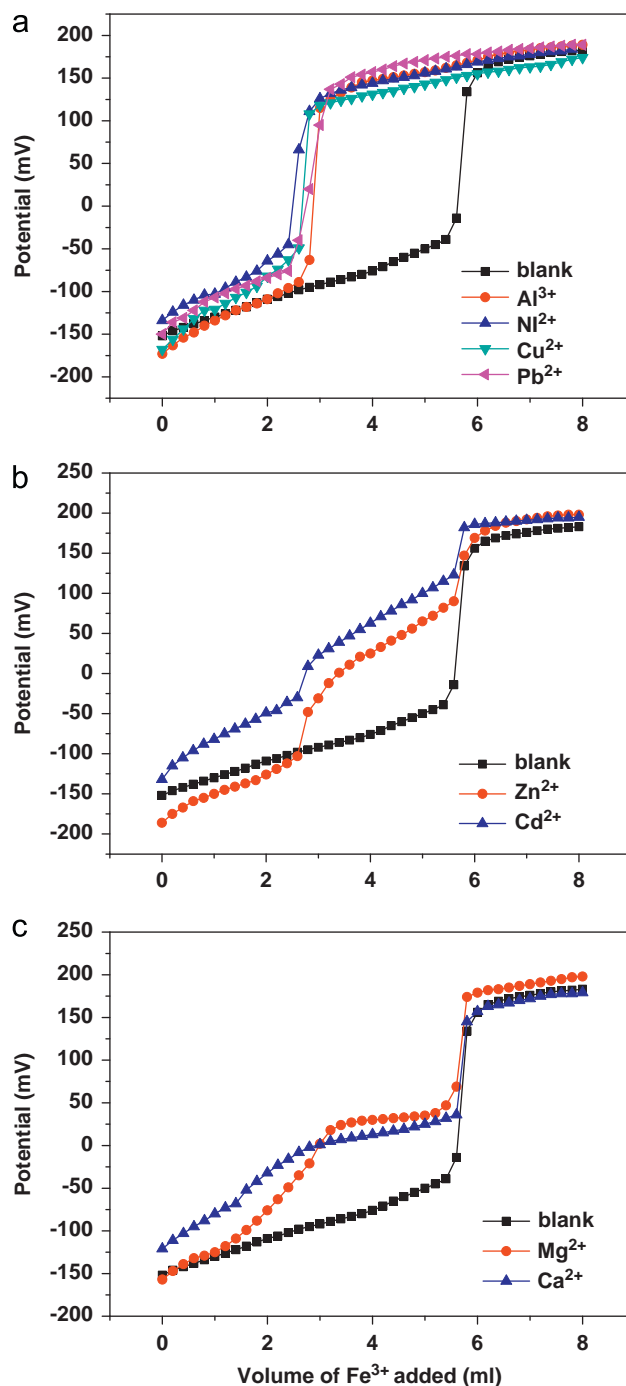

Fig. 9. Classification of metal ions on the basis of potentiometric response (a) Group I (b) Group II (c) Group III.

observed that only Group II metal ions (Zn^{2+} and Cd^{2+}) exchanged EDTA to Fe^{3+}. The observation is attributed to kinetics of metal-EDTA exchange. Although the exchange of EDTA between Group I metal ions and Fe^{3+} is thermodynamically feasible, the contradiction may be due to slow exchange rate with respect to potentiometric time scale. Rate of EDTA exchange is accelerated or slowed by the pH change and every metal-EDTA complex has an optimum pH value at which the rate of EDTA exchange is slowest [32]. The working and optimum pH for Group I metal ions is almost same due to which the EDTA exchange is very slow. However, the working and optimum pH for Group II metal ions are different and are therefore prone to a faster EDTA exchange as a result of which the titration curve shows two

Table 3
Potentiometric response, optimum complexation pH, and stability constant data of three metal ion groups.

Group	Metal ion	log K	pH	Potentiometric response
I	Cu^{2+}	18.80	4–5	Single potential break corresponding to excess EDTA
	Ni^{2+}	18.63		
	Pb^{2+}	18.04		
	Al^{3+}	16.30		
II	Zn^{2+}	16.50	7–8	Two potential breaks corresponding to free and exchanged EDTA
	Cd^{2+}	16.46		
III	Ca^{2+}	10.69	8–9	No prominent potential break
	Mg^{2+}	08.79	9–10	
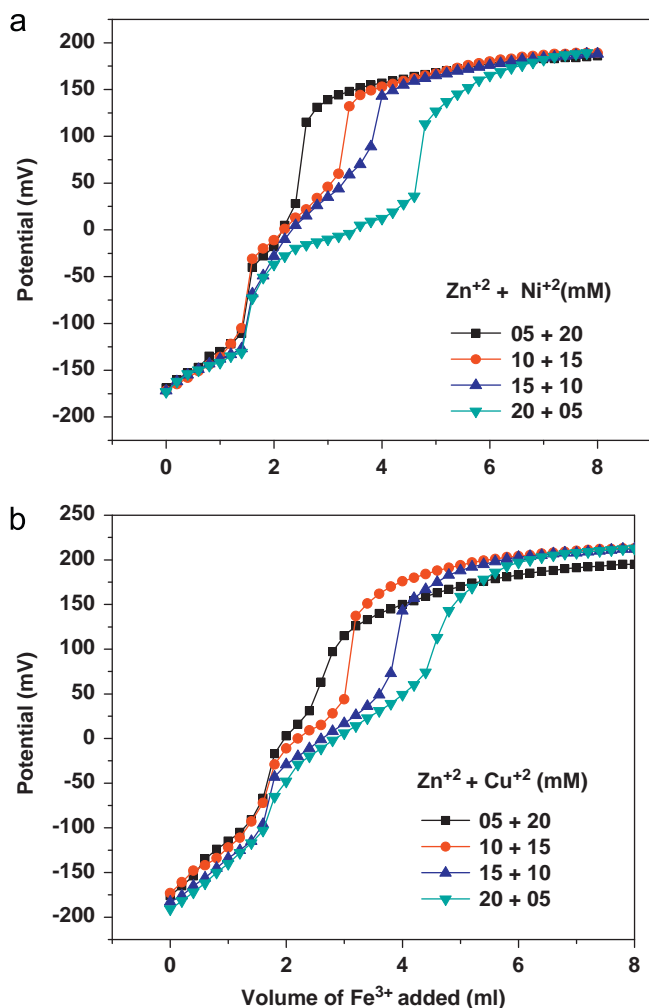
Fig. 10. Estimation of bimetallic solutions using pseudo-indicator method (a) Zn^{2+} and Ni^{2+} (b) Zn^{2+} and Cu^{2+}.

inflection points first corresponding to free EDTA and second corresponding to exchanged EDTA. The presence of an activation barrier was further validated by performing the titration at higher temperatures (upto 45 °C). Some deformation in post equivalence region of the titration curve was observed with increase in temperature. However, this temperature induced deformation did not shape as clear second potential break even at 45 °C. Compared to Group I and II, the metal ions of Group III did not show a clear potential break. The observation is attributed to very low EDTA binding constants for Group III metal ions on account of large difference between working and optimum pH for EDTA binding.

The model was further explored for the simultaneous estimation of two non-redox metal ions, in which one exchanged EDTA with Fe^{3+} while the other did not. Two equivalence points corresponding to free EDTA and to the total exchange of EDTA between metal ion and Fe^{3+} were observed for these titrations. In addition, simultaneous estimation of two mixed binary systems of Group I and Group II was also investigated (Fig. 10). For the two binary mixtures relative amounts of both the metal ions were varied keeping the total amount constant. Since free EDTA in all the cases would be same, as a result first potential break in titration curves was observed at the same position in all cases. However a shift in the second equivalence point proportionate to the number of millimoles of Zn^{2+} was observed. The Zn^{2+} ions in the two binary mixtures exchanged EDTA with Fe^{3+} and hence the shift observed in the second potential break in accordance with the amount of Zn^{2+} in the mixture. Out of the two studied mixed binary systems Ni^{2+}/Zn^{2+} showed more prominent inflection points compared to Cu^{2+}/Zn^{2+}. This is because Ni^{2+} is more inert than Cu^{2+} for the exchange of bound EDTA to Fe^{3+}. Worth to mention the stoichiometric positioning of potential breaks was obtained in both the cases.

4. Conclusion

A pseudo-indicator method for the estimation of non-redox metal ions like Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} potentiometrically using platinum as indicator electrode is presented. The model has a novelty of changing the ratio of oxidised or reduced states in a typical Nernstian fashion through precipitation or complexation without an actual electron transfer. The work also explores the Spectrophotometric validation of the Nernst equation and determination of the standard electrode potentials through spectro-electrochemical titration.

Acknowledgements

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