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Alkali Metal Cation Effects in a Prussian Blue Surface-Modified Electrode

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Graphite electrodes were surface modified first by coating them in a glow discharge with iron pentacarbonyl (the resulting deposit called an iron-containing plasma deposit) or iron pentacarbonyl and ethane in a 1:1 molar ratio (the resulting deposit called an iron-containing plasma polymer) and then further surface modified by electrochemical reaction with hexacyanoferrate ion in water. This results in a Prussian blue surface modified electrode, which was characterized by cyclic voltammetry in dry propylene carbonate and in 1 vol % water/propylene carbonate containing K^+, Na^+, or Li^+ electrolyte cations. Depending on the potential of the electrode, the surface adherent iron hexacyanoferrate is present as Berlin green, $[KFe^{3+}Fe^{II}(CN)_6]_{1/2}[Fe^{3+}Fe^{III}(CN)_6]_{1/2}$, "soluble" Prussian blue, $KFe^{3+}Fe^{II}(CN)_6$, or Everitt's salt, $K_2Fe^{2+}Fe^{II}(CN)_6$, when K^+ is the cation of the bulk electrolyte. When Na^+ or Li^+ salts are used as the background electrolyte, the electrode surface bound iron hexacyanoferrate changes from the totally oxidized species $Fe^{3+}Fe^{III}(CN)_6$ to Everitt's salt, $M_2Fe^{2+}Fe^{II}(CN)_6$, with one or two intermediate redox processes. The redox potentials for these processes are influenced by the alkali-metal countercation. The dependence of peak currents on scan rates suggests that the electrode redox processes are kinetically controlled by electrolyte cation migration in and out of the surface-bound Prussian blue lattice. Adherence of the surface-bound Prussian blue is remarkable in a 1 vol % water/propylene carbonate solution. No decrease in peak current signals was observed after 9 days of continuous redox cycling using an iron-containing plasma deposit Prussian blue surface modified electrode. A unique characteristic of this Prussian blue surface modified electrode is that it is permeable to K^+, Na^+, and Li^+ cations and exhibits a selectivity sequence in dry propylene carbonate or a 1 vol % water/propylene carbonate solution in the order $K^+ > Na^+ > Li^+$. It is presumed that these alkali-metal countercations occupy interstitial cavities in the cubic Prussian blue lattice. Results are presented which suggest that the hydrated cation enters these cavities and not the naked cation when the solvent is 1 vol % water/propylene carbonate or 100% water. However, when the solvent is dry propylene carbonate, the naked cation enters the Prussian blue lattice and not the solvated cation. Results obtained from experiments using the Li^+ cation in propylene carbonate and water/propylene carbonate mixtures suggest that the countercation lattice sites associated with the low-spin Fe(III/II) redox couple are chemically distinguishable from those associated with the high-spin Fe(3+/2+) redox couple.

Introduction

The study of methods for modifying the surface of an electrode has received considerable attention recently.[2] In our laboratories we are investigating the use of metalated plasma polymers and plasma deposits as an electrode surface modification technique. We have surface modified graphite electrodes by depositing a thin film resulting from the plasma polymerization of $Fe(CO)_5$ and C_2H_6 as comonomers, and $Fe(CO)_5$ alone, directly on the electrode surface. These films serve as suitable anchoring sites for electrochemically generated Prussian blue (ferric ferrocyanide) to produce a surface-modified electrode, which may be oxidized and reduced in neutral aqueous solution to Berlin green (ferric ferricyanide) and Everitt's salt (ferrous ferrocyanide), respectively.[3]

Since the time of discovery of Prussian blue by Diesbach in 1704[4] several studies have been made of the structure and chemistry of this insoluble mixed-valence iron compound.[5-7] Despite this long interest, it was not until 1978 that a report of the electrochemistry of Prussian blue was made.[8a] Since then several reports concerning the electrochemical properties of Prussian blue[3,8-11] and related compounds[8c,12-14] have ap-

peared. Prussian blue is a mixed-valence species with high-spin iron(3+)[15] ligated by six N atoms and low-spin iron(II)[15] ligated by six carbon atoms of cyanide and formulated as ferric ferrocyanide.[5,7] In situ Mössbauer measurements[10d] have conclusively shown that the reduction of Prussian blue to Everitt's salt (or Prussian white) proceeds via the reduction of high-spin iron(3+) to iron(2+). Interest in Prussian blue and related surface modified electrodes originates partly from their potential application as electrochromic devices, electrocatalysts, and cathode materials for batteries, in chemical analysis, and in ion exchange.

In this report we have extended our initial work on Prussian blue surface modified electrodes in neutral aqueous medium to propylene carbonate solvent and to a 1 vol % water/propylene carbonate mixture. We have studied the effects of the electrolyte cation and cation solvation on the electrochemistry of electrode surface bound Prussian blue. Results obtained suggest that the hydrated cations enter the interstitial cavities of the surface-bound Prussian blue and that these

(1) (a) Duke University. (b) Research Triangle Institute.
(2) See for example: (a) Calvert, J. M.; Schemehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* 1983, 22, 2151 and references therein. (b) Doblhofer, K.; Dürr, W.; Jauch, M. *Electrochim. Acta* 1982, 27, 677 and references therein. (c) Ryan, M. D.; Wilson, G. S. *Anal. Chem.* 1982, 54, 20R. (d) Murray, R. W. *Acc. Chem. Res.* 1980, 13, 135. (e) Snell, K. D.; Kennan, A. G. *Chem. Soc. Rev.* 1979, 8, 259.
(3) Crumbliss, A. L.; Lugg, P. S.; Patel, D. L.; Morosoff, N. *Inorg. Chem.* 1983, 22, 3541.
(4) Kaufman, G. B. "Inorganic Coordination Compounds: Nobel Prize Topics in Chemistry"; Heyden: Philadelphia, 1981; Chapter 4.
(5) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* 1967, 10, 247.
(6) Ludi, A.; Güdel, H. W. *Struct. Bonding (Berlin)* 1973, 14, 1.
(7) Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: New York, 1976; pp 121–126.
(8) (a) Neff, V. D. *J. Electrochem. Soc.* 1978, 125, 886. (b) Ellis, D.; Eckhoff, M.; Neff, V. D. *J. Phys. Chem.* 1981, 85, 1225. (c) Rajan, K. P.; Neff, V. D. *J. Phys. Chem.* 1982, 86, 4361.

(9) (a) Kellawi, H.; Rosseinsky, D. R. *J. Electroanal. Chem. Interfacial Electrochem.* 1982, 131, 373. (b) Mortimer, R. J.; Rosseinsky, D. R. *J. Electroanal. Chem. Interfacial Electrochem.* 1983, 151, 133. (c) Goncalves, R. M. C.; Kellawi, H.; Rosseinsky, D. R. *J. Chem. Soc., Dalton Trans.* 1974, 991.
(10) (a) Itaya, K.; Akahoshi, H.; Toshima, S. *J. Electrochem. Soc.* 1982, 129, 1498. (b) Itaya, K.; Shibayama, K.; Akahoshi, H.; Toshima, S. *J. Appl. Phys.* 1982, 53, 804. (c) Itaya, K.; Ataka, T.; Toshima, S. *J. Am. Chem. Soc.* 1982, 104, 4767. (d) Itaya, K.; Ataka, T.; Toshima, S.; Shinohara, T. *J. Phys. Chem.* 1982, 86, 2415.
(11) Messina, R.; Perichon, J. *J. Appl. Electrochem.* 1980, 10, 655.
(12) Itaya, K.; Ataka, T.; Toshima, S. *J. Am. Chem. Soc.* 1982, 104, 3571.
(13) (a) Bocarsly, A. B.; Sinha, S. *J. Electroanal. Chem. Interfacial Electrochem.* 1982, 137, 157. (b) Bocarsly, A. B.; Sinha, S. *J. Electroanal. Chem. Interfacial Electrochem.* 1982, 140, 167. (c) Sinha, S.; Humphrey, B. D.; Fu, E.; Bocarsly, A. B. *J. Electroanal. Chem. Interfacial Electrochem.* 1984, 162, 351. (d) Sinha, S.; Humphrey, B. D.; Bocarsly, A. B. *Inorg. Chem.* 1984, 23, 203. (e) Humphrey, B. D.; Sinha, S.; Bocarsly, A. B. *J. Phys. Chem.* 1984, 88, 736.
(14) Siperko, L. M.; Kuwana, T. *J. Electrochem. Soc.* 1983, 130, 396.
(15) Arabic numerals are used to designate the oxidation state of the high-spin iron cations and Roman numerals that of the low-spin iron.

lattice sites which are associated with the high-spin and low-spin iron redox couples are chemically nonequivalent.

Experimental Section

Materials. Ethane was obtained from Airco, Inc., and used without purification. Iron pentacarbonyl was obtained from Aldrich Chemical Co., stored as received at -78 °C, and warmed to 0 °C during plasma polymerizations. $Na_3Fe(CN)_6$ and $Li_4Fe(CN)_6$ were obtained from Pfaltz and Bauer, and $K_3Fe(CN)_6$ was purchased from Fisher. Lithium, sodium, and potassium perchlorates (RIC/ROC, B & A) and nitrates (Fisher) were recrystallized from water/acetone (85%/15%) prior to use. Potassium hexafluorophosphate was obtained from Aldrich. Propylene carbonate was obtained from Aldrich, distilled under vacuum, and stored over molecular sieves. Carbon rods (0.3 cm × 3.8 cm) used for plasma polymer deposition and cyclic voltammetric measurements were obtained from Ultracarbon (Ultra F purity) and extracted with hot CH_3CN for 18 h prior to use. Contrary to our previous report,[3] the graphite electrodes were abraded with optical polish and felt cloth prior to use in order to rid the surface of loose carbon. Although there was a small increase in longevity of the surface-bound Prussian blue, no significant differences in behavior were observed between the polished and unpolished electrodes.

Methods. Electrode surface modification was carried out by plasma polymerization of a $Fe(CO)_5/C_2H_6$ mixture (iron-containing plasma polymer) or $Fe(CO)_5$ alone (iron-containing plasma deposit) in an inductively coupled cylindrical reactor[16] containing the graphite electrode. The conditions for plasma polymerization and reactor configuration were as previously reported.[3] Except for tenacity of Prussian blue adherence to the electrode, no difference was observed between the iron-containing plasma polymer and iron-containing plasma deposit surface modified electrodes. Data shown in the figures were obtained with the iron-containing plasma deposit surface modified electrodes. Since the graphite electrode surface is rough, the coating is discontinuous and it is not possible to determine the actual thickness of the plasma film electrode coating. However, a nominal loading may be calculated (on the basis of the assumption that the surface is smooth) and regulated by controlling the exposure time to the plasma. Nominal loadings for the iron-containing plasma polymer or plasma deposit used in this work are 10–25 $\mu g/cm^2$. Characterization of the iron-containing plasma polymer and iron-containing plasma deposit is described elsewhere.[17,18] The physical and chemical characteristics of the iron-containing plasma polymer and iron-containing plasma deposit are entirely reproducible with use of controlled preparative conditions. At the plasma polymerization conditions used for this study, both the iron-containing plasma polymer and iron-containing plasma deposit contain both high-spin iron(III) present as Fe_2O_3 (particle size <30 Å) and high-spin iron(III) bound in a carboxylate and/or β-diketonate coordination environment.

Cyclic voltammetry was performed with a Bioanalytical Systems CV-1B triangular wave generator, a Ag/AgCl reference electrode, Pt auxiliary electrode, and iron-containing plasma polymer or plasma deposit surface modified working electrode in propylene carbonate with an appropriate electrolyte. Cyclic voltammograms were recorded with a Houston Instruments Model 100 x-y recorder. The potential measured midway between the cathodic and anodic peak potentials (E_{pc}, E_{pa}) is referred to as E_{av} and is reported relative to the Ag/AgCl reference electrode. No correction for junction potentials was made. For purposes of comparison, the $Fe(C_5H_5)_2/Fe(C_5H_5)_2^+$ couple exhibits E_{av} at 0.37 V in our cell with use of either dry propylene carbonate or 1 vol % water/propylene carbonate and 0.1 M $KClO_4$ as the electrolyte. In all experiments 0.54 cm^2 of the working electrode surface was exposed to the electrolyte solution.

Two methods for depositing iron hexacyanoferrate on the iron-containing plasma polymer or iron-containing plasma deposit modified electrode surface were used. Method I utilized a one-cell three-electrode (surface-modified working electrode, Ag/AgCl reference electrode, Pt auxiliary electrode) system. A potential of 0.0 V applied to the working electrode in aqueous 5 mM $M_3Fe(CN)_6$ (M = K^+ or Na^+) solution (0.1 M electrolyte) resulted in a 1.6-V potential at the auxiliary electrode, which caused a decomposition of some of the

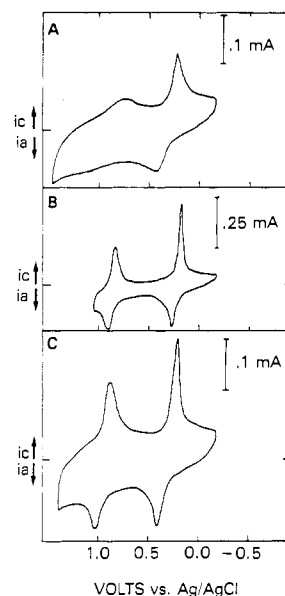**Figure 1.** Cyclic voltammograms for a Prussian blue surface modified electrode prepared according to method I (0.1 M KNO_3 and 5 mM $K_3Fe(CN)_6$, scan rate 10 mV/s: (A) in dry propylene carbonate (0.1 M KPF_6); (B) in water (0.1 M KNO_3); (C) in 1 vol % water/propylene carbonate (0.1 M KPF_6).

$Fe(CN)_6^{3-}$.[19] This solution was stirred for 2.25 h, which resulted in a deposition of Everitt's salt onto the working electrode surface. The working electrode was then converted to Berlin green by holding the potential at 1.14 V in the appropriate aqueous electrolyte until there was no current flowing, removed, vacuum-dried, and examined by cyclic voltammetry in propylene carbonate. In order to deposit Everitt's salt onto an iron-containing plasma polymer or plasma deposit surface modified graphite electrode from an aqueous 5 mM solution of $M_4Fe(CN)_6$ (M = K^+, Na^+, or Li^+), method II is used. This is because a potential of 0.0 V applied to this solution does not produce a sufficiently positive potential at the auxiliary electrode to cause decomposition of $Fe(CN)_6^{3-/4-}$.[19] However, $Fe(CN)_6^{3-/4-}$ can be directly oxidized at a potential of 1.6 V, thus forming the required solution of iron hexacyanoferrate. Method II utilized a two-cell three-electrode system in which the working and auxiliary electrodes were isolated with use of an agar salt bridge. A Pt working electrode was held at 1.6 V in an aqueous 5 mM $Li_4Fe(CN)_6$ solution (0.1 M $LiNO_3$ electrolyte) for 2.25 h with stirring. This oxidized solution was used in accordance with method I (Li^+ electrolyte cation) to coat a plasma polymer or plasma deposit surface modified electrode with Everitt's salt. The electrode was removed from the solution, vacuum-dried, and examined by cyclic voltammetry in propylene carbonate containing 0.1 M $LiClO_4$.

Results

Neither the iron-containing plasma polymer or iron-containing plasma deposit coated graphite electrode exhibits any redox signals when cyclic voltammograms are obtained in propylene carbonate with K^+, Na^+, or Li^+ perchlorates as the electrolyte (scanning at 10 mV/s from $+1.4$ to -1.25 V). An identically treated electrode cycled in aqueous KNO_3 or $NaNO_3$ reveals a broad cathodic wave at -1.0 V and a weak-intensity anodic wave at -0.55 V.[3]

Method I (Experimental Section) was used to prepare an iron hexacyanoferrate surface modified electrode in the Everitt's salt form, $K_2FeFe(CN)_6$. After the film was converted to Berlin green, the electrode was vacuum-dried and cycled in dry propylene carbonate containing 0.1 M KPF_6 (no hexacyanoferrate) to obtain a cyclic voltammogram as shown in Figure 1A. The redox signals are very broad and weak compared to those in the cyclic voltammogram obtained with use of the same electrode in aqueous KNO_3 (Figure 1B). It

(16) Yasuda, H.; Lamaze, C. E. *J. Appl. Polym. Sci.* **1973**, *17*, 1519.
(17) Morosoff, N.; Patel, D. L.; Lugg, P. S.; Crumbliss, A. L. *J. Appl. Polym. Sci.*: *Appl. Polym. Symp.* **1984**, *38*, 83.
(18) Morosoff, N.; Patel, D. L.; White, A. R.; Umana, M.; Crumbliss, A. L.; Lugg, P. S.; Brown, D. B. *Thin Solid Films* **1984**, *117*, 33.

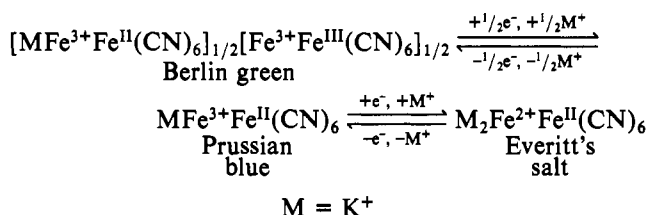(19) Dewet, J. F.; Rolle, R. *Z. Anorg. Allg. Chem.* **1965**, *96*, 336.

Table I. E_{av} Values for Prussian Blue Surface Modified Electrodes

| solvent[a] | electrolyte cation | E_{av},[b] V | | ΔE_{av},[c] V |
		Fe-(III/II)	Fe-(3+/2+)	
H_2O	K	0.89	0.21	0.68
pc/H_2O	K	0.96	0.34	0.62
H_2O	Na	1.06	0.0	1.06
pc/H_2O	Na	1.20	0.11	1.09
H_2O	Li	d	d	
pc/H_2O	Li	1.05	-0.09	1.14

[a] Legend: H_2O, pure H_2O, data from ref 3; pc/H_2O, 1 vol % H_2O in propylene carbonate. [b] E_{av} values determined as described in the Experimental Section expressed relative to the Ag/AgCl reference electrode for low-spin, Fe(III/II), and high-spin, Fe(3+/2+), redox couples. [c] Difference between columns 3 and 4. [d] Not observed; see text.

was found that the resolution of the cyclic voltammogram shown in Figure 1A (propylene carbonate, 0.1 M KPF_6) can be enhanced by adding 1 vol % water, as shown in Figure 1C.[20] This cyclic voltammogram persists unchanged for the duration of the observation time (several hundred cycles; see below). The E_{av} values in 1 vol % water/propylene carbonate are 0.96 and 0.34 V; see Table I. The potential difference between the first and second redox couples is approximately the same as in pure water; see Table I. Integration of the cathodic waves shows a ratio of ca. 0.5 (peak area at 0.96 V/peak area at 0.34 V). With these data we present in Scheme I the stoichiometry for the transformations of the electrode surface bound iron hexacyanoferrate in 1 vol % water/propylene carbonate containing 0.1 M KPF_6.

Scheme I[15]

$$[MFe^{3+}Fe^{II}(CN)_6]_{1/2}[Fe^{3+}Fe^{III}(CN)_6]_{1/2} \underset{-1/2e^-, -1/2M^+}{\overset{+1/2e^-, +1/2M^+}{\rightleftharpoons}}$$
$$\text{Berlin green}$$

$$MFe^{3+}Fe^{II}(CN)_6 \underset{-e^-, -M^+}{\overset{+e^-, +M^+}{\rightleftharpoons}} M_2Fe^{2+}Fe^{II}(CN)_6$$
$$\text{Prussian} \qquad\qquad\qquad \text{Everitt's}$$
$$\text{blue} \qquad\qquad\qquad\qquad \text{salt}$$

$$M = K^+$$

Scheme I is consistent with our previous observations in 100% aqueous medium.[3] The reduction of low-spin iron(III) occurs at $E_{av} = 0.96$ V (Berlin green $\rightleftharpoons$ Prussian blue), and the reduction of high-spin iron(3+) occurs at $E_{av} = 0.34$ V (Prussian blue $\rightleftharpoons$ Everitt's salt). Of particular importance are the formulas for Berlin green and Prussian blue. Prussian blue is formulated as the "soluble" form, $KFe^{3+}Fe^{II}(CN)_6$, rather than the "insoluble" form, $Fe^{3+}_4[Fe^{II}(CN)_6]_3$,[7] on the basis of the presence of cation effects (see below), the absence of any effect observed for PF_6^-, ClO_4^-, NO_3^-, or Cl^- anions, and the stoichiometry of electron transfer. Photothermal spectroscopic measurements (UV–vis and FTIR) of the electrode surface obtained after various potentials ($E > 0.96$ V; 0.96 V $> E > 0.34$ V; $E < 0.34$ V) have been applied to the Prussian blue surface modified electrode are consistent with the formulas presented in Scheme I.[21,22]

Role of the Electrolyte Cations. Method I was also used with $Na_3Fe(CN)_6$ in aqueous $NaNO_3$ to prepare an iron hexacyanoferrate surface modified electrode in the Everitt's

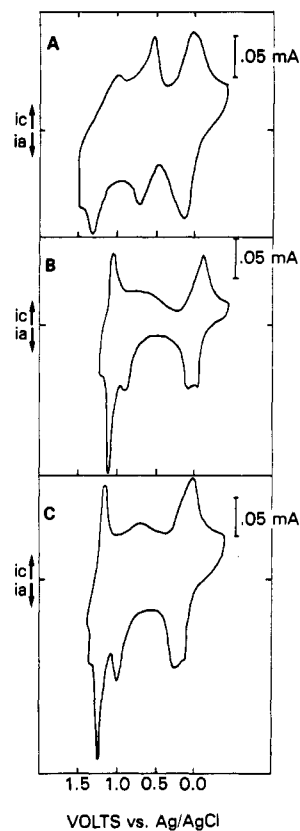**Figure 2.** Cyclic voltammograms for a Prussian blue surface modified electrode prepared according to method I (0.1 M $NaNO_3$ and 5 mM $Na_3Fe(CN)_6$), scan rate 10 mV/s: (A) in dry propylene carbonate (0.1 M $NaClO_4$); (B) in water (0.1 M $NaNO_3$); (C) in 2 vol % water/propylene carbonate (0.1 M $NaClO_4$).
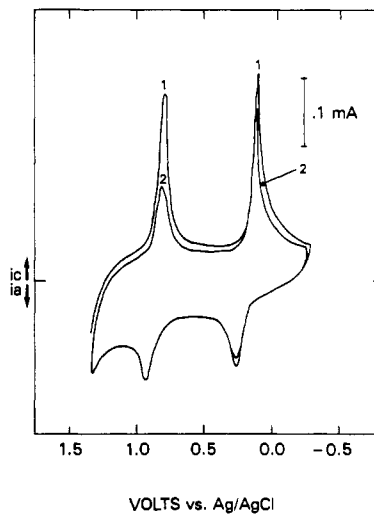

Figure 3. Cyclic voltammogram obtained with use of the working electrode from Figure 2A, which was removed from solution at 1.4 V, rinsed, and cycled in aqueous 0.1 M KNO_3. Cycle 2 was the same as each successive cycle (scan rate 10 mV/s).[24]

salt form with a Na^+ countercation, $Na_2FeFe(CN)_6$.[23] After the film was converted to Berlin green (Experimental Section), the electrode was dried and cycled in dry propylene carbonate containing 0.1 M $NaClO_4$ from +1.38 to –0.53 V at 10 mV/s. A representative voltammogram that persists unchanged for

(20) This system of 1 vol % water/propylene carbonate has a ratio of approximately 6:1 water molecules to K^+ cations. The results obtained with KPF_6 can be duplicated with $KClO_4$ even though the concentration of $KClO_4$ is <0.1 M in propylene carbonate due to the poor solubility of $KClO_4$ in this solvent.

(21) Childers, J. W.; Crumbliss, A. L.; Lugg, P. S.; Palmer, R. A.; Morosoff, N.; Patel, D. L. *J. Phys., Colloq. (Orsay, Fr.)* **1983**, *44*, C6-285.
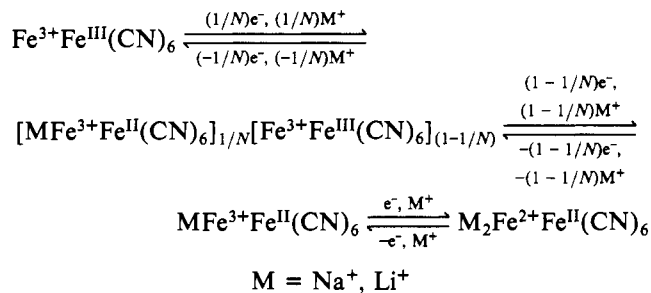
(22) Crumbliss, A. L.; Lugg, P. S.; Childers, J. W.; Palmer, R. A. *J. Phys. Chem.*, in press.

(23) It is necessary that the electrodes be prepared with use of method I with Na^+ as the counterion in order to obtain cyclic voltammograms as shown in Figure 2. Electrodes prepared with use of method I and K^+ as the counterion give more complex voltammograms when cycled in a solution containing Na^+.

the duration of the observation time (several hundred cycles; see below) is shown in Figure 2A. Three broad redox couples are apparent at E_{av} = 1.1, 0.61, and 0.07 V with corresponding cathodic and anodic peak areas in the ratio of 0.3:0.4:1. The shapes and the potentials of the redox couples in propylene carbonate containing Na^+ (Figure 2A) differ considerably from those observed for the same electrode cycled in aqueous Na^+ (Figure 2B). The electrode was removed from propylene carbonate solution (0.1 M $NaClO_4$) at 1.4 V and cycled in aqueous KNO_3 to obtain the cyclic voltammogram shown in Figure 3. On the first cycle the integrated cathodic peak currents for the low- and high-spin redox couples are in the ratio of ca. 1:1. For each successive cycle the voltammogram exhibits the characteristic signature for surface-bound Prussian blue in aqueous KNO_3, in which the ratio of the low-spin to high-spin integrated cathodic peak currents is ca. 0.5:1.[24]

It was found that by adding 2 vol % water to the system containing propylene carbonate and 0.1 M $NaClO_4$ (Figure 2A) a new cyclic voltammogram that persisted for several hundred cycles (see below) was exhibited as shown in Figure 2C. The striking similarity between Figure 2B (aqueous solution containing 0.1 M $NaNO_3$) and Figure 2C (propylene carbonate solution containing 2 vol % H_2O and 0.1 M $NaClO_4$) should be noted. The E_{av} values for the two extreme redox couples in Figure 2C are 1.2 and 0.11 V, with relative integrated peak areas in the ratio ca. 0.5:1, respectively; see Table I. There is also an ill-defined couple that occurs at ~0.75 V in the 2 vol % water/propylene carbonate system (Figure 2C) as well as the aqueous system (Figure 2B). Scheme II is proposed for the redox processes that take place in propylene carbonate, water/propylene carbonate, and aqueous solutions with the Prussian blue surface modified electrode and Na^+ as the countercation.

Scheme II[15]

$$Fe^{3+}Fe^{III}(CN)_6 \underset{(-1/N)e^-, \, (-1/N)M^+}{\overset{(1/N)e^-, \, (1/N)M^+}{\rightleftharpoons}}$$

$$[MFe^{3+}Fe^{II}(CN)_6]_{1/N}[Fe^{3+}Fe^{III}(CN)_6]_{(1-1/N)} \underset{-(1-1/N)e^-, \atop -(1-1/N)M^+}{\overset{(1-1/N)e^-, \atop (1-1/N)M^+}{\rightleftharpoons}}$$

$$MFe^{3+}Fe^{II}(CN)_6 \underset{-e^-, \, M^+}{\overset{e^-, \, M^+}{\rightleftharpoons}} M_2Fe^{2+}Fe^{II}(CN)_6$$

$$M = Na^+, Li^+$$

Parts A and B of Figure 4 are plots showing the linear relationship between peak current and the square root of the scan rate in 1 vol % water/propylene carbonate containing Na^+ or K^+ as the electrolyte cation.[25] This is consistent with results obtained in aqueous solution[3] and may be interpreted that the electrode redox kinetics are influenced by diffusion of the Na^+ or K^+ counterion through the surface bound iron hexacyanoferrate lattice.[26] The separation between cathodic and anodic peak currents (i_c, i_a) decreases from 800 to 90 mV on decreasing the scan rate from 150 to 2 mV/s for propylene carbonate containing either Na^+ or K^+ as the electrolyte cation.

An electrode prepared by method I with use of $Na_3Fe(CN)_6$ and $NaNO_3$ and then cycled in dry propylene carbonate

(24) Prussian blue surface modified electrodes prepared from $Na_3Fe(CN)_6$ and $NaNO_3$ and then cycled in aqueous $NaNO_3$, removed from solution at 1.2 V, and then cycled in aqueous KNO_3 shows a voltammogram identical with that shown in Figure 3.

(25) Electrodes prepared with use of method I and then cycled in *dry* propylene carbonate gave cyclic voltammograms with poor resolution even at slow scan rates (10 mV/s); therefore, peak currents were not measured as a function of the scan rate.

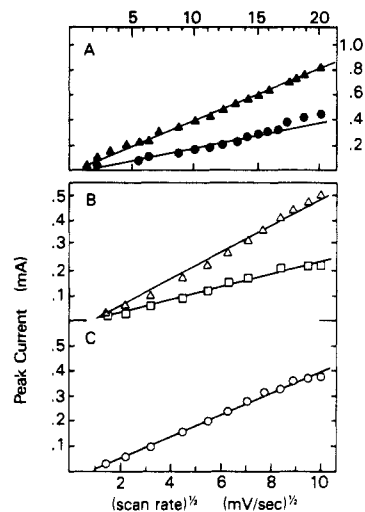(26) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980.

Figure 4. Plots of cathodic peak currents vs. square root of the scan rate in 1 vol % water/propylene carbonate containing (A) 0.1 M $KClO_4$ ((▲) $Fe^{3+/2+}$ redox, (●) $Fe^{III/II}$ redox), (B) 0.1 M $NaClO_4$ ((△) $Fe^{3+/2+}$ redox, (□) $Fe^{III/II}$ redox), and (C) 0.1 M $LiClO_4$ ((○) $Fe^{3+/2+}$ redox).

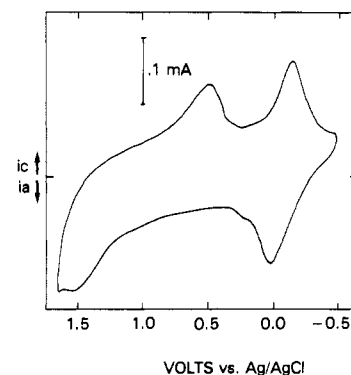**Figure 5.** Cyclic voltammogram of Prussian blue surface modified electrode prepared according to method I ($NaNO_3$ and $Na_3Fe(CN)_6$) in dry propylene carbonate (0.1 M $LiClO_4$; scan rate 10 mV/s).
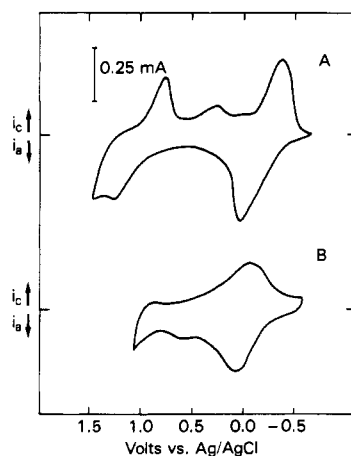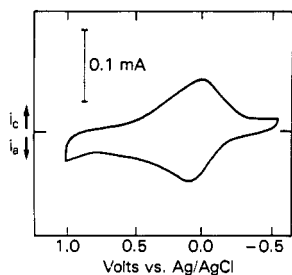

Figure 6. Cyclic voltammogram obtained in 1 vol % water/propylene carbonate (0.1 M $LiClO_4$) with a Prussian blue surface modified working electrode prepared according to method I (0.1 M KNO_3 and $K_3Fe(CN)_6$): (A) cycle 1 at 10 mV/s; (B) cycle 626 at 10 mV/s.

containing 0.1 M $LiClO_4$ exhibits the characteristic cyclic voltammogram shown in Figure 5. Repeated cycling of this electrode results in only a small loss (10%) of the original signal intensity after 2000 cycles. When this electrode is removed from the solution at 1.4 V, and then cycled in aqueous KNO_3, the ratio of the cathodic currents for the two peaks is ca. 1:1 on the first sweep and ca. 0.5:1 on repeated cycles. This is

Figure 7. Cyclic voltammogram obtained in 1 vol % water/propylene carbonate (0.1 M LiClO$_4$) with a Prussian blue surface modified working electrode prepared according to method II (0.1 M LiNO$_3$ and Li$_4$Fe(CN)$_6$), scan rate 10 mV/s.

Figure 8. Cyclic voltammogram obtained in 1 vol % water/propylene carbonate (0.1 M KClO$_4$) with a Prussian blue surface modified working electrode prepared according to method II (0.1 M LiNO$_3$ and Li$_4$Fe(CN)$_6$), scan rate 10 mV/s.

Figure 9. Cyclic voltammogram obtained in 1 vol % water/propylene carbonate (0.05 M KClO$_4$ and 0.05 M NaClO$_4$) with a Prussian blue surface modified working electrode prepared according to method I (0.1 KNO$_3$ and K$_3$Fe(CN)$_6$), scan rate 10 mV/s.

the same as is observed when Na$^+$ (rather than Li$^+$) is the countercation as shown in Figure 3.

When a propylene carbonate solution containing 1 vol % H$_2$O and 0.1 M LiClO$_4$ is used with a Prussian blue surface modified electrode prepared according to method I (0.1 M KNO$_3$ and 5 mM K$_3$Fe(CN)$_6$), the characteristic cyclic voltammogram shown in Figure 6a is obtained. Two well-resolved redox couples are observed at E_{av} values of +1.05 and −0.1 V. This is in contrast to aqueous solution experiments, where no cyclic voltammogram is observed when Li$^+$ is the electrolyte cation.[3]

Repeated cycling in 1 vol % water/propylene carbonate containing 0.1 M LiClO$_4$ (200 cycles from +1.39 to −0.5 V) results in a deterioration of the low-spin iron redox couple at 1.05 V with multiple peaks and shoulders becoming apparent. Finally, after 600 cycles only one redox couple is present with E_{av} at 0.03 V, as shown in Figure 6B. When an iron-containing plasma deposit coated electrode is used, the integrated area of this residual peak is 30% less than that of the initial redox signal at E_{av} = −0.09 V. An iron-containing plasma polymer coated electrode prepared in the same manner exhibited approximately a 50% decrease in the high-spin redox signal after 600 cycles in propylene carbonate containing 0.1 M LiClO$_4$. This difference is attributed to possible swelling and loss of polymer coating from the electrode surface in propylene carbonate (see below).

Figure 4C is a plot of peak current as a function of the square root of the scan rate for the high-spin redox couple in 1 vol % water/propylene carbonate containing 0.1 M LiClO$_4$. The linearity of this relationship, along with a decrease in cathodic and anodic peak current (i_{pc}, i_{pa}) separation with a decrease in scan rate, is consistent with the electrode kinetics being influenced by the diffusion of Li$^+$ ions into the surface-bound iron hexacyanoferrate for the Prussian blue ⇌ Everitt's salt redox couple.

In an attempt to simplify the Li$^+$-containing electrode system and to eliminate any effects that may arise from using K$^+$ ions in the surface modification procedure, a Prussian blue surface modified electrode was prepared with Li$^+$ as the only countercation present. This is described as method II in the Experimental Section. A single redox couple at E_{av} = 0.07 V was observed in 1 vol % water/propylene carbonate with 0.1 M Li$^+$ as the electrolyte cation; see Figure 7. This corresponds to the Prussian blue ⇌ Everitt's salt redox couple. This redox signal did not decay for the duration of the observation time (several hundred cycles; see below) upon cycling from +1.0 to −0.51 V. When this electrode was placed in a 1 vol % water/propylene carbonate solution containing 0.1 M KPF$_6$, a cyclic voltammogram was obtained with a single redox couple at E_{av} = 0.29 V; see Figure 8. This corresponds to the high-spin iron redox couple portion of the cyclic voltammogram normally obtained with a Prussian blue surface modified electrode (method I prepared in K$^+$ electrolyte) in 1 vol % water/propylene carbonate containing 0.1 M KPF$_6$
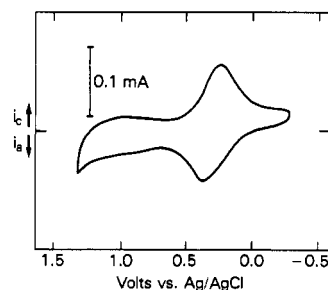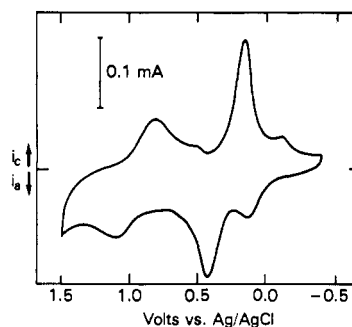
(cf. Figure 1). When this electrode is returned to 1 vol % water/propylene carbonate containing 0.1 M LiClO$_4$, the single redox couple at 0.07 V reappears as shown in Figure 7.

When water (10% by volume) is added to the 1 vol % water/propylene carbonate solution containing Li$^+$ as the electrolyte cation, both redox couples disappear for the electrode prepared by method I and the high-spin iron couple (the only one present) disappears for the electrode prepared by method II. When these electrodes are returned to an aqueous KNO$_3$ solution, no redox activity is observed. This suggests that the totally hydrated Li$^+$ ion becomes bound inside the Prussian blue lattice. This is the most likely explanation for the absence of a cyclic voltammogram for the Prussian blue surface modified electrode in aqueous solution when Li$^+$ is the electrolyte cation.[3]

Experiments using all possible permutations of two electrolyte cations (0.05 M M'$^+$ and 0.05 M M$^+$, Na$^+$ ≠ M'$^+$ = K$^+$, Na$^+$, Li$^+$) in dry propylene carbonate or 1 vol % water/propylene carbonate establishes a preference of the surface bound Prussian blue lattice for a countercation in the order K$^+$ > Na$^+$ > Li$^+$. For example, a cyclic voltammogram obtained in 1 vol % water/propylene carbonate containing a mixed electrolyte, 0.05 M KClO$_4$ and 0.05 M NaClO$_4$, shows predominantly "K$^+$ character"; see Figure 9. This K$^+$ signature for the cyclic voltammogram dominates regardless of whether Na$^+$ or K$^+$ is used in the iron hexacyanoferrate surface modification procedure. An electrode cycled in dry propylene carbonate or 1 vol % water/propylene carbonate containing 0.05 M LiClO$_4$ and 0.05 M NaClO$_4$ or KClO$_4$ exhibits a cyclic voltammogram characteristic of the Na$^+$ or K$^+$ electrolyte cation, respectively.

Surface Adherence. Experiments were performed to determine the tenacity of adherence of the redox-active Prussian blue on the electrode surface in propylene carbonate as the plasma polymer film is changed from the iron-containing plasma polymer to iron-containing plasma deposit, and the

electrolyte cation is varied. Our results, which are summarized below, demonstrate that in 1 vol % water/propylene carbonate the iron-containing plasma deposit provides the better anchor for Prussian blue. No difference in stability was noted between Na^+ and K^+ electrolyte cations. The Li^+ electrolyte cation presents a unique case due to the disappearance of the low-spin redox couple (see above). We have also found that electrode longevity is significantly enhanced in 1 vol % water/propylene carbonate over 100% aqueous solution.

An iron-containing plasma deposit surface modified Prussian blue electrode was cycled in 1 vol % water/propylene carbonate with $KClO_4$ or $NaClO_4$ electrolyte from +1.38 to -0.53 V at 10 mV/s for 2000 cycles (313 h) with no decrease in peak current due to either redox couple. An iron-containing plasma polymer surface modified Prussian blue electrode treated at the same conditions exhibited a 25% depletion in peak current signal for both redox couples. Identical electrodes (iron-containing plasma polymer and plasma deposit) when cycled 2000 times in aqueous medium exhibited a 70% loss in the peak current signal for both redox couples.

We have reported that the iron sites in the plasma polymer and plasma deposit are distributed throughout a hydrocarbon plasma polymer backbone,[17,18] with the iron atoms as probable sites of Prussian blue attachment through a cyanide bridge.[3] Consequently, should any swelling of the plasma polymer or plasma deposit occur, this may contribute to the loss of surface adherent Prussian blue. It is possible that swelling occurs in the case of the iron-containing plasma polymer in 1 vol % water/propylene carbonate.

Discussion

Prussian blue surface modified electrodes prepared from graphite electrodes coated with an iron-containing plasma polymer or iron-containing plasma deposit film are redox active in dry propylene carbonate containing K^+, Na^+, or Li^+ electrolyte cations. The addition of 1–2 vol % water to the propylene carbonate produces cyclic voltammograms with more sharply defined oxidation and reduction peaks. Depending on the potential of the electrode, the surface adherent iron hexacyanoferrate is present as Berlin green, $[KFeFe(CN)_6]_{1/2}$-$[FeFe(CN)_6]_{1/2}$, "soluble" Prussian blue, $KFeFe(CN)_6$, or Everitt's salt, $K_2FeFe(CN)_6$ (Scheme I), when K^+ is the cation of the bulk electrolyte. When Na^+ or Li^+ is used, the iron hexacyanoferrate changes from the totally oxidized species $FeFe(CN)_6$ to Everitt's salt, $M_2FeFe(CN)_6$, with one or two intermediate redox processes (Scheme II). The longevity of the surface-bound redox-active Prussian blue is optimized in a 1 vol % water/propylene carbonate solution by using an iron-containing plasma deposit film to anchor the Prussian blue to the electrode surface. The tenacity of this electrode in 1 vol % water/propylene carbonate is remarkable, there being no observed decrease in peak current signal after 9 days of continuous cycling.

The linear dependence of the peak currents on the square root of the scan rate (Figure 4) suggests that the electrode kinetics are influenced by a diffusion process.[26] This may be contrasted with the predicted behavior for surface-bound species, which is a linear dependence of peak current directly on the scan rate, such as observed by Bocarsly and co-workers[13] for chemically derivatized nickel electrodes. Prussian blue derivatized electrode surfaces prepared by Neff and co-workers[8b] exhibit a linear peak current dependence on the scan rate only for scan rates less than 5 mV/s, which is consistent with our observations. We propose that our electrode kinetics are primarily influenced by the diffusion of the electrolyte cation into and out of the surface bound Prussian blue lattice, and not the transport of an electron from one iron center to the next. This hypothesis is based on the significant differences in the cyclic voltammograms (peak potentials, peak shapes,

relative integrated current areas) as the electrolyte cation is changed from K^+ to Na^+ to Li^+, as well as the cation selectivity $(K^+ > Na^+ > Li^+)$. To put these diffusion effects into context, it is useful to consider the open lattice structure of the Prussian blue film on the electrode surface. A single-crystal X-ray structure of the soluble form of Prussian blue is not available, but the dimensions of the channels in the cubic lattice structure may be inferred from data for insoluble Prussian blue and Prussian blue analogues.[5-7,27,28] Open channels exist in the lattice whose dimensions may reasonably be assumed to be ca. 3.2 Å. The alkali-metal countercations in Prussian blue and Everitt's salt reside in these channels, which are defined by $-C\equiv N-$ groups along the edges and alternating high-spin $Fe(3+)$ and low-spin $Fe(II)$ at the corners for Prussian blue and high-spin $Fe(2+)$ and low-spin $Fe(II)$ for Everitt's salt. The zeolitic character of Prussian blue analogues has been reported.[29] Our Prussian blue surface modified electrode exhibits a definite preference for alkali-metal cation $(K^+ > Na^+ > Li^+)$ in aqueous, propylene carbonate, and mixed water/propylene carbonate solutions. This is in reverse order to ionic radius and in the order of increasing hydration radius $(K^+, 1.25$ Å; $Na^+, 1.83$ Å; $Li^+, 2.37$ Å$)^{30}$ determined by ionic mobility. This suggests that the solvent sheath plays a role in this ion selectivity.

Our results obtained in water, 1 vol % water/propylene carbonate, and dry propylene carbonate lead us to propose that it is the hydrated cation and not the naked cation that enters the Prussian blue lattice. A Prussian blue surface modified electrode cycled in aqueous or 10 vol % water/propylene carbonate containing Li^+ results in total loss of redox activity, even when the electrode is returned to aqueous K^+. Lithium cations are very highly hydrated in aqueous solution with up to 21 molecules of H_2O associated with each Li^+ cation.[31] It is feasible that the hydrated Li^+ may enter the outermost channels of the Prussian blue lattice and then become trapped, blocking access to all channels into the lattice. Therefore, even when changing the countercation of the bulk electrolyte no redox signal is observed. Analysis of the electrode surface by FTIR spectroscopy shows that a Prussian blue surface modified electrode held at a reducing potential (corresponding to Everitt's salt) in aqueous Li^+ exhibits an IR spectrum consistent with Berlin green. This suggests that the bulk of the surface-bound iron hexacyanoferrate cannot be reduced in the presence of aqueous Li^+.[22] This is most likely due to the large hydration shell of Li^+.

A Prussian blue surface modified electrode cycled in dry propylene carbonate containing Li^+ remains electroactive for thousands of cycles. A cyclic voltammogram of this electrode in aqueous K^+ solution shows the full signature characteristic of this countercation, as shown in Figure 1B. Lithium cation does not become trapped in the lattice when propylene carbonate is used presumably because the solvent shell is stripped from the Li^+ prior to entering the lattice. The Stokes radius for Li^+ in propylene carbonate is 3.37 Å, which is too large to enter the Prussian blue lattice.[31] The large separation in peak potentials seen in Figure 5 is consistent with this hypothesis as removal of the propylene carbonate solvent sheath

(27) (a) Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A. *Inorg. Chem.* **1977**, *16*, 2704. (b) Herren, F.; Fisher, P.; Ludi, A.; Halg, W. *Inorg. Chem.* **1980**, *19*, 956.

(28) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford University Press: London 1975; pp 753–756.

(29) See, for example: (a) Seifer, G. B. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1962**, *7*, 621. (b) Shriver, D. F.; Brown, D. B. *Inorg. Chem.* **1969**, *8*, 42. (c) Prout, W. E.; Russell, E. R.; Groh, H. J. *J. Inorg. Nucl. Chem.* **1965**, *27*, 473. (d) Kourin, V.; Rais, J.; Million, B. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1111.

(30) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions"; Butterworths: London, 1958.

(31) Burgess, J. "Metal Ions in Solution"; Halstead Press: New York, 1978.

could result in a slower diffusion of the ions into and out of the surface bound Prussian blue lattice. Partial hydration of the Li^+ cation in a 1 vol % water/propylene carbonate mixture may create a semihydrated Li^+ cation that is of the appropriate size to enter and exit the Prussian blue lattice.

A Prussian blue surface modified electrode cycled in dry propylene carbonate with K^+ electrolyte exhibits a very weak and broad set of redox couples as shown in Figure 1A. This may be due to slow exchange of the propylene carbonate molecules solvating the K^+ cation. Potassium cation solvated by propylene carbonate has a Stokes radius of 2.75 Å, which is too large to enter the Prussian blue lattice channels.[31] Upon addition of 1 vol % water to the propylene carbonate containing 0.1 M K^+, a well-resolved cyclic voltammogram is obtained. Water, even in small quantities, is known to preferentially coordinate to metal cations[32] in propylene carbonate solution. We propose that the water in propylene carbonate solvates the K^+ and that the hydrated cation (Stokes radius 1.25 Å)[31] is then of the appropriate size to enter the Prussian blue lattice.

Our observed redox activity in the presence of Na^+ or Li^+ is in contrast to the observations of Neff[8] and Itaya.[10] The reasons for this significant difference in behavior are not clear, but in our case we identify the surface-bound Prussian blue as the soluble ($MFeFe(CN)_6$) rather than the insoluble ($Fe_4[Fe(CN)_6]_3$) form, and our method of electrode preparation, which involves anchoring the Prussian blue to iron sites in an iron-containing plasma polymer or iron containing plasma deposit coating, is significantly different from that of these other investigators. Bocarsly and co-workers[13] have found a selectivity sequence in water (including activity for Li^+ in water) similar to that reported here for a chemically derivatized nickel electrode containing a very thin film of surface-bound $[Ni^{II}_x(M(CN)_6)_y]^{n-}$ (M = Ru, Fe). Messina and Perichon[11] report that a carbon-paste Prussian blue membrane electrode is permeable to Li^+ cations in propylene carbonate.

Both the high-spin and low-spin iron redox potentials were found to be sensitive to alkali-metal cation and, to a lesser extent, the change from water to water/propylene carbonate solvent (Table I). In effect, the potential range over which Prussian blue is stable with respect to oxidation or reduction is enhanced on changing the electrolyte cation from K^+ to Na^+ or Li^+. This is in contrast to the solution behavior of low-spin $[Fe(CN)_6]^{3-/4-}$, which shows a large redox potential shift with solvent[33-35] and a small variation with alkali-metal countercation.[36-38] Both effects are attributed to acceptor interactions with the N atom of coordinated cyanide: solvation in the former and weak ion pairing in the latter case. Such acceptor interactions may be largely responsible for the shift to a more positive redox potential for $[Fe(CN)_6]^{3-/4-}$ in a Prussian blue lattice (where high-spin Fe^{3+} acts as an acceptor for the N atom of cyanide: Fe^{II}—C≡N—Fe^{3+}) relative to that in solution. (For example, in aqueous solution $[Fe(CN)_6]^{3-/4-}$ redox occurs at 0.29 V and Fe(III/II) redox for electrode surface bound Prussian blue occurs at 0.89 V). However, due to the polymeric nature of Prussian blue whereby each N atom is coordinated to a Fe, the cation dependence of the redox potential cannot be explained by direct N atom interactions.

Evidently the identity of the alkali-metal ion in the countercation sites of the Prussian blue lattice influences both the high-spin and low-spin iron redox potentials by some unknown mechanism.

In addition to the unique permeability of our Prussian blue surface modified electrode to Na^+ and Li^+ counterions, our results suggest that there is a chemical distinction between the countercation lattice sites associated with the high-spin and low-spin redox couples. The experimental observations that support this hypothesis are summarized as follows: (1) When the Prussian blue surface modified electrode is prepared by method II (i.e. with only Li^+ countercation present), no low-spin iron redox couple is observed in 1 vol % water/propylene carbonate (Figures 7 and 8). (2) Repeated cycling of the Prussian blue surface modified electrode prepared by method I in 1 vol % water/propylene carbonate containing Li^+ results in the gradual disappearance of the low-spin iron redox couple (Figure 6). (3) When this electrode is placed in 1 vol % water/propylene carbonate containing 0.1 M K^+ electrolyte, the cyclic voltammogram shows a shift in the high-spin couple E_{av} value to that characteristic of the K^+ counterion but still does not show a low-spin iron redox couple. (The resulting cyclic voltammogram is identical with that shown in Figure 8.) (4) When a method I prepared electrode is cycled in 1 vol % water/propylene carbonate (0.1 M $LiClO_4$) over only the high-spin redox couple several hundred times and then cycled in 1 vol % water/propylene carbonate containing 0.1 M KPF_6, *both* the low-spin and high-spin redox couples characteristic of the K^+ countercation are observed. (5) FTIR spectra taken of an electrode surface prepared by method II and corresponding to that used to obtain the cyclic voltammograms shown in Figure 7 show that even at an oxidizing potential Berlin green is not formed on the electrode surface.[22]

Our interpretation of these observations is that once hydrated Li^+ is in the lattice sites associated with the *low-spin* Fe(III/II) redox couple it cannot diffuse out, whereas there is a reversible flux of hydrated Li^+ associated with the *high-spin* Fe(3+/2+) redox couple. This is a consequence of the high degree of hydration of Li^+, relative to that of K^+ and Na^+. It may be that there is a certain degree of Li^+/K^+ (or Na^+) exchange that occurs at the low-spin Fe(III/II) redox site. This is consistent with the observation that the low-spin Fe(III/II) redox couple ($[MFe^{3+}Fe^{II}(CN)_6] \rightleftharpoons [MFe^{3+}Fe^{II}-(CN)_6]_{1/2}[Fe^3Fe^{III}(CN)_6]_{1/2}$) only involves the exchange of half of the countercations on each cycle, which may provide the reason for the disappearance of the low-spin couple only after several hundred cycles in 1 vol % water/propylene carbonate containing 0.1 M Li^+ (Figure 6) when the Prussian blue surface modified electrode is prepared by method I. That is, after a number of cycles all of the K^+ (or Na^+) ions in the low-spin sites have been completely substituted by Li^+, which cannot diffuse out of these lattice sites. When the Prussian blue surface modified electrode is prepared by method II, there are only Li^+ ions in these sites and we see only the high-spin iron redox couple (Figure 7). Our statement of nonequivalence of the low-spin and high-spin countercation lattice sites comes from the observation that only the low-spin redox couple is affected by Li^+ in this way. Additional spectroscopic experiments that investigate the electrode surface as a function of potential, electrolyte cation, and solvent support this hypothesis of high-spin and low-spin countercation lattice site distinction and are reported elsewhere.[22] The distinction between lattice sites, the countercation selectivity ($K^+ > Na^+ > Li^+$), and dependence of E_{av} on countercation suggest possible development of these surface-modified electrodes as analytical devices.

Registry No. $KFeFe(CN)_6$, 25869-98-1; $Fe(CO)_5$, 13463-40-6;

(32) Coetzee, J. F.; Umemoto, K. *Inorg. Chem.* **1976**, *15*, 3109.
(33) Gritzner, G.; Danksagmüller, K.; Gutmann, V. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *72*, 177.
(34) Gutmann, V.; Gritzner, G.; Danksagmüller, K. *Inorg. Chim. Acta* **1976**, *17*, 81.
(35) Gritzner, G.; Danksagmüller, K.; Gutmann, V. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *90*, 203.
(36) Kolthoff, I. N.; Tomsicek, W. J. *J. Phys. Chem.* **1935**, *39*, 945.
(37) Nichugovskii, G. F.; Shvedov, V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1969**, *14*, 156.
(38) Hanania, G. I. H.; Irvine, D. H.; Eaton, W. A.; George, P. *J. Phys. Chem.* **1967**, *71*, 2022.

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Kinetics, Mechanism, and Thermodynamics of Aqueous Iron(III) Chelation and Dissociation: Influence of Carbon and Nitrogen Substituents in Hydroxamic Acid Ligands

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Thermodynamic and kinetic studies were performed to investigate the complexation of aqueous high-spin iron(III) by 12 bidentate hydroxamic acids, $R_1C(O)N(OH)R_2$, (R_1 = CH_3, C_6H_5, 4-$NO_2C_6H_4$, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$; R_2 = CH_3, C_6H_5, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 4-IC_6H_4, 3-IC_6H_4, 4-NCC_6H_4, 3-NCC_6H_4, 4-$CH_3C(O)C_6H_4$), in acid medium. Both complex formation and dissociation (aquation) reactions were investigated by stopped-flow relaxation methods over a range of [H^+] and temperatures. A two-parallel-path mechanism without proton ambiguity is established for the reaction of $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ with $R_1C(O)N(OH)R_2$ to form $Fe(H_2O)_4(R_1C(O)N(O)R_2)^{2+}$. Equilibrium quotients, $\Delta H°$ and $\Delta S°$ values, rate constants, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for both reaction paths in the forward and reverse directions are reported. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are found to be linearly related and compensating. On the basis of an analysis of the equilibrium quotients, rate constants, and activation parameters for the reaction in both directions, an associative interchange (I_a) mechanism is proposed for hydroxamic acid ligand substitution at $Fe(H_2O)_6^{3+}$. Similar trends for these parameters are observed for the reaction at $Fe(H_2O)_5OH^{2+}$, suggesting an associative interchange character for this reaction path also. However, coordinated water dissociation appears to be dominant, and some associative character for this path may be the result of H-bonding interactions between the undissociated hydroxamic acid and coordinated –OH. Electron-donating and -withdrawing R_1 and R_2 substituents were selected in order to determine the relative influence of the C and N substituent on the hydroxamic acid and to determine the optimum hydroxamic acid structure for kinetic and thermodynamic stability of the iron(III) chelate. Kinetic and thermodynamic chelate stabilization are enhanced by increasing electron density on the carbonyl oxygen atom, which is promoted by electron donors in the R_1 position and delocalization of the N atom lone pair of electrons into the C–N bond. The influence of the R_2 substituent appears to be dominant with an electron-releasing alkyl group as the preferred R_2 substituent for kinetic and thermodynamic stability. The optimum hydroxamic acid ligand for kinetic and thermodynamic stability of the iron(III) chelate was found to be 4-$CH_3OC_6H_4C(O)N(OH)CH_3$.

Introduction

Hydroxamic acids have broad application as corrosion inhibitors, antifungal agents, food additives, flotation reagents in extractive metallurgy, pharmaceutical, and analytical reagents.[1] Several of these applications depend on the strong metal-complexing ability of the hydroxamates. Of particular interest and relevance to this report is the high affinity of the hydroxamate group for iron(III). Siderophores, which are microbially generated chelators produced to increase the bioavailability of iron to these organisms, are known to contain hydroxamic acid functional groups.[2,3] Synthetic and naturally occurring hydroxamic acids have been investigated for use as therapeutic agents for iron removal from transfusion-induced iron-overloaded patients.[4,5] For a number of reasons it is of interest to obtain an understanding of the kinetic and thermodynamic contribution to iron(III) complex stability with

hydroxamic acid ligands, as well as the mechanism for iron-(III) chelation and release (reaction 1). Previous work in our

$$Fe(H_2O)_6^{3+} + R_1C(O)N(OH)R_2 \xrightleftharpoons{\ H_2O\ }$$
$$Fe(H_2O)_4(R_1C(O)N(O)R_2)^{2+} + H_{aq}^+ + 2H_2O \quad (1)$$
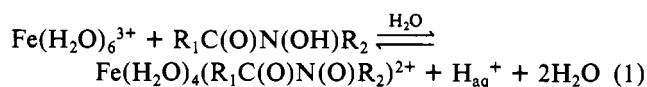
laboratory has dealt with the thermodynamics, kinetics, and mechanism of reaction 1 with a series of synthetic hydroxamic acids where R_1 = CH_3 and C_6H_5 and R_2 = CH_3, C_6H_5, and H.[6] We have applied the mechanistic model developed for reaction 1 to iron(III) dissociation from the siderophore ferrioxamine B[7,8] in acid solution and at conditions where the dissociation reaction is catalyzed by synthetic hydroxamic acids.[9]

In this report we describe a systematic investigation of the electronic influence of the substituent on the C (R_1 group) and the N (R_2 group) atoms of the hydroxamate moiety on the thermodynamics, kinetics, and mechanism of reaction 1. Two series of synthetic hydroxamic acids were used: the substituted *N*-methylbenzohydroxamic acids (I) (referred to as the R_1 series) and the substituted *N*-phenylacetohydroxamic acids (II) (referred to as the R_2 series). Complex formation constants, kinetics of complex formation and dissociation, and associated

(1) (a) Kehl, H., Ed. "Chemistry and Biology of Hydroxamic Acids"; Karger: New York, 1982. (b) Bauer, L.; Exner, O. *Angew. Chem., Int. Ed. Engl.* **1974,** *13,* 376. (c) Agrawal, Y. K. *Russ. Chem. Rev. (Engl. Transl.)* **1979,** *48,* 948. (d) Agrawal, Y. K.; Roshania, R. D. *Bull. Soc. Chim. Belg.* **1980,** *89,* 159. (e) Agrawal, Y. K. *Rev. Anal. Chem.* **1980,** *5,* 3. (f) Chatterjee, B. *Coord. Chem. Rev.* **1978,** *26,* 281.
(2) Neilands, J. B. *Annu. Rev. Biochem.* **1981,** *50,* 715.
(3) Neilands, J. B. *Adv. Inorg. Biochem.* **1983,** *5,* Chapter 6.
(4) Martell, A. E.; Anderson, W. F.; Badman, D. G., Eds. "Development of Iron Chelators for Clinical Use"; Elsevier: New York, 1981.
(5) Brown, D. A.; Chidambaram, M. B. In "Metal Ions in Biological Systems"; Sigel, H., Ed.; Marcel Dekker: New York, 1982; Vol. 14, Chapter 5.

(6) Monzyk, B.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1979,** *101,* 6203.
(7) Monzyk, B.; Crumbliss, A. L. *Inorg. Chim. Acta* **1981,** *55,* L5.
(8) Monzyk, B.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1982,** *104,* 4921.
(9) Monzyk, B.; Crumbliss, A. L. *J. Inorg. Biochem.* **1983,** *19,* 19.