

Solution Redox Couples for Electrochemical Energy Storage

I. Iron (III)-Iron (II) Complexes with O-Phenanthroline and Related Ligands

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ABSTRACT

Iron (III)-Iron (II) complexes with o-phenanthroline and related ligands have been examined by electrochemical techniques in aqueous H₂SO₄ media with respect to their suitability as redox couples for electrochemical energy storage. The iron (II) complexes undergo a rapid 1 electron oxidation at graphite and platinum electrodes to yield iron (III) complexes; these complexes showed varying stabilities depending on the nature of the substituents on the complexes. The iron (II) complexes examined in this study were formed with (i) monodentate, (ii) bidentate, or (iii) tridentate ligands. The redox couples have a higher E° value which has been a positive consideration in the storage. Although the aquo iron (II)-iron (III) couple has an E° less than the complexes, it certainly has shown greater promise in terms of storage stability. The kinetics of iron (II) complexation has been followed by cyclic voltammetry.

A redox flow cell (or battery) (1-8) is one in which the chemical species which participate in the electrode reactions are soluble. The cell is charged with the input of electrical energy to drive the overall cell reaction in a thermodynamically uphill direction and the oxidized species produced at an inert electrode in one half-cell and the reduced form from the other are stored in external vessels. Electricity is produced in these cells when the stored reactants flow back into the cell and react at the electrodes. Thus these cells are of interest as secondary or rechargeable batteries. The energy densities of these systems (i.e., energy stored per unit weight of battery) suffer in comparison to more conventional secondary batteries which utilize solid reactants, because of the weight of the solvent and electrolyte. However, they offer the possibility of much better cycle life, since the repeated charge and discharge cycles do not involve phase changes and the accompanying changes of electrode morphology. These systems are of interest in stationary applications such as electrical energy storage and in utility load leveling.

Another related area involving soluble redox couples in energy devices is that of photoelectrochemical (PEC) (or liquid junction photovoltaic) cells with semiconductor electrodes (9). These cells, which are based on the light-driven redox processes of solution species at semiconductors, are of two types. In the PEC cell without energy storage, a single redox couple is employed, and the electrode reaction at the counterelectrode is the reverse of the photo-redox process at the semiconductor. In PEC cells with storage [types of photoelectrosynthetic cells (9)], the reactants formed during irradiation are stored and employed to generate electricity, in the same or a separate cell, during dark periods.

The redox couples for these applications, represented by the reaction in [1]



must satisfy a number of requirements: (i) both forms, O and R, must be highly soluble to minimize the storage volume and mass and to allow high mass transfer rates and current densities during charging and discharging; (ii) the formal potential, E° , of one couple must be highly positive, and E° of the other highly negative to maximize the cell voltage and energy density; (iii) the heterogeneous reaction rate for the charging and discharging reactions at the inert electrodes should be rapid (i.e., the standard rate constant, k° , for [1] should be large) so that the electrode reactions occur at their mass transfer controlled rates; (iv) both O and R should be stable during generation and storage, and this stability pertains to reaction with solvent, electrolyte, atmosphere, and electrode materials, and, for metal complexes, stability with respect to ligand loss; (v) the materials should be safe, inexpensive, and abundant; (vi) the couple should not be corrosive and react with cell materials, or the storage vessel, indeed, in PEC cells the redox couple is often called upon to stabilize and protect the semiconductor electrode from photocorrosion (10, 11); and (vii) for PEC cells, the redox species should not absorb light in the wavelength region of semiconductor absorption.

A number of redox couples have been proposed for such systems. These include Fe(III)/Fe(II) (HCl) (5, 6); Cr(III)/Cr(II) (HCl) (4-6); Ti(IV)/Ti(III) (7); Br₂, Br⁻ (12-14); and, for PEC cells, S²⁻, S₂²⁻ and Se²⁻, Se₂²⁻ (15, 16). A difficulty in a storage cell is the possible intermixing of the components of the two half-cells, because of imperfect separators or membranes, which leads not only to loss of capacity and efficiency but more seriously to cross-contamination of the redox solutions. Approaches to minimizing this intermixing problem include the use of a single element system in three oxidation states [e.g., Cr(VI), Cr(III)//Cr(III), Cr(II) (4)] or the use of two oxidation states of the same element with the redox potentials shifted by complexation with different ligands.

The work reported here, as well as other current investigations (1, 2), is concerned with the application of metal ion coordination compounds as redox

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couples in flow cells. By suitable choice of ligand the formal potential of the couple can be shifted in the desired direction. Moreover such complexes may show improved characteristics with respect to stability and color in comparison to the uncomplexed species. The chemical principles related to the formation and properties of metal complexes are well developed and many new and potentially useful ligands have been reported. We describe here investigations of the Fe(III)/Fe(II) couple with ligands related to o-phenanthroline and bipyridine. Iron species were chosen for this initial investigation because iron is an abundant and inexpensive element with many highly soluble compounds. Such couples may be useful in the positive half-cell of redox flow systems or with n-type semiconductors in PEC cells.

Experimental

Reagents.—1,10-(or o-)phenanthroline (phen), 2,9-dimethylphenanthroline (2,9-dmp), 4,7-dimethylphenanthroline (4,7-dmp), and 4-methylphenanthroline (mp) were obtained from Alfa Chemicals. 2,2'-Bipyridine (bpy) was obtained from Aldrich Chemical Company. Tripyridine triazine (tpt), 4-cyanopyridine (cp), and 2-pyridine carboxaldehyde-2-pyridyl hydrazine (p-cph) were obtained from J. T. Baker Company. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was reagent grade (Matheson, Coleman and Bell). Surfactants IGEPAL-Co430 (MW = 396) and 530 (MW = 484) were obtained from GAF Corporation (Atlanta, Georgia) and "Texas-1" (MW = 404) was made by Dr. Y. B. Youssef of The University of Texas. The former two surfactants carry ethylene oxide groups and the latter is the sodium salt of 8(p-phenyl sulfanato) hexadecane. All solutions were prepared with doubly distilled water and the solutions were degassed with prepurified gas that was passed through a chromous sulfate solution and then distilled water.

Apparatus.—A Model 173 potentiostat in combination with a Model 179 digital coulometer (Princeton Applied Research Corporation, Princeton, New Jersey) was employed for all electrochemical experiments. The current-voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder. The current time curves were recorded on a Model 564 storage oscilloscope (Tektronix) during potential-step chronoamperometry and on a National Panasonic strip-chart recorder during coulometric experiments.

Procedure.—The usual supporting electrolyte was aqueous H_2SO_4 prepared by suitable dilution of concentrated H_2SO_4 . All solutions were degassed with nitrogen before the electrochemical experiments. The complexes were usually prepared directly in the electrochemical cell by mixing known concentrations of ferrous sulfate and the ligand. A mole ratio of ligand/Fe(II) of greater than 5 was used. Controlled potential electrolyses were conducted with a large area graphite sheet electrode (area, 6.5 cm^2) (Ultra Carbon, Sherman, Texas) with continuous nitrogen gas bubbling. Some of the electrochemical experiments were carried out in the dark. All of the potentials were measured with respect to an aqueous saturated calomel electrode (SCE). An H-cell with a porous sintered-glass disk separating the two compartments was used in coulometric investigations. For cyclic voltammetric investigations, a single compartment cell with a solution capacity of 5 ml was employed, with either platinum wire ($A = 0.12 \text{ cm}^2$), platinum disk ($A = 0.14 \text{ cm}^2$), or graphite rod (taken from a C-cell battery, area $A = 0.14 \text{ cm}^2$) working electrodes. The platinum electrodes were pretreated by fast pulsing between +1.0 to -1.0V in H_2SO_4 .

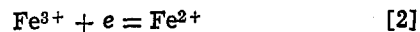
The solubilities of the complexes were estimated by dissolving the specified concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

and an excess of ligand in 0.5M H_2SO_4 . The complex formed would precipitate at this initial ion concentration. The precipitate was then just dissolved in the solution by adding 0.5M H_2SO_4 solution gradually. The concentration and the solubility were then estimated by the degree of the dilution of the solution (Table I). These measurements were done at room temperature.

The stabilities of ferrous and ferric complexes were monitored with a Cary 14 spectrophotometer. The ferric complexes were prepared either by electrochemical oxidation of the ferrous complexes or by Ce(IV) oxidation in H_2SO_4 medium.

Results

To shift the potential of the half-reaction



toward values positive of the E° (+0.77V vs. NHE), ligands which form more stable complexes with Fe(II) are required. Since Fe^{2+} (d^6) is a good π -donor cation, ligands with low-lying vacant π^* orbitals complex strongly with it (17). Fe^{3+} has poorer π -donor properties because of its higher charge. Thus ligands such as bpy and phen (Fig. 1) are known to shift the potential of the redox couple in a positive direction. Further manipulation of the potential is possible by substitution on the rings of these ligands. A number of highly stable complexes of these ligands are known (17). The structure and abbreviations for those ligands used in this study are shown in Fig. 1 and Table II.

Solubilities.—Table I is a list of the solubilities of the complexes in aqueous 0.5M H_2SO_4 . Uncomplexed Fe(II) and Fe(III)-sulfate salts are quite soluble and yield solutions with metal ion concentrations $\sim 1\text{M}$. The solubility of the complexes vary with the nature of the ligand. The ligands themselves are soluble in acidic media to $\sim 2\text{M}$ (e.g., phen, 2,9-dmp). The complexes in 1M concentrations form solutions which are viscous and deeply colored. The uncomplexed Fe(II) and Fe(III) ions in H_2SO_4 are quite transparent in the visible region.

E° values.—The formal potentials of the various Fe(II)/Fe(III) complexes were evaluated from the cyclic voltammetric peak potential values at low scan rates ($E_{pa} = E^\circ + 0.028/n$) (see Table II). The complexes with cp, tpt, 2,9-dmp, and p-cph show more positive peak potentials, but the reversible potential values are difficult to estimate because of the instability of the ferric complex. The E° -values for the other ligands are all more positive than E° for the aquo Fe ($3+/2+$) couple in H_2SO_4 . In the phen-complexes substitution of methyl groups produces less positive peak potentials; while nitro- and chloro-group substitution yields more positive potentials compared to complexes with the unsubstituted ligand. Similar observations have been made by Fan and

Table I. Estimated solubilities of ferrous-ferric couples and ligands*

Substance	Solubility (g/100 ml)	Concentration (M)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	27.8	1.0
$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	44.0	0.8
$\text{Fe}(\text{phen})_3\text{SO}_4$	52.6	0.8
$\text{Fe}(\text{bpy})_3\text{SO}_4$	43.8	0.7
$\text{Fe}(2,9\text{-dmp})\text{SO}_4$	37.2	1.0
$\text{Fe}(\text{tp})_3\text{SO}_4$	22.4	0.3
Phenanthroline	40.0	2.2
Bipyridyl	31.6	2.0
Terpyridine	44.0	1.8
4-Cyanopyridine	10.5	1.0

* Measured in 0.5M H_2SO_4 . See experimental section for method.

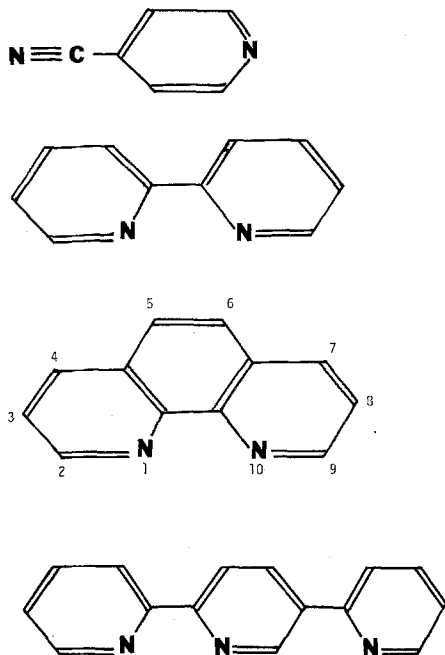


Fig. 1. Structure of ligands used in the study

Faulkner (18) at a phthalocyanine covered metal electrode.

Cyclic Voltammetric Measurements

Electron transfer kinetics.—Cyclic voltammetry (*cv*) was employed to survey a system with respect to heterogeneous electron transfer kinetics and stability of the Fe(III)-L species. Since the heterogeneous electron transfer rate constants, k^0 , are all moderately large ($>10^{-3}$ cm/sec), at low scan rates, v , the electrochemical behavior (in the absence of fast following reactions) is characteristic of a Nernstian reaction and show ΔE_p -values ~ 60 mV ($\Delta E = E_{pa} - E_{pc}$). When v is increased, shifts of E_{pa} and an increase in ΔE_p are observed signaling the onset of effects of the heterogeneous electron transfer rate (in the absence of uncompensated resistance effects) (19-21). Information about k^0 can then be obtained from the variation of E_{pa} or ΔE_p with v using methods developed by Matsuda and Ayabe (19) and Nicholson (20). The approach taken here was to determine the value of ψ from the E_p - v behavior (assuming $\alpha \sim 1/2$), where

$$\psi = \frac{k^0}{\sqrt{\pi a D_{Fe^{2+}}}} \quad [3]$$

where $a = nFv/RT$ and $D_{Fe^{2+}}$ is the diffusion coefficient of the Fe(II) ion in the medium employed. The

diffusion coefficients of Fe(II) and Fe(III) were determined from the peak currents i_{pa} and i_{pc} . For the aquo-species in 0.5M H_2SO_4 , $D_{Fe^{2+}} = D_{Fe^{3+}} = 2.5 \times 10^{-6}$ cm²/sec. Typical D -values for the complexed Fe(II) species determined by *cv* are listed in Table II. With these D -values and the measured ψ -values, k^0 was obtained. These are also listed in Table II. For example, in a typical study with 10 mM Fe(II)-phen complex in 0.5M H_2SO_4 , the *cv* wave showed $E_{pa} = 0.85V$ and, on scan reversal, $E_{pc} = 0.79V$ at $v = 50$ mV/sec. When v increased, ΔE_p increased, and at $v = 50$ V/sec, $\Delta E_p = 0.09V$; $v = 100$ V/sec, $\Delta E_p = 0.10V$; $v = 200$ V/sec, $\Delta E_p = 0.12V$; $v = 500$ V/sec, $\Delta E_p = 0.18V$. These measurements were made with full *iR* compensation. From these values, an average value of $k^0 = 5.8 \times 10^{-2}$ cm/sec was obtained. With the Fe(II) coordination compounds only values for 0.5M H_2SO_4 are listed in Table II, since in 3M H_2SO_4 protonation of the ligands (with pK_a 's $\sim 4-6$) competes very strongly with complexation with Fe(II) and appreciable complexation does not occur.

Values of k^0 for the Fe(3+/2+) couple in the absence of added ligand were also obtained in 0.5 and 3M H_2SO_4 , yielding values of 1.6×10^{-3} and 1.2×10^{-2} cm/sec, respectively. Typical *cv* curves are shown in Fig. 2. The electrochemical oxidation of Fe(II) in aqueous H_2SO_4 has been previously investigated at platinum and carbon paste electrodes (22, 23). The results are in general agreement with those found here. The rate of the electrode reaction appears to depend on the concentration of the acid as well as the nature of the electrode surface (*e.g.*, the presence of oxide films). However, the coordinated species generally have larger k^0 -values than the aquo-species under similar conditions (0.5M H_2SO_4).

Stability (*cv*).—Stability of the coordination compound and the product of the electrode reaction can also be monitored by *cv*. Consider the oxidation of FeL_x^{2+} . The observed *cv* behavior depends on the ligand, L, and the tendency of FeL_x^{3+} formed during the anodic sweep to decompose (Fig. 3). During the time scale of the *cv* sweep the Fe(III) complexes with phen (or bpy) and tp are stable while that with cp is not. In the latter case oxidation of the stable Fe(II) complex leads to the Fe(III) form which decomposes rapidly, probably by loss of ligand to form a different Fe(III) species. The general reaction sequence is thus

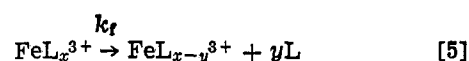
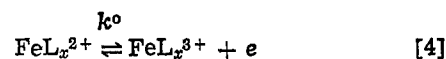


Table II. Thermodynamic and kinetic constants for ferrous-ferric couples*

Ligands	E^0 (V vs. SCE)	k^0 (cm/sec)	k_1^{**} (sec ⁻¹ × 10 ²)	k_1^{\dagger} (M ⁻¹ sec ⁻¹ × 10 ⁻⁴)	D (cm ² sec ⁻¹ × 10 ⁹)	Abbreviation of ligand
Aquo	0.45	1.6×10^{-3} $1.2 \times 10^{-2\dagger}$			2.5	H ₂ O
Bipyridine	0.82	5.6×10^{-2}	0.063	3.0	1.11	bpy
o-Phenanthroline	0.82	5.8×10^{-2}	0.012	3.0	1.22	phen
4-Methyl-o-phenanthroline	0.73	4.9×10^{-2}	0.005	—	1.07	mp
4,7-Dimethyl-o-phenanthroline	0.69	2.5×10^{-2}	0.003	6.3	1.00	4,7-dmp
2,9-Dimethyl-o-phenanthroline	0.82		>0.6			2,9-dmp
5-Chloro-o-phenanthroline	0.97‡		0.14			CIP
5-Nitro-o-phenanthroline	1.07‡		0.91			Np
Terpyridine	0.82	6.0×10^{-3}	0.18	800	1.80	tp
2-Pyridinecarboxaldehyde	0.67		>0.6			p-cph
Tripyridinetrizaine	1.24		>0.6			tpt
4-Cyanopyridine	0.82		>0.6			cp

* Medium 0.5M H_2SO_4 ; electrode material graphite. $T = 23 \pm 2^\circ C$.

** Rate constant value refers to decomposition of ferric complexes determined by spectrophotometry. The value (>0.6) was estimated by *cv*.

† Rate constant for the complexation of ferrous ion determined by *cv* method.

‡ Medium 3M H_2SO_4 .

§ K. Ogura and K. Miyamoto, *Electrochimica Acta*, 22, 1357 (1977).

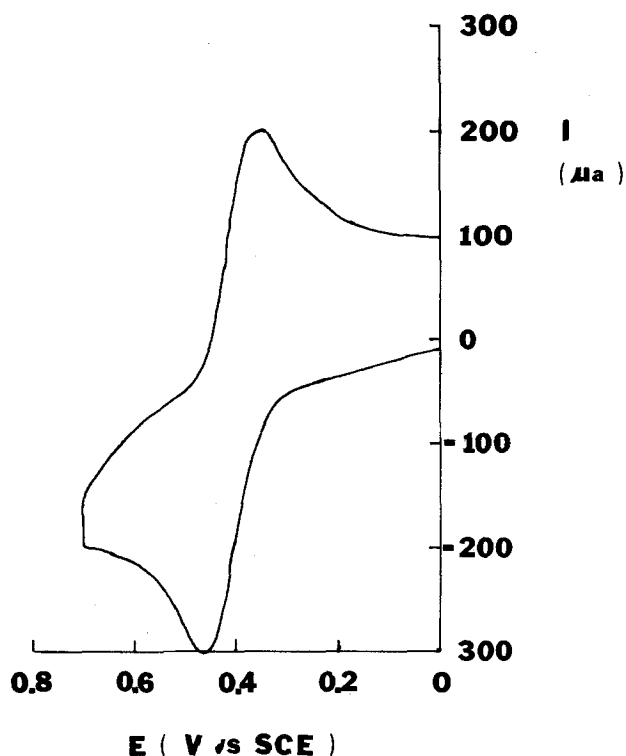


Fig. 2. (a) Cyclic voltammogram curve for the oxidation of 10 mM Fe^{2+} in aqueous 3M H_2SO_4 working electrode: Graphite, reference electrode: aqueous saturated calomel electrode. $v = 0.50$ V/sec.

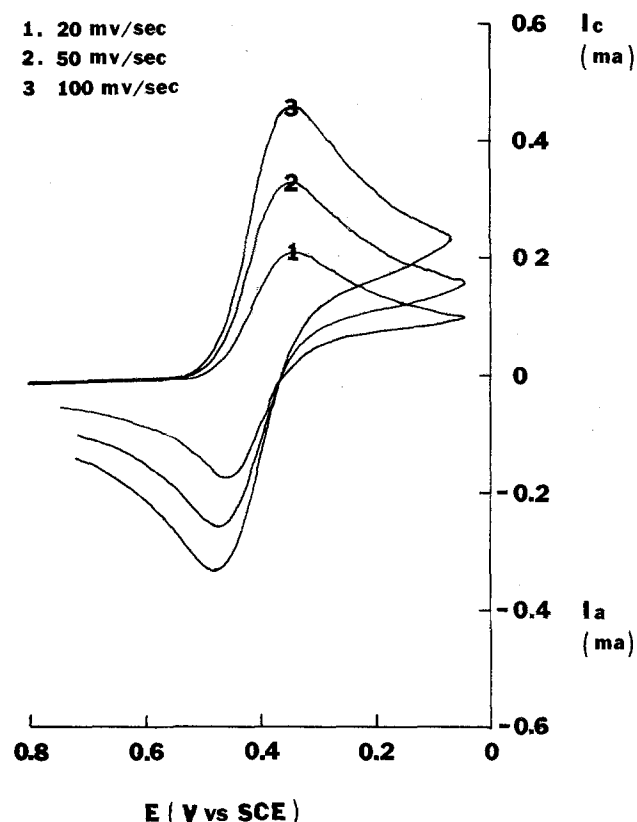


Fig. 2. (b) The current-voltage curve after controlled potential exhaustive electrolysis at $+0.80\text{V}$ in $0.5\text{M H}_2\text{SO}_4$.

(for simplicity, the state of protonation of the ligand is not indicated in the equations). Instability on the cv time scale for v up to 50 V/sec was also found for 2,9-dmp and several other ligands, as indicated in Table II.

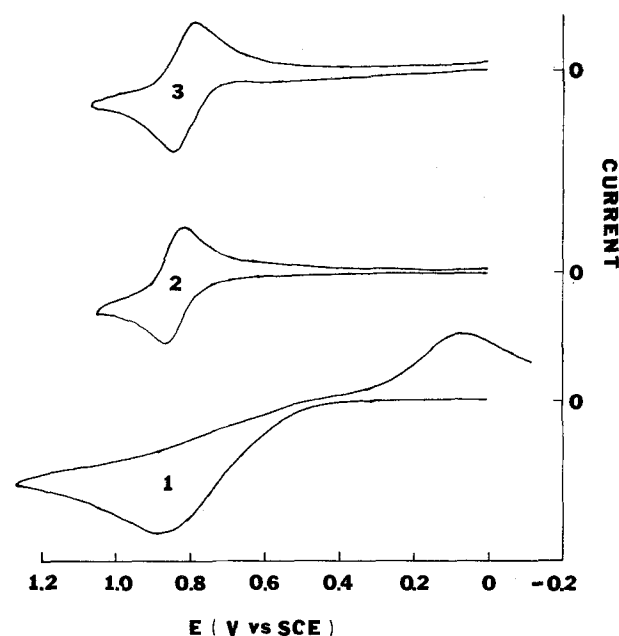
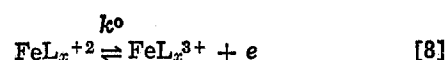
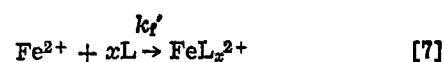
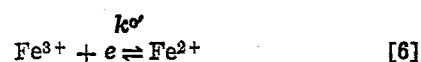


Fig. 3. Cyclic voltammograms for $\text{Fe}(\text{II})$ ion coordinated with: 1, monodentate (cp); 2, bidentate (bpy); 3, tridentate (tp) at graphite electrode. Solution contained 10 mM aquo $\text{Fe}(\text{II})$ ion and at least 50 mM ligand. $v = 0.05$ V/sec.

The rate of formation of the $\text{Fe}(\text{II})$ -ligand complexes was also of interest and this was determined by cv for complexes with bpy, phen, 4,7-dmp, and tp. In all cases the $\text{Fe}(\text{III})$ complex is thermodynamically unstable in $0.5\text{M H}_2\text{SO}_4$, although it is kinetically inert so that it decomposes to Fe^{3+} and free ligand quite slowly. Thus if one prepares a solution containing a mixture of free Fe^{3+} and L essentially no complexation occurs. Upon reduction of the Fe^{3+} to Fe^{2+} rapid reaction with L takes place so that on scan reversal oxidation of $\text{Fe}(\text{II})$ occurs both as free Fe^{2+} and as FeL_x^{2+} , i.e., the reaction sequence is



Typical results for a solution containing 5 mM Fe^{3+} and 300 mM phen in $0.5\text{M H}_2\text{SO}_4$ at a Pt electrode are shown in Fig. 4. Note that at very slow sweep rates ($v = 20$ mV/sec) the anodic peak for Fe^{2+} oxidation following Fe^{3+} reduction is barely detectable, while the $\text{Fe}(\text{phen})_3^{2+}$ oxidation wave is fully developed. At higher sweep rates i_{pa} for Fe^{2+} oxidation increases and the $\text{Fe}(\text{phen})_3^{2+}$ oxidation wave becomes relatively smaller. At very high sweep rates ($v = 100$ V/sec) only the Fe^{2+} oxidation is observed with the same general characteristics as the uncomplexed Fe^{3+} couple in the absence of phen at this v . The rate constant, k_f' for Fe^{2+} disappearance can be estimated from the ratio of i_{pa}/i_{pc} for the $\text{Fe}^{3+/2+}$ couple. Typical data for the cv of these complexes is shown in Table III along with the rate constants obtained using the treatment of a second-order following (EC) reaction (24). Since the ligand concentrations are high, the EC reaction is essentially pseudo-first order and the treatment of this EC-reaction scheme (25) also applies. The calculated values of k_f' are based on the free ligand concentration, $[\text{L}]$, at the given H_2SO_4 concentration which is in equilibrium with the various protonated forms. The pK_a values employed in calculation of $[\text{L}]$ were:

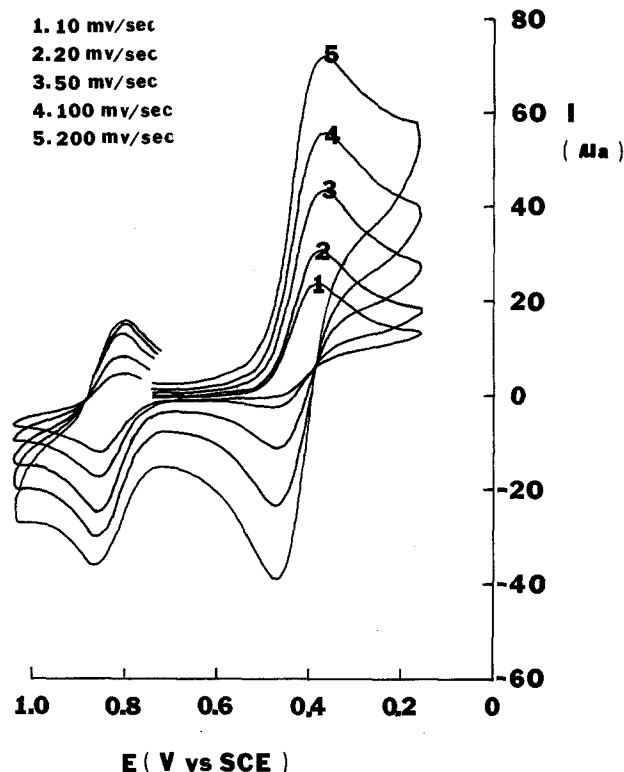


Fig. 4. Cyclic voltammogram for 5 mM Fe(III) reduction in the presence of phenanthroline (300 mM) at a platinum electrode.

bpy, $pK = 4.47$; phen, $pK = 4.98$; tp, $pK_1 = 2.64$, $pK_2 = 4.33$ (26, 27). The k'_i -values obtained by this procedure are listed in Table II.

A digital simulation of current-voltage curves was carried out for the reduction of Fe(III) in the presence of the ligands. In this simulation the following mechanism was assumed. Reaction [6] was followed by

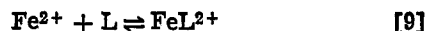
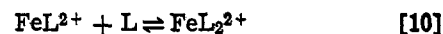


Table III. Electrochemical studies of complexation rate of Fe^{2+} : complexation with bipyridine, o-phenanthroline and terpyridine*

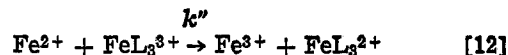
Sweep rate (V/sec)	t_{pa}/t_{pc}	τ (sec)	$k_{app}\dagger$ ($\text{M}^{-1} \text{sec}^{-1}$)	$k_{ct}\ddagger$ ($\text{M}^{-1} \text{sec}^{-1} \times 10^{-5}$)
Concentration of bipyridine: 0.3M				
0.05	0.230	5.00	4.00	0.27
0.05	0.275	4.00	3.51	0.24
0.05	0.254	4.00	4.11	0.28
0.10	0.307	2.50	4.52	0.31
0.10	0.367	2.00	3.94	0.27
0.10	0.341	2.00	4.56	0.31
0.20	0.435	1.25	4.49	0.30
0.20	0.539	1.00	3.65	0.25
0.20	0.458	1.00	5.06	0.34
0.50	0.619	0.50	5.54	0.38
0.50	0.656	0.40	6.80	0.42
Concentration of o-phenanthroline: 0.3M				
0.02	0.256	12.50	1.30	0.29
0.05	0.474	5.00	0.94	0.21
0.10	0.528	2.50	1.52	0.34
0.20	0.747	1.25	1.82	0.34
0.50	0.780	0.50	2.46	0.55
1.00	0.857	0.25	5.78	1.28
Concentration of terpyridine: 0.02M				
0.05	0.617	11.00	3.80	82.8
Concentration of terpyridine: 0.04M				
0.05	0.416	11.20	4.11	75.8

* Medium 0.5M H_2SO_4 . Working electrode platinum. (Area = 0.14 cm^2). Adsorption of the organic on the electrode sometimes produced irreproducibility. Temperature of the solutions $\sim 25^\circ\text{C}$. Concentration of $\text{Fe}^{3+} = 5.0 \text{ mM}$.

† Calculated employing the total concentration of the ligand and assuming formation of the mono-complex is rate determining.
‡ Calculated with the effective ligand concentration using pK_a values reported in text.



and reaction [8], where k^o and k^o' are heterogeneous electron transfer rate constants. If [9] is taken as the rate-determining step and neglecting dissociation rate, the simulated curves are nearly identical to the experimental one as shown in Fig. 5. The small discrepancy for the Fe^{3+} reduction wave might be due to the onset of background reduction. The second oxidation wave (that of FeL_3^{2+}) and its corresponding reversal reduction wave might also be perturbed by the occurrence in homogeneous solution of the reaction



Although the Fe^{2+} concentration in the vicinity of the electrode at the potentials of these waves is small, this reaction is known to be rapid, $k'' = 2.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ for $\text{L} = \text{bpy}$ in $0.5\text{M } \text{H}_2\text{SO}_4$ (28). The inclusion of this reaction in the simulation did not affect the observed i - E curves for k'' -values up to $10^4 \text{ M}^{-1} \text{ sec}^{-1}$. Within the number of iterations used in the simulation explicit values of k'' higher than this could not be employed. However, even if k'' is assumed to be at the mass transfer controlled limit, so that Fe^{2+} and FeL_3^{3+} cannot coexist in a simulation space element, the effect of the i - E curves, shown as dashed lines in Fig. 5, is small.

It is interesting to compare these results of complexation of Fe^{2+} by bpy with those obtained by stopped flow methods (29), where a second-order

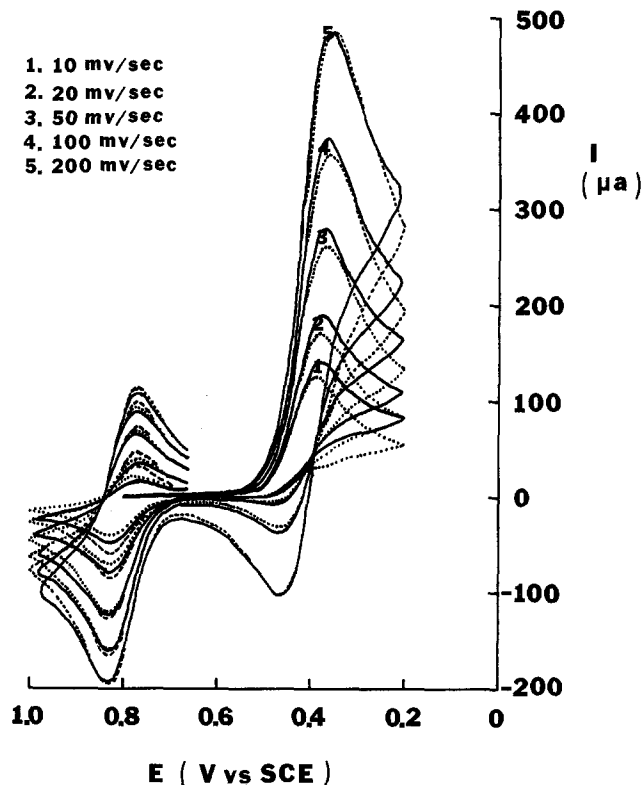


Fig. 5. Digital simulation for the ECE process of the ferric-bipyridine system in $0.5\text{M } \text{H}_2\text{SO}_4$. (—) Experimental curves; digital simulation curves (---) assuming infinite rate of reaction [12] and (···) assuming rate of reaction [12] = 0. $C_{\text{Fe}^{3+}} = 20 \text{ mM}$, $C_{\text{bpy}} = 300 \text{ mM}$, $k_{app} = 2.5 \text{ M}^{-1} \text{ sec}^{-1}$; $D_{\text{Fe}^{3+}} = 2.5 \times 10^{-6} \text{ cm}^2/\text{sec}$, $D_{\text{Fe}(\text{bpy})_3^{3+}} = 2.6 \times 10^{-6} \text{ cm}^2/\text{sec}$. Area of platinum electrode = 0.148 cm^2 .

$E^o(\text{Fe}^{3+,2+}) = 0.41\text{V}$, $E^o(\text{Fe}(\text{bpy})_3^{3+,2+}) = 0.80\text{V}$, $\alpha(\text{Fe}^{3+,2+}) = 0.5$, $\alpha(\text{Fe}(\text{bpy})_3^{3+,2+}) = 0.5$, $k_s(\text{Fe}^{3+,2+}) = 1.61 \times 10^{-3} \text{ cm}^2/\text{sec}$, and $k_s(\text{Fe}(\text{bpy})_3^{3+,2+}) = 5.64 \times 10^{-2} \text{ cm}^2/\text{sec}$.

rate constant of $2.8 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ at 0.2°C was reported. This rate constant was assigned to the first step in the complexation formation of $\text{Fe}(\text{bpy})_2^{2+}$ (reaction [9]). The addition of the second and third bpy ligands is faster; for the third step the rate constant is $1.4 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$, while for phen the rate of addition of the third ligand is $1.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ (29). The medium and temperature effects on the dissociation rates of the bpy and phen complexes have been investigated by Basolo *et al.* (30).

Controlled Potential Coulometric (cpc) Measurements

The long term stability and current efficiency for the processes on cycling were investigated by controlled potential electrolysis techniques. The oxidation of Fe^{2+} in the uncomplexed form carried out at 0.2V past the anodic *cv* peak showed an n_{app} (faraday/mol) of 0.98-1.00. The current decayed smoothly to the background value and a plot of $\log i$ vs. t yielded a straight line (31) (Fig. 6). Reversal electrolysis, reduction of the electrogenerated Fe^{3+} , carried out at $\sim 0.10\text{V}$, consumed essentially the same number of coulombs as in the forward electrolysis. These experiments were carried out at concentrations up to 1M and electrolysis times of ~ 0.5 hr.

Oxidation of $\text{Fe}(\text{II})$ -complexes with bpy, phen, 2,9-dmp, and tp were carried out at 1.0V vs. SCE at a graphite electrode. In all cases the oxidations consumed 0.95-1.00 faraday/mol (see Table IV) and the current-time curve decayed smoothly to background. For electrolysis times ~ 1.0 hr, reversal electrolysis of the solution at 0.10V consumed about the same number of coulombs as the forward electrolysis. Repetitive electrolysis, cycling between the oxidized and reduced forms four times at 0.5 hr intervals produced similar results.

To examine the lifetime of the complex $\text{Fe}(\text{III})$ species, *cv* experiments were undertaken on solution following cpc oxidation. For ordinary cpc electrolysis of 30 min to 1 hr duration, *cv* showed reduction waves of height and location consistent with the presence of FeL_x^{3+} . However, when these solutions were allowed

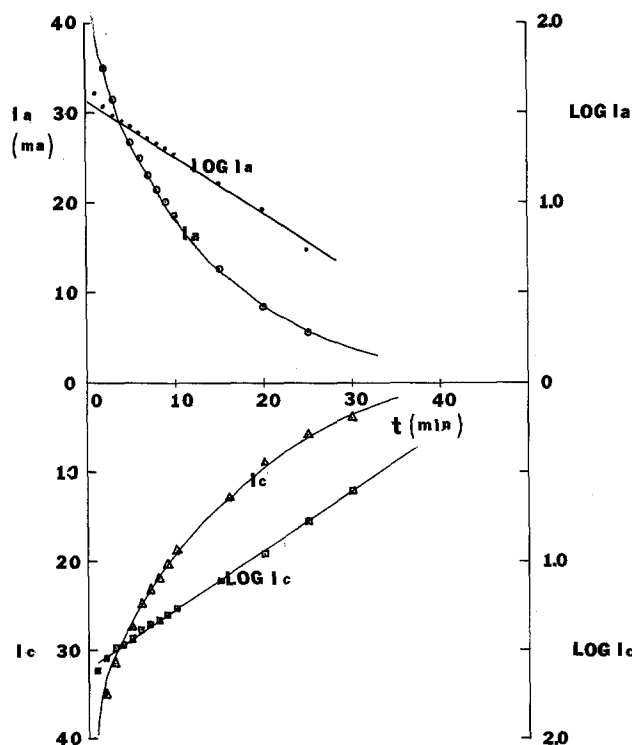


Fig. 6. Current-time curve during exhaustive electrolysis of 10 mM $\text{Fe}(\text{phen})_3^{2+}$ in aqueous H_2SO_4 at a graphite working electrode.

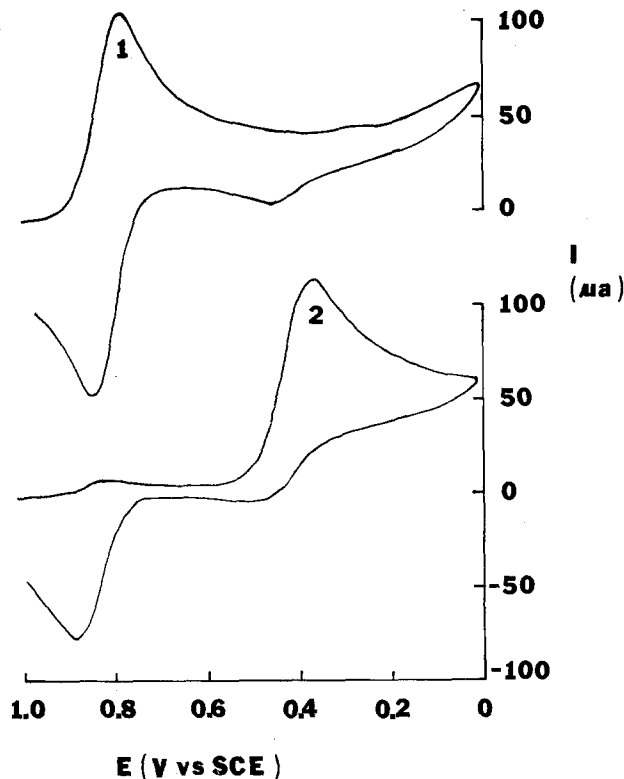


Fig. 7. Stability of $\text{Fe}(\text{phen})_3^{3+}$ in 1N H_2SO_4 . Upper curve: cyclic voltammogram for 10 mM $\text{Fe}(\text{phen})_3^{2+}$ immediately after controlled potential electrolysis at +1.0V at graphite electrode. Lower curve: cyclic voltammogram of the same solution after standing 24 hr in air.

to stand for times of 10-20 hr (Fig. 7), *cv* revealed that i_{pc} for FeL_x^{3+} reduction decreased and a wave for uncomplexed Fe^{3+} appeared. Thus a slow decomposition of the FeL_x^{3+} species ($L = \text{bpy}, \text{phen}, \text{mp}, 4,7\text{-dmp}$) does occur. The rate of decomposition of the FeL_x^{3+} was determined by spectrophotometry, as described below.

Stability of $\text{Fe}(\text{III})$ Species

Since the long duration storage capabilities of these systems appear limited by the stability of FeL_x^{3+} , measurements of the rate of decomposition of the $\text{Fe}(\text{III})$ species and some attempts at stabilization were carried out. The stability of $\text{Fe}(\text{III})$ complexes were examined spectrophotometrically. The $\text{Fe}(\text{III})$ complexes were formed by chemical oxidation by mixing millimolar concentrations of $\text{Fe}(\text{II})$ complexes and excess $\text{Ce}(\text{IV})$ sulfate in 0.5M H_2SO_4 and monitoring the disappearance of the $\text{Fe}(\text{III})$ complex absorption (32). The rate constants for the first-order decay of the FeL_x^{3+} species, k_t , are listed in Table V. Substitution of a methyl group on phen more than doubles the half-life with 4,7-dmp being the most stable of the complexes examined. The 2,9-dmp complex is very unstable, because in this case the placement of the methyl groups produces steric hindrance to bonding between the $\text{Fe}(\text{III})$ and the phenanthroline nitrogens.

The background medium also appears to play a role in the rate of decomposition of $\text{Fe}(\text{III})$ complexes. Thus $\text{Fe}(\text{phen})_3^{3+}$ is reported to be stable in high concentrations of H_2SO_4 (22, 23). We found, in bulk electrolysis experiments with the complexes, that the stability was decreased in H_2SO_4 solutions at a pH of ~ 1 , compared with 0.5M H_2SO_4 . The stability of $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ complexes has been studied previously (33, 34). The general conclusions are that the instability of the complex can be attributed to nucleophilic attack by water, resulting in replacement of the ligands by water molecule. The exact nature of

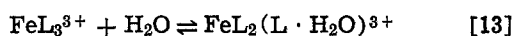
Table IV. Controlled potential electrolysis of ferrous ions*

Moles taken	Q _r ^o (C)	Moles of Fe ²⁺ (oxdn)	Q _b ^o (C)	Moles of Fe ²⁺ recovered (redn)	n _{app} [†] (faradays mol ⁻¹)
Free Fe ²⁺ ions					
0.061 × 10 ⁻³	6.39	0.066 × 10 ⁻³	6.08	6.3 × 10 ⁻⁵	1.08
0.061 × 10 ⁻³	6.64	0.068 × 10 ⁻³	6.28	6.5 × 10 ⁻⁵	1.10
1.19 × 10 ⁻³	114.5	1.18 × 10 ⁻³	109.1	1.13 × 10 ⁻³	0.99
3.00 × 10 ⁻³	285.3	2.96 × 10 ⁻³	265.0	2.75 × 10 ⁻³	0.98
3.00 × 10 ⁻³	288.6	2.99 × 10 ⁻³	269.2	2.78 × 10 ⁻³	0.99
1.50 × 10 ⁻³	1706.9	1.70 × 10 ⁻³	1470.0	1.52 × 10 ⁻³	1.10
3.00 × 10 ⁻³	2826.8	2.93 × 10 ⁻³	2830.0	2.93 × 10 ⁻³	0.98
Fe (phen) ₃ ²⁺					
4.67 × 10 ⁻⁴	42.77	4.43 × 10 ⁻⁴	45.20	4.68 × 10 ⁻⁴	0.95
4.67 × 10 ⁻⁴	43.57	4.51 × 10 ⁻⁴	41.00	4.24 × 10 ⁻⁴	0.97
1.07 × 10 ⁻³	104.10	1.07 × 10 ⁻³	92.00	0.95 × 10 ⁻³	1.00
Fe (2,9-dmp) ₃ ²⁺					
3.10 × 10 ⁻⁴	34.05	3.52 × 10 ⁻⁴	33.00	3.4 × 10 ⁻⁴	1.10
3.10 × 10 ⁻⁴	33.75	3.49 × 10 ⁻⁴	—	—	1.10
Fe (tp) ₃ ²⁺					
2.00 × 10 ⁻⁴	19.55	2.02 × 10 ⁻⁴	19.80	2.0 × 10 ⁻⁴	1.02
4.00 × 10 ⁻⁴	44.45	4.60 × 10 ⁻⁴	—	—	1.10

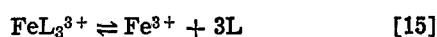
* Working electrode: graphite. Forward electrolysis was carried out at +1.0V and reverse electrolysis at 0.0V.

† Values for oxidation.

the intermediate complex is not clear. Some authors (35) favor the reaction sequence



In our studies we observed the formation of free Fe³⁺ in 0.5M H₂SO₄ from FeL₃³⁺ upon standing for long duration, even in the presence of excess ligand. This demonstrated that total replacement of the ligand by H₂O eventually occurs, i.e.



(where L = phen, bpy). When excess ligand is not present, a cathodic peak at +0.10V appears on standing, which might represent dimeric species such as a bridge complex formed (18) by the following reaction

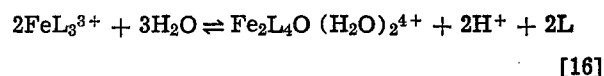


Table V. Cyclic voltammetric data on the bulk electrolysis products*

Sweep rate (V/sec)	E _{pa} (V)	i _{pa} (mA)	E _{pc} (V)	i _{pc} (mA)	Remarks
Unbound Fe ²⁺ Conc = 1M					
0.02	0.48	3.80	0.40	—	Before bulk electrolysis
0.05	0.48	5.20	0.40	—	Before bulk electrolysis
0.02	—	—	0.40	3.90	After electrolysis at +0.80V
0.05	—	—	0.40	5.60	After electrolysis at +0.80V
Reversal electrolysis at 0.0V					
0.02	0.48	3.80	0.40	—	
0.05	0.48	5.20	0.40	—	
Fe (phen) ₃ ²⁺ Conc = 20.0 mM					
0.02	0.86	0.14	0.80	0.14	
0.05	0.86	0.22	0.80	0.22	
0.02	—	—	0.80	0.14	After bulk electrolysis at +1.0V
0.05	—	—	0.80	0.22	After bulk electrolysis at +1.0V
Reversal electrolysis at +0.26V					
0.02	0.86	0.15	0.80	0.15	
0.05	0.86	0.23	0.80	0.23	
Fe (2,9-dmp) ₃ ²⁺ Conc = 20.0 mM					
0.02	0.80	0.11	0.12	0.03	Before bulk electrolysis
0.05	0.87	0.17	0.08	0.08	Before bulk electrolysis
0.02	—	—	0.10	0.11	After oxidation at +1.0V
0.05	—	—	0.08	0.17	After oxidation at +1.0V
After reversal electrolysis at 0.0V					
0.02	0.80	0.11	0.12	0.03	
0.05	0.87	0.17	0.08	0.08	

* Measurements were made at graphite electrode in the same medium used for controlled potential electrolysis.

Since attack by water causes decomposition of the Fe(III) species, blocking of the central metal ion by a hydrophobic environment or decreasing the water activity in the bulk solution may improve stability. Indeed the improved stability of the 4-mp and 4,7-dmp may partially represent such an effect, although the electron-donating properties of the methyl groups may also play a role. Attempts at providing a more hydrophobic environment were made by introducing various surface active agents and monitoring the concentration of the Fe(III) complex by cv. Results for the Fe(bpy)₃³⁺ complex are shown in Fig. 8 in 0.5M H₂SO₄ solutions containing butanol, heptanol, and the surfactant IGEPAL. Considerable improvement was noticed with 1-butanol in the medium. The abrupt changes in cyclic voltammetric peak current in the presence of a few surfactants (e.g., curve 8) occurs when phase separation takes place.

Electrolysis of Fe(II) complexes was also conducted in the presence of 1M AlCl₃ or 1M MgSO₄ or saturated solutions of Li₂SO₄. The decay of the Fe(III) complex concentration was noticed even in the presence of the above salts. When saturated solutions were used, the solutions became viscous and the

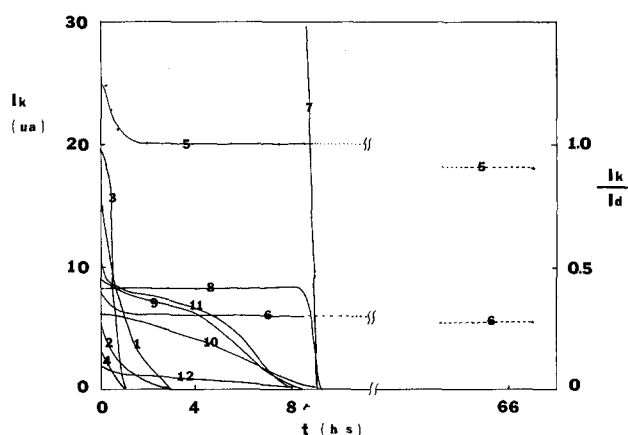


Fig. 8. The decay of Fe(III)-bpy complex in 1N H₂SO₄ in the presence of stabilizing agents. The Fe(III)-bpy complex was obtained by controlled potential electrolysis of Fe(II)-bpy complex. *i_k* = cyclic voltammetric peak current after controlled potential electrolysis (cathodic peak at +0.80V) *i_d* is the diffusional peak current. *i_k* = 1, 3, 5, 7, 9, and 11 and *i_k*/*i_d* = 2, 4, 6, 8, 10, and 12, *i_k* (*t* = 0) = 36 μA for line 7. 1, 2 = No stabilizer; 3, 4 = Texas-1 (excess); 5, 6 = 5 ml 1-butanol; 7, 8 = IGEPAL Co-430; 9, 10 = IGEPAL Co-530; 11, 12 = 1-heptanol.

duration of electrolysis was very long; with Li_2SO_4 saturated solution in 0.5M H_2SO_4 , electrolysis of 12.6 mmols $\text{Fe}(\text{phen})_3^{3+}$ took about 4 hr. At the end of electrolysis, a cathodic peak at 0.31V for free $\text{Fe}(\text{III})$ was observed in the cyclic voltammograms.

Discussion

Aquo $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ couple in 6N H_2SO_4 appears to be well suited as a redox positive couple for an extended period of time and appears to meet the major requirements of stability, solubility, fast electron exchange, and high electrical conductivity in the acid medium. A measurement of electron transfer rate constant in the 2N HCl medium was undertaken to compare it with H_2SO_4 medium. At platinum disk or graphite electrodes, an average of five measurements gave k^0 values of 1.9×10^{-3} and 1.34×10^{-3} cm/sec, respectively. These values are slightly smaller than the value obtained in H_2SO_4 (see Table I). However, a disadvantage of using HCl medium is the somewhat less positive background limiting potential value compared with H_2SO_4 (22). An advantage of H_2SO_4 medium over Cl for PEC cells is the lighter colors of the $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ species in this medium.

Complexation of $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ couple can provide higher E^0 -values [e.g., 1.07V for np compared to 0.53V (vs. SCE)] and faster electrode kinetics. The solubility of the complexes is approximately the same as uncomplexed $\text{Fe}(\text{II})$ or $\text{Fe}(\text{III})$. While the $\text{Fe}(\text{II})$ complexes are highly stable over days in the absence of O_2 , $\text{Fe}(\text{III})$ complexes decay in the medium employed by loss of ligand (see Fig. 7). This process results in loss of stored energy since the redox couple so produced is at a less positive potential. However, this loss is slightly compensated by the fast complexation of $\text{Fe}(\text{II})$ by ligand during a discharge cycle. Note that if the rate of complexation of $\text{Fe}(\text{II})$ were rapid enough, the $\text{Fe}(\text{III})$ reduction wave would shift to potentials near those for the oxidation of the complexed $\text{Fe}(\text{II})$ species.

Conclusions

The results here describe how coordination of the central metal ion can affect the potential and the kinetics of the electrode reaction to produce systems which might be utilizable in redox flow batteries. The aquo iron ($3+/2+$) system in H_2SO_4 appears to be an alternative to the iron ($3+/2+$) system in HCl media currently under investigation. Complexation with phenanthroline or bipyridyl-type ligands results in significant positive shifts in the potential of the redox couple. The solubility of these couples appears satisfactory, but instability of the ferric form results in partial loss of capacity upon long-term storage.

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