Fe(III)/Fe(II) — LIGAND SYSTEMS FOR USE AS NEGATIVE HALF-CELLS IN REDOX-FLOW CELLS

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Summary

Cyclic voltammetric and controlled-potential electrolysis studies of Fe(III)/Fe(II) complexes with diethylenetriaminepentaacetic, nitrilotriacetic and ethylenediaminetetraacetic acids show that the formal potential of the iron redox couple shifts markedly to negative values. The stability and heterogeneous rate constants appear to favour the application of such systems as the negative half-cell on an all-iron flow cell.

Introduction

For the past few years, considerable effort has been devoted to the search for stable redox systems for use in flow cells [1]. A typical flow cell employs two, fully soluble, redox couples; the storage capacity is determined by the solution concentration and the cell size.

Various redox couples (*e.g.*, Fe(III)/Fe(II) [2, 3], Cr(III)/Cr(II) [2 - 4], Ti(IV)/Ti(III) [5]) have been proposed for use as positive and negative half-cells in redox batteries. These couples, suffer, however, from serious efficiency losses. The latter can be minimized by employing the same element, in different oxidation states, in both half-cells [4, 6, 7]. This approach requires the use of different complexing agents to provide a workable difference in redox potential. Bard and co-workers [8, 9] have examined such a possibility in a study of Fe(III)/Fe(II) and Co(III)/Co(II) couples complexed with *o*-phenanthroline and bipyridine ligands. In the case of the Fe(III)/Fe(II) system, for example, it was found that the redox potential was shifted to more positive values on complexation and thus provided a positive half-cell.

The work reported here examines further the Fe(III)/Fe(II) couple and aims to identify potential ligands that are capable of shifting the redox potential to more negative values, thereby making a negative half-cell possible. An all-iron redox cell may then become a distinct possibility. Since it

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is qualitatively known that chelating agents such as diethylenetriaminepenta-acetic acid nitrilotriacetic acid and ethylenediaminetetraacetic acid cause negative shifts in the potential of the Fe(III)/Fe(II) couple, these ligands have been examined in more detail. In particular, an attempt has been made to optimize the conditions necessary for their use in an all-iron, redox flow-cell.

Experimental

Diethylenetriaminepentaacetic acid (DTPA) obtained from Fluka (Switzerland), nitrilotriacetic acid (NTA) from BDH (England), ethylene-diaminetetraacetic acid (EDTA) from Glaxo Laboratories (Bombay, India), and ferrous ammonium sulphate from Sarabhai Merck Ltd. (India) were used without further purification. Electrochemical investigations were carried out with a Model 173 potentiostat in combination with a Model 179 digital coulometer and a Model 175 universal programmer (all from PAR, Princeton, NJ). Current–voltage and current–time curves were recorded on a Model 2100 A3 recorder (Anika, India). For coulometric studies, a Model 377A coulometric cell system (PAR, Princeton, NJ) was employed.

The supporting electrolyte consisted of an aqueous sulphuric acid solution containing potassium sulphate. The sulphuric acid was prepared by suitable dilution of concentrated stock reagent with double-distilled water. All solutions were purged with nitrogen prior to experiment. The complexes were prepared directly by mixing given concentrations of ferrous ammonium sulphate and the ligands in a ligand/Fe(II) mole ratio >5.

Platinum foil was used for both the working and counter electrodes. Controlled-potential electrolysis studies were conducted on a mercury-pool electrode. All potentials are reported with regard to a saturated calomel reference electrode (SCE), and all measurements were carried out at a constant temperature of 25 ± 2 °C.

Results and discussion

Typical cyclic voltammograms for the Fe(III)/Fe(II)–DTPA system at pH 6.5 are shown in Fig. 1. It can be seen that the potential shifts to lower values relative to an uncomplexed Fe(III)/Fe(II) system. The system is reversible, as indicated by $i_{p,a}/i_{p,c} = 1.0$, where $i_{p,a}$ and $i_{p,c}$ are the anodic and cathodic peak currents, respectively. Similar cyclic voltammograms were obtained with NTA and EDTA. The formal potentials (E') with the three different ligands under study are given in Table 1.

The effect of pH on the cyclic voltammogram (CV) is demonstrated in Fig. 2. With increase in pH over the range 1 - 6, the general appearance of the CV curve improves and indicates a greater reversibility, as well as stabilization, of Fe(II) complexed species; also, the formal potentials shift to more
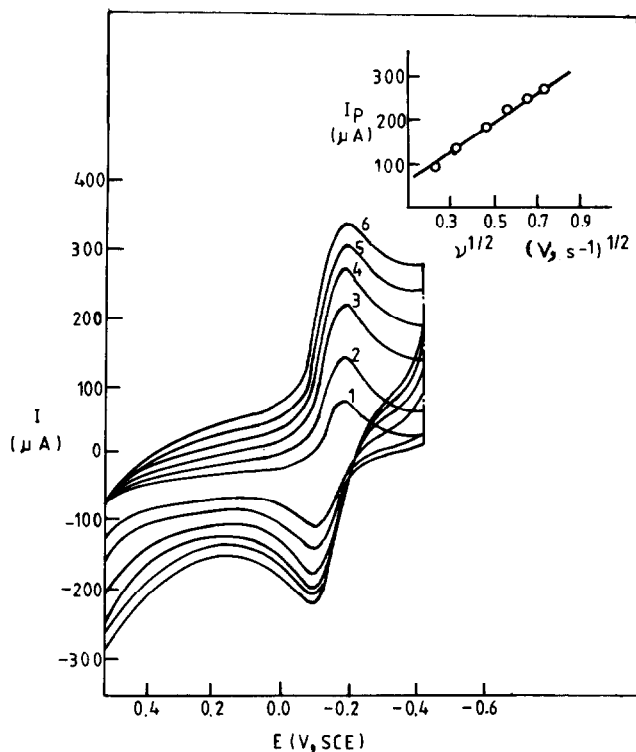
Fig. 1. Cyclic voltammograms for 1 mM Fe(III)/Fe(II) with 0.05 M DTPA. (Inset) peak current vs. square-root of sweep rate. Curves 1 - 6 for sweep rates of 50, 100, 200, 300, 400 and 500 mV s^{-1}, respectively.

TABLE 1

Kinetic and electrochemical constants for an Fe(III)/Fe(II) couple with different chelating agents[a]

System	pH	E' (V)	D ($\times 10^{-6}$ cm s^{-1})	k^o ($\times 10^{-3}$ cm s^{-1})
Fe(III)/Fe(III)[b]	2.0	+0.45	3.24	3.25
Fe(III)/Fe(II)–NTA	2.8	−0.093	0.33	12.4
Fe(III)/Fe(II)–DTPA	2.5	−0.070	0.20	15.6
Fe(III)/Fe(II)–EDTA	2.8	−0.114	1.50	34.9

[a]K_2SO_4 (0.5 M) medium, pH adjusted with H_2SO_4 for all the systems except Fe(III)/Fe(II) system.
[b]In 0.1 M H_2SO_4 medium without addition of any ligand.

negative values (Fig. 3). A similar observation was made by Kolthoff and co-workers [10] for the iron–EDTA system. The negative shift of the Fe(III)/Fe(II) formal potential may be explained in terms of the formation of more stable Fe(III) complexes. This behaviour is opposite to that of
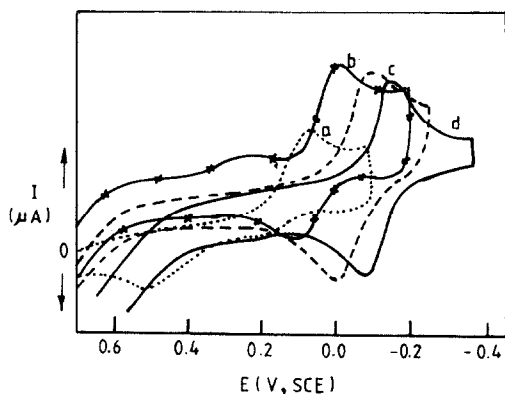
Fig. 2. Cyclic voltammogram for 1 mM Fe(III)/Fe(II) with 0.05 M DTPA at pH: (a) 1.08; (b) 1.75; (c) 2.5; (d) 4.05.
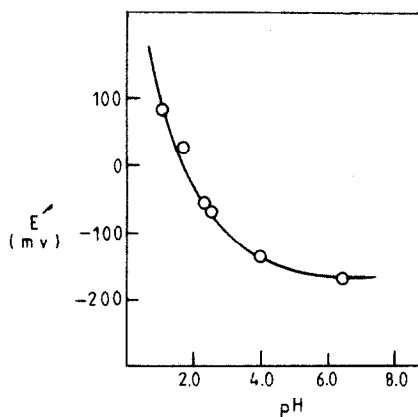
Fig. 3. Variation of formal potential of Fe(III)–DTPA complex with pH.

phenanthroline and bipyridyl ligands which cause a positive shift in the formal potential and form more stable Fe(II) complexes [8].

The heterogeneous electron-transfer rate constant (k^o) was obtained by the method described by Nicholson [11], according to which it is possible to determine the rate constant at high scan rates because the kinetics of electron transfer become competitive with the rate of potential change. In our system, it was found that a scan rate of 100 mV s^{-1} corresponds to this situation. The working curve (ref. 11, Fig. 3) was then employed to obtain the redox kinetic potential values (ψ) where:

$$\psi = \frac{k_o}{(\pi a D_o)^{1/2}} \tag{1}$$

Here, $a = nF/RT$ and D_o is the diffusion coefficient of Fe(II) or Fe(III) (assumed to be the same) determined from the peak currents $i_{p,a}$ or $i_{p,c}$ using the equation [12]:

$$i_p = (2.69 \times 10^5)n^{3/2}AD_o^{1/2}C^\circ\nu^{1/2} \tag{2}$$

where: i_p is the peak current; n is the number of electrons transferred; A is the electrode area (cm^2); D_o is the diffusion coefficient of the species being oxidized/reduced (cm^2 s^{-1}); C° is the concentration of the same species in the bulk solution (mol ml^{-1}); ν is the scan rate (V s^{-1}). From a plot of i_p versus $\nu^{1/2}$ (eqn. (2)) a straight line was obtained with slope proportional to $D_o^{1/2}$ (inset, Fig. 1). The diffusion coefficients for the aquo Fe(III)/Fe(II) species in 0.1 M H$_2$SO$_4$ and those for the complexed Fe(III) species are listed in Table 1. The heterogeneous rate constants (k°) were now obtained using eqn. (1). For the Fe(III)–complex species, the k^o values vary over the range 0.012 - 0.035 cm s^{-1}.

The heterogeneous rate constant for the uncomplexed Fe(III)/Fe(II) couple in 0.1 M H_2SO_4 is 3.25×10^{-3} cm s^{-1} and this is in fair agreement with the value 1.6×10^{-3} cm s^{-1} previously reported [13, 14]. In general, the complexed species have larger k° values than the uncomplexed species. Bard and coworkers [8] also found similar trends in their investigations with phenanthroline and bipyridine ligands.

The stability of the complexes was investigated by controlled-potential coulometric (CPC) studies. In controlled potential electrolysis, the current decreases exponentially (Fig. 4(a)) according to the equation [13]:

$$i(t) = i^\circ \exp(-i^\circ A/nFC^\circ V)t \tag{3}$$

where: V is the volume of the solution; A is the area of the electrode; i° is the initial current density. The parameter n can be obtained from the slope of the plot of log i versus t (Fig. 4(b)). The product $i^\circ A$ is simply the total initial current.

Reduction of complexed Fe^{3+} species (forward electrolysis, Fig. 4, I) was carried out at a potential of -0.7 V. Covering all cases, electrolysis consumed 0.93 - 1.06 F $mole^{-1}$. A similar result has been found by other workers [8]. Reverse electrolysis (backward electrolysis, Fig. 4, II) was carried out at a potential of $+0.05$ V. The number of coulombs (Q) consumed was approximately the same as for forward electrolysis (Fig. 4). The relevant data are shown in Table 2. To examine the life-time of the complexed-Fe(II) species, CV experiments were undertaken on the solution following CPC reduction. The voltammogram after electrolysis for 20 - 40
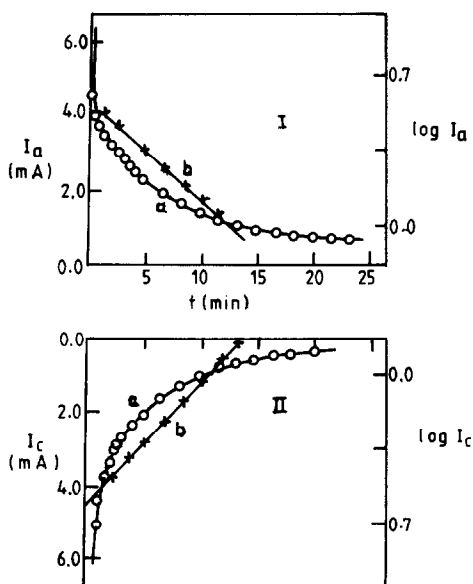

Fig. 4. Current–time curve during exhaustive electrolysis in 1 mM Fe(III)/Fe(II) DTPA at a mercury-pool electrode.

TABLE 2

Controlled-potential electrolysis data

Moles taken[a] ($\times10^{-5}$)	Q_f (C)	Mole reduced ($\times10^{-5}$)	Q_b (C)	Moles Fe^{3+}–complex oxidized (recovered) ($\times10^{-5}$)
Fe^{3+}–(DTPA)				
1.49	1.531	1.587	1.521	1.576
1.49	1.520	1.575	1.508	1.563
1.49	1.521	1.576	1.511	1.566
Fe^{3+}–(NTA)				
1.5	1.360	1.409	1.346	1.395
1.5	1.355	1.404	1.352	1.401
Fe^{3+}–(EDTA)				
1.5	1.383	1.433	1.473	1.526
1.5	1.470	1.523	1.464	1.517

[a]Number of moles present in the total volume of solution electrolysed.

min had a well-defined peak consistent with the presence of an Fe(II)–ligand. After storing the solution for 24 h in air, however, the curve showed a faintly developed peak corresponding to free Fe^{2+} (Fig. 5). This indicates a very slow decomposition of Fe^{3+}–ligand species with time and suggests that the complexes are reasonably stable.
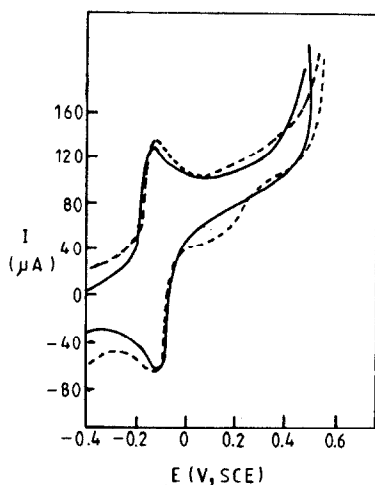

Fig. 5. Stability of Fe(III)/Fe(II)–DTPA in K_2SO_4: ———, immediately after controlled potential electrolysis at -0.7 V; — — —, after standing in air for 24 h.

Conclusion

The electrochemical studies of the Fe(III)/Fe(II) couple in presence of EDTA, DTPA and NTA demonstrate that stable Fe(III) complexes are formed. The electron-transfer kinetics and the shift of the formal potential in the negative direction both appear to satisfy the requirements of a redox-flow cell. An all-iron redox-flow cell therefore appears feasible in which the above ligands would be used in the negative half-cell and phenanthroline and bipyridyl ligands in the positive half-cell. The medium employed has a suitable pH. Controlled-potential coulometric studies show that forward and backward electrolyses consume equal amounts of electrical charge.

Acknowledgement

List of symbols

i_{pa} Anodic peak current
$i_{p,c}$ Cathodic peak current
$E^{\prime}$ Formal potential
ψ Redox kinetic potential
k° Heterogeneous rate constant
D_o Diffusion coefficient
a Tafel parameter
n Number of electrons involved in a redox process
A Area of the electrode
C° Concentration of redox species in bulk
ν Scan rate
α Transfer coefficient
Q Charge
i° Initial current density

References

1 L. H. Thaller, *NASA TMX-71540*, NASA, U.S. Dept. of Energy, 1974; and *U.S. Pat. 3996064* (1974).
2 L. H. Thaller, Redox flow energy storage systems, *NASA-TM-79143*, *Terrestrial Energy Systems Conf. sponsored by Am. Inst. Aeronautics and Astronautics, Orlando, Florida, June 4 - 6, 1979, NASA-TM 79067, Jan. 1979.*

3 L. H. Thaller, Redox flow development and demonstration, *Symp. on Load Levelling sponsored by Electrochem. Soc., Atlanta, Georgia, Oct. 10 - 13, 1979.*

4 K. D. Beccu and G. Crespy, Large scale energy storage by means of dissolved redox-flow systems, *SPE meeting, Grenoble, France, April 9, 1976.*

5 R. F. Savinell, C. C. Liu, R. T. Galasco, S. H. Chiang and J. F. Coetzee, *J. Electrochem. Soc., 126* (1979) 357.

6 E. Sum and K. S. Kazacos, *J. Power Sources, 15* (1985) 179.

7 E. Sum, M. Rychcik and K. S. Kazacos, *J. Power Sources, 16* (1985) 85.

8 Y. W. D. Chen, K. S. V. Santhanam and A. J. Bard, *J. Electrochem. Soc., 128* (1981) 1460.

9 Y. W. D. Chen, K. S. V. Santhanam and A. J. Bard, *J. Electrochem. Soc., 129* (1982) 61.

10 I. M. Kolthoff and C. Auerbach, *J. Am. Chem. Soc., 74* (1952) 1452.

11 R. S. Nicholson, *Anal. Chem., 37* (1965) 1351.

12 H. Matsuda and Y. Ayabe, *Z. Elektrochem., 59* (1955) 494.

13 R. N. Adams, *Electrochemistry at Solid Electrodes*, Marcel Dekker, New York, 1969.

14 D. H. Angill and T. Dickinson, *J. Electroanal. Chem., 35* (1972) 55.