

CHEMISTRY AND ELECTROCHEMISTRY OF IRON COMPLEXES

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[Received: 14 October 1998 Accepted: 7 May 2000]

A brief review of chemistry and electrochemistry of ferro/ferricyanide system Fe(II)/Fe(III) system in sulphuric acid, tartrate, oxalate, citrate and EDTA is presented. Factors influencing the rate of ferro/ferricyanide and Fe(II)/Fe(III) redox processes are discussed. The stability of Fe(II)/Fe(III) complexes in various medium is compared and experimental support is provided.

Keywords: Iron complexes, ferro/ferricyanide, ferrous/ferric electrode processes, complex stability.

INTRODUCTION

In recent years, the coordination theory has found increasing application in many types of chemical work. Its usefulness in the selection of organic precipitants for metallic ions and in explaining biological phenomena is well known. It is also the basis for our understanding of the role of metal ions in leather tanning, in the dyeing of cloth and in regulating plant growth. Coordinating agents are used in winning metals from their ores, in electroplating, in catalyzing reactions and in obviating the effects of undesirable catalysis, in precipitation of metallic ions and in preventing their precipitation and in many other ways [1]. The tendency to form complexes is generally greater with ferric than with ferrous iron. Fe(II) forms stable complexes with a coordination number of six only with cyanide ion to form ferrocyanide anion.

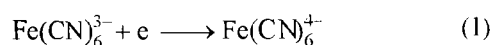
For complexes of coordination number six, the electron structures are divided into 'inner orbital' and 'outer orbital' types. In the former, relatively stable *d* orbitals of lower principal quantum numbers are combined with S_p orbitals of higher quantum numbers. In the latter type all of the orbitals have the same principal number and therefore the *d* orbitals have a lower stability. There is a discontinuity in substitution rates when the unshared electron occupies the last available inner *d* orbital. Inner and outer orbital complexes are subdivided into labile and inert groups [2]. A brief account of the chemistry and electrochemistry of

ferro/ferricyanide system, Fe(II)/Fe(III) system in sulphuric acid, tartrate, oxalate, citrate and EDTA is dealt in this review.

Cyanide complexes of iron

A substantial account of the chemistry of complex cyanides of the transition metals has been given in [3]. The range of oxidation states at present known to be exhibited in cyanocomplexes is reported to be greatest for iron. There are nitroso cyano complexes in which the metal has formal oxidation states of -2 and -1 and carbonyl cyanocomplexes of iron (0).

Fe(II) forms cationic complexes with a coordination number of 6. The metal cyanide bond is strongly covalent and favours the Fe(II) state as compared to Fe(III) state. The electrode potential indicates that the ferricyanide is more stable (i.e.) poor oxidizing agent than the corresponding hydrated ferric ion [2]. The standard reduction potential, E^0 is 0.356 V vs SCE [4-5] and 0.361 vs Ag/AgCl [6] for the following reaction:



Factors influencing the rate of ferro/ferricyanide electrode process

The kinetics of ferro/ferricyanide system is frequently used to check up the validity of the modern theories of electrode kinetics [7-11]. It is due to the fact that both oxidized and

reduced forms of the complex are quite stable and their structure is well known [12-16]. Further, the changes consequential to electrode reaction are believed to occur beyond the first coordination sphere [17-18].

The kinetics of ferro/ferricyanide reaction has been studied on oxide free platinum [7,19-21] and gold [8] electrode surfaces. This system has been invariably used as a probe by research workers on different forms of carbon electrode [22] including glassy carbon (GC) electrodes [23- 27]. The factors which influence the rate of ferro/ferricyanide electrode process are briefly presented.

Effect of alkali metal cation

Significant changes in the rate constant of this system are reported in solutions containing different concentrations of background electrolyte [28-33]. The rate of ferro/ferricyanide redox system shows a first order dependence on the concentration of the cationic component of the alkali metal cations and their catalytic influence on the electrode process increases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ as described in [31]. Thereby an active participation of the alkali metal cation in the ferro/ferricyanide redox reaction is suggested which gives rise to a first order dependence of the rate on the concentration of the cation M^+ .

Hydrogen ion concentration

The rate of ferro/ferricyanide reactions does not show dependence on $p\text{H}$ at metal electrodes such as Au and Pt [34]. In the case of GC electrodes it has been established [34] that the rate of some outer-sphere processes show a clear reproducible dependence on the solution $p\text{H}$. This is attributed to the property of the electrode itself and not to the electroactive species. A chemical origin for the dependence of the rate of reaction on the $p\text{H}$ of the medium has been suggested. The dependence is probably caused by the protonation of chemical functional groups at the electrode surface.

Electrode material

Standard electrochemical rate constants ought not to depend appreciably on the electrode material (because the nature of the electrode material only affects the rate constant via a second order term which contains the work function of the relevant metal) as reported in [34]. However, in practice the measured electrochemical rate constants actually depend a great deal on the nature of the electrode material as also on the pre-treatment given to the electrode. This may be

accounted for by different double layer structures at different electrode materials as well as different electrical double layer effects due to variation in surface characteristics of differently pre-treated electrode materials.

Though numerous studies on ferro/ferricyanide were carried out, the nature of its electrode reaction is not well understood and appears to be complex [36]. A simple electron transfer reaction is widely suggested [14-19]. The formation of a trinuclear complex with the cation of the background electrolyte in between and its adsorption on the electrode /surface has been suggested [30-37]. Partial charge transfer model is also applied to explain the nature of this reaction [38].

Effect of electrode pre-treatment

As discussed already the quantitative results obtained for certain redox couples depend strongly on the method of surface preparation immediately before the use as well as on the previous history of the electrode. Various pre-treatment procedures have been evolved and reported from time to time to improve the electrode activity depending on the redox system taken for investigation.

As far as the ferro/ferricyanide redox reaction is concerned, the contribution [24,39] is very significant. These authors were able to get reversible cyclic voltammograms for the reduction of ferricyanide in 1 M KCl at scan rates upto 1 Vs^{-1} . The GC electrode surface was pre-treated by them by an elaborate procedure [23] of manual abrasion using a series of silicon carbide papers of decreasing roughness (down to $30 \mu\text{m}$) and cloth polishing, care being taken not to damage the teflon surrounding the glassy carbon and to ensure coplanarity. The integrity of the carbon- teflon seal was verified by inspection with a low power reflectance microscope.

It is a fact that different electrochemical procedures are required to activate GC towards different redox couples in aqueous media [26,40]. However, many redox reactions in organic solvents are found to be relatively insensitive to changes in the nature of the electrode surface obtained by different pre-treatment procedures [41-42].

The enhanced activity, based on heat treatment temperature (HTT) of GC electrodes subjected to preanodization at +1.5 V, towards ferro/ferricyanide and several other electrode reactions has been observed [43]. On the contrary, preanodization followed by precathodization resulted in

half-wave potential less anodic than that found on freshly polished electrode [26].

Fe(II)/Fe(III) in simple and other complex media

The standard electrode potential of the Fe(II)/Fe(III) couple is +0.5 V vs SCE which is somewhat more positive than the anodic dissolution potential of mercury. The diffusion current resulting from the reduction of uncomplexed ferrous ion starts at the potential of the anodic mercury dissolution [44]. However, in the presence of complexing agents it has been possible to shift half wave reduction potential to more cathodic values, for the purpose of analytical estimations.

Factors influencing the rate of Fe(II)/Fe(III) electrode processes — Influence of substrate

Electrode reactions can be divided into two general classes: (1) the reactants and/or the products experiencing strong interaction with the electrode forming chemibonds between the electrode and a reactant or a product species; (2) the reactant and/or the products do not form any chemibond with the electrode.

The reactions of the first type are important for the study of electrocatalysis and the basis of the models for the electrocatalytic type of reaction arises from the theories of charge transfer pioneered as reported in [45]. In the mechanism of homogeneous redox kinetics, a basic doubt exists concerning whether the mechanism involves an atom transfer reaction [46] or an electron transfer reaction in solution [47]. The atom transfer theory [46] does not take into account the double layer structure.

The rate of a redox reaction were it to occur by an atom-transfer mechanism, would depend on the substrate, as reported in [48], for the influence of a substrate on the hydrogen evolution reaction. On the contrary if the mechanism is electron transfer no such dependence should exist.

Various phenomenological evidences eg. the solvent isotope effect in homogeneous redox reactions [46,49-50] and the suggestion of a dependence of i_0 for electronic redox reaction upon the electrode material, which could be inferred by comparing the rates observed for the reduction of Fe^{3+} to Fe^{2+} on Hg, Au, Ag [17], Pt [17,51] and on oxides [52] leave doubt as to non- involvement of the reacting species with the electrode material. There is some evidence in the literature that the state of the surface of platinum e.g. obtained by activation procedures affects the exchange current density of the redox reaction [19,53]. The rate

measurements alone do not offer in all systems sufficient information to test the theories as described in [54]. These authors [54] have recorded the heat of activation and the rate at the reversible potential of the $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ reaction as a function of change of substrates for a number of non-oxide forming noble metals and alloys and found that the rate of Fe(II)/Fe(III) reaction depended on the noble metal employed. They have found that in 1 M H_2SO_4 the rate of gold is only one-tenth of that on platinum. The rate of a redox reaction is likely to vary with the nature of the electrode material, but only as a consequence of concomitant changes in the double layer as reported in [55-56]. The structure of the double layer is controlled by the rational potential of the electrode, which in turn depends on the work function of the metal. When the electrode material is changed, the rational potential, at the same applied electrode potential is altered and consequently the potential different across the diffuse layer is also different. Others [8] have got almost same values of rate constant on gold and platinum and say that it is to be expected in concentrated solutions and electrode potentials more than 0.35 V from the zero charge potential, the potential difference across the double layer would be essentially independent of electrode potential and hence work function.

Effect of supporting electrolyte

It has been reported that the standard rate constant of the ferrous- ferric reaction depends on the nature and concentration of the background electrolyte employed. Thus k_s decreased with increase in the sulphate ion concentration and pH as described in [53]. He attributed this to an increase in the amount of Fe^{3+} complexed with SO_4^{2-} , each successive complex reducing at a lower rate. Similar results were reported [57] and the following explanations are given by them.

- α The electrode surface may have different activities in different electrolytes
- α The activities of the ions, rather than their concentrations should be used in calculating the rate constants and change in the ionic strength of the supporting electrolyte is likely to alter the activity coefficients.

It is generally known [56] that the Fe(II)/Fe(III) system exhibits waves with higher standard rate constants in hydrochloric acid than in sulphuric acid.

Acids other than perchloric and sulphuric have not been extensively studied as media for the reduction of Fe(III) at

other electrodes. Fe(III) reduction is quite fast in all media and is reversible in HClO_4 .

The effect of temperature

The effect of temperature on the reduction rate of Fe(III) on GC electrode was studied in different acids [55]. In all media, both $E_{1/2}$ and current increased with increasing temperature as predicted by the Arrhenius equation and the temperature coefficients of the diffusion coefficients. The K_s values increased in all the acids. In HNO_3 there was increase upto 313 K and at higher temperatures the value decreased. This is suggested to be due to a deleterious effect of the hot acid on the electrode surface. With increasing temperature, the wave quality in H_2SO_4 deteriorated. The current stability also decreased considerably and until repolished the electrode surface exhibited irreversible waves for the reversible system (eg. Fe(III)/Fe(II) in HClO_4).

Effect of electrode pre-treatment

The nature of the electrode material, the double layer structure and the effect of supporting electrolyte etc. have been emphasized by several authors as important factors influencing the rate of electrode reaction taking Fe(II)/Fe(III) redox reaction as a probe to test the validity of these propositions. The pre-treatment of the electrode has not been given any special emphasis in earlier studies as affecting the rate of electrode reaction. In studies with carbon electrodes the effect of chemical and electrochemical pre-treatments on rate constants of several electrode reactions has been reported by several authors [58-59]. Systematic investigations [43] have been carried out to decide the potential at which the surface alternations, causing the acceleration of the electrode kinetics, take place. It has been found that activation of GC electrode occurs at fairly positive potentials. However, they recommend a cycling between a positive and negative potential for conditioning the surface 'oxide' which occurs both through its successive reduction and renewal.

A dramatic change in rate constant for Fe(III)/Fe(II) in 1 M H_2SO_4 , brought about by changing the pre-treatment from polishing with 0.3 μm alumina to polishing followed by dipping in chromic acid at room temperature and subsequent thorough washing with distilled water has been reported [60]. Not only did a significant increase (about 100 fold) in rate constant results from the chromic acid treatment but the reproducibility of the waves improved markedly. These authors attribute this to increase in double layer capacity arising from a change in the nature of the surface, as a result

of chromic acid treatment. However, on wax impregnated graphite electrodes the rate constant for Fe(II)/Fe(III) system increased only slightly and with carbon paste electrodes the disintegration of the paste occurred with chromic acid treatment.

Tartrate complexes

Due to the involvement of OH group in the chelating process tartrate complexes are generally more stable than the succinate complexes. The considerably more positive half-wave potentials in oxalate medium when compared with citrate and tartrate media show that the oxalate complex of ferrous ion is stronger than the citrate and tartrate complexes towards oxidation [44].

The electrochemical studies on Fe(II)/Fe(III) in tartrate medium at a carbon electrode have not been reported in literature [61] although the system has been studied on a mercury electrode polarographically. The polarographic studies show that the system behaves reversibly in solutions of pH 7 and the half-wave potentials of anodic and cathodic waves are identical in alkaline solutions, however, the anodic wave is observed at a much more positive potential than the cathodic wave.

Oxalate complexes

As compared with tartrate the half-wave reduction potentials in oxalate medium are more positive. Therefore, oxalate complex of ferrous ion is stronger and that of ferric ion is weaker than the citrate and tartrate complexes. This is connected with the fact that complexation with tartrate and citrate directly involves replacement by ferric or ferrous ion of the hydrogens of the hydroxyl groups which are lacking in oxalate ion.

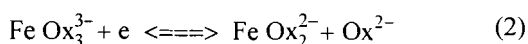
Consideration of the half-wave potential of the tris (oxalate) ferrate (III) ion as a function of oxalate ion concentration revealed that the formula of the iron (III) complex produced in a 0.0001 to 0.0002 molar solution of iron (III) ion in the presence of 0.15 molar oxalate ion concentration is $[\text{Fe}(\text{C}_2\text{O}_4)_2]^-$. But when the concentration of oxalate ion is in excess the species is the complex $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-}$ [62].

Ferric oxalate complexes are numerous and stable. The tendency to form them is so great that calcium oxalate will dissolve in ferric chloride solution. The complex oxalate salts belong to two series, the dioxalato, which are greenish yellow and the trioxalato which are emerald green and much more stable. Ferrous oxalate is difficult to prepare owing to the tendency of the anion to reduce the cation.

Fe(II)/Fe(III) oxalate system has been extensively used as a probe to assess different techniques in polarography, since the system is perfectly reversible on DME. This reaction scheme has been used as a probe in staircase voltammetry [63] and in second harmonic a.c. polarography [64].

Polarographic waves of Fe(II) and Fe(III), oxalate complexes are reversible in neutral or acidic solutions and disappear in alkaline solutions due to Fe(OH)₃ precipitation [62].

The overall electrochemical reaction at the DME is given to be [13] $\text{Fe Ox}_3^{3-} + e \rightarrow \text{Fe Ox}_3^{4-}$ provided that $[\text{Ox}^{2-}]$ 0.2 M. In contrast the reaction is essentially,



when $10^{-2} < [\text{Ox}^{2-}] < 0.2 \text{ M}$ also the pH of the solution will indeed influence the polarographic behaviour of this system since H₂C₂O₄ is a weak acid.

In the evaluation of kinetic parameters for this system on DME faradaic rectification polarography (FRP) galvanostatic double pulse (GDP) method and a.c. polarography have been extensively used [65-69]. On DME the electron transfer rate for Fe(II)/Fe(III) oxalate system is quite fast, of the order of 1 cm/sec. Both FRP and GDP are suitable for the measurement of electron transfer rates faster than 1 cm/sec. In GDP method it is necessary that known amount of oxidant and the reductant must be contained in the electrolyte solution. This is not the case in the FRP method.

Citrate complexes

It has been established that the citrate ion can lose its hydroxyl hydrogen as well as the carboxyl hydrogen and can coordinate with a bivalent metal such as copper or iron even in acid solution. This suggests the possibility of formation of both six and seven membered rings in the citrate complexes, the six membered ring forming

TABLE I: Stability of iron complexes [2]

Ligand	Species	Stability or equilibrium constant (log ₁₀ values)
Cyanide	Iron (III)	31.0 (stepwise addition of ligand)
EDTA	Iron (III)	25.1 (Gross addition of ligand)
	Iron (III)	14.3 -do-
Citrate	Iron (III)	25.0 -do-
Oxalate	Iron (III)	21.6 -do-
Tartrate	Iron (III)	18.1 -do-

preferentially [62,70]. Due to the involvement of OH group in the chelation process, the citrate complexes are more stable than their oxalate complexes.

In solutions containing 0.5 M sodium citrate and 0.005 percent gelatin the half wave potential of the ferric to ferrous wave is a linear function of pH between 4 and 12 and its value vs SCE at 25° follows the equation

$$E_{1/2} = 0.426 - 0.108 \text{ pH} \quad (3)$$

EDTA complexes

Trivalent iron forms one of the most stable complexes with EDTA and other chelates while the divalent iron complexes are considerably less stable [70]. The EDTA complex of Fe(III) is too strong to react with the usual reagents. Trivalent iron is thus not precipitated by ammonia in the presence of EDTA and did not separate out as ferric hydroxide with 0.2 M NaOH.

Diffusion current is observed in polarography only when excess of ferric iron is present in solutions containing trisodium salt of EDTA and 0.4 M potassium nitrate as supporting electrolyte and 0.01 percent gelatin. Another wave at 0.0 V vs SCE results from the reduction of the complexed iron. Observation of a separate wave with lower diffusion current for the complexed iron implies that the rate of dissociation of the complex is relatively small [42]. The stability constants of some of the Fe(III) complexes are given in Table I.

Stability of Fe(II)/Fe(III) complexes in various media

Even though no systematic approach on the study of stability of various Fe(II)/Fe(III) complexes has been attempted, from the cyclic voltammetric peak shift values in different media [71] it has been possible to comment on the relative complexing capacity of various complexing agents reported

TABLE II: Peak potential values (vs NCE) for Fe(II) oxidation on Glassy Carbon electrode in different media. Potential scan rate: 0.05 Vs⁻¹

Fe(II) in	E _{p,a} / V	E _{p,c} / V
0.5 M H ₂ SO ₄	0.48	0.28
0.5 M H ₂ SO ₄ + 0.2 M sodium tartrate	0.42	0.27
0.5 M H ₂ SO ₄ + 0.2 M sodium oxalate	0.28	0.05
0.5 M H ₂ SO ₄ + 0.2 M sodium citrate	0.04	-0.20
0.2 M NaOH + 0.2 M sodium tartrate	0.13	-0.45
0.2 M NaOH + 0.2 M EDTA	0.08	-0.26

in the present work. The peak potential values ($E_{p,a}$ and $E_{p,c}$) obtained for the Fe(II)/Fe(III) redox reaction in pure sulphuric acid media as well as various other complexing media containing sulphuric acid at a scan rate of 0.05 Vs^{-1} are given in Table II.

As far as the cathodic shift in reduction potential is concerned more shift is observed in citrate medium than in oxalate and tartrate medium. Therefore, the following order of complexing capacity is assigned for Fe(II) in these media.



Therefore, it is clear that citrate has got tendency to form stable complex with Fe(III) which becomes difficult to reduce as shown by the more cathodic reduction potential compared to oxalate and tartrate medium. The stability constant values given in Table I support this fact.

Among tartrate and EDTA complexes of Fe(III) iron in alkaline medium the reduction peak for Fe(III) tartrate complex occurs at a more negative potential compared to that in EDTA medium. Therefore, tartrate complex of Fe(III) in alkaline medium is stabler compared to EDTA complex.

CONCLUSION

The urgency for reviewing the topic, "Chemistry and electrochemistry of iron complexes" is felt very significant in the present day context. Taking into account the inevitable role these complexes play in the modification of electrode surfaces and preparation of tailor-made electrodes for specified applications. The author of the present review has contributed significantly to the development of modification of electrode surfaces with metal hexacyanoferrates, their analogues and derivatives. This review will provide prior knowledge to the readers in coordination complexes with implications on electrochemistry and will be helpful for the pursuit of research on modified electrodes.

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