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Iron Reduces Iron: A Spectroelectrochemical Insight of Ligand Effect on Iron Redox Potential

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ABSTRACT

The electron transfer reaction between two oxidation states of a transition metal redox couple is amazingly interesting. The present study describes a combined spectrophotometric and potentiometric investigation of redox reaction involving iron (III) and iron(II) oxidation states. The electron transfer reaction is seen to occur between iron-(III)phenanthroline complex and a series of iron-(II) complexes with water, EDTA, DPTA, NTA, Tiron and diphosphate ligands. The relative propensity of selected ligands towards this reaction, displayed in the potentiometric titration plots can be corroborated with the redox potential modification of Fe(III)-Fe(II) redox couple. The ligand effect on redox potential of the iron redox couple as the underlying concept of the reaction, has been thoroughly investigated and thermodynamically modeled. The differing abilities of EDTA and Tiron ligands towards the spontaneity of this reaction under different pH conditions were potentiometerically observed and spectrophotometrically rationalized with the degree of ligand chelation vis-a-vis complex stability and the resultant redox potential. The experiment can serve as a model for unique environmental and biological redox reactions and can be explored further for designing of novel redox systems for redox flow cells.

Keywords: iron oxidation states, ligand effect, potentiometric titrations, spectrophotometry, EDTA, DPTA, Tiron, speciation analysis, thermochemical cycle, and iron redox couple

1. INTRODUCTION

Redox reactions are the important class of chemical reactions at work all around us encompassing natural as well as manmade domains of life. These reactions involve transfer of electrons guided by a key thermodynamic parameter, expressing the affinity of a chemical species to gain or lose electrons the redox potential. The efficacy (release and uptake) of electron transfer between the two chemical entities can be predicted from electrochemical series and primarily depends on the difference in their reduction potential see equation 1.

$$\Delta G^{0} = -nFE^{0}cell \qquad (1)$$
where $E^{0}cell = E^{0}_{0}$ - $E^{0}_{reductant}$

From equation 1, it is evident that, if the potential difference between oxidant and reductant reduces to zero, the redox reaction becomes non spontaneous. Accordingly a redox reaction involving same substance both as oxidant and reductant has $E^{0}_{_{\rm cell}}$ = 0 and is hence not feasible. Therefore, a redox reaction in which iron(II) reduces iron(III) back to iron(II) can be amazingly interesting. Transition metals have multiple oxidation states separated by a finite potential value and the reduction potential of Fe(III)-Fe(II) redox couple is 0.771V vs NHE [1]. Complexation reaction of the transition metal oxidation states in a redox couple is a favorable factor for modulation of redox potential of transition metal redox systems [2]. Depending upon the relative stabilization of the two oxidation states in a transition metal redox couple, different ligands can tune the formal redox potential of the Fe(III)-Fe(II) redox couple to a range of values [3]. Hence iron complexes in the presence of different ligands, even though involving the same Fe(III)-Fe(II) redox couple, can behave as different oxidizing/reducing agents, capable of transferring electron amongst themselves [4]. Hence, due to ligand modulated redox potentials, a redox reaction in which iron(II) reduces iron(III) can be possible. In continuation of our interests on complexation modulated redox behavior of transition metal systems [5-9], we, herein present a spectro electrochemical evidence of a ligand driven redox reaction between iron oxidation states in which an iron(II) complex reduces iron(III) phenanthroline complex to iron(II)phenanthroline complex and itself gets oxidized to iron(III) complex. The relative propensity of different ligands towards this ligand driven redox reaction has also been investigated. The thermodynamic efficacy of the selected group of ligands towards the electron transfer between two

iron oxidation states was found to be in accordance with their capacity to lower the iron(III)-iron(II) reduction potential [10]. The influence of complexation parameters was also investigated through a comparative study of ligand effect on iron redox couple under two pH conditions (4.0 and 6.5). The effect of pH has been corroborated with the speciation analysis of iron complexation with the studied ligands. This work provides a spectro-electrochemical insight of ligand effect on iron redox potential, as underlying reason for the interesting redox reaction in which iron reduces iron.

2. MATERIALS AND METHODS 2.1 Reagents and Solutions

All solutions were freshly prepared from analytical-grade chemicals of Merck India make using nitrogen gas purged double distilled water. The stock solution of 2×10⁻¹ M 1,10- phenanthroline was prepared from 1,10-phenanthroline monohydrate (3.9648 g in 100 mL of distilled water prior acidified with 10 mL of 1.0 M sulphuric acid). The stock solutions of 0.02 M iron(II), and 0.1 M ligands were prepared by dissolving the calculated amount of iron-(II) sulfate hexahydrate {FeSO4.6H2O}. imino diacetic acid(IDA, $H_7C_4O_4N$), diethylenetriamine pentaacetic acid (DPTA, C14H23N3O10), 4, 5-dihydroxy-1,3-benzenedisulfonicacid disodium salt (Tiron, C₆H₄Na₂O₆S₂), nitrilotriaceticacid (NTA, C₆H₉NO₆), diphosphate (DP, Na₂H₂P₂O₇), and ethylene diaminetetraacetic acid disodium salt dihydrate (EDTA-Na₂)·2H₂O $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O_2$). The 1 × 10⁻³ M iron-(III) solution for speciation analysis was prepared from ammonium ferric sulphatedodecahydrate.(NH₄)Fe(SO4)₂·12H₂O. The necessary acid medium of redox reaction was maintained using 1.0 M H₂SO₄ solution.

2.2 Instrument and Physical Measurements

Spectrophotometric measurements were carried on Shimadzu 1650 UV-visible spectrophotometer with thermostatic control. Potentiometric measurements were carried on Eutech PC5500 ion analyzer over a thermostatic magnetic stirrer using platinum indicator and calomel reference electrode at 25°C under nitrogen environment in a self-fabricated assembly described in our previous work [18].

2.3 General Procedures of Potentiometric Titrations

All potentiometric estimations were performed at room temperature (28°C ± 2°C) under nitrogen atmosphere over a magnetic stirrer. The analytical samples were titrated with 2×10^{-2} M iron (II) solution, added in increments of 0.2 ml throughout titration. The EMF values were recorded when change was within ± 2 mV. In a typical potentiometric experiment, in a pre step to titration, 0.02 M [Fe(Phen)₃]²⁺ solution was prepared by the addition of 1, 10 phenanthroline ligand to iron(II) solution in 1:3 molar ratio in presence of 2.0 M sodium acetate buffer (pH 4). The prepared complex [Fe(Phen)₃]²⁺, was quantitatively oxidized to [Fe(Phen)₃]³⁺ using standardized 2×10^{-2} M cerium(IV) solution. The concerns regarding decomposition necessitated the preparation of a series of freshly prepared [Fe(Phen)₃]³⁺ analyte [11] with varying concentration. These were then quickly titrated with 2×10^{-2} M iron(II) solution and the EMF was recorded. This is because the [Fe(Phen)₂]³⁺ complex is proposed not to exist in solution when 1,10-phenanthroline is added directly to iron(III) ions in solution and instead an oxo bridged diiron complex [(H₂O)(Phen), FeOFe(Phen)₂(H₂O)]⁴⁺ is reported to be the

predominant form [12,13]. However the exact composition of diiron species is dependent on Fe³⁺: Phen ligand molar ratio, counter ion of ferric salt and the pH of solution [14]. In order to circumvent this complicacy, we attempted to prepare more stable and readily formed red colored [Fe(Phen),]²⁺ and carefully oxidized it to blue [Fe(Phen),]³⁺ to be sure of the composition of analytical species in the sample solution. For spectrophotometric estimations, a series of six samples each containing 1.0 ml of 1×10^{-3} M freshly prepared solution of [Fe(Phen),]²⁺ were taken. To each sample, 0.5 ml of 6.0 M sulphuric acid and 1.0 ml of standardized 1×10^{-3} N potassium permanganate solution was added to oxidize red colored [Fe(Phen)₂]²⁺ to blue [Fe(Phen),]³⁺solution. To the blue [Fe(Phen),]³⁺ solution in the six samples, sequential

a decrease in the absorption due to dilution effect was observed. The ligand effect of the selected ligands on the [Fe(Phen)₃]³⁺ iron(II) redox reaction was studied at around pH 4.0 maintained by 1×10^{-4} M H₂SO₄. The ligand to metal molar ratio was appropriately adjusted for an octahedral composition of iron (3:1 for bidentate and 1:1 for hexadentate). In a typical titration set, 7.0 ml of 2×10^{-2} M freshly prepared [Fe(Phen)₂]³⁺ was titrated with 2×10^{-2} M iron(II) complex solution prepared by the dissolution of calculated amount of ligand(as solid compound) in the aqueous solution of 2×10^{-2} M iron(II) maintained at pH 4.0. The cell potential

addition of 1×10^{-3} M iron(II) was made in a

dose dependent manner (0.0, 0.2, 0.4, 0.6, 0.8, 1.0) and the absorbance of each solution

was recorded in the wavelength range of

350-800 nm. The observed changes in

the absorbance are depicted in Figure 2.

On addition of iron(II) solution in excess

to stoichiometric amount of [Fe(Phen)₃]³⁺,

was measured after each addition of iron(II) complex { $[Fe(L)_x]^{(2-nx)+}$ } titrant, when the change in potential was less than ± 2 mV. The pH of the titration mixture was measured at the start and the completion of the titration.

The spectrophotometric analysis of Tiron-Fe(III) complexation reactions at pH 4.0 and 8.5 was attempted using molar ratio method. In a series of nine labelled 5.0 ml volumetric flasks, 1.0 ml of 1×10^{-3} M Fe(III) was taken. To each flask, a sequential addition of (0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6) 1×10^{-3} M Tiron ligand solution was made, and their pH was adjusted around 3.5-4.0 with 1×10^{-4} M H₂SO₄ solution over a pH meter. A similar set of experiments in which, 1.0 ml of 1×10^{-3} M Fe(III) was also taken in nine labeled 5.0 mL volumetric flasks, followed by a sequential addition of (0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0) of 1×10^{-3} M Tiron ligand solution. The pH was adjusted around 8.5-9.0 using 4.0 M aqueous ammonia over a pH meter. The absorbance of both sets of solutions after dilution to 5.0 ml with distilled water, (maintaining the pH) was recorded over 400-800 nm wavelength range and are depicted in Figures 8 and 9.

3. RESULT AND DISCUSSION

The equilibrium constant K, for a redox reaction of metal ions, can be estimated from standard reduction potentials of metal ions involved in the reaction [15]. Thus equilibrium constant (K) of the redox reaction involving iron(II) and iron(III) can be calculated using equation 2:

Fe²⁺ + Fe³⁺
$$\rightleftharpoons$$
 Fe³⁺ + Fe²⁺
Log K = $\frac{E_{Fe} - E_{Fe}}{0.059}$ (2)

 $\log K = 0.0$

Where $E_{Fe} = E_{Fe} = 0.771 \text{ V} [16]$ are standard reduction potentials of Fe(III) /Fe(II) redox couple. The value of K = 0.0, indicates a non spontaneous redox reaction between iron(II) and iron(III). Indeed, no redox reaction appears to occur between iron(II) and iron(III) in their free or aqua complex form. However, the phenomena of iron(II) reducing iron(III) was interestingly observed through emergence of red coloration upon addition of colorless iron-(II) solution to the light blue colored solution of iron-(III) tris-phenanthroline complex ${[Fe(Phen)_3]^{3+}}$ Figure1. The formation of iron(II) trisphenanthroline complex { $[Fe(Phen)_2]^{2+}$ } was also evidenced from the increasing intensity of red coloration upon gradual addition of iron(II) solution. The corresponding electron transfer reaction is represented in equation 3.

$$\begin{split} & [\operatorname{Fe}(\operatorname{phen})_3]^{3+} + [\operatorname{Fe}(\operatorname{OH}_2)_6]^{2+} \to [\operatorname{Fe}(\operatorname{phen})_3]^{2+} \\ & + [\operatorname{Fe}(\operatorname{OH}_2)_6]^{3+} \\ & (3) \\ & (\operatorname{Light Blue}) \text{ (colorless) (Deep red) (Light yellow)} \end{split}$$

Where phen is 1,10-phenanthroline ligand.



Figure 1. Visible color changes depicting reduction of $[Fe(Phen)_3]^{3+}$ by $[Fe(OH_2)_6]^{2+}$. The visible color perception of the redox reaction was further confirmed through spectrophotometric investigation at the respective λ max of { $[Fe(Phen)_3]^{3+}$ } and { $[Fe(Phen)_3]^{2+}$ }. Figure 2. The observed spectral changes at the lambda max corresponding to $[Fe(Phen)_3]^{3+}$ and $[Fe(Phen)_3]^{2+}$ support the electron transfer concept with no ligand exchange.



Figure 2. Spectrophotometric response of $[Fe(Phen)_3]^{3+}$ reduction by $[Fe(OH_2)_a]^{2+}$.

The Figure 2, depicts three absorption bands. The band around 350 nm is characteristic of conjugated $pi(\pi)$ systems and can be assigned to the absorbance of the phenanthroline ligands. The intense absorption band around 510 nm is assigned to the iron (II) tris-phenanthroline complex $[Fe(Phen)_2]^{2+}$ [17] while as the low intensity absorption band around 600 nm can be ascribed to iron(III)-tris-phenanthroline complex [17]. It is evident from Figure 2, that on the sequential addition of iron-(II) to the solution of [Fe(Phen)₃]³⁺, the intensities of absorption bands corresponding to $[Fe(Phen)_{3}]^{2+}$ (λ 510 nm) and $[Fe(Phen)_{3}]^{3+}$ (λ 600 nm) increased and decreased respecttively. The intensity of the absorption band at 510 nm corresponding to [Fe(Phen)₂]²⁺ displayed a decreasing trend in intensity (dotted line in Figure 2) due to dilution effects, when the amount of iron (II) became excess to the necessary stoichiometric requirement of the redox reaction (equation3). Thus the spectrophotometric response clearly confirms the electron transfer reaction without any ligand exchange between iron(II) and [Fe(Phen)₃]³⁺ complex authenticating the iron reduces iron concept.

The plausible explanation for this

interesting observation, lies in the ligand modulation of the iron(III)-iron(II) redox potential [18]. The electrochemical behavior of transition metal ions gets modified by the complexation, which leads to a different reduction potential in the complexed state compared to the free/uncomplexed state. The complexation effect on redox potential, can be explained in terms of differential stabilization of transition metal oxidation states in the redox couple and is often expressed as equation 4 [18].

$$E_{\text{complex}} = E_{\text{aqua}} - \frac{RT}{nF} \ln \frac{\beta^{\text{III}}}{\beta^{\text{II}}}$$
(4)

Where $E_{complex}$ is the redox potential of iron(III)-iron(II) redox couple in complexed form and β^{III} and β^{II} are the formation constants of iron(III) and iron(II) respectively with the given ligand. According to equation 4, the ratio of formation constants β^{III}/β^{II} modulates the redox potential of a iron(III)-iron(II)redox couple in complexes. Therefore ligands which stabilize iron(III) more than iron(II) give β^{III}/β^{II} ratio > 1 and hence $E_{complex} < E_{aqua}$, while as ligands which stabilize iron(II) more than iron(III) give β^{III}/β^{II} ratio < 1 and consequently $E_{complex} >$ E_{aqua}. 1,10-Phenanthroline (Phen) is a strong pi acceptor type bidentate ligand with two nitrogen donor sites in the aromatic phenanthrene structure. The formation constant values (log β^{II} = 21.3) and (log β^{III} =14.1) of Phen complexes with two iron oxidation states 2+ and 3+ respectively [19], Phen forms more stable complex with iron(II) than iron(III). Consequently, the Phen complexed potential of iron(III)-iron(II) redox couple (1.14 V) is higher than its free state redox potential [20]. An equilibrium constant value of $\log K = 6.27$ was calculated for the redox reaction involving [Fe(phen)₂]³⁺ reduction by $[Fe(OH_2)_6]^{2+}$ (equation 3) using the (equilibrium constant calculation)

equation 2. The calculated log K = 6.27, corresponds to a free energy change of 3.6 KJ mole⁻¹ and cell potential of 0.698 V. Thus from thermodynamic perspective, the redox reaction involving reduction of $[Fe(phen)_{2}]^{3+}$ by $[Fe(OH_{2})_{2}]^{2+}$ is a spontaneous reaction. The significant cell potential value (0.698V) of the iron reducing iron redox reaction depicted in equation 3, predicts a sharp endpoint in the potentiometric titration of this redox reaction [21]. The potentiometric response of the reduction of $[Fe(phen)_3]^{3+}$ by $[Fe(OH_2)_6]^{2+}$ (equation 3) is shown in Figure 3. From Figure 3, it is clear that a noticeable potential change occurs at the equivalence point of the redox reaction. On reversing the mode of titration, an exactly reverse trend in variation of potential was observed (Figure 3). This indicates that the redox reaction can be monitored potentiometerically by either adding $[Fe(OH_2)_6]^{2+}$ as titrant to $[Fe(phen)_3]^{3+}$ (red curve in Figure 3) or by adding $[Fe(phen)_{3}]^{3+}$ as titrant to $[Fe(OH_{2})_{4}]^{2+}$ (blue curve in Figure 3) with the similar analytical estimations under both the cases [22].



Figure 3. Potentiometric response of the redox reaction under two types of titration modes.

The potentiometric method was optimized for titration parameters like temperature, pH and concentration range. The redox reaction was found to be sufficiently fast around 20°C to allow quick equilibration on platinum electrode [23] for a smooth potentiometric titration data. The pH was found to influence titration in many ways: speciation in case of different iron complexes, a very low pH (<1) unfavor's stability of iron(III) phen complex. At higher pH (>5), the free/uncomplexed iron(III) formed in the reaction begin to precipitate giving a suspension. Thus a pH range of 3-5, was found to compromise different pH based factors for an optimum potentiometric titration. The optimum concentration range of the redox reaction was determined by the concentration profile depicted in Figure 4.



Figure 4. Concentration profile of $[Fe(Phen)_3]^{3+}$ reduction by $[Fe(OH_2)_6]^{2+}$ (Normalized EMF values for clear potentiometric response).

Motivated by the ligand modulated electron transfer between $[Fe(phen)_3]^{3+}$ and $[Fe(OH_2)_6]^{2+}$, we attempted to investigate the influence of some selected ligands having a range of binding propensities towards iron(III) metal ion, in order to build up and systematize, the complexation effect on the

redox potential of iron redox couple. [24]. Thus five selected ligands have iron (III) metal ion binding constants in the increasing order: aqua < Diphosphate (DP) < Nitrilotriacetic acid (NTA) < Diethylene triaminepentaaceticacid (DTPA) < Ethylene diaminetetraaceticacid (EDTA). The potentiometric response of selected ligands on the reduction of [Fe(phen),]³⁺ by ${[Fe(L)_{x}]^{(2-nx)+}}$; where L is the selected ligand with n units of negative charge per ligand molecule and x is the number of ligand molecules attached to iron(II) is as shown in Figure 5. The reported work can also be proposed as a potentiometric titration method for estimation of iron (II) or iron (III) metal ions in solution. The analytical figures of merit for the proposed method include: a fairly low detection limit of 10.0 mgL⁻¹ for iron(II) and 20.0 mg L⁻¹ for iron(III). A wide dynamic range of 0.1-100 mM for iron(II) and 0.5-50 mM for iron(III).

From Figure 5, it is seen that the different EMF changes occur at the equivalence point of titration plots in case of selected ligands. This indicates the dissimilar strength of iron(II) complexes with selected ligands $\{[Fe(L)_x]^{(2-nx)+}\}$ as titrants towards the same analyte $[Fe(phen)_3]^{3+}$. The relative trend in which selected ligands bring the potential change EDTA > DTPA > NTA > DP > H₂O at the equivalence point corroborates well with their efficacy towards iron (III) stabilization [24].

The distinctive influence of selected ligands on potentiometric behavior of the $[Fe(phen)_3]^{3+}$ reduction by $\{[Fe(L)_x]^{(2-nx)+}\}$ titrants can be explained by coordination coupled electron transfer [25] Figure 6.



Figure 5. Comparative ligand effect on $[Fe(Phen)_3]^{3+}$ reduction by selected iron(II) complexes $\{[Fe(L)_x]^{(2-nx)+}\}$ (Normalized EMF values).



Figure 6. Coordination coupled electron transfer between $[Fe(phen)_3]^{3+}$ and $[Fe(OH_2)_6]^{2+}$ in presence of selected iron(III) stabilizing ligands.

From Figure 6, it is clear that, in the presence of iron(III) stabilizing ligand (L), the free energy of complexation step G_3 adds to the free energy of electron transfer in step G_2 giving an overall free energy change of reaction as $(G_3 + G_2) - G_1$, compared to $(G_2 - G_1)$ in the absence of any ligand. The magnitude of G_3 component of overall free energy change of the reaction is in direct proportion to the stability of iron(III) complex with the ligand L (β^{III} value). Higher the formation constant of iron(III) complex with ligand (L), more is its contribution towards G_3 and higher is the

free energy change of the reaction and consequently, larger is the EMF change at equivalence point in the titration plot. The correlation of the iron(III) and iron(II) ligand stabilization {log β^{III}/β^{II} } with corresponding complexed state reduction potential of iron(III)-iron(II) redox couple is depicted in Table 1. It is evident from the data of table 1 that ligands which stabilize iron (III) more than iron(II) {log β^{III} >log β^{II} }, lower the reduction potential of iron(III)-iron(II) redox couple. The data entries in Table 1, are in conformity with the observed

potentiometric titration plots of the corresponding iron complexes in Figure 5. An important observation regarding change in reduction potential of iron(III)iron(II) redox couple, on account of different degree's of complex formation with the same ligand under differing pH conditions was observed in case of 4, 5-dihydroxy-1, 3-benzene di sulfonic acid disodium salt (Tiron) ligand. The redox potentials of iron(III)-iron(II) redox couple in presence of EDTA and Tiron are + 0.08 V and -0.509 V vs NHE, respectively [31].

Table 1. Ligand stabilization of iron(III) vs iron(II) correlation with reduction potential.

Ligand	Donor	Log	Log	Log	Expt	Ref
	Site	(β^{III})	(β^{II})	$\{\beta^{III}/$	$E^{\overline{o}}$	
		Fe ³⁺	Fe ²⁺	β^{II}	(V)	
1,10-phenanthroline	N, N	14.1	21.0	- 7.0	1.14	[2]
Aqua	Ο	-	-	-	0.771	[1]
Ethylenediaminetetra acetic acid (EDTA)	N, O ⁻	25.1	14.3	10.8	0.08	[26]
Diethylenetriaminepenta acetic Acid (DPTA)	N, O ⁻	28.0	16.5	11.5	0.054	[27]
4,5-dihydroxy-1,3-benzene disulfonic acid disodium salt (Tiron)	O ⁻ ,O ⁻	-	-	-	+0.352* -0.509**	[28]
Nitrilotri-acetic acid (NTA)	N, O ⁻ ,O ⁻	15.9	8.2	7.7	+0.318*	[29]
Diphosphate (DP)	0-,0-	12.4	6.4	6.0	-1.04	[30]

* pH=4 ** pH = 6-8

Hence in accordance with the thermodynamic model described in Figure 6, iron(II) in the form of Tiron complex should be a more stronger reductant than [Fe^{II}EDTA]² for the iron reducing iron redox

reaction and therefore, a larger potential change at equivalence point is expected in the titration plot with Tiron than EDTA. Contrary to this, the potentiometric titration plot of $[Fe(phen)_{,}]^{3+}$ with iron(II) in the

presence of Tiron ligand displayed a smaller potential change as compared to titration plot with EDTA ligand at pH 4.0. Considering the origin of this discrepancy to be in pH effect on redox potentials [32], we attempted to modulate the pH of the titration solution. On raising the pH to 6.5 with dilute ammonia slowly, the anticipated larger potential change in case of Tiron ligand compared to EDTA was observed Figure 7.



Figure 7. Comparative titration plots of EDTA and Tiron ligand effect on $[Fe(phen)_3]^{3+}$ redox reaction at pH 4.0 and 6.5.

The probable explanation for the observed pH influence in case of Tiron ligand can be correlated with iron-(II) Tiron complex speciation. Strassman et al, have predicted that complexes of different compositions are predominant in the complexation reaction of iron(II) with Tiron under different pH conditions[31]. Furthermore, depending upon number of Tiron chelate rings in the iron-(II) coordination sphere under dissimilar pH conditions, different stability constants and corresponding reduction potentials of resulting iron-Tiron complexes were also observed [33]. Therefore, it can be envisaged that pH 4.0 was not optimal for the formation of tris complex of Tiron ligand with iron-(II) due to which the reduction potential of resulting iron(II)-Tiron (bis chelate)

complex at pH 4.0 could not be lower than the corresponding iron(II)-EDTA complex at the same pH. However the formal reduction potential of iron-(II) Tiron (tris chelate) complex formed around pH 6.5 is quite lower than the corresponding iron(II)-EDTA. Because of this, a larger potential jump in case of iron(II) Tiron titration plot at pH 6.5 was observed Figure 7. The pH of the titration solution could not be raised beyond 6.5 as it leads to the undesired precipitation reactions. To verify our assertion of iron(III)-Tiron complex speciation, we did a parallel spectrophotometric study of iron(III) -Tiron complexation reaction under acidic (pH 4.0) and alkaline (pH 8.5) conditions. The spectrophotometric titration of solutions with a fixed analytical concentration of iron(III) and different molar ratios of iron(III) and Tiron ligand at pH 4.0 and 8.5 are shown in Figures 8 and 9 which verify the involvement of 1:1 and 1:3 molar ratios of iron-(III) and Tiron at pH 4.0 and pH 8.5, respectively. This was in accordance with other literature reports [6, 34, 35]



Figure 8. Spectra of different Fe(III)- Tiron molar ratio solutions at pH 4.0. Insert: maximum absorbance as a function of mole ratio for each curve.



Figure 9. Spectra of different Fe(III)-Tiron molar ratio solutions at pH 8.5. Insert: maximum absorbance as a function of mole ratio for each curve.

Thus spectrophotometric investigation of pH influence on iron(III) Tiron speciation analysis reveals the formation of [Fe(Tiron) $(OH_2)_4$]⁻ and [Fe(Tiron)_3]⁹⁻ at pH 4.0 and 8.5, respectively. The increase of chelation at higher pH brings enhanced stabilization of iron-(III) in tris complex with concomitant decrease in the redox potential, thus favoring effective electron transfer.

CONCLUSION

The work highlights complexation effect on iron(III)-iron(II) redox couple and its utilization for an inquisitive electron transfer reaction between iron{II and III} oxidation states. The dual techniques of potentiometry and spectrophotometry have been used to investigate the reduction of iron(III)-phenanthroline complex ${[Fe(phen)_{3}]^{3+}}$ by a series of iron(II) complexes with water, EDTA, DPTA, NTA, Tiron and diphosphate ligand fields. The efficiency of iron(II) complexes involving these ligands towards reduction of {[Fe(phen)₃]³⁺} was envisaged potentiometerically, and corroborated with their ability to decrease the iron(III)-iron(II)

reduction potential. A thermodynamic model correlating free energy of electron transfer reaction/cell potential with relative ligand strength was also predicted. The pH effect on redox potential was studied through potentiometric titration of ${[Fe(phen)_3]^{3+}}$ by iron(II) complexes with EDTA and Tiron ligands at pH 4.0 and 6.5. The observed pH effect, was corroborated with predominance of different composition of iron(II) Tiron complexes under different pH conditions. The degree of ligand chelation vis-a-vis complex stability and resultant redox potential was explored through spectrophotometric speciation analysis of iron(III) Tiron complexation reaction under different pH conditions.

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