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Electrochemistry in near-critical and supercritical fluids

Part 8. Methyl viologen, decamethylferrocene, $Os(bpy)_3^{2+}$ and ferrocene in acetonitrile and the effect of pressure on diffusion coefficients under supercritical conditions

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ABSTRACT

The cyclic voltammetry (CV) of methyl viologen (MV^{2+}), decamethylferrocene (DMFc), $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and ferrocene (Fc) was studied at high temperatures and pressures in a small cell (7.5 ml) where the pressure and temperature could be varied independently. While the CV of MV^{2+} and $Os(bpy)_3^{3+}$ remained well-behaved with reversible or quasi-reversible waves only into the near-critical region (up to ca. 230 ° C), Fc and DMFc showed well-defined behavior under supercritical conditions. The diffusion coefficient of ferrocene was measured at a supercritical temperature (280 ° C) as a function of pressure, and the experimental results were correlated to values calculated by the Stokes–Einstein relation.

INTRODUCTION

We report here further studies of electrode reactions in near-critical and supercritical acetonitrile (MeCN). We have been interested in electrochemistry under these conditions, because small changes in pressure and temperature in the near-critical and supercritical region of a fluid can result in large changes in solvent properties. For example, the viscosity and dielectric constant of a supercritical fluid (SCF) are related to the density, which can be readily varied by changes in the temperature and pressure of the system. Moreover, SCF have been used extensively for extraction [1] and chromatography [2]. Previous studies from our laboratory and elsewhere have dealt with the use of NH_3 [3,4], water [5–7[, CO_2/H_2O [8], MeCN [9,10], and SO_2 [11] as media for voltammetric investigations under near-critical and

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supercritical conditions. There have been reports of the application of H_2O [7] and CO_2/MeOH [12] for electrosynthetic applications as well.

MeCN has been used extensively as a solvent in electrochemistry for many years. This solvent has a critical temperature (T_c) of 274.7 ° C and a critical pressure (P_c) of 48.3 bars. Crooks first described electrochemistry in near-critical and supercritical MeCN [9,10] where the stainless steel cell employed did not allow easy independent variation of T and P. We present here further studies with MeCN in a small Inconel cell previously used in experiments with NH_3 [4], where the pressure can be varied independently of the temperature. We might note that the low critical pressure of MeCN allows a wider range of conditions in the supercritical region than NH_3 and H_2O. We describe studies of the electrochemistry of systems such as $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine), methyl viologen (MV^{2+}), and decamethylferrocene (DMFc) up to temperatures of 233, 277, and 282° C, respectively. We have chosen these three different systems to study in near-critical and supercritical MeCN, because they have been widely studied in this solvent at room temperature and are reasonably stable at the high temperatures employed. In addition, their half-wave potentials lie within the potential limits of MeCN at high temperatures. The stability of these compounds and the electrogenerated products at the higher temperatures is also discussed.

We also describe measurements of the diffusion coefficient (D) of ferrocene (Fc) by chronoamperometry at 280 ° C as a function of pressure up to 250 bar (reduced pressure, $P_r = P/P_c = 6.2$) are reported. These results are compared with those predicted by the Stokes–Einstein relationship, which relates D to the viscosity of the system. The density and other data are reported by Frank et al. [13,14], who measured thermodynamic parameters of MeCN up to 450° C and 2500 bar. However, the viscosity of MeCN under near-critical and supercritical conditions is not available to our knowledge and was therefore calculated from a semiempirical equation, presented by Steil and Thodos [15], in which the reduced density is related to the viscosity of polar solvents and gases as dense and liquid phases.

EXPERIMENTAL

MeCN (spectrophotometric grade, Mallinckrodt, St. Louis, MO) was dried over CaH_2 and distilled into P_2O_5 twice and then into basic alumina and finally into a glass vessel. Three freeze-pump-thaw cycles were carried out before placing the storage vessel into the dry box. DMFc and Fc were vacuum sublimed and the $MV(PF_6)_2$ was made by mixing aqueous solutions of $MVCl_2$ and KPF_6. The precipitate was recrystallized twice from acetone and dried overnight under vacuum. $Os(bpy)_3(PF_6)_2$ was prepared by the method of Gaudiello et al. [16]. Tetraethylammonium trifluoromethanesulfonate (TEA CF_3SO_3) was used for studies under supercritical conditions. At lower temperatures, $NaCF_3SO_3$ was used. These were prepared and recrystallized following previous methods [9,10,17]. Briefly, these electrolytes were prepared from an aqueous solution of tetraethylammonium hydroxide or sodium carbonate that was neutralized with trifluoromethanesulfonic acid (3M, St. Paul MN). The solution was dried, and the remaining solids were recrystallized from acetone three times and dried under vacuum at 100 ° C (TEA CF_3SO_3) and 200 ° C ($NaCF_3SO_3$) for 3 days.

A 7.5 ml high pressure (HP) cell, made from Inconel 600, and the high pressure apparatus similar to that employed in previous studies with NH_3 [4], was used in all experiments. The cell was either rinsed thoroughly with acetone and deionized water (Millipore, Bedford, MA) or was cleaned with 3 : 1 H_2SO_4/H_2O_2 (30%) and rinsed thoroughly with deionized water. After the cleaning process, the cell was oven-dried overnight and mounted, with the proper electrodes, under vacuum ($< 10^{-5}$ Torr) at 100 ° C for ca. 12 h before use. The solution was transferred to the HP cell and a stainless steel ampoule (25 ml) inside a dry box. The high pressure cell and ampoule were connected to a pressure generator. The pressure generator was placed under vacuum before opening it to the ampoule, which would fill the high pressure system.

A 0.008 cm^2 tungsten working electrode was used in all experiments and prepared following previous methods [3,4]. Briefly, the tungsten was sealed in uranium glass and then attached to a Pyrex-to-Kovar graded seal. The Kovar was silver-soldered to a stainless steel tube.

The electrochemical measurements were done using a Princeton Applied Research (PAR) 175 universal programmer, a PAR 173 potentiostat/galvanostat and a PAR 179 digital coulometer. The currents were recorded on a Norland 3001 digital oscilloscope for fast sweep rates (v) and chronoamperometric measurements or, at lower v, a Bausch & Lomb Houston Instruments Model 2000 recorder. A platinum gauze and a silver wire were used as counter and quasi-reference electrodes, respectively. All potentials are reported vs. AgQRE. All chronoamperometric measurements were made over a time span of 1–100 ms. The conductivity was measured between the counter and the working electrodes with an ac conductance meter.

RESULTS AND DISCUSSION

The electrochemistry of MV^{2+}, $Os(bpy)_3^{2+}$ and DMFc was studied in MeCN up to near-critical and supercritical temperatures. The effect of T and P on the stability of parent compound and products, the potentials for the redox processes, and the diffusion coefficients (D) was investigated.

MV^{2+}. The cyclic voltammetric behavior of MV^{2+} was studied up to 277 ° C. Cyclic voltammograms of MV^{2+} from 25 ° C to 272 ° C and 182 bar are given in Fig. 1. The cyclic voltammetric (CV) waves are reversible or quasi-reversible up to 200 ° C; above this temperature the electrochemical behavior becomes more complex and the waves are less well-defined. Typical CV data are given in Table 1. The normalized current function of the first reduction wave, $i_{pc}/v^{1/2}cA$ (i_{pc}, cathodic peak current; c, concentration; A, electrode area) increases by a factor of about two between 25 and 200 ° C, reflecting the four-fold increase in the diffusion coefficient. The increased peak splittings, ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$, where E_{pc} and E_{pa} are cathodic and anodic peak potentials) at the higher temperatures probably reflects mainly the increase in solution resistance and contributions of IR drop to ΔE_p. The

TABLE 1

Cyclic voltammetric data for MV^{2+} [a]

T/ °C	P/ bar	Density/ g cm^{-3}	$[MV(PF_6)_2]$ /mM	[TEAC F_3SO_3] /M	v/ V s^{-1}	$E_{1/2}(1)$ /V vs. AgQRE	$\Delta E_p(1)$ /mV	$E_{1/2}(2)$/V vs. AgQRE	$\Delta E_p(2)$ mV	$i_{pc}(1)v^{-1/2}c^{-1}A^{-1}$/ A $s^{1/2}$ $V^{-1/2}$ M^{-1} cm^{-2}	$i_{pc}(2)v^{-1/2}c^{-1}A^{-1}$/ A $s^{1/2}$ $V^{-1/2}$ M^{-1} cm^{-2}	$\frac{i_{pa}(2)}{i_{pc}(2)}$
25	1.0	0.78	5.0	0.2	0.5	−0.230	60	−0.630	60	0.49	0.49	1.00
106	8.6	0.69	4.4	0.18	0.5	−0.180	100	−0.620	100	0.71	0.71	0.94
200	53	0.57	3.7	0.15	0.5	−0.125	150	−0.613	125	0.96	0.99	0.84

[a] The solution contained the indicated amount of $MV(PF_6)_2$ and TEA CF_3SO_3. The electrode was a 0.008 cm^2 tungsten electrode and the scan was between −0.2 and −1.1. V vs. AgQRE.

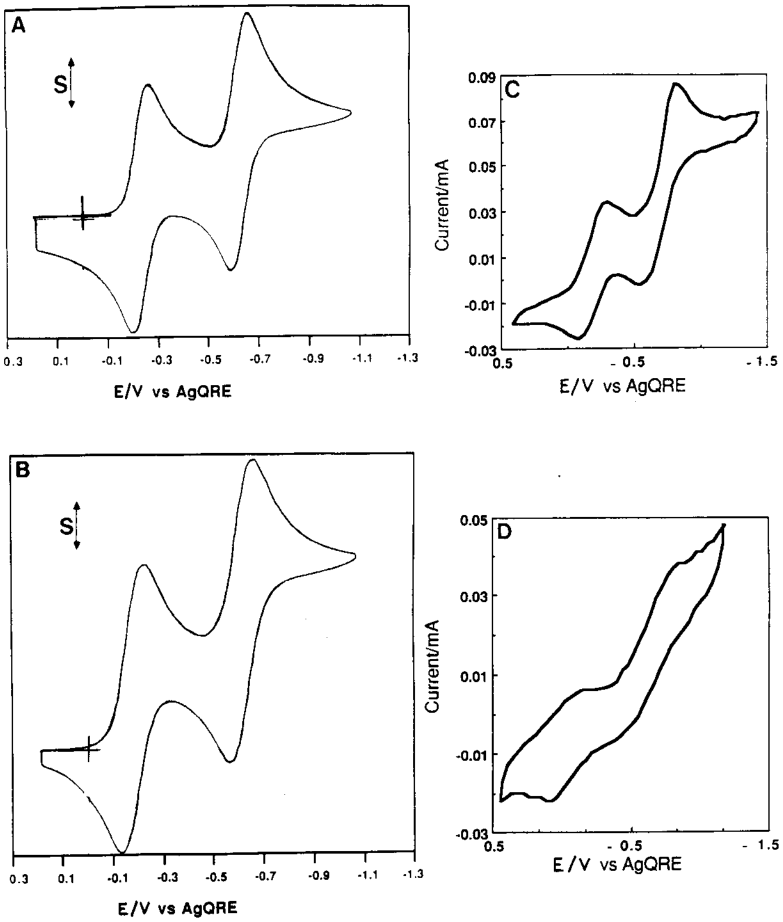

Fig. 1. CV of $MV(PF_6)_2$ at different temperatures and pressures.

	$T°$/C	P/bar	$[MV^{2+}]$ /mM	c/M		v/ V s^{-1}	S/ mA cm^{-2}
				$TEACF_3SO_3$	$NaCF_3SO_3$		
(A)	24	1.01	5	0.2		0.5	0.5
(B)	106	8.63	4.4	0.18		0.5	0.7
(C)	234	106	3.35		0.13	0.5	
(D)	277	182	3.12		0.10	1.0	

dielectric constant (ϵ) of MeCN decreases from 36 at 25 ° C to 17 at 200 ° C (53 bar). The half-wave potential, $E_{1/2}$, for each wave can be obtained by averaging the peak potentials. The difference between the $E_{1/2}$-values of the first and second waves increases as the temperature increases, representing a relatively greater stabilization of the radical cation, $MV^{\cdot+}$ (i.e., a smaller extent of disproportionation to MV and MV^{2+}) at higher T. This perhaps reflects the greater stabilization of $MV^{\cdot+}$ as the

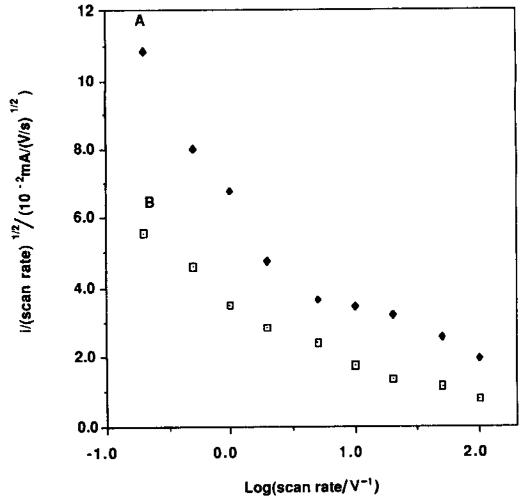

Fig. 2. Normalized current of the 1st (B) and 2nd (A) cathodic peak of MV^{2+} vs. log(scan rate) at 234° C and 106 bar ($P_r = 2.2$).

medium becomes less polar. Similar stabilization effects in the viologen system have been observed in micellar systems [18].

At higher temperatures (> 200° C), the behavior becomes more complicated (Figs. 1C, D and 2). For example, at 234° C the peak current of the second cathodic wave, i_{pc2}, is larger than that of the first wave. Moreover, the current function $i_{pc2}/v^{1/2}c$ depended strongly on v (Fig. 2), while $i_{pc1}/v^{1/2}$ was somewhat less dependent on v. The waves became less well-defined at still higher temperatures, and at 300° C, under supercritical conditions, the wave for the oxidation of $MV^{\cdot+}$ to MV^{2+} was peak-shaped, suggesting some precipitation of $MV^{\cdot+}$ on the electrode surface. Note that ϵ for MeCN at 300° C (84 bar) is about 7 [13,14]. At the higher temperatures the currents tend to plateau towards steady-state values as D increases. This effect was observed with all of the redox couples and is discussed below.

Decamethylferrocene. The CV waves of DMFc are reversible or quasi-reversible from 25° C to the supercritical region (282° C) (Fig. 3). The increase in ΔE_p found at the higher temperatures again probably results from an increase in uncompensated resistance. Typical CV data are given in Table 2. Note that D for DMFc, calculated from i_{pa}, assuming a reversible wave at the given temperature, increases from 1.8×10^{-5} cm^2/s at 25° C (1.01 bar) to 9.3×10^{-4} cm^2/s at 248° C (116 bar). The large increases of D parallel similar changes seen in MeCN [9,10] and other solvents [3–5,11] and reflect the strong decrease in viscosity of the solutions at higher temperatures. As previously discussed in connection with studies in SO_2 [11], this increase in D leads to increasing importance of hemispherical diffusion, as determined by the factor D/r (where r is the radius of the working electrode disk).

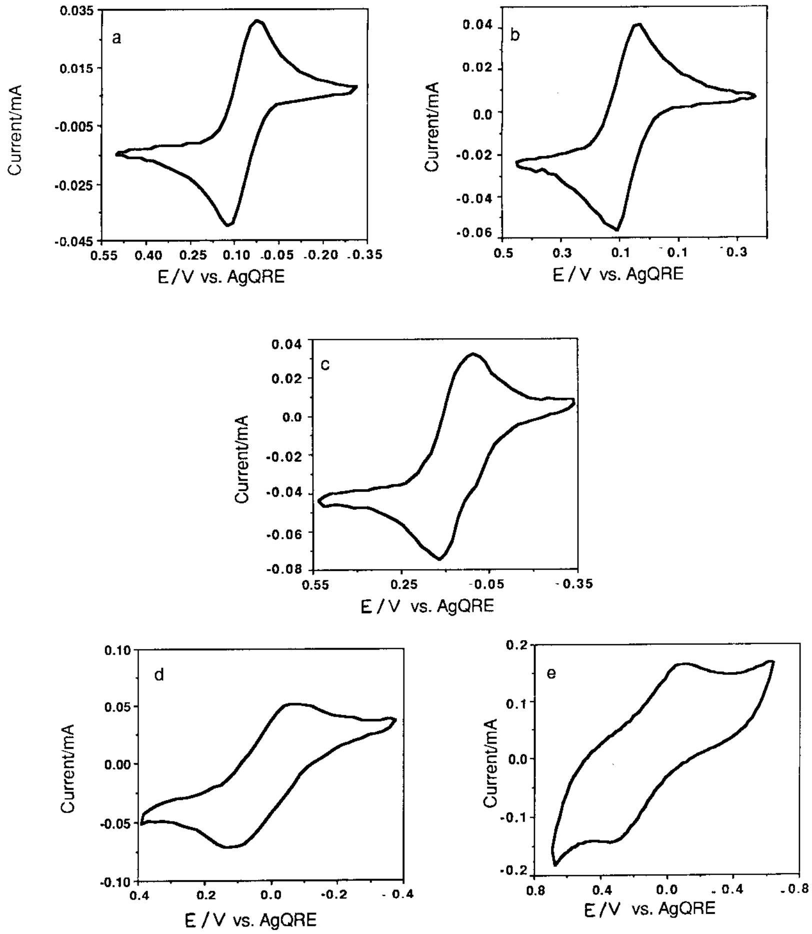

Fig. 3. CV of DMFc from 25° C to 282° C.

	$T°/C$	P/bar	v/V s^{-1}	[DMFc]/mM	[NaCF$_3$SO$_3$]/M
(a)	25	1.01	1	5.0	0.2
(b)	104	19	1	4.45	0.18
(c)	200	64	1	3.57	0.14
(d)	248	116	1	2.84	0.11
(e)	282	168	1	2.82	0.11

As D/r increases, the CV limiting currents becomes more plateau-shaped. While this effect is frequently found for ultramicroelectrodes [19], it is manifested with larger electrodes, such as those used here, only when D shows large increases.

Os(bpy)$_3^{2+}$. The CV behavior of Os(bpy)$_3^{2+}$ in MeCN as a function of T is similar to that of the other redox species (Fig. 4). The normalized i_{pa}-values increase strongly with T and the waves again show a plateau-shape as D increases (Table 3).

TABLE 2

Cyclic voltammetric data for decamethylferrocene [a]

T/ °C	P/ bar	[DMFc] /mM	[$NaCF_3SO_3$] /M	v/ $V s^{-1}$	$i_{pa}v^{-1/2}c^{-1}A^{-1}$/ $A s^{1/2} V^{-1/2} M^{-1} cm^{-2}$	10^4D/ $cm^2 s^{-1}$	Dr^{-1}/ $cm s^{-1}$	$\frac{i_{pc}}{i_{pa}}$	$E_{1/2}$/V vs. AgQRE	ΔE_p/ mV
25	1.01	5.00	0.20	1	1.01	0.18	3.5×10^{-4}	1.00	0.081	60
104	19	4.45	0.18	1	1.54	0.74	1.5×10^{-3}	1.00	0.072	78
200	63	3.57	0.14	1	1.89	2.00	3.9×10^{-3}	0.96	0.064	115
248	116	2.84	0.11	1	2.85	9.30	0.02	0.96	0.038	170

[a] Solution contained indicated amounts of DMFc and $NaCF_3SO_3$. A 0.008 cm^2 tungsten electrode was employed. The potential scan was between −0.3 to 0.5 V vs. AgQRE at 25° C, 104° C, and 200° C and −0.35 to 0.4 V vs. AgQRE at 248° C.

TABLE 3

Cyclic voltammetric data of $Os(bpy)_3^{3+}$

T/ °C	P/ bar	Density /$g cm^{-3}$	[$Os(bpy)_3(PF_6)_2$] /mM	[TEA CF_3SO_3] /M	v/$V s^{-1}$	$E_{1/2}(1)$/V vs. AgQRE	ΔE_p/ mV	$i_{pa}(1)v^{-1/2}c^{-1}A^{-1}$/ $A s^{1/2} V^{-1/2} M^{-1} cm^{-2}$	$\frac{i_{pc}}{i_{pa}}$
25	1.0	0.78	5.0	0.20	0.1	1.01	60	0.46	1
106	59	0.69	4.4	0.18	0.2	1.06	1.10	0.76	1
223	122	0.55	3.5	0.14	0.2	$E_a = 1.18$	–	1.84	–

[a] The solution contained the indicated amounts of $Os(bpy)_3(PF_6)_2$ and TEA CF_3SO_3. The working electrode was 0.008 cm^2 tungsten and was scanned between 0 and +1.3 V vs. AgQRE.

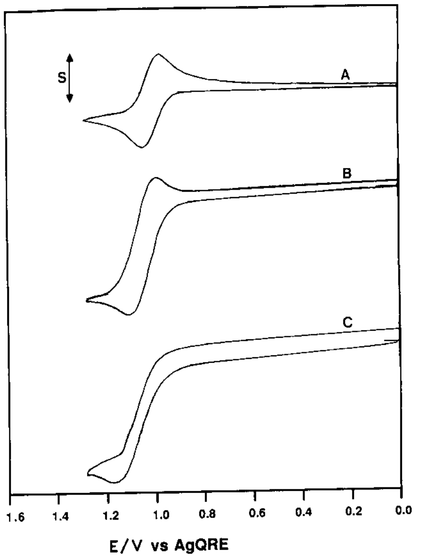

Fig. 4. CV of $Os(bpy)_3(PF_6)_2$ at different temperatures.

	T °/C	P/bar	$[Os(bpy)_3(PF_6)_2]$ /mM	$[NaCF_3SO_3]$ /M	v/V s^{-1}	S/mA
(A)	25	1.01	5.0	0.20	0.1	0.62
(B)	106	59	4.4	0.18	0.2	0.63
(C)	223	122	3.5	0.14	0.2	1.25

Effect of T on $E_{1/2}$. Although the absolute values of $E_{1/2}$ with respect to a true reference electrode or couple are not available because a quasi-reference electrode was employed in these studies, the relative changes in $E_{1/2}$ with T are probably meaningful. The results for the redox species discussed above are shown in Fig. 5. DMFc, which could be studied over the widest temperature range because of its high stability, showed the smallest variation of $E_{1/2}$ with T and was remarkably constant up to ca. 230 ° C. The $E_{1/2}$ values for the $Os(bpy)_3^{3+/2+}$ couple and for the $MV^{2+/+}$ (vs. the $MV^{+/0}$) couple show somewhat larger variations with T, suggesting that solvation effects are more important for the more highly charged cations. DMFc appears to be a useful reference redox couple in MeCN at high T.

Effect of pressure of diffusion coefficient under supercritical conditions. The stability of Fc at high temperatures permitted the measurement of D under supercritical conditions. An especially interesting aspect of a supercritical fluid is the ability to change its characteristics strongly (e.g., ϵ, density, viscosity) by changes in P. The D-value for Fc was measured by chronoamperometry [20] by a potential step from -0.05 to $+1.05$ V vs. AgQRE for a solution containing 2.5 mM Fc and 0.1 M $NaCF_3SO_3$ at 280 ° C ($T_r = 1.02$) and $P_r = 1.94$. Since the solution volume is a

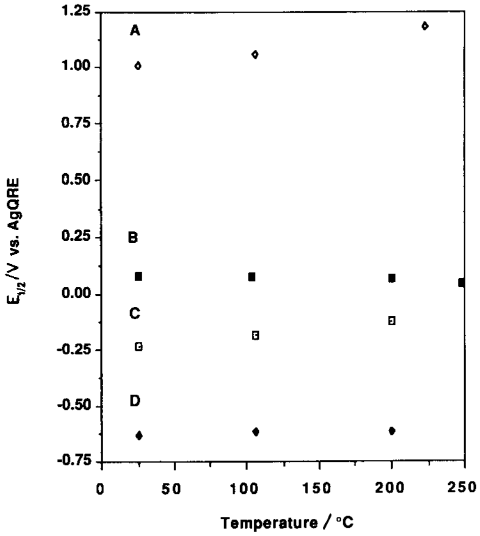

Fig. 5. $E_{1/2}$ vs. temperature for (a) $Os(bpy)^{2+/3+}$; (b) $DMFc^{0/+}$; (c) $MV^{2+/+}$; (d) $MV^{+/0}$.

function of P, the concentrations of the Fc and electrolyte were corrected at each P. By using the small Inconel cell, where P could be varied independently of T, we were able to measure D, at 280 °C ($T_r = 1.02$) for pressures of 67.6 ($P_r = 1.40$) to 250 bar ($P_r = 5.19$). This experiment was carried out to determine how the diffusion coefficient changed with viscosity at supercritical T and P. The viscosity, η, increases with increasing pressure and is related to D by the Stokes–Einstein (S–E) relationship [9]:

$$D = kT/A\pi\eta r \tag{1}$$

where r is the radius of ferrocene (0.25 nm) [6]. The parameter, A, is given by

$$A = 6(1 + 2\eta/\beta r)/(1 + 3\eta/\beta r)$$

where β is a slip coefficient. For a non-slip particle-solvent boundary condition, $\beta = \infty$, and for a free-slip condition $\beta = 0$, so that A ranges from 4 to 6. For Fc, A is probably close to 6, since the Fc molecule is larger than MeCN and closer to a free-slip condition.

The D value for Fc was calculated from the slope of a plot of i vs. $t^{-1/2}$ for times up to 100 ms. The concentration of Fc at a given T and P was calculated from the previously reported density of MeCN [13,14]. However, experimental values of η under these conditions are not available. Thus, η was estimated by the following equation of state that relates residual viscosity ($\eta - \eta^\circ$) to the reduced density (ρ_r) [15]:

$$(\eta - \eta^\circ)\xi = 0.0607(9.045\rho_r + 0.63)^{1.739} \quad \text{for} \quad 0.1 \leqslant \rho_r \leqslant 0.9$$

$$\log\{4 - \log[(\eta - \eta^\circ)\xi]\} = 0.6439 - 0.1005\rho - \Delta$$

where $\Delta = 0$ for $0.9 \leqslant \rho_r \leqslant 2.2$

$$\Delta = (4.75)(10^{-4})(\rho_r^3 - 10.65)^2 \quad \text{for} \quad 2.2 \leqslant \rho_r \leqslant 2.6$$

where η is the dense gas viscosity in μP ($1\mu\text{P} = 10^{-7}$ Pa s); η° is low-pressure gas viscosity in μP (at 280 °C, $\eta^\circ = 135$ μP for acetonitrile [15]), and ρ_r is the reduced gas density. The critical density of acetonitrile is 0.237 g ml^{-1} [13,14]. ξ is calculated from the following equation.

$$\xi = T_c^{1/6}/(M^{1/2}P_c^{2/3})$$

where T_c is in K, P_c is in atm and M is the molar mass in g. For acetonitrile, $\xi = 0.034$.

From these equations we can determine the residual viscosity at different reduced densities, and by knowing η°, we can estimate the viscosity of MeCN. The D values at 280 °C from $P_r = 1.40$ (190 μP) to 5.19 (690 μP) are presented in Table 4. As the pressure was increased, the diffusion constant decreased from 8.5×10^{-4} cm^2/s at $P_r = 1.4$ to 2.9×10^{-4} cm^2/s at $P_r = 5.19$. Figure 6 presents a plot of D vs. viscosity for the experimental results and the S–E relationship values. The experimental D values tend to be higher than those predicted by the S–E relationship for $A = 6$, but closer to, and slightly below, that for $A = 4$. This suggests that the change of D with pressure in supercritical MeCN fluids is not only governed by the change in η, but by other factors, such as changes in the effective value of r, because of changes in the solvating power of the solvent. A similar explanation was proposed to rationalize why the diffusion constant of Cu^{2+} was higher than that predicted by the S–E relationship in water at high temperature [5].

TABLE 4

Experimental and theoretical diffusion coefficients of ferrocene at 280 °C to 250 bar

Pressure/ bar	P_r [a]	Density /g cm^{-3}	Viscosity /μP	$10^4 D/\text{cm}^2\ \text{s}^{-1}$	
				Exp.	SE [b]
67.6	1.40	0.29	277	8.5	5.84
80.2	1.66	0.34	332	7.1	4.86
108	2.24	0.41	456	4.9	3.55
129	2.67	0.44	526	4.5	3.08
146	3.03	0.46	574	4.0	2.82
165	3.41	0.47	617	3.9	2.62
183	3.79	0.48	657	3.4	2.47
203	4.21	0.49	697	3.2	2.33
217	4.50	0.50	722	3.1	2.24
238	4.92	0.51	758	3.0	2.14
250	5.19	0.52	778	2.9	2.08

[a] P_r = reduced pressure = P/P_c.

[b] Diffusion coefficient according to the Stokes–Einstein relationship with $A = 6$.

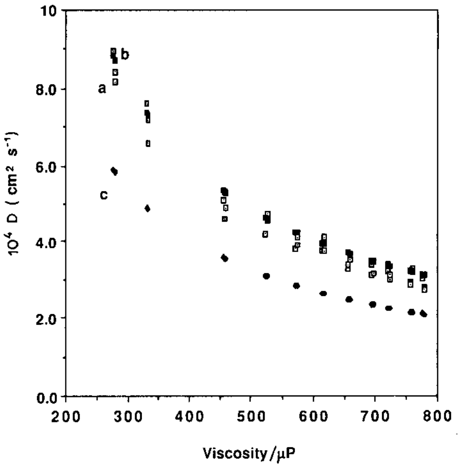

Fig. 6. D of Fc at 280 °C vs. viscosity: (a) experimental; (b) $A = 4$ and (c) $A = 6$ (Stokes–Einstein relation; see text).

Cyclic voltammograms of Fc at 280 °C and two different reduced pressures are shown in Fig. 7. The normalized anodic peak current increased with a decrease in P_r, from 6.44 mA/cm^2 at $P_r = 4.78$ to 9.3 mA/cm^2 at $P_r = 1.94$. Moreover, more IR compensation was needed for the CV at $P_r = 1.94$ than for $P_r = 4.78$, since the dielectric constant and the density of the solvent increase with an increase in pressure (see Table 1). Therefore, the concentration of the electrolyte changed from 0.10 M at $P_r = 1.94$ to 0.13 M at $P_r = 4.78$. The conductivity of the solution between working and counter electrodes at 280 °C increased by 200 μS from $P_r = 1$ to $P_r = 4$ (Fig. 8).

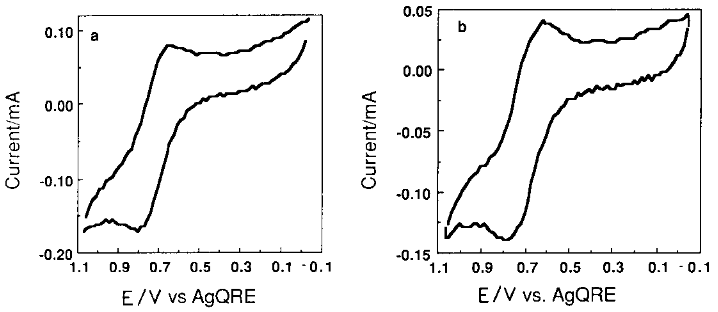

Fig. 7. CV of Fc at a 280 °C at different pressures.

	T/°C	P_r	v/V s^{-1}	[Fc]/mM	[NaCF$_3$SO$_3$]/M
(a)	280	1.94	2	2.5	0.10
(b)	280	4.78	2	3.39	0.13

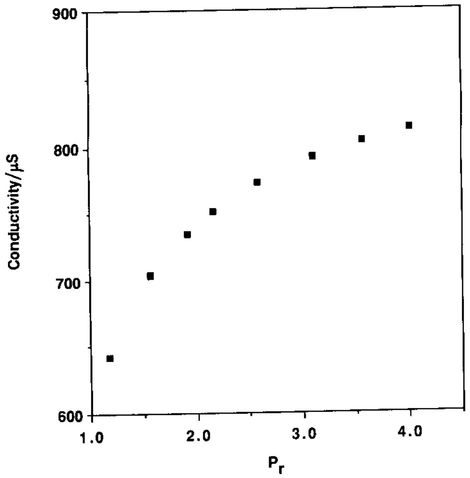

Fig. 8. Conductivity between working and auxiliary electrodes vs. P_r at 280 °C for 0.2 M $NaCF_3SO_3$ (concentration at 25 °C) in MeCN.

These results suggest that electrochemical methods are useful in the measurement of D as a function of pressure under supercritical conditions. Short experimental times are required in the measurement, since the low viscosity and possible thermal gradients in the system could contribute to the onset of convective processes, which would become more important as the thickness of the diffusion layer increases. Moreover, the contribution from non-linear diffusion processes, which are more important at longer times, would complicate the analysis of the experimental results. However, measurements cannot be made at very short times because of significant contributions by double layer charging processes to the total measured current. Thus, the "time window" that is useful for determination of D under supercritical conditions is a rather narrow one, e.g., roughly 5 to 100 ms. We might indicate that previous measurements of D as a function of P under supercritical conditions have been reported [21,22].

CONCLUSIONS

Several compounds were examined in near-critical and supercritical MeCN. Although $Os(bpy)_3^{2+}$ and MV^{2+} were fairly stable in the near-critical region, useful electrochemical results could not be obtained under supercritical conditions. However, both Fc and DMFc could be used, and either would be a useful molecule for probing MeCN properties at high T. Fc and DMFc should also be convenient reference redox couples for measuring potentials of other systems. Although the conductivity of MeCN under high temperature conditions is rather low, it appears adequate for useful voltammetric measurements, especially with ultramicroelectrodes. Near-critical and supercritical MeCN might also prove interesting for synthetic applications.

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