Electrochemical Studies of Inorganic Redox Processes in n-Butyronitrile over a Wide Range of Temperature and Scan Rates at Conventional and Microsized Electrodes: Iron Protoporphrin IX Dimethyl Ester Chloride

A. M. BOND, T. F. MANN, G. A. TONDREAU*

Department of Chemical and Analytical Sciences, Deakin University, Geelong, Vic. 3217 (Australia)

and D. A. SWEIGART

Department of Chemistry, Brown University, Providence, RI 02912 (U.S.A.)

(Received April 13, 1989; revised September 12, 1989)

Abstract

The nuances accompanying the charge transfer process for the electrochemical reduction of iron protoporphrin IX dimethyl ester chloride, Fe(ppdme)Cl, in n-butyronitrile, are revealed directly by either cyclic voltammetry at conventionally sized electrodes over the temperature range from –100 to +100 °C or by using scan rates encompassing the millivolt per second to thousands of volts per second range with microelectrodes.

Both approaches lead to the conclusion that the reduction processes are best described by the square reaction scheme given below which includes chloride exchange with solvent and/or electrolyte and cross redox reactions.

$$\begin{tikzcd}
{[\mathrm{Fe(ppdme)}]^+} \arrow[r, shift left, "+e^-"] \arrow[d, shift right, "-\mathrm{Cl}^-"'] & \mathrm{Fe(ppdme)} \arrow[l, shift left, "-e^-"] \arrow[r, shift left, "+e^-"] \arrow[d, shift right, "-\mathrm{Cl}^-"'] & {[\mathrm{Fe(ppdme)}]^-} \arrow[l, shift left, "-e^-"] \arrow[d, shift right, "-\mathrm{Cl}^-"'] \\
\mathrm{Fe(ppdme)Cl} \arrow[u, shift right, "+\mathrm{Cl}"'] \arrow[r, shift left, "+e^-"] & {[\mathrm{Fe(ppdme)Cl}]^-} \arrow[u, shift right, "+\mathrm{Cl}^-"'] \arrow[l, shift left, "-e^-"] \arrow[r, shift left, "+e^-"] & {[\mathrm{Fe(ppdme)Cl}]^{2-}} \arrow[u, shift right, "+\mathrm{Cl}^-"'] \arrow[l, shift left, "-e^-"]
\end{tikzcd}$$

In contrast, data from conventional narrow range time domain experiments employed at a single temperature could be interpreted as the simple reaction scheme.

$$\mathrm{Fe(ppdme)Cl} + e^- \rightleftharpoons [\mathrm{Fe(ppmdme)Cl}]^- + e^- \rightleftharpoons [\mathrm{Fe(ppdme)Cl}]^{2-}$$

Introduction

Voltammetric techniques are now being widely used in inorganic chemistry to study thermodynamic and kinetic aspects of the redox properties of metal complexes. Broadly speaking, electrochemical processes can be classified as reversible or irreversible [1–3]. Reversible electrochemical processes are a measure of the energetics of electron transfer reactions where all reactions including the charge transfer step and coupled chemical reactions are in equilibrium on the appropriate voltammetric timescale (e.g. time scale of d.c., a.c., or pulse voltammetry etc.). Reversible electrode processes therefore provide useful thermodynamic information but give no mechanistic, kinetic or other chemical information concerning the reactants or products. On the other hand, irreversible processes are those where the rate determining step is, for example, a slow electron transfer or a slow chemical reaction accompanying electron transfer. Measurement of the electrode processes under irreversible conditions provides considerable mechanistic information. The 'trick' in voltammetry to obtain mechanistic information is therefore to provide an appropriate time scale of measurement so that reduction or oxidation processes encompass both the reversible and irreversible time regimes.

The majority of voltammetric studies of inorganic redox processes have been undertaken at ambient temperatures (10 to 25 °C) and over narrow time domains, e.g. scan rates of 50 to 500 mV s^{-1} in cyclic voltammetry, drop times of 0.5 to 5 s in d.c. polarography and pulse widths of 10 to 100 ms in pulse voltammetry. Under these conditions very little meaningful kinetic information can be gleaned from the measurements, as the time and temperature regimes are too small to detect nuances associated with the charge transfer process.

However, recent developments in voltammetric techniques, many of which are now present in commercially available instrumentation, imply that the voltammetric time domain available in many laboratories can usually be made shorter than the rate of the chemical steps accompanying electron transfer, and that many of the limitations previously

---

*On leave from: Department of Chemistry, Southern Oregon State College, Ashland, OR 97520, U.S.A.

0020-1693/90/$3.50

imposed in kinetic studies should no longer apply. For example, the use of microelectrodes allows voltammetric scan rates in excess of one million volts per second to be used [4, 5]. With time domains of this order, rate constants of certain types of second and higher order processes occurring at essentially diffusion controlled rates can be measured [6]. In addition to much shorter time domains becoming routinely available, temperature ranges encompassing several hundred degrees are now readily accessible for voltammetric studies. Over these very wide temperature ranges, rate constants of processes having typical activation energies will vary by several orders of magnitude. Consequently for a fixed time domain of measurement, processes may be made to appear in equilibrium (reversible) or not in equilibrium (irreversible) by varying the temperature over a wide range.

In the present paper, the power of utilizing the wide time domain and temperature range available will be illustrated in an electrochemical study of iron porphyrin complexes in the solvent n-butyronitrile. Part of this paper is therefore didactic in nature and provides complimentary concepts to those contained in a recent review [7]. Figure 1 shows the cyclic voltammetry of the iron tetraphenylporphyrin chloride complex recorded at a typical temperature of 20 °C and time domain (scan rate of 300 mV s^{-1}). Two chemically reversible reduction and two chemically reversible oxidation processes are observed. The observation of a series of reversible processes is relatively common for iron porphyrin complexes when studied by voltammetry at ambient temperatures and slow scan rates [8–11]. Of interest in the present work is the two reduction processes. Our present report is aimed at illustrating by use of modern voltammetric techniques how simply it can be shown that these processes are not simple one electron charge transfer processes, as could be concluded from a conventional measurement (Fig. 1). Rather, they involve fast rates of electron transfer with fast rate constants for both ligand loss and gain after electron transfer. n-Butyronitrile was chosen as the aprotic organic solvent because of its relatively high dielectric constant (20.31) [12], excellent liquid range (117 to −111.9 °C [12], wide accessible potential range and excellent solvating ability for both the metal porphyrin complexes and relatively inert electrolytes. Conventional electrodes were used at conventional scan rates over the temperature range of +100 to −100 °C to provide one method of identifying the presence of the chemical steps accompanying the electron transfer. The use of such a wide temperature range has rarely been employed, but is obviously advantageous [13]. Cyclic voltammetry at microelectrodes using fast scan rates was used to provide an extremely wide time domain and provide data complementing that obtained by use of variable temperature. The complexes studied were iron protoporphyrin IX dimethyl ester chloride, Fe(ppdme)Cl and iron tetraphenylporphyrin chloride, Fe(tpp)Cl.

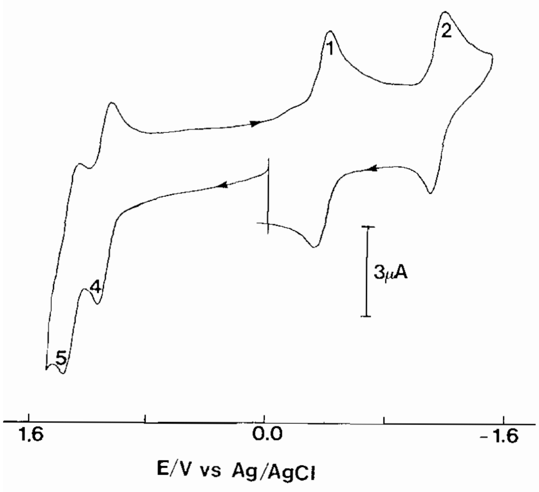
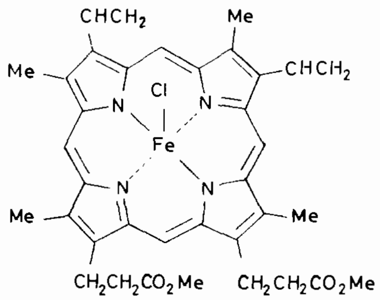
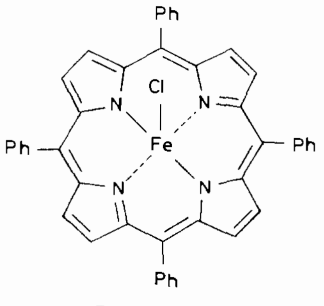


Fig. 1. Cyclic voltammogram obtained at a conventionally sized platinum disk electrode with a scan rate of 300 mV s^{-1} for reduction and oxidation of 1.0×10^{-3} M Fe(tpp)Cl in n-butyronitrile (0.1 M TBAP) at 20 °C.



[Fe (ppdme) Cl]



[Fe(tpp)Cl]

The voltammetric processes for Fe(tpp)X (X = N_3^-, Cl^-) and related complexes have been reported at ambient and low temperatures using conventionally sized electrodes and conventional techniques [8–11, 14] in solvents such as dimethylformamide and other organic solvents but not in n-butyronitrile or at elevated temperatures or with microelectrode short time domain methodology. In these other studies, the importance of the equilibria involving various species were ususally deduced by varying the concentration of X^-, by theoretical calculation of the shapes of the current voltage curves or by combining spectroscopic information with voltammetric evidence. In the present paper direct voltammetric observation of the various species is provided.

Experimental

Chemicals

Hemin chloride, Fe(pp)Cl, was used as purchased from Eastman Kodak. $\{Fe(ppdme)\}_2O$ was prepared from hemin chloride by a standard literature method [15], and converted to Fe(ppdme)Cl by bubbling dry HCl through a dichloromethane solution. Fe(ppdme)-Cl was isolated by evaporating the dichloromethane solution to dryness. Fe(ppdme)Cl was purified by recrystallization from a dichloromethane/pentane solvent mixture. Fe(tpp)Cl was synthesized from $\{Fe(tpp)\}_2O$ by a standard procedure [16]. n-Butyronitrile was purchased from TCI and purified by passing the solvent through an activated neutral alumina chromatographic column followed by fractional distillation from CaH_2. Tetrabutylammonium perchlorate (TBAP) was recrystallized from acetone/ether and bis(triphenylphosphine)iminium chloride (PPNCl) was recrystallized from acetone/hexane. Tetrahexylammonium hexafluorophosphate ($THAPF_6$) was made by metathesis of $(C_6H_{13})_4NI$ and HPF_6, and recrystallized from 95% ethanol. All electrolytes were vacuum dried for at least 48 h prior to use.

Electrochemical Instrumentation

Conventional cyclic voltammograms were obtained at scan rates of 50 to 700 mV s^{-1} with a BAS CV 27 instrument using a three electrode potentiostated mode and recorded on a Houston Model 100 X-Y recorder. The working electrode was either a platinum, gold or glassy carbon disk (1–2 mm radius) and the counter electrode was a platinum wire. The reference electrode was an Ag/AgCl electrode made up in CH_2Cl_2 (0.1 M TBAP) saturated LiCl. The reference electrode was connected to the test solution via a salt bridge containing n-butyronitrile (0.1 M TBAP). The voltammetric processes were similar at all working electrodes and only data obtained at the platinum disk electrode are reported. Argon saturated with n-butyronitrile was bubbled through the solution for one hour prior to undertaking voltammetric experiments and then maintained as a blanket over the solution during measurements. The complete absence of oxygen is essential. The oxygen reduction product, superoxide, is very stable in n-butyronitrile and deleteriously influences the voltammetry of Fe(ppdme)Cl.

Temperature measurements were taken using a Matronics MAT 100 K thermocouple. Measurements at low temperature were obtained by placing the cell in a slush bath prepared by mixing liquid nitrogen and a variety of solvents such as dichloromethane, methanol, ethanol or n-butyronitrile. Correction for any potential drift in the reference electrode was made by frequent referencing to the oxidation potential of a 5×10^{-4} M solution of ferrocene.

Fast scan experiments (50 to 5000 V s^{-1}) with microdisk electrodes (radius 12.5 to 50 μm) sealed in soda glass and prepared according to methods based on those described in the literature [4] were performed using a two electrode rather than three electrode arrangement. The triangular voltage used in fast scan rate cyclic voltammetry was applied with a PAR (Princeton Applied Research Corp.) Model 175 Function Generator. The current was measured with a current-to-voltage converter based on an OP-37 operational amplifier. The voltage and measured current was then fed to a Gould Model 4035 Digital Storage Oscilloscope and the data recorded in this way transferred to a Houston model 100 X-Y recorder for visual display. A platinum wire pseudo reference electrode was used to minimize ohmic IR drop in fast scan rate experiments instead of the higher resistance Ag/AgCl reference electrode. Platinum microdisk electrodes were polished with a 0.05 μm alumina aqueous slurry on a micro polishing cloth.

Conductivity measurements were performed on Fe(ppdme)Cl, Fe(tpp)Cl and PPNCl with standard conductivity cells and indicate the porphyrins are only slightly ionized relative to PPNCl in n-butyronitrile.

Results

Studies over a Wide Temperature Range with Conventional Sized Electrodes

Figure 2(a) shows a cyclic voltammogram (scan rate $\nu = 300$ mV s^{-1}) with a conventionally sized electrode for the reduction of Fe(ppdme)Cl at 100 °C, which is near the boiling point of n-butyronitrile. Under these conditions, two apparently reversible one electron reduction processes are observed which resemble those reported for reduction of Fe(tpp)Cl at ambient temperatures (see Fig. 1). However, as shown in Fig. 2(b), subtle departures from reversible behaviour are observed at 20 °C for the Fe(ppdme)Cl complex. While the two processes still appear to be superficially reversible at 20 °C, the peak height of reduction process 1 is substantially larger than reduction process 2 and the ratio of the reduction peak height, i_p^{red}, to oxidation peak height, i_p^{ox}, i_p^{red}/i_p^{ox}, for

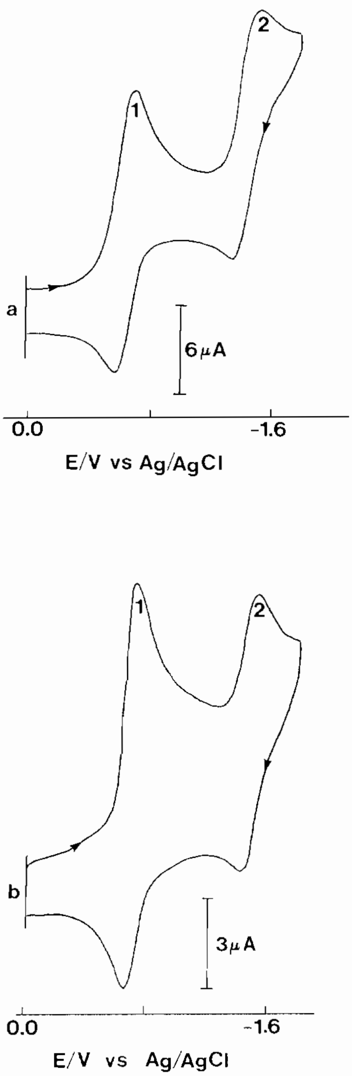


Fig. 2. Cyclic voltammograms obtained at a conventionally sized platinum disk electrode with a scan rate of 300 mV s^{-1} for reduction of 1.0×10^{-3} M Fe(ppdme)Cl in n-butyronitrile (0.1 M TBAP) at: (a) 100 ℃; (b) 20 ℃.

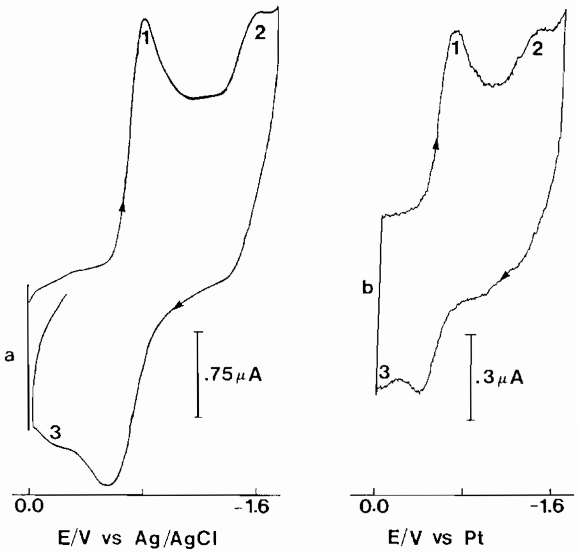


Fig. 3. Cyclic voltammograms for reduction of 1.0×10^{-3} M Fe(ppdme)Cl in n-butyronitrile (0.1 M TBAP) at: (a) −100 °C, scan rate = 300 mV s^{-1} using a conventionally sized platinum disk electrode; (b) 20 ℃, scan rate = 200 V s^{-1} using a 50 μm radius platinum disk microelectrode.

process 1 is much greater than unity. This implies that process 1 is no longer diffusion controlled at the lower temperature and indicates that chemical reactions accompany the electron transfer process. By the time the temperature is lowered to −100 ℃, which is close to the freezing point of n-butyronitrile, process 2 has become very small relative to process 1 and a new process 3 is observed on the reverse and subsequent cycles at potentials slightly less negative than process 1. This situation is shown in Fig. 3(a) and confirms that there is considerable complexity associated with the two reduction processes that are deceptively simple at +100 ℃. The more than 200 ℃ temperature range available in n-butyronitrile can be used advantageously to directly reveal the presence of a species giving rise to additional electrode processes 3.

Studies of Fast Scan Rates with Microelectrodes

The use of microelectrodes, enables very fast scan rates to be used in n-butyronitrile with minimal IR drop. This technique is complementary to the variable temperature studies in the sense that fast scan rate data resembles low temperature data obtained at slow scan rates in that process 3 can be directly revealed at fast scan rates (compare Fig. 3(a) and (b)). Figure 3(a) which was obtained at −100 ℃ at a conventional electrode and scan rate of 300 mV s^{-1} and Fig. 3(b), the cyclic voltammogram obtained at a microelectrode at 20 ℃ but with a scan rate of 200 V s^{-1} are remarkably similar in appearance. That is, lowering of temperature or increasing the scan rate leads to similar voltammetry. This observation must be consistent with the proposed mechanism.

Figure 4(a)–(d) shows that as the scan rate is increased the chemical reversibility of reduction process 1 is decreased. Concomitantly, a new process appears at less negative potentials which coincides with process 3 observed at very low temperatures and conventionally used scan rates. The reversibility of process 3 is shown in Fig. 5. At a scan rate of 5000 V s^{-1} (Fig. 4(d)) process 3 is clearly defined and process 1 is completely irreversible. Figure 4(c) and 4(d), shows the situation where the switching potential is more negative than process 2. Under fast scan rate

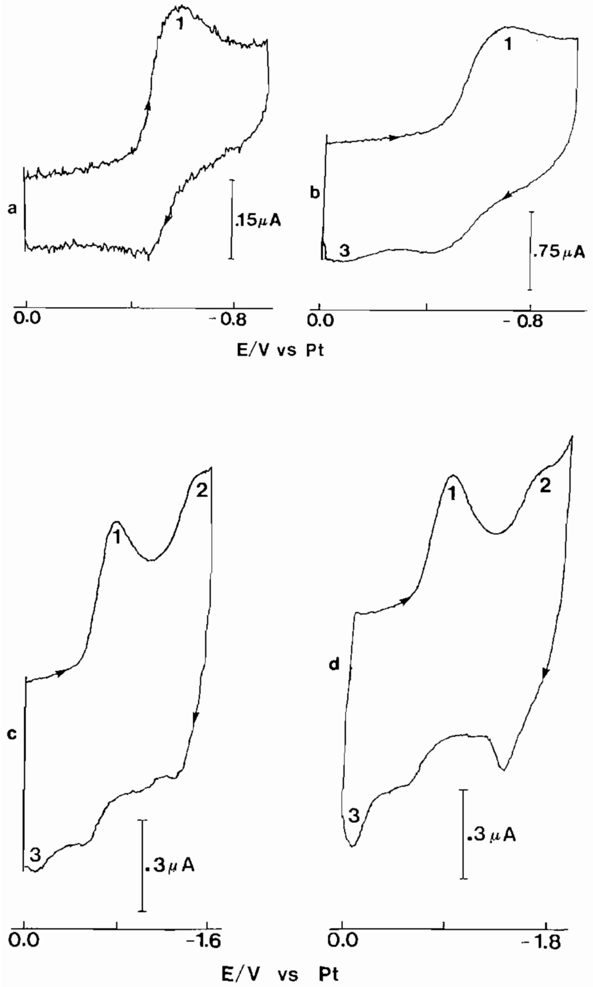


Fig. 4. Cyclic voltammograms obtained at a platinum disk microelectrodes for reduction of 1.0 × 10^{-3} M Fe(ppdme)Cl in n-butyronitrile (0.5 M TBAP) at 20 °C. Scan rates: (a) 50 V s^{-1}, 50 μm radius electrode; (b) 500 V s^{-1}, 50 μm radius electrode; (c) 1000 V s^{-1}, 25 μm radius electrode; (d) 5000 V s^{-1}, 12.5 μm radius electrode.

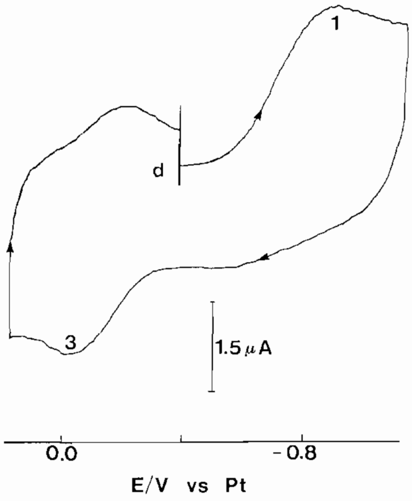


Fig. 5. Cyclic voltammogram obtained at a 25 μm radius platinum disk microelectrode showing the reversibility of process 3 for reduction of 1.0 × 10^{-3} M Fe(ppdme)Cl in n-butyronitrile (0.5 M TBAP) at 20 °C. Scan rate 5000 V s^{-1}.

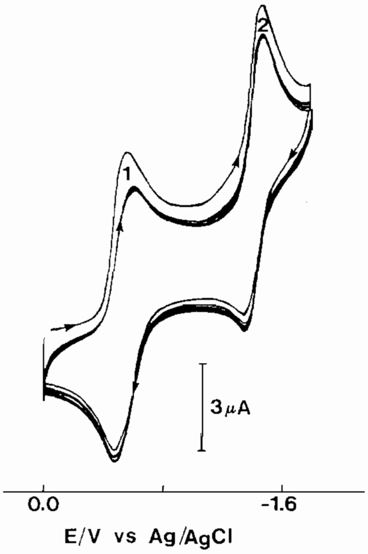


Fig. 6. Cyclic voltammogram obtained at a conventionally sized platinum disk electrode for reduction of 1.0 × 10^{-3} M Fe(ppdme)Cl in n-butyronitrile (0.1 M PPNCl) at 20 °C at a scan rate of 300 mV s^{-1}.

conditions, reduction process 2 shifts to a more negative potential because of IR drop, but attains a degree of chemical reversibility as process 1 becomes chemically irreversible. In fact, as shown in Fig. 4(c) and (d), the oxidation currents associated with processes 2 and 3 (reverse scan data) increase at a similar rate until at very fast scan rates where process 1 is completely irreversible it is obvious that processes 2 and 3 correspond to reduction and oxidation of the product of process 1.

Figure 6 shows a cyclic voltammogram obtained with conventional electrodes and conditions when chloride is used in place of perchlorate as the electrolyte. In the chloride media and with a scan rate of 300 mV s^{-1}, processes 1 and 2 both have similar reduction peak heights. Furthermore, process 1 approaches the diffusion controlled response in the sense that $(i_p^{red}/i_p^{ox}) \rightarrow 1$ and $i_p^{red}/v^{1/2} \rightarrow$ constant. In fact the cyclic voltammogram in Fig. 6 with a chloride electrolyte and a temperature of 20 °C closely resembles that in Fig. 2(a) with a perchlorate electrolyte and a temperature of 100 °C. While a change in the electrolyte from perchlorate to chloride has a significant effect, changing the electrolyte from perchlorate to hexafluorophosphate (not shown) has only a marginal effect. Clearly, the concentration of the chloride ligand plays a major role in the observed voltammetry as is the case with temperature and scan rate.

Data for Fe(tpp)Cl are qualitatively similar to those described in detail for Fe(ppdme)Cl, except for an approximately 80 °C offset, e.g. the cyclic voltammogram in Fig. 1 obtained at 20 °C for Fe(tpp)Cl resembles that obtained at 100 °C for Fe(ppdme) in Fig. 2(a).

Discussion

The observed temperature, scan rate and chloride concentration dependence of processes 1 and 2 and generation of process 3 from both low temperature and fast scan rate voltammetry enables a detailed understanding of the reduction mechanism to be gained as follows.

Process 3 which is observed at either low temperatures or fast scan rates, in the absence of deliberately added chloride, and which occurs at the least negative potential, can be assumed to predominantly arise from the Fe(III)/Fe(II) charge transfer process

$$\mathrm{Fe(ppdme)^+ + e^- \rightleftharpoons Fe(ppdme)} \qquad (1)$$

Process 3 may involve weak solvent and/or electrolyte interactions [17].

The position and degree of chemical reversibility of process 1 is dependent on the concentration of chloride, temperature and scan rate and must intimately involve the presence of the chloride ligand. This alternative Fe(III)/Fe(II) charge transfer step can therefore be represented approximately as

$$\mathrm{Fe(ppdme)Cl + e^- \rightleftharpoons [Fe(ppdme)Cl]^-} \qquad (2)$$

The dependencies on temperature scan rate and chloride concentration provide definitive evidence that the chloride dissociation and association reactions accompany the electron transfer steps as described in eqns. (3) and (4).

$$\mathrm{Fe(ppdme)Cl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{[Fe(ppdme)]^+ + Cl^-} \qquad (3)$$

$$\mathrm{[Fe(ppdme)Cl]^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Fe(ppdme) + Cl^-} \qquad (4)$$

Processes 1 and 3 will converge if all steps in the electrochemistry are in equilibrium and under these conditions will be measured as a single Fe(III)/Fe(II) process, rather than being split into two discrete Fe(III)/Fe(II) steps. Processes 1 and 3 actually form components of the completely general square reaction scheme.

$$\begin{tikzcd}
{\mathrm{[Fe(ppdme)]^+}} \arrow[r, shift left, "+e^-"] \arrow[d, shift left, "+Cl^-"] \arrow[dr, leftrightarrow] & \mathrm{Fe(ppdme)} \arrow[l, shift left, "-e^-"] \arrow[d, shift left, "+Cl^-"] \arrow[dl, leftrightarrow] \\
\mathrm{Fe(ppdme)Cl} \arrow[u, shift left, "-Cl^-"] \arrow[r, shift left, "+e^-"] & {\mathrm{[Fe(ppdme)Cl]^-}} \arrow[l, shift left, "-e^-"] \arrow[u, shift left, "-Cl"]
\end{tikzcd} \qquad (5)$$

Voltammetric data imply that the cross redox reaction

$$\mathrm{[Fe(ppdme)Cl]^- + [Fe(ppdme)]^+ \rightleftharpoons Fe(ppdme) + Fe(ppdme)Cl} \qquad (6)$$

represented by the X symbol may also occur.

Conductivity data prove that the equilibrium position for eqn. (3) lies substantially to the left in n-butyronitrile.

In contrast the equilibrium position in eqn. (4) lies a considerable distance to the right. Thus, to a first order approximation, process 1 is predominantly described under normal conditions of measurement by the reversible eqn. (7).

$$\mathrm{[Fe(ppdme)Cl] + e^- \rightleftharpoons [Fe(ppdme)Cl]^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Fe(ppdme) + Cl^-} \qquad (7)$$

At very fast scan rates, or low temperatures, processes 2 and 3 exhibit related characteristics under conditions of cyclic voltammetry and must result from reduction and oxidation respectively of a common product. Under these conditions, process 1 also becomes irreversible and the voltammetric response is approximately represented in eqn. (8), with reduction and oxidation of Fe(ppdme) giving rise to charge transfer processes 2 and 3 respectively.

$$\begin{tikzcd}
\mathrm{Fe(ppdme)Cl} \arrow[r, shift left, "+e^-"] & {\mathrm{[Fe(ppdme)Cl]^-}} \arrow[l, shift left, "-e^-"] \arrow[r, "k_2"] & {\mathrm{[Fe(ppdme)]^+}} \arrow[d, shift right, "+e^-"'] \\
 & & \mathrm{Fe(ppdme) + Cl^-} \arrow[u, shift right, "-e^-"'] \arrow[d, shift right, "+e^-"'] \\
 & & {\mathrm{[Fe(ppdme)]^-}} \arrow[u, shift right, "-e^-"']
\end{tikzcd} \qquad (8)$$

That is, time domains or temperatures can be reached where the back reaction, or rate constant k_{-2}, is too slow to enable equilibrium to be obtained within the time scale of the voltammetric experiment. It is this condition which allows process 3 to be observed as a discrete step.

Process 2, which is an Fe(II)/Fe(I) step, can be represented by eqn. (9).

$$\begin{tikzcd}
\mathrm{Fe(ppdme)} \arrow[r, shift left, "+e^-"] \arrow[d, shift right, "{+\mathrm{Cl}^-\; k_{-2}}"'] & {[\mathrm{Fe(ppdme)}]^-} \arrow[l, shift left, "-e^-"] \arrow[d, shift right, "{+\mathrm{Cl}^-\; k_{-3}}"'] \\
{[\mathrm{Fe(ppdme)Cl}]^-} \arrow[u, shift right, "{-\mathrm{Cl}^-\; k_2}"'] & {[\mathrm{Fe(ppdme)Cl}]^{2-}} \arrow[u, shift right, "{-\mathrm{Cl}^-\; k_3}"']
\end{tikzcd} \tag{9}$$

The reversible half-wave potential, $E^r_{1/2}$ for process 2 when represented solely as

$$\mathrm{Fe(ppdme)} + e^- \rightleftharpoons \mathrm{Fe(ppdme)}^- \tag{10}$$

is considerably more negative than process 3, when represented as in eqn. (1) with the separation in half-wave potentials for processes 1, 2 and 3 being determined by the equilibrium constants associated with eqns. (3) and (4). The fact that the separations are large, means that the cross redox reactions as given in eqn. (11) are highly favoured, and may also contribute to the electrochemical response.

$$[\mathrm{Fe(ppdme)Cl}]^- + [\mathrm{Fe(ppdme)}]^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{Fe(ppdme)} + \mathrm{Fe(ppdme)Cl} \tag{11}$$

By extrapolation of arguments based on the potential differences between processes 1 and 3 it would be predicted that a further process 4 as described in eqn. (12) should exist at a very negative potential [14f] which is outside the available potential range in n-butyronitrile.

$$\begin{tikzcd}
{[\mathrm{Fe(ppdme)Cl}]^-} \arrow[r, shift left, "+e^-"] \arrow[d, shift right, "{-\mathrm{Cl}^-\; k_2}"'] & {[\mathrm{Fe(ppdme)Cl}]^{2-}} \arrow[l, shift left, "-e^-"] \arrow[d, shift right, "{+\mathrm{Cl}^-\; k_3}"'] \\
\mathrm{Fe(ppdme)} \arrow[u, shift right, "{+\mathrm{Cl}^-\; k_{-2}}"'] & {[\mathrm{Fe(ppdme)}]^-} \arrow[u, shift right, "{-\mathrm{Cl}^-\; k_{-3}}"']
\end{tikzcd} \tag{12}$$

Examples of thermodynamically favoured cross redox reactions associated with the presumed existence of process 4 (eqn. (12)) are given by eqns. (13) and (14).

$$[\mathrm{Fe(ppdme)Cl}]^{2-} + \mathrm{Fe(ppdme)} \rightleftharpoons [\mathrm{Fe(ppdme)Cl}]^- + [\mathrm{Fe(ppdme)}]^- \tag{13}$$

$$[\mathrm{Fe(ppdme)Cl}]^{2-} + [\mathrm{Fe(ppdme)}]^+ \rightleftharpoons [\mathrm{Fe(ppdme)Cl}^-] + \mathrm{Fe(ppdme)} \tag{14}$$

Process 4 also provides the 'missing current' in the sense that the sum of the reduction current from processes 1, 2, 3 and 4 should correspond to an overall two electron Fe(III)/Fe(I) process. Experimentally, currents less than this are observed under conditions where process 4 is predicted to be important.

At elevated temperatures, all reactions accompanying electron transfer increase in rate and approach equilibrium. This results in the observation of two one electron, reversible, reduction steps designated as processes 1 and 2 where formally process 1 is a combination of all the Fe(III)/Fe(II) steps and process 2 is a combination of all the Fe(II)/Fe(I) steps. As the temperature is lowered and/or the scan rate increased, equilibrium conditions can no longer be maintained relative to the voltammetric time scale. In the extreme case where totally non-equilibrium conditions apply and cross redox reactions do not influence the voltammetry, four reduction processes would be theoretically expected with the first two corresponding to a total one electron reduction ($\mathrm{Fe^{III}/Fe^{II}}$) and the second two corresponding to a further total one electron reduction ($\mathrm{Fe^{II}/Fe^{I}}$). A summary of the overall mechanism (ignoring some cross redox reactions) is given in eqn. (15).

$$\begin{tikzcd}
{[\mathrm{Fe(ppdme)}]^+} \arrow[r, shift left, "+e^-"] \arrow[d, shift right, "+\mathrm{Cl}^-"'] \arrow[dr, leftrightarrow] & \mathrm{Fe(ppdme)} \arrow[l, shift left, "-e^-"] \arrow[r, shift left, "+e^-"] \arrow[d, shift right, "+\mathrm{Cl}^-"'] \arrow[dl, leftrightarrow] \arrow[dr, leftrightarrow] & {[\mathrm{Fe(ppdme)}]^-} \arrow[l, shift left, "-e^-"] \arrow[d, shift right, "+\mathrm{Cl}^-"'] \arrow[dl, leftrightarrow] \\
\mathrm{Fe(ppdme)Cl} \arrow[r, shift left, "+e^-"] \arrow[u, shift right, "-\mathrm{Cl}^-"'] & {[\mathrm{Fe(ppdme)Cl}]^-} \arrow[l, shift left, "-e^-"] \arrow[r, shift left, "+e^-"] \arrow[u, shift right, "-\mathrm{Cl}^-"'] & {[\mathrm{Fe(ppdme)Cl}]^{2-}} \arrow[l, shift left, "-e^-"] \arrow[u, shift right, "-\mathrm{Cl}^-"']
\end{tikzcd} \tag{15}$$

Equation (15) can be contrasted to reaction scheme (16) which may have been postulated on the

$$\mathrm{Fe(ppdme)Cl} + e^- \rightleftharpoons [\mathrm{Fe(ppdme)Cl}]^- + e^- \rightleftharpoons [\mathrm{Fe(ppdme)Cl}]^{2-} \tag{16}$$

basis of measurements solely made under standard temperatures and time domains. That is, access to a wide range of temperatures and scan rates enables voltammograms to be observed between the extreme of complete chemical reversibility and complete chemical irreversibility and aids the understanding of what appears to be a deceptively simple redox process under conventional temperature and time domain conditions.

The voltammetry of Fe(tpp)Cl in n-butyronitrile follows the same mechanism as for Fe(ppdme)Cl but with a different set of equilibrium and rate constants. For a scan rate of 300 mV s^{-1}, comparison of Figs. 1 and 2 reveal that similar voltammograms are obtained for Fe(tpp)Cl and 20 ℃ and Fe(ppdme)Cl at 100 ℃. The reduction of Fe(tpp)Cl has been studied in a range of other solvents on previous occasions and shown to exhibit a mechanism consistent with that proposed in this study [14a]. The present study clearly reveals in a direct manner and without resort to a detailed theoretical analysis [14a, 18] that the processes are complex. Ready access to a wide temperature and/or time domain, should generally enhance the understanding of all voltammetric processes. It is hoped that the present example will encourage a wider adoption of such methodology.

Acknowledgements

This work was supported financially by the Australian Research Grant Scheme and by the grant of a Fellowship from the Australian–American Education Foundation to G.A.T. The contribution of both these organizations is gratefully acknowledged.

References

1 J. Heyrovský and J. Kůta, *Principles of Polarography*, Academic Press, New York, 1966.

2 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 1980.

3 A. M. Bond, *Modern Polarographic Methods in Analytical Chemistry*, Marcel Dekker, New York, 1980.

4 A. M. Bond, K. B. Oldham and C. G. Zoski, *Anal. Chim. Acta, 216* (1989) 177.

5 (a) M. Fleischmann, S. Pons, D. R. Rolison and P. P. Schmidt (eds.), *Ultramicroelectrodes*, Datatech Systems Publishers, Morganton, NC, 1987; (b) R. M. Wightman and G. O. Wipf, in A. J. Bard (ed.), *Electroanalytical Chemistry*, Vol. 15, Marcel Dekker, New York, 1989, pp. 269–363.

6 C. A. Armatore, A. Jutand and F. Pfluger, *J. Electroanal. Chem., 218* (1987) 361.

7 C. D. Baer, C. A. Camaioni-Neto, D. A. Sweigart, A. M. Bond, T. F. Mann and G. A. Tondreau, *Coord. Chem. Rev., 93* (1989) 1.

8 J. H. Fuhrhop, in K. M. Smith (ed.), *Porphyrins and Metalloporphyrins*, Elsevier, New York, 1975, Ch. 14.

9 R. H. Felton, in D. Dolphin (ed.), *The Porphyrins*, Vol. V, Academic Press, New York, 1978, Ch. 3.

10 D. G. Davis, in D. Dolphin (ed.), *The Porphyrins*, Vol. V, Academic Press, New York, 1978, Ch. 4.

11 (a) K. M. Kadish, in A. B. P. Lever and H. B. Gray (eds.), *Iron Porphyrins*, Addison-Wesley, Reading, MA, 1982, Part 2, Ch. 4; (b) K. M. Kadish, *Prog. Inorg. Chem., 34* (1986) 435.

12 C. K. Mann, in A. J. Bard (ed.), *Electroanalytical Chemistry*, Vol. 3, Marcel Dekker, New York, 1969, pp. 57–134.

13 (a) R. M. Crooks and A. J. Bard, *J. Phys. Chem., 91* (1987) 1274; (b) A. J. Bard, W. M. Flarsheim and K. P. Johnston, *J. Electrochem., 135* (1988) 2001; (c) R. M. Crooks and A. J. Bard, *J. Electroanal. Chem., 240* (1988) 253; (d) T. Nagaoka and S. Okazaki, *J. Phys. Chem., 89* (1985) 2340.

14 (a) D. Lexa, P. Rentien, J. M. Savéant and F. Xu, *J. Electroanal. Chem., 191* (1985) 253; (b) D. Lexa, M. Momenteau, P. Rentien, G. Rytz, J. M. Savéant and F. Xu, *J. Am. Chem. Soc., 106* (1984) 4755; (c) L. A. Bottomley and K. M. Kadish, *Inorg. Chem., 20* (1981) 1348; (d) P. Cocolios and K. M. Kadish, *Israel J. Chem., 25* (1985) 138; (e) D. Feng and M. D. Ryan, *Inorg. Chem., 26* (1987) 2480; (f) A. M. Bond and D. A. Sweigart, *Inorg. Chim. Acta, 123* (1986) 167; (g) W. Byers, J. A. Cossham, J. O. Edwards, A. T. Gordon, J. G. Jones, E. T. P. Kenny, A. Mahmood, J. McKnight, D. A. Sweigart, G. A. Tondreau and T. Wright, *Inorg. Chem., 25* (1986) 4767.

15 J. H. Fuhrhop and K. M. Smith, in K. M. Smith (ed), *Porphyrins and Metalloporphyrins*, Elsevier, New York, Ch. 19, p. 175.

16 C. L. Coyle, P. A. Rofson and E. H. Abbott, *Inorg. Chem., 12* (1973) 2007.

17 K. M. Kadish and R. K. Rhodes, *Inorg. Chem., 22* (1983) 1090.

18 J. M. Savéant and F. Xu, *J. Electroanal. Chem., 208* (1986) 197.