J. Electroanal. Chem., 243 (1988) 117–131
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ELECTROCHEMISTRY IN NEAR-CRITICAL AND SUPERCRITICAL FLUIDS

PART VI. THE ELECTROCHEMISTRY OF FERROCENE AND PHENAZINE IN ACETONITRILE BETWEEN 25 AND 300 ° C

RICHARD M. CROOKS and ALLEN J. BARD
Department of Chemistry, The University of Texas, Austin, TX 78712 (U.S.A.)

(Received 22nd July 1987; in revised form 27th October 1987)

ABSTRACT

Cyclic voltammetry in MeCN at various temperatures and pressures, including supercritical conditions, are described. The reduction wave of phenazine in MeCN/CF_3SO_3Na was reversible or nearly reversible up to 200 ° C. Above 200 ° C, the second reduction wave coalesced with the first. The oxidation of ferrocene in CH_3CN was quasi-reversible between 25 and 285 ° C. Above the critical temperature (T_c) the standard heterogeneous electron transfer ($k°$) decreased. The diffusion coefficients (D) of phenanzine and ferrocene up to T_c are reported, and the determination of viscosity of high temperature/high pressure liquids and fluids based on the measurements of D via the Stokes–Einstein equation is suggested.

INTRODUCTION

Previous reports from this laboratory have demonstrated that inorganic supercritical fluids (SCF), such as water and ammonia, are suitable solvents for electrochemical studies [1]. Wightman and co-workers [2] recently described electrochemical studies in near-critical CO_2 with water. We describe here electrochemistry in the organic supercritical fluid acetonitrile (MeCN), where the voltammetric reduction of phenazine (Ph) and oxidation of ferrocene (Fc) between 25 and 300 ° C were investigated. The one-electron oxidation wave of Fc at low scan rates was reversible or nearly reversible throughout this temperature range. At the highest temperatures the electrochemistry of Ph was complex and is discussed only qualitatively. The diffusion coefficients and the heterogeneous electron transfer rate for Fc and Ph were estimated in supercritical MeCN.

The characteristics of SCF suitable for electrochemical studies have been discussed previously [1d]. MeCN presents a number of advantages and disadvantages compared to H_2O and NH_3. For example, because of its lower critical pressure (P_c), MeCN is more compressible than NH_3 within the limited pressure range available

0022-0728/88/$03.50

for electrochemical experiments. Moreover, the decrease of the dielectric constant (ϵ) with temperature (T) is not as large for MeCN as for H_2O or NH_3. Finally, MeCN is easier to handle experimentally than the inorganic fluids, since it is less corrosive and has a lower P_c.

The higher critical temperature of MeCN ($T_c = 275\,^\circ C$) vs. NH_3 is a disadvantage for two reasons. First, the solvent is more likely to react with electrochemically generated substrates at higher temperatures. This can result in undesirable reactions of reactant or products. Second, the useful polarizable range of most electrodes in SCF decreases with increasing temperature.

We have chosen MeCN as the solvent for this preliminary investigation of organic SCF for several reasons. There is extensive literature of room-temperature studies in MeCN that can be used to predict the electrochemical response of reactions that occur in MeCN at elevated temperature and pressure. MeCN has a low critical pressure ($P_c = 48$ bar), which results in a broad range of available densities [3a]. This is important, since the solvating power of a SCF is controlled by its density. Finally, the polarizable range of MeCN at room temperature is large (ca. 5 to 6 V) and should provide a broad enough potential window for a wide variety of electrochemical investigations at higher temperatures. Polar organic SCF, such as MeCN, have received little attention in the literature. Franck [3] has measured ϵ, and other thermodynamic parameters for a number of fluids at elevated temperature, including MeCN. At room temperature $\epsilon = 38$, while in the supercritical phase, ϵ can be adjusted between about 5 and 15 within the pressure range of our experimental apparatus.

Ph [1d,4] and Fc [5] were chosen as substrates because their electrochemistry has been studied at 25 °C in MeCN and because their electrochemical reactions occur near the middle of the MeCN potential range. In most previous investigations tetraalkylammonium (TAA) salts have been used as supporting electrolyte because they are less subject to ion pairing than metal salts. However, TAA salts may not be thermally stable in supercritical MeCN; therefore, CF_3SO_3Na was used as supporting electrolyte in all experiments reported here. This limited the scope of our results somewhat, since some radical anions precipitate in the presence of alkali metal ions.

The three ring heterocycle Ph undergoes a quasi-reversible reduction to the stable radical anion ($Ph^{\cdot -}$) at room temperature in MeCN. The standard rate constant for heterogeneous electron transfer is 0.02 cm/s [4c]. Further reduction to the dianion (Ph^{2-}) is possible. Ph^{2-} has been reported to be both stable [4b] and unstable [4c] on the voltammetric time scale. At room temperature we have found the stability of Ph^{2-} to depend on the purity of the solvent and type of electrolyte. However, even when extreme precautions were taken to ensure solution purity, Ph^{2-} had a lifetime of only a few seconds in MeCN. In ammonia, both $Ph^{\cdot -}$ and Ph^{2-} were stable on the voltammetric time scale between 25 and 150 °C (supercritical) [1d]. These results suggest that Ph^{2-} undergoes a slow reaction with MeCN at room temperature and a slightly faster reaction if impurities are present.

Fc is oxidized to the ferricinium ion (Fc^+) in a one-electron (quasi-) reversible process in MeCN at room temperature. The standard rate constant of the heterogeneous electron transfer has been variously reported to be in the range 10^{-3} to 1 cm/s [5c,f]. The Fc/Fc^+ couple was chosen for this study, since it has frequently been used as an internal standard, or reference redox couple, for potential measurements in non-aqueous systems [5b,e]. Moreover, the oxidation of Fc is relatively insensitive to small amounts of water and other impurities.

EXPERIMENTAL

The cell, electrodes, and other apparatus have been described in detail in previous reports [1c,e]. For all experiments described here, the 75 ml stainless steel cell (type 2 cell) and tungsten working electrode ($A = 0.0083$ cm^2) were used. The glass liner in this cell assured that there would be no metal-ion contamination of the solution at subcritical temperature. However, stainless steel does not appear to be corroded by supercritical MeCN. This makes MeCN particularly attractive for future investigations, since the type 1 cell [1d], with its advantage of temperature-independent pressure control, can be used for electrochemical studies.

Chemicals

The electrolyte, CF_3SO_3Na, was prepared and purified by the same procedure as the CF_3SO_3K used in previous work [1d], except CF_3SO_3H was neutralized with Na_2CO_3. Ferrocene (Alfa, Danvers, MA) and phenazine (Aldrich, Milwaukee, WI) were vacuum sublimed once before use. HPLC grade MeCN (Mallinckrodt, Paris, KY) was distilled from CaH_2 and twice from P_2O_5 onto activated basic aluminium oxide (Woelm Super 1, Woelm Pharma, GmbH and Co., F.R.G.) and finally subjected to several freeze–pump–thaw cycles to remove oxygen. All chemicals were stored in an inert atmosphere box until needed.

Procedure

The procedure used for preparing the cell has been described [1e]. The only modification to the previously described procedure involved addition of solvent to the cell. For the experiments reported here, MeCN was added directly to the cell along with substrate and electrolyte in the dry box.

Electrochemical measurements

All electrochemical measurements were made by cyclic voltammetry (CV) or chronocoulometry [1d,e,6]. In all CV measurements positive feedback iR compensation was employed. $E_{1/2}$ values were obtained by averaging the cathodic and anodic peak potentials ($E_{p,c}$ and $E_{p,a}$) obtained from the cyclic voltammograms for Fc [6]. Because of interference from the second reduction of Ph, reliable $E_{1/2}$ data could not be obtained for Ph above 200 ° C. Therefore, at $T > 200$ ° C, $E_{1/2}$ was estimated from the difference in $E_{p,c}$ and $E_{p,a}$, but it may not be thermodynamically significant because of the occurrence of following reactions. The estimated error for the potential measurements is ± 15 mV below 200 ° C and ± 25 mV above 200 ° C.

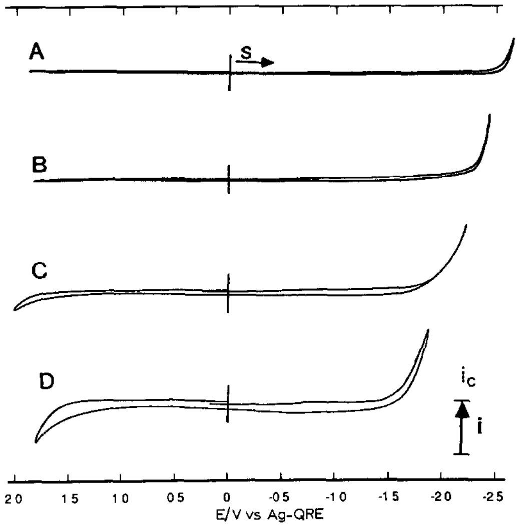

Fig. 1. Cyclic voltammetry of acetonitrile+CF_3SO_3Na (background polarization) as a function of temperature. (A) $T = 25\,°C$; $P = 1.0$ bar; $c\{CF_3SO_3Na\} = 0.20$ M; $v = 0.2$ V/s; $i = 20$ μA. (B) $T = 100\,°C$; $P = 1.7$ bar; $c\{CF_3SO_3Na\} = 0.18$ M; $v = 0.2$ V/s; $i = 20$ μA. (C) $T = 200\,°C$; $P = 18.6$ bar; $c\{CF_3SO_3Na\} = 0.14$ M; $v = 0.5$ V/s; $i = 50$ μA. (D) $T = 300\,°C$; $P = 200$ bar; $c\{CF_3SO_3Na\} = 0.11$ M; $v = 1.0$ V/s; $i = 50$ μA. All scans began and ended at the vertical mark (0 V vs. Ag-QRE). In (A) and (B) the positive voltage limit is not shown since the tungsten disk electrode (area = 0.0083 cm^2) was passivated at $E > +2.0$ V. The length of the line labeled "i" represents the current scale as defined above. The tungsten electrode had an area of 0.0083 cm^2.

All potentials are reported versus the silver quasi-reference electrode (Ag-QRE) [1d]. The Ag-QRE provided a reasonably stable reference potential over a period of several hours in MeCN, but because it does not provide a thermodynamically meaningful potential, no quantitative thermodynamic conclusions are drawn from the potential data. In future experiments it would be useful to include a reference redox couple, such as Fc/Fc^+ [5b], in the cell with the substrate under investigation to provide a more stable and meaningful reference potential.

The current ratios, $i_{p,a}/i_{p,c}$ for the first reduction of Ph or $i_{p,c}/i_{p,a}$ for the oxidation of Fc, were calculated using Nicholson's [7] semi-empirical technique. $i_{p,a}$ and $i_{p,c}$ are the anodic and cathodic peak currents [6].

RESULTS AND DISCUSSION

Background processes

Cyclic voltammetric curves for CH_3CN, CF_3SO_3Na solutions at a tungsten disk electrode between 25 and 300 °C are shown in Fig. 1. For comparison, the current sensitivity, electrolyte concentration and density were roughly the same as those used for the voltammetry of Ph and Fc. The electrolyte, CF_3SO_3Na, is not electrochemically active within the polarizable limits of MeCN at any temperature [8]. This permits the broadest possible potential range to be accessed. Additionally, the alkali metal trifluoromethanesulfonates (triflates) are very easily purified, and since they have high decomposition temperatures (i.e., > 300 ° C) [8b], they can be thoroughly dehydrated, even though the Na and Li salts are deliquescent. Finally, the alkali metal triflates are inert towards many chemical reactions, are poor ligands, and are soluble in most solvents with $\epsilon > 5$. Na and Li triflates are sufficiently soluble in MeCN up to 300 ° C that solution resistance is low. The K salt is insoluble below 100 ° C and is heavily ion paired above this temperature.

Tetraalkylammonium (TAA) salts have been used as supporting electrolytes in organic solvents because they are bulky, so that ion pair formation is sterically hindered. It would be convenient to use TAA electrolytes in SCF where ions pairing can be particularly troublesome, because small sterically accessible ions, such as the anion radicals of tetracyanoquinodimethane ($TCNQ^{\cdot -}$) or 1,4-dinitrobenzene ($1,4\text{-}DNB^{\cdot -}$), form ions paired complexes with Na^+ that are insoluble in MeCN at room temperature. However, both $TCNQ^{\cdot -}$ and $1,4\text{-}DNB^{\cdot -}$ were soluble and showed reversible electrochemistry up to 150 ° C in the presence of tetra-n-butylammonium (TBA) triflate. TBA triflate is thermally unstable in MeCN above 200 ° C, which precludes its use as an electrolyte in most supercritical organic solvents.

For the work described here, it was necessary to choose substrates, such as Ph and Fc, that are not particularly sensitive to ion pairing with Na^+ in MeCN. The delocalization of the unpaired electron over the large aromatic $Ph^{\cdot -}$ ion probably prevents extensive ion pairing, while localization of charge on the protected metal center and the bulky sulfonate ion prevent precipitation of Fc^+.

With CF_3SO_3K as a supporting electrolyte in ammonia, the resistance of the solution increased with temperature up to the T_c. This was probably caused by ion pairing and a decrease in the specific solvating forces of ammonia [9]. The conductivity of the $MeCN/CF_3SO_3Na$ system approximately doubled as the temperature was raised from 25 to 100 ° C, and continued a gradual increase to 300 ° C. Increased ionic mobility is probably responsible for this effect.

The most important features in Fig. 1 are the absence of major impurity peaks between the background limits and the large useful potential range, even in the SCF, Fig. 1d. The absence is especially important, since it means MeCN, and probably other suprcritical organic solvents, do not corrode metal cells. The background voltammetry was not substantially changed from that shown in Fig. 1d when the solution was allowed to contact the metal cell for up to 8 h at 300 ° C and 200 bar. Upon cooling to room temperature, no new waves were observed.

The typical available potential range in MeCN is between 5 and 6 V at 25 ° C, depending upon electrolyte impurities [6]. The anodic limit of our system at this temperature, Fig. 1a, was reduced somewhat because the electrode formed a passivating film, probably tungsten oxide, positive of +2.0 V. The source of the oxide may have been trace water or oxygen in the solvent. Overall, the useful range decreased from 4.5 V at 25 ° C to between 3.0 and 3.5 V at 300 ° C.

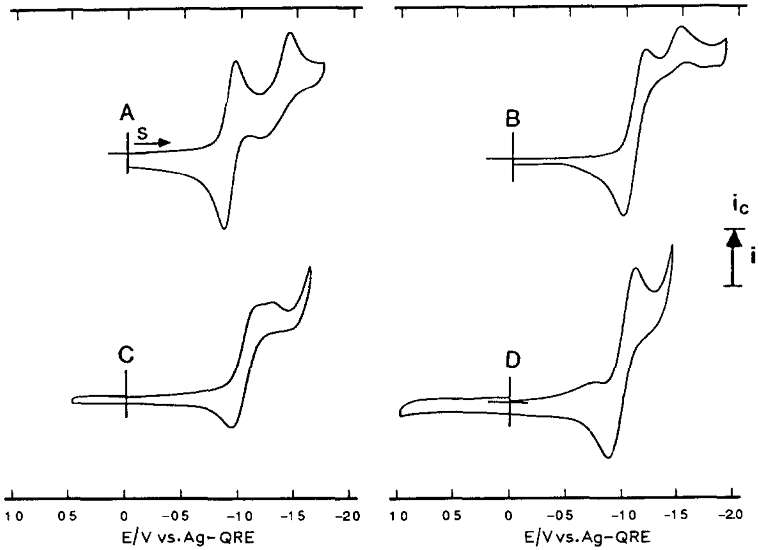

Fig. 2. Cyclic voltammetry of the reduction of phenazine (Ph) in acetonitrile + CF_3SO_3Na as a function of temperature: (A) $T = 100\,°C$; $P = 1.7$ bar; $c_{Ph} = 8.2$ mM; $c\{CF_3SO_3Na\} = 0.18$ M; $v = 0.5$ V/s; $i = 50$ μA. (B) $T = 200\,°C$; $P = 15.6$ bar; $c_{Ph} = 6.5$ mM; $c\{CF_3SO_3Na\} = 0.14$ M; $v = 0.5$ V/s; $i = 50$ μA. (C) $T = 250\,°C$; $P = 34.2$ bar; $c_{Ph} = 5.1$ mM; $c\{CF_3SO_3Na\} = 0.11$ M; $v = 0.5$ V/s; $i = 100$ μA. (D) $T = 300\,°C$; $P = 175$ bar; $c_{Ph} = 5.2$ mM; $c\{CF_3SO_3Na\} = 0.11$ M; $v = 1.0$ V/s; $i = 100$ μA. All scans began and ended at the vertical mark (0 V vs. Ag-QRE).

At the positive limit at any temperature, a passivating polymer film formed on the electrode surface, which sometimes could be removed by the application of a short high-voltage pulse. The film was probably polyacetonitrile, which has been suggested to form in the positive background processes in MeCN solutions at room temperature [10]. Potential excursions into the negative background did not affect subsequent electrochemical measurements.

Phenazine

The cyclic voltammetry of Ph between 100 and 300 °C is shown in Fig. 2. The data derived from these and other voltammograms are collected in Table 1. At 25 °C the first wave is reversible at slow scan rates, but above 1 V/s $i_{p,a}/i_{p,c}$ decreases and ΔE_p increases from near the theoretical value of 59 mV to 188 mV at 20 V/s. In a previous study by Sawyer [4c], a similar variation of ΔE_p with v was reported, and was attributed to a slow electron transfer. However, in this case the diminished value of $i_{p,a}/i_{p,c}$ suggests a different or additional process, such as a following chemical reaction (EC mechanism). For most EC reactions $i_{p,a}/i_{p,c}$ increases with scan rate [6], but for a reversible dimerization, $i_{p,a}/i_{p,c}$ decreases with v in a way that is in qualitative agreement with the results reported here [11]. Millefiori [4b] found that a series of related aza-aromatics (e.g., quinoxaline,

TABLE 1

Cyclic voltammetric data for phenazine

v/V s^{-1}	ΔE_p/mV	$-E_{1/2}$/V [a]	$i_{p,c}v^{-1/2}c^{-1}$/μA $s^{1/2}$ $V^{-1/2}$ M^{-1}	$i_{p,a}/i_{p,c}$
$T = 25\,°C$, $P = 1$ bar, $D = 2.4 \times 10^{-5}$ cm²/s, $c = 9.1$ mM, $\rho = 0.78$ g/cm³				
0.1	64	1.165	9.6	1.00
0.2	68	1.152	9.5	0.97
0.5	72	1.122	9.7	0.93
1.0	88	1.118	9.7	0.90
2.0	115	1.111	9.4	0.88
4.0	131	1.111	9.1	0.87
8.0	157	1.102	8.8	0.86
10.0	168	1.100	8.7	0.85
15.0	181	1.101	8.5	0.86
20.0	188	1.098	8.3	0.85
Theoretical [b]	59			1.00
Average		1.118	9.1	0.90
σ		0.023	0.5	0.05
$T = 100\,°C$, $P = 1.7$ bar, $D = 6.6 \times 10^{-5}$ cm²/s, $c = 8.2$ mM, $\rho = 0.70$ g/cm³				
0.1	98	1.123	17.0	–
0.2	96	1.122	15.6	0.92
0.5	104	1.120	15.1	0.96
1.0	109	1.120	14.7	0.96
2.0	115	1.121	14.5	0.96
4.0	117	1.120	14.4	0.96
8.0	119	1.119	14.2	0.95
10.0	121	1.120	14.3	0.95
15.0	131	1.119	14.1	0.95
20.0	135	1.117	13.9	0.95
Theoretical	74			1.00
Average		1.102	14.8	0.95
σ		0.002	0.9	0.01
$T = 200\,°C$, $p = 18.6$ bar, $D = 1.9 \times 10^{-4}$ cm²/s, $c = 6.5$ mM, $\rho = 0.56$ g/cm³				
0.5	188	1.121	22.3	0.85
1.0	190	1.118	20.1	0.93
2.0	203	1.110	19.3	1.00
4.0	205	1.113	19.4	1.00
8.0	221	1.105	19.9	0.98
10.0	233	1.111	20.0	0.98
15.0	238	1.113	20.4	0.97
20.0	256	1.112	20.6	0.97
Theoretical	94			1.00
Average		1.113	20.3	0.96
σ		0.005	0.9	0.05

Estimated parameters for phenazine in supercritical AN [c]

T/°C	P/bar	$-E_{1/2}$/mV	ρ/g cm^{-3}	c/mM	D/cm² s^{-1}
300	175	1.032	0.45	5.2	2.5×10^{-4}

[a] Since $i_{p,a}/i_{p,c} \neq 1$ at fast scan rates the most reliable values of $E_{1/2}$ were at the lowest scan rates.

[b] For a one-electron reversible process with stable product.

[c] $E_{1/2}$ and D were estimated assuming the single wave observed at this temperature was a two-electron

pyrazine, and acridine) dimerized in MeCN at 25 °C when 0.1 *M* tetra-n-ethylammonium perchlorate was used as supporting electrolyte. Others have shown that alkali metal ions promote the dimerization of anion radicals in MeCN and other

TABLE 2

Heterogeneous rate constants for ferrocene and phenazine

Ferrocene

v/V s^{-1}	ΔE_p/mV	a [a]	ψ [b]	$k°$/cm s^{-1}
T = 25 °C, P = 1 bar, D = 2.6×10^{-5} cm^2/s, c = 6.1 mM, η = 0.345 cp				
20.0	87	7.8×10^2	0.90	0.23
40.0	92	1.6×10^3	0.75	0.27
60.0	110	2.3×10^3	0.46	0.20
80.0	114	3.1×10^3	0.42	0.21
100.0	124	3.9×10^3	0.35	0.20
Average				0.22 ± 0.05
σ				0.03
T = 100 °C, P = 1.7 bar, D = 6.5×10^{-5} cm^2/s, c = 5.4 mM, η = 0.17 cp				
5.0	85	1.6×10^2	0.98	0.17
10.0	94	3.1×10^2	0.70	0.18
20.0	104	6.2×10^2	0.52	0.19
40.0	104	1.2×10^3	0.52	0.26
60.0	104	1.9×10^3	0.52	0.32
80.0	107	2.5×10^3	0.49	0.35
100.0	113	3.1×10^3	0.43	0.34
Average				0.26 ± 0.05
σ				0.08
T = 200 °C, P = 18.6 bar, D = 8.6×10^{-5} cm^2/s, c = 4.3 mM, η = 0.15 cp				
1.0	102	2.5×10	0.55	0.045
2.0	102	4.9×10	0.55	0.063
5.0	107	1.2×10^2	0.49	0.093
10.0	109	2.5×10^2	0.47	0.12
20.0	109	4.9×10^2	0.47	0.17
40.0	113	9.8×10^2	0.43	0.22
60.0	121	1.5×10^3	0.37	0.24
80.0	115	2.0×10^3	0.41	0.30
100.0	156	2.5×10^3	0.19	0.16
Average				0.16 ± 0.05
σ				0.09

Estimated parameters for ferrocene in supercritical AN

T/°C	P/bar	a	c/mM	D/cm^2 s^{-1}	ψ	η/cp	ΔE_p/mV	$k°$/cm s^{-1}
275	125	21	3.7	2.4×10^{-4}	0.31	0.07	(at 1 V/s) 130	0.04 ± 0.02

TABLE 2 (continued)

Phenazine

v/V s^{-1}	ΔE_p/V	a[a]	ψ[b]	k°/cm s^{-1}
$T = 100\,^\circ C$, $P = 1.7$ bar, $D = 6.6\times10^{-5}$ cm^2/s, $c = 8.2$ mM, $\eta = 0.17$ cp				
1.0	109	3.1×10	0.47	0.04
2.0	115	6.2×10	0.41	0.05
4.0	117	1.2×10^2	0.39	0.06
8.0	119	2.5×10^2	0.38	0.09
10.0	121	3.1×10^2	0.37	0.09
15.0	131	4.7×10^2	0.30	0.09
20.0	135	6.2×10^2	0.28	0.10
Average				0.07 ± 0.03
σ				0.02
$T = 200\,^\circ C$, $P = 18.6$ bar, $D = 1.9\times10^{-4}$ cm^2/s, $c = 6.5$ mM, $\eta = 0.15$ cp				
1.0	190	2.5×10	0.12	0.02
2.0	203	4.9×10	0.11	0.02
4.0	205	9.8×10	0.10	0.02
8.0	221	2.0×10^2	0.09	0.03
Average				0.02 ± 0.01
σ				0.01

[a] $a = Fv/RT$.
[b] $k^\circ = \psi\,(\pi a D)^{1/2}$.

solvents [12]. Therefore, a reversible dimerization may be responsible for the behavior of Ph at room temperature. This subject was not explored further.

At moderate temperature (100 to 200 ° C) $i_{p,a}/i_{p,c}$ was near the theoretical value of 1.0 expected for an electron transfer resulting in a stable product [6]. The same behavior was observed for dimerization reactions in ammonia as the temperature was raised [1e]. That is, increased temperature reduced the equilibrium constant for the dimerization (i.e., the rate of the back reaction became significant). In this temperature regime, ΔE_p increases with v, but since $i_{p,a}/i_{p,c}$ is ca. 1, it probably represents the effect of a quasi-reversible heterogeneous electron transfer. Above 200 ° C the second reduction of Ph is too close to the first to allow accurate estimates of ΔE_p or $i_{p,a}/i_{p,c}$ (Figs. 2c,d).

The heterogeneous electron transfer rate constant (k°) can be estimated from the difference between the cathodic and anodic peak potentials (ΔE_p) and the diffusion coefficients of the oxidized and reduced substrate (D_O and D_R) from Nicholson's treatment [13]. The relevant equations are

$$k^\circ = \left[\psi(\pi a D_O)^{1/2}/\gamma^{\alpha}\right] \tag{1}$$

$$a = nFv/RT \tag{2}$$

$$\gamma = (D_O/D_R)^{1/2} \tag{3}$$

where ψ (which is obtained from a working curve) is a dimensionless parameter dependent on the magnitude of ΔE_p, v is the scan rate, R is the gas constant, F is the Faraday constant, and α is the transfer coefficient. If D_R is set equal to D_O, the calculation is simplified somewhat. Only ΔE_p values that fell in the sensitive region of the ψ working curve ($85\ \text{mV} \leqslant \Delta E_p \leqslant 221\ \text{mV}$) were used to calculate the average value of k°.

In the absence of solvent reorganization, transition state theory predicts an increase in k° with temperature [14]. A slight decrease in k° is observed for Ph as the temperature is raised from 100 to 200 °C, Table 2; however, the change in k° with temperature is small and probably within the precision limits for the estimation of k°. Nevertheless, large changes in solvation are expected near Tc, which could be responsible for a decrease in k° with increasing temperature. A similar dependence of k° on temperature was found for Fc, suggesting that the decrease in k° may be real. A contribution from uncompensated resistance effects to ΔE_p may also be present; note, however, that the solution resistance decreased as the temperature was raised.

$E_{1/2}$ values (vs. a quasi-reference electrode) for the first reduction of Ph are listed in Table 1. Over a range of about 200 °C, the $E_{1/2}$ values are fairly constant vs. Ag-QRE. This is contrary to previous results in ammonia [1d,e,11a], where the potential shifted about -2 mV/°C vs. the onset of solvated electrons (e_s^-). There, e_s^- serves as an internal potential standard, but no such convenient reference potential is readily available for MeCN at elevated temperatures. $E_{1/2}$ was estimated in supercritical MeCN by assuming that the single wave (Fig. 2d) was a two-electron process resulting in a stable product. This is probably not a completely valid assumption, and the error in this measurement may be significant.

The second wave for the reduction of Ph corresponds to the formation of the dianion (Ph^{2-}) at 25 °C in most aprotic solvents with TAA electrolytes [4]. In the presence of Na^+, Ph^{2-} is not stable between 25 and 300 °C, Fig. 2. This may be the result of ion pairing or a following reaction, such as dianion-substrate coupling. A quantitative analysis of this wave was beyond the scope of this initial study. The important result derived from the voltammetry of Ph is that the two waves coalesce into a single wave at ca. 275 °C. This probably represents a two-electron reduction of Ph. The presence of the reverse wave at 300 °C, Fig. 2d, suggests that the product of the reduction is at least somewhat stable on the voltammetric time scale, even in the SCF. The presence of the prewave is indicative of a following reaction, which is probably protonation of the dianion by nucleophilic attack on MeCN or trace water. Upon cooling the SCF back to room temperature, the voltammetry of Fig. 2a is recovered except for a shift in potential, demonstrating that Ph itself is not reactive towards MeCN at elevated temperature.

Diffusion coefficients were evaluated for Ph in MeCN between 25 and 300 °C. D_O ranged from $2.4 \times 10^{-5}\ \text{cm}^2/\text{s}$ at 25 °C to $2.5 \times 10^{-4}\ \text{cm}^2/\text{s}$ at 300 °C, Table 1. These results are consistent with those reported previously for Ph in ammonia [1d,11a], and the room temperature value is only slightly lower than that reported by Sawyer [4c], $2.9 \times 10^{-5}\ \text{cm}^2/\text{s}$. A detailed analysis of the diffusion data is precluded because the viscosity (η) of MeCN at elevated temperature and pressure has not been measured. To calculate D_O above 200 °C, a step to a potential negative of both Ph waves was necessary, and η, the number of electrons transferred, was assumed to be 2.

Ferrocene

Cyclic voltammograms for the oxidation of Fc between 25 and 275 °C are shown in Fig. 3, and the data derived from this figure are collected in Table 3. At subcritical temperature we observed an uncomplicated one electron oxidation of Fc to Fc^+. Evidence for this includes near theoretical ΔE_p values at low scan rates, E_p independent of v over four decades, and $i_{p,c}/i_{p,a} = 1$ over a 250 °C temperature range. The low temperature results are in accord with previously published results for the oxidation of Fc at room temperature [5].

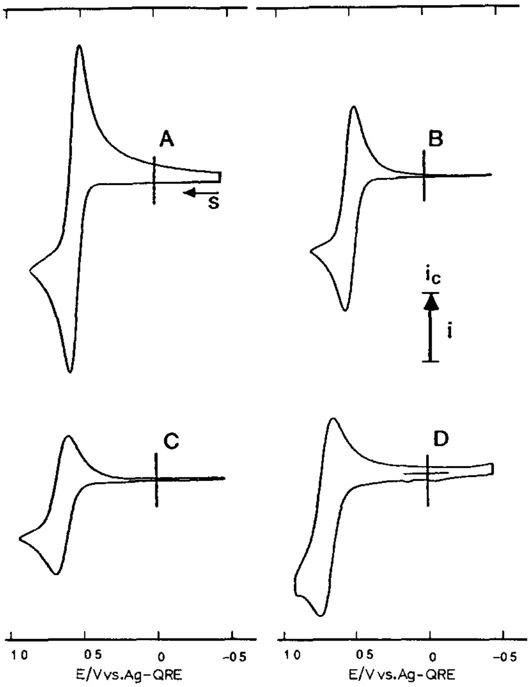

Fig. 3. Cyclic voltammetry of the oxidation of ferrocene in acetonitrile + CF_3SO_3Na as a function of temperature: (A) $T = 25$ °C; $P = 1.0$ bar; $c_{Fc} = 6.1$ mM; $c\{CF_3SO_3Na\} = 0.20$ M; $v = 0.2$ V/s; $\iota = 10$ μA. (B) $T = 100$ °C; $P = 1.7$ bar; $c_{Fc} = 5.4$ mM; $c\{CF_3SO_3Na\} = 0.18$ M; $v = 0.2$ V/s; $i = 20$ μA. (C) $T = 200$ °C; $P = 18.6$ bar; $c_{Fc} = 4.3$ mM; $c\{CF_3SO_3Na\} = 0.14$ M; $v = 0.5$ V/s; $i = 50$ μA. (D) $T = 275$ °C; $P = 125$ bar; $c_{Fc} = 3.7$ mM; $c\{CF_3SO_3Na\} = 0.11$ M; $v = 1.0$ V/s; $i = 50$ μA. The vertical mark is at 0 V (vs. Ag-QRE); all scans began at −0.5 V. The length of the line labeled "i" represents the current scale as defined above. The tungsten electrode had an area of 0.0083 cm^2.

TABLE 3

Cyclic voltammetric data for ferrocene

v/V s^{-1}	ΔE_p/mV	$E_{1/2}$/V	$i_{p,a}v^{-1/2}c^{-1}/\mu$A s$^{1/2}$ V$^{-1/2}$ M^{-1}	$i_{p,c}/i_{p,a}$
$T = 25\,°C$, $P = 1$ bar, $D = 2.6\times10^{-5}$ cm^2/s, $c = 6.1$ mM, $\rho = 0.78$ g/cm^3				
0.1	58	0.617	11.5	0.96
0.2	59	0.616	11.4	0.97
0.5	61	0.616	11.2	0.97
1.0	65	o.615	10.7	1.00
2.0	72	0.614	10.5	1.00
5.0	78	0.614	10.4	1.01
10.0	80	0.615	10.3	1.02
20.0	87	0.620	10.0	1.02
40.0	92	0.627	9.7	1.03
60.0	110	0.625	9.4	1.04
80.0	114	0.621	9.3	1.03
100.0	124	0.620	9.1	1.04
Theoretical [a]	59			1.00
Average		0.618	10.2	1.01
σ		0.004	0.8	0.03
$T = 100\,°C$, $P = 1.7$ bar, $D = 6.5\times10^{-5}$ cm^2/s, $c = 5.4$ mM, $\rho = 0.70$ g/cm^3				
0.2	80	0.557	15.1	0.83
0.5	78	0.551	14.7	0.96
1.0	80	0.556	14.1	0.97
2.0	82	0.557	13.8	0.99
5.0	85	0.559	13.5	1.00
10.0	94	0.556	13.5	1.02
20.0	104	0.549	13.2	1.02
40.0	104	0.551	13.1	1.03
60.0	104	0.547	12.9	1.04
80.0	107	0.554	12.7	1.04
100.0	113	0.552	12.7	1.05
Theoretical	74			1.00
Average		0.554	13.5	1.00
σ		0.004	0.6	0.06
$T = 200\,°C$, $P = 18.6$ bar, $D = 8.6\times10^{-5}$ cm^2/s, $c = 4.3$ mM, $\rho = 0.56$ g/cm^3				
0.5	109	0.686	17.0	–
1.0	102	0.688	16.5	0.86
2.0	102	0.690	16.0	0.94
5.0	107	0.691	15.8	1.00
10.0	109	0.694	15.8	1.02
20.0	109	0.696	15.7	1.04
40.0	113	0.700	15.9	1.06
60.0	121	0.700	16.5	1.07
80.0	115	0.701	16.6	1.08
100.0	156	0.705	16.3	1.07
Theoretical	94			1.00
Average		0.695	16.2	1.02
σ		0.006	0.4	0.07

TABLE 3 (continued)

Estimated parameters for ferrocene in supercritical AN						
$T/°C$	P/bar	$E_{1/2}$/V	ρ/g cm^{-3}	c/mM	D/cm^2 s^{-1}	ΔE_p/mV (at 1 V/s)
275	125	0.730	0.47	3.7	2.4×10^{-4}	130

[a] For a one-electron reversible process with stable product.

Measurement of ΔE_p, $E_{1/2}$ and $i_{p,c}/i_{p,a}$ above T_c were in general agreement with the lower temperature measurements, but the precision of these measurements was not as high because of the proximity of the wave to the background. Mild filming of the electrode may have occasionally occurred above T_c. However, upon cooling the Fc/MeCN solution to room temperature, no evidence of electrode filming was observed, and the original voltammetric behavior returned, except for a slight shift in potential. A UV–visible absorption spectrum of the cooled solution was identical to the initial Fc/MeCN solution, indicating that Fc does not react with hot MeCN. The Fc/Fc$^+$ couple could serve as a reference redox couple for potential measurements made in organic solvents at elevated temperature, since its E_p value was independent of v and constant for several hours vs. Ag-QRE at a particular temperature.

From the tabulated values of ΔE_p as a function of v, Table 2, $k°$ was estimated for Fc between 25 and 275°C. The range of $k°$ is from 0.22 cm/s at 25°C and 1 bar to 0.04 cm/s at 275°C and 125 bar. At 25°C, $k°$ is within the range of previously published results (10^{-3}–1 cm/s) [5]. The decrease of $k°$ with increasing temperature is most pronounced in the critical region, where changes in solvation and ϵ are expected to be greatest. Since there were no serious complications in measuring ΔE_p throughout the 250°C range, these results probably represent a real decrease in $k°$ with increasing temperature. To our knowledge, $k°$ has not previously been measured at temperatures as high as those used here. SCF may provide the means for studying unusual effects on heterogeneous and homogeneous electron transfer rates brought about by major changes in solvation. More data from other redox substrates in the high temperature regime are necessary to determine the generality of the results reported here.

Over the temperature range 25 to 275°C, D_R for Fc increased from 2.6×10^{-5} to 2.4×10^{-4} cm^2/s, Table 3. This result is of the same order of magnitude as that found for Ph. The room temperature value is in agreement with previously published results of 2.2×10^{-5} cm^2/s for Fc in MeCN [5c,d].

The Stokes–Einstein equation has been shown to be valid over a broad range of temperatures and solution conditions [1]. From the known value of η for MeCN at 25°C, 0.345 cp [15], η can be estimated at any temperature using the Stokes–Einstein equation,

$$D = kT/6\pi r\eta \tag{4}$$

if the effective molecular radius, r, of Fc (0.25 nm) does not change with temperature. In ammonia many substrates have been shown to have relatively constant r over a broad temperature range [1d]. The calculated viscosity of MeCN is 0.07 cp at 275 ° C and 125 bar. Other values are listed in Table 2.

CONCLUSIONS

We have demonstrated that electrochemical measurements in supercritical MeCN are possible. Furthermore, two substrates, Fc and Ph, were stable throughout the temperature range studied. Ph gave two voltammetric waves at 25 ° C; the first was a reversible one-electron reduction, and the second was a quasi-reversible reduction, the product of which was only moderately stable. In the SCF these waves coalesced into a single wave. Fc showed reversible to quasi-reversible voltammetric waves throughout the temperature range studied, and Fc^+ was stable on the voltammetric time scale.

Preliminary evidence suggests that k° decreases slightly at elevated temperature and more sharply in the critical region. Because of the difficulty in measuring ΔE_p accurately above T_c and because of the possibility of processes other than the heterogeneous electron transfer control ΔE_p, more data should be obtained for other substrates before this trend is considered to be general. The decrease in k°, which would arise from difference in the solvent reorganization energy, is not wholly unexpected because of the unique solvating properties of near-critical and supercritical fluids. Near the critical point changes in ϵ with pressure are steepest. This region should be of special interest in future investigations of solvation effects on rates.

The diffusion coefficients of Fc and Ph increased by an order of magnitude over a temperature range of about 270 ° C. The Stokes-Einstein equation along with the diffusion coefficient were used to estimate the viscosity of MeCN at several temperatures. This is a simple method for determining viscosity, if the effective molecular radius of the substrate does not change greatly in the temperature/pressure rang of interest.

ACKNOWLEDGEMENT

The support of this research by the Office of Naval Research (N00014-84-K-0428) is gratefully acknowledged.

REFERENCES

1 (a) A.C. McDonald, F.-R.F. Fan and A.J. Bard, J. Phys. Chem., 90 (1986) 196; (b) W.M. Flarsheim, Y.-M. Tsou, I. Tractenberg, K.P. Johnston and A.J. Bard, ibid., 90 (1986) 3857; (c) R.M. Crooks, F.-R.F. Fan and A.J. Bard, J. Am. Chem. Soc., 106 (1984) 6851; (d) R.M. Crooks and A.J. Bard, J. Phys. Chem., 91 (1987) 1274; (e) R.M. Crooks and A.J. Bard, J. Electroanal. Chem., 240 (1988) 253.

2 M.E. Philips, M.R. Deakin, M.V. Novotny and R.M. Wightman, J. Phys. Chem. 91 (1987) 3934.

3 (a) A.Z. Francesconi, E.U. Franck and H. Lentz, Ber. Bunsenges. Phys. Chem., 79 (1979) 897; (b) E.U. Franck Kelm (Ed.), High Pressure Chemistry, Reidel, Boston, 1978, p. 243; (c) E.U. Franck, Ber. Bunsenges. Phys. Chem., 88 (1984) 820; (d) E.U. Franck and R. Duel, Faraday Discuss. Chem. Soc., 66 (1978) 191; (e) R. Diguet, R. Duel and E.U. Franck, Ber. Bunsenges. Phys. Chem., 89 (1985) 800.

4 (a) R.L. Ward, J. Am. Chem. Soc., 84 (1962) 332; (b) S.J. Millefiori, Heterocycl. Chem., 7 (1970) 145; (c) D.T. Sawyer and R.Y. Komai, Anal. Chem., 44 (1972) 715; (d) E.W. Stone and A.H. Maki, J. Chem. Phys., 39 (1963) 1635; (e) B.J. Tabner and J.R. Yandle, J. Chem. Soc. (A), (1968) 381.

5 (a) A.J. Zara, S.S. Machado, L.O.S. Bulhões, A.V. Benedetti and T. Rabockai, J. Electroanal. Chem., 221 (1987) 165; (b) R.R. Gagné, C.A. Koval and G.G. Lisensky, Inorg. Chem., 19 (1980) 2855; (c) M.I. Montenegro and D. Pletcher, J. Electroanal. Chem., 200 (1986) 371; (d) T. Kuwana, D.E. Bublitz and G. Hoh, J. Am Chem. Soc., 82 (1960) 5811; (e) J.W. Diggle and A.J. Parker, Electrochim. Acta, 18 (1973) 975; (f) A.M. Bond, T.L.E. Henderson, T.F. Mann, W. Thormann and C.G. Zoski, J. Electroanal. Chem., submitted.

6 A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980.

7 R.S. Nicholson, Anal. Chem., 38 (1966) 1406.

8 (a) K. Rousseau, G.C. Farrington and D. Dolphin, J. Org. Chem., 37 (1972) 3968; (b) R.D. Howells and J.D. McCown, Chem. Rev., 77 (1977) 69.

9 D. Nicholls in R.J.H. Clark (Ed.), Inorganic Chemistry in Liquid Ammonia, Elsevier, New York, 1979, pp. 10–20.

10 (a) J. Ouyang and A.J. Bard, J. Electroanal. Chem., 222 (1987) 331; (b) G. Tourillon, P.-C. Lacaze and J.-E. Dubois, ibid., 100 (1979) 247; (c) P.C. Lacaze and G. Tourillon, J. Chim. Phys., 76 (1979) 371; (d) C.V. Oprea, M. Popa and N. Hurduc, Polymer J., 16 (1984) 191.

11 (a) R. Crooks, Ph. D. Dissertation, Univ. of Texas at Austin, 1987, 4, and references therein; (b) C. Amatore, D. Garreau, M. Hammi, J. Pinson and J.M. Savéant, J. Electroanal. Chem., 184 (1985) 1.

12 (a) W.V. Childs, J.T. Maloy, C.P. Keszthelyi and A.J. Bard, J. Electrochem. Soc., 118 (1971) 874; (b) M.J. Hazelrigg and A.J. Bard, ibid., 122 (1975) 211; (c) O.R. Brown, R.J. Butterfield and J.P. Millington, Electrochim. Acta, 27 (1982) 1655.

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

14 R.A. Marcus, (a) Annu. Rev. Phys. Chem., 15 (1964) 155, and references therein; (b) J. Chem. Phys., 24 (1956) 966.

15 R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, 53rd ed., CRC Press Cleveland OH, 1972, p. F-37.