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 $E^\text{o}$ value which has been a positive consideration in the storage. Although the aquo iron (II)-iron (III) couple has an $E^\text{o}$ 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 over-all 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 photovoltaic (PEC) (or liquid junction photovoltaic) devices, or the reaction in [1]

\[ \text{O} + n\text{e} \rightarrow \text{R} \quad [1] \]

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, $E^\text{o}$, of one couple must be highly positive, and $E^\text{o}$ 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, $k^\circ$, 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(II), 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...
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 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 (tpi), 4-cyanopyridine (cp), and 2-pyridine carboxaldehyde-2-pyridyl hydrazine (p-cph) were obtained from J. T. Baker Company. FeSO$_4$·7H$_2$O was reagent grade (Matheson, Coleman and Bell). Surfactants IGEFA- CO$_{3}$H$_2$O (MW = 500) and 530 (MW = 484) were obtained from GAF Corporation (Atlanta, Georgia) and "Texas-1" (MW = 404) was made by Dr. Y. B. Youseff 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 and then distilled water.

**Apparatus.**—A Model 173 potentiosstat 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$_2$SO$_4$ prepared by suitable dilution of concentrated H$_2$SO$_4$. 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 ferric complexes were prepared either by electrochemical oxidation of the ferrous complexes or by Ce(IV) oxidation in H$_2$SO$_4$. Uncomplexed Fe(II) and Fe(III)-sulfate salts are quite soluble and yield solutions with metal ion concentrations ~1M. The solubility of the complexes vary with the nature of the ligand. The ligands themselves are soluble in acidic media to ~2M (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$_2$SO$_4$ are quite transparent in the visible region.

**Results**

To shift the potential of the half-reaction

$$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$$


and an excess of ligand in 0.5M H$_2$SO$_4$. The complex formed would precipitate at this initial ion concentration. The precipitate was then just dissolved in the solution by adding 0.5M H$_2$SO$_4$ 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$_2$SO$_4$. medium.

**SOLUTION REDOX COUPLES**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Solubility (g/100 ml)</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO$_4$·7H$_2$O</td>
<td>27.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe(phen)$_3$SO$_4$</td>
<td>44.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Fe(bpy)$_2$SO$_4$</td>
<td>45.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Fe(2,9-dmp)SO$_4$</td>
<td>37.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe(tp)SO$_4$</td>
<td>52.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Phenanthrolined</td>
<td>40.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Bipyridine</td>
<td>31.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Terepyridine</td>
<td>44.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4-Cyanopyridine</td>
<td>10.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Measured in 0.5M H$_2$SO$_4$. See experimental section for method.*
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$_2$SO$_4$, $D_{Fe^{2+}} = 2.5 \times 10^{-6}$ cm$^2$/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 $k_0$ 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$_2$SO$_4$, the cv wave showed $E_{pa} = 0.85$V and, on scan reversal, $E_{pc} = 0.79$V at $v = 50$ mV/sec. When $v$ increased, $\Delta E_p$ increased, and at $v = 50$ V/sec, $\Delta E_p = 0.90$V; $v = 100$ V/sec, $\Delta E_p = 0.10$V; $v = 200$ V/sec, $\Delta E_p = 0.12$V; $v = 500$ V/sec, $\Delta E_p = 0.18$V. These measurements were made with full ir compensation. From these values, an average value of $k_0 = 5.8 \times 10^{-2}$ cm$^2$/sec was obtained. With the Fe(II) coordination compounds only values for 0.5M H$_2$SO$_4$ are listed in Table II, since in 3M H$_2$SO$_4$ 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$_2$SO$_4$, yielding values of $1.6 \times 10^{-3}$ and $1.2 \times 10^{-2}$ cm$^2$/sec, respectively. Typical cv curves are shown in Fig. 2. The electrochemical oxidation of Fe(II) in aqueous H$_2$SO$_4$ 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$_2$SO$_4$).

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$_2^{2+}$. The observed cv behavior depends on the ligand, L, and the tendency of FeL$_2^{2+}$ 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

$$\text{FeL}_2^{2+} \rightarrow \text{FeL}_2^{3+} + e^- \quad [4]$$

$$k_f$$

$$\text{FeL}_2^{3+} \rightarrow \text{FeL}_2^{4+} + yL \quad [5]$$

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

<table>
<thead>
<tr>
<th>Ligands</th>
<th>$E^{\circ}$ (V vs. SCE)</th>
<th>$k_0$ (cm$^2$/sec)</th>
<th>$k_0$ (sec$^{-1} \times 10^5$)</th>
<th>$k_f$ (sec$^{-1} \times 10^4$)</th>
<th>$D$ (cm$^2$ sec$^{-1} \times 10^8$)</th>
<th>Abbreviation of ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquo</td>
<td>0.45</td>
<td>1.6 $\times 10^{-4}$</td>
<td>1.2 $\times 10^{-4}$</td>
<td>0.005</td>
<td>3.0</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>Bpyridine</td>
<td>0.82</td>
<td>5.6 $\times 10^{-4}$</td>
<td>3.0</td>
<td>1.22</td>
<td>1.07</td>
<td>bpy</td>
</tr>
<tr>
<td>o-Pyridylinaline</td>
<td>0.62</td>
<td>3.3 $\times 10^{-4}$</td>
<td>3.0</td>
<td>1.22</td>
<td>1.07</td>
<td>omp</td>
</tr>
<tr>
<td>4-Methyl-o-phenanthroline</td>
<td>0.73</td>
<td>4.9 $\times 10^{-4}$</td>
<td>3.0</td>
<td>1.22</td>
<td>1.07</td>
<td>phen</td>
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<tr>
<td>4,7-Dimethyl-o-phenanthroline</td>
<td>0.69</td>
<td>2.3 $\times 10^{-4}$</td>
<td>3.0</td>
<td>1.22</td>
<td>1.07</td>
<td>phen</td>
</tr>
<tr>
<td>2,6-Dimethyl-o-phenanthroline</td>
<td>0.82</td>
<td>0.6</td>
<td>0.6</td>
<td>1.00</td>
<td>4.5-dmp</td>
<td>phen</td>
</tr>
<tr>
<td>5-Chloro-o-phenanthroline</td>
<td>0.971</td>
<td>0.14</td>
<td>0.6</td>
<td>1.00</td>
<td>4.5-dmp</td>
<td>phen</td>
</tr>
<tr>
<td>3-Nitro-phenanthroline</td>
<td>1.079</td>
<td>0.9</td>
<td>0.6</td>
<td>1.00</td>
<td>4.5-dmp</td>
<td>phen</td>
</tr>
<tr>
<td>Terephridine</td>
<td>0.92</td>
<td>6.0 $\times 10^{-3}$</td>
<td>3.0</td>
<td>1.22</td>
<td>1.07</td>
<td>tp</td>
</tr>
<tr>
<td>2-Pyridinethaldehyde</td>
<td>0.72</td>
<td>&gt;0.6</td>
<td>0.6</td>
<td>1.00</td>
<td>4.5-dmp</td>
<td>p-phen</td>
</tr>
<tr>
<td>Tripyridinethaldehyde</td>
<td>1.24</td>
<td>&gt;0.6</td>
<td>0.6</td>
<td>1.00</td>
<td>4.5-dmp</td>
<td>p-phen</td>
</tr>
<tr>
<td>4-Cyanopyridine</td>
<td>0.62</td>
<td>&gt;0.6</td>
<td>0.6</td>
<td>1.00</td>
<td>4.5-dmp</td>
<td>cp</td>
</tr>
</tbody>
</table>

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* Medium 0.5M H$_2$SO$_4$ 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.

Fig. 2. (a) Cyclic voltammetric curve for the oxidation of 10 mM Fe$^{3+}$ in aqueous 3M H$_2$SO$_4$ working electrode: Graphite, reference electrode: aqueous saturated calomel electrode. $v = 0.50$ V/sec.

1. 20 mv/sec
2. 50 mv/sec
3. 100 mv/sec

E (V vs SCE)

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

E (V vs SCE)

Typical results for a solution containing 5 mM Fe$^{3+}$ and 300 mM phen in 0.5M H$_2$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$^{3+}$ oxidation following Fe$^{3+}$ reduction is barely detectable, while the Fe(phen)$_2^{3+}$ oxidation wave is fully developed. At higher sweep rates the oxidation increases and the Fe(phen)$_2^{3+}$ oxidation wave becomes relatively smaller. At very high sweep rates ($v = 100$ V/sec) only the Fe$^{3+}$ 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, $k'_r$ for Fe$^{3+}$ disappearance can be estimated from the ratio of $i_{pa}/i_{pc}$ for the 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 $k'_r$ are based on the free ligand concentration, [L], at the given H$_2$SO$_4$ concentration which is in equilibrium with the various protonated forms. The pK$_a$ values employed in calculation of [L] were:

- $k_{c}^{o}$ for Fe$^{3+}$ + e$^{-}$ $\rightarrow$ Fe$^{2+}$
- $k'_{r}$ for Fe$^{3+}$ + xL $\rightarrow$ FeL$_x^{2+}$
- $k_{p}$ for FeL$_x^{2+}$ $\rightarrow$ FeL$_{x+1}^{2+}$ + e

The rate of formation of the Fe(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 Fe(III) complex is thermodynamically unstable in 0.5M H$_2$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 Fe(II) occurs both as free Fe$^{3+}$ and as FeL$_x^{2+}$, i.e., the reaction sequence is:

[6] $k_{c}^{o}$

Fe$^{3+}$ + e$^{-}$ $\rightarrow$ Fe$^{2+}$

[7] $k'_{r}$

Fe$^{3+}$ + xL $\rightarrow$ FeL$_x^{2+}$

[8] $k_{p}$

FeL$_x^{2+}$ $\rightarrow$ FeL$_{x+1}^{2+}$ + e

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 $k'_{r}$ are based on the free ligand concentration, [L], at the given H$_2$SO$_4$ concentration which is in equilibrium with the various protonated forms. The pK$_a$ values employed in calculation of [L] were:
Table III. Electrochemical studies of complexation rate of Fe^{2+}: complexation with bipyridine, o-phenanthroline and tripyridine

<table>
<thead>
<tr>
<th>Sweep rate (V/sec)</th>
<th>f$<em>{ps}$/f$</em>{be}$</th>
<th>$r$ (sec)</th>
<th>$k_{app}$ (M$^{-1}$ sec$^{-1}$)</th>
<th>$k_{cat}$ (M$^{-1}$ sec$^{-1}$) x 10$^{-4}$</th>
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</thead>
<tbody>
<tr>
<td>Concentration of bipyridine: 0.3M</td>
<td></td>
<td></td>
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<tr>
<td>0.05</td>
<td>0.230</td>
<td>5.00</td>
<td>4.00</td>
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<tr>
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<td>0.375</td>
<td>4.00</td>
<td>3.51</td>
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<tr>
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<tr>
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<td>0.307</td>
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<td>0.31</td>
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<tr>
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<td>3.84</td>
<td>0.57</td>
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<td>0.341</td>
<td>2.00</td>
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<td>0.405</td>
<td>1.25</td>
<td>4.49</td>
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<td>0.20</td>
<td>0.539</td>
<td>1.00</td>
<td>3.63</td>
<td>0.25</td>
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<td>0.539</td>
<td>1.00</td>
<td>4.68</td>
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<td>0.619</td>
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<td>0.656</td>
<td>0.40</td>
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<td>Concentration of o-phenanthroline: 0.3M</td>
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<td>0.236</td>
<td>12.50</td>
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<td>0.05</td>
<td>0.474</td>
<td>5.00</td>
<td>0.94</td>
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<tr>
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<td>0.528</td>
<td>2.50</td>
<td>1.62</td>
<td>0.34</td>
</tr>
<tr>
<td>0.20</td>
<td>0.747</td>
<td>1.35</td>
<td>1.82</td>
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<tr>
<td>1.00</td>
<td>0.857</td>
<td>0.55</td>
<td>5.78</td>
<td>1.28</td>
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<td>Concentration of terpyridine: 0.02M</td>
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<tr>
<td>0.05</td>
<td>0.617</td>
<td>11.00</td>
<td>3.60</td>
<td>82.8</td>
</tr>
<tr>
<td>0.05</td>
<td>0.618</td>
<td>11.20</td>
<td>4.11</td>
<td>75.8</td>
</tr>
</tbody>
</table>

*Medium 0.5M H$_2$SO$_4$. Working electrode platinum. (Area = 0.14 cm$^2$). Adsorption of the organic on the electrode sometimes produced irreproducibility. Temperature of the solutions ~25°C. Concentration of Fe$^{2+}$ = 5.0 mM.

$\text{FeL}_2^{2+} + \text{L} \rightleftharpoons \text{FeL}_2^{2+}$ [10]

$\text{FeL}_2^{2+} + \text{L} \rightleftharpoons \text{FeL}_2^{2+}$ [11]

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$^{2+}$ reduction wave might be due to the onset of background reduction. The second oxidation wave (that of FeL$_2^{2+}$) and its corresponding reversal reduction wave might also be perturbed by the occurrence in homogeneous solution of the reaction

$\text{Fe}^{2+} + \text{FeL}_2^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{FeL}_3^{2+}$ [12]

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, $k'' = 2.2 \times 10^8$ M$^{-1}$ sec$^{-1}$ for L = bpy in 0.5M H$_2$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$^4$ M$^{-1}$ 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$_3^{2+}$ 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
rate constant of 2.8 × 10^4 M⁻¹ sec⁻¹ at 0.2°C was reported. This rate constant was assigned to the first step in the complexation formation of Fe(bpy)²⁺ (reaction [9]). The addition of the second and third bpy ligands is faster; for the third step the rate constant is 1.4 × 10^5 M⁻¹ sec⁻¹, while for phen the rate of addition of the third ligand is 1.5 × 10^6 M⁻¹ 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 Fe²⁺ in the uncomplexed form carried out at 0.2V past the anodic peak showed an napp (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 Fe³⁺, carried out at ~0.10V, 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 Fe(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 0.98-1.00 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 Fe(III) species, cpc 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 FeLx³⁺. However, when these solutions were allowed to stand for times of 10-20 hr (Fig. 7), cv revealed that for FeLx³⁺ reduction decreased and a wave for uncomplexed Fe³⁺ appeared. Thus a slow decomposition of the Fe₃⁺ species (L = bpy, phen, mp, 4,7-dmp) does occur. The rate of decomposition of the FeL₃³⁺ was determined by spectrophotometry, as described below.

**Stability of Fe(III) Species**

Since the long duration storage capabilities of these systems appear limited by the stability of FeL₃³⁺, measurements of the rate of decomposition of the Fe(III) species and some attempts at stabilization were carried out. The stability of Fe(III) complexes were examined spectrophotometrically. The Fe(III) complexes were formed by chemical oxidation by mixing millimolar concentrations of Fe(II) complexes and excess Ce(IV) sulfate in 0.5M H₂SO₄ and monitoring the disappearance of the Fe(III) complex absorption (32). The rate constants for the first-order decay of the FeL₃³⁺ species, kₐ, 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 Fe(III) and the phenanthroline nitrogens.

The background medium also appears to play a role in the rate of decomposition of Fe(III) complexes. Thus Fe(phen)₃³⁺ is reported to be stable in high concentrations of H₂SO₄ (22, 23). We found, in bulk electrolysis experiments with the complexes, that the stability was decreased in H₂SO₄ solutions at a pH of ~1, compared with 0.5M H₂SO₄. The stability of Fe(II) and Fe(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...
the intermediate complex is not clear. Some authors favor the reaction sequence

\[ \text{FeL}_2^{3+} + \text{H}_2\text{O} \rightarrow \text{FeL}_2(\text{L} \cdot \text{H}_2\text{O})^{3+} \]  

and

\[ \text{FeL}_2(\text{L} \cdot \text{H}_2\text{O})^{3+} \rightarrow \text{FeL}_2(\text{L} \cdot \text{OH})^{2+} + \text{H}^+ \]  

In our studies we observed the formation of free Fe\(^{3+}\) in 0.5M \(\text{H}_2\text{SO}_4\) from \(\text{FeL}_2^{3+}\) upon standing for long duration, even in the presence of excess ligand. This demonstrated that total replacement of the ligand by \(\text{H}_2\text{O}\) eventually occurs, i.e.

\[ \text{FeL}_2^{3+} \rightarrow \text{Fe}^{3+} + 3\text{L} \]  

(where \(\text{L} = \text{phen, bpy}\)). 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

\[ 2\text{FeL}_2^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{L}_4\text{O}(\text{H}_2\text{O})^{2+} + 2\text{H}^+ + 2\text{L} \]  

(16)

Table IV. Controlled potential electrolysis of ferrous ions

<table>
<thead>
<tr>
<th>Moles taken</th>
<th>(Q^+) (C)</th>
<th>(Q^{3+}) (oxdn)</th>
<th>(Q^-) (C)</th>
<th>(Q_{\text{recov}}) (redn)</th>
<th>(n_{\text{app}}) (faraday mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-4})</td>
<td>0.061</td>
<td>6.39</td>
<td>0.066</td>
<td>6.08</td>
<td>0.08</td>
</tr>
<tr>
<td>(10^{-5})</td>
<td>0.061</td>
<td>6.94</td>
<td>0.066 \times 10^{-5}</td>
<td>6.28</td>
<td>0.08</td>
</tr>
<tr>
<td>(10^{-6})</td>
<td>3.18</td>
<td>114.3</td>
<td>2.96 \times 10^{-4}</td>
<td>255.0</td>
<td>2.75 \times 10^{-4}</td>
</tr>
<tr>
<td>(10^{-7})</td>
<td>3.00</td>
<td>295.9</td>
<td>2.95 \times 10^{-4}</td>
<td>292.9</td>
<td>2.78 \times 10^{-4}</td>
</tr>
<tr>
<td>(10^{-8})</td>
<td>1.30</td>
<td>1706.3</td>
<td>1.70 \times 10^{-4}</td>
<td>1570.0</td>
<td>1.52 \times 10^{-4}</td>
</tr>
<tr>
<td>(10^{-9})</td>
<td>3.00</td>
<td>2823.8</td>
<td>2.93 \times 10^{-4}</td>
<td>2830.0</td>
<td>2.93 \times 10^{-4}</td>
</tr>
</tbody>
</table>

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

† Values for oxidation.

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)\(_3^{3+}\) complex are shown in Fig. 8 in 0.5M \(\text{H}_2\text{SO}_4\) solutions containing butanol, heptanol, and the surfactant IGEFAL. 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 \(\text{AlCl}_3\) or 1M \(\text{MgSO}_4\) or saturated solutions of \(\text{Li}_2\text{SO}_4\). 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...
duration of electrolysis was very long; with Li$_2$SO$_4$ saturated solution in 0.5M H$_2$SO$_4$, electrolysis of 12.6 mmols Fe(phen)$_3^{3+}$ took about 4 hr. At the end of electrolysis, a cathodic peak at 0.31V for free Fe(III) was observed in the cyclic voltammograms.

Discussion

Aquor Fe(II)/Fe(III) couple in 6N H$_2$SO$_4$ 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$_2$SO$_4$ medium. At platinum disk or graphite electrodes, an average of five measurements gave k values of 1.9 x 10^{-3} and 1.34 x 10^{-3} cm/sec, respectively. These values are slightly smaller than the value obtained in H$_2$SO$_4$ (see Table I). However, a disadvantage of using HCl medium is the somewhat less positive background limiting potential value compared with H$_2$SO$_4$ (22). An advantage of H$_2$SO$_4$ medium over CI for PEC cells is the lighter colors of the Fe(II) and Fe(III) species in this medium.

Complexation of Fe(II)/Fe(III) couple can provide higher Eo-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 Fe(II) or Fe(III). While the Fe(II) complexes are highly stable over days in the absence of O$_2$, Fe(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 Fe(II) by ligand during a discharge cycle. Note that if the rate of complexation of Fe(II) were rapid enough, the Fe(III) reduction wave would shift to potentials near those for the oxidation of the complexed Fe(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$_2$SO$_4$ 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.

Acknowledgment

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