Preliminary note

Electrochemistry in near-critical and supercritical fluids

Part 7. SO₂

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We describe here the cyclic voltammetry (CV) and chronoamperometry of $Fe(bpy)_3^{+2}$ (bpy = 2,2′-bipyridine) in SO_2 at temperatures up to 174°C, above the critical point of SO_2 ($T_c = 158$°C, $P_c = 77.8$ atm), and discuss the effect of temperature on the diffusion coefficient (D) and the electrochemical behavior. Near-critical and supercritical fluids are of interest because the solvent properties are very different from those of the liquid form and are adjustable over a wide range by variation of the temperature and pressure. Recent studies have demonstrated that electrochemical experiments can be carried out in supercritical H_2O [1], NH_3 [2], $CO_2 + H_2O$ [3] and MeCN [4]. Extension of this methodology to SO_2 is important because this solvent has been shown to be a very valuable one for electrochemical studies [5]. It is an aprotic solvent with a reasonable dielectric constant that has a wide potential window out to positive potentials of about +4.7 V vs. SCE [6]. This allows the electrochemical generation and study of highly oxidizing species and thus provides a useful complement to NH_3, which has a far negative limit. Moreover, the relatively low critical temperature and pressure of SO_2 makes SO_2 a convenient high temperature solvent, compared, for example, to MeCN and H_2O.

All experiments were carried out with a cell constructed of Inconel 600 with a volume of 7.5 ml [2b]. The SO_2, purified by previously-described methods [6], was distilled into a stainless steel ampoule connected to the electrochemical cell containing the supporting electrolyte, tetraethyl ammonium hexafluoroarsenate (TEAAsF₆), and the electroactive species. This cell and its contents had been placed under vacuum at 100°C overnight to dry. The electrochemical cell was connected to a pressure generator [2b] which could be used to adjust the pressure to the desired value at any temperature. The synthesis and purification of TEAAsF₆ and $Fe(bpy)_3(AsF_6)_2$ followed previous practice [6]. Either a 10 or 25 μm diameter platinum disk sealed-in-glass ultramicroelectrode was used as working electrode.
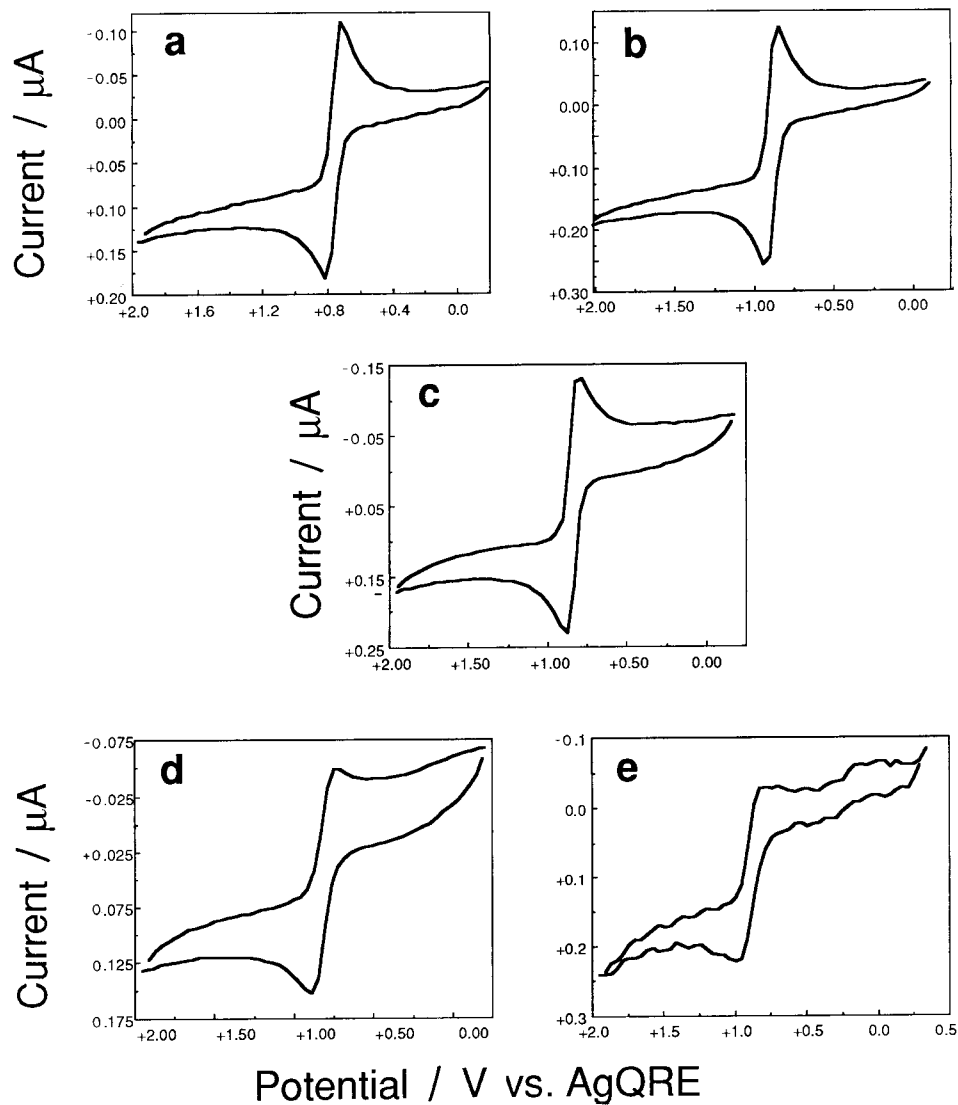
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Fig. 1. Cyclic voltammetry (10 V/s) of $Fe(bpy)_3^{+2}$ as a function of temperature and pressure. (a) $T = 25°C$, $P = 13.2$ bar, $c\{Fe(bpy)_3(AsF_6)_2\} = 11$ mM, $c\{TEAAsF_6\} = 0.2$ M; (b) $T = 50°C$, $P = 25$ bar, $c\{Fe(bpy)_3(AsF_6)_2\} = 10.1$ mM, $c\{TEAAsF_6\} = 0.19$ M; (c) $T = 100°C$, $P = 47$ bar, $c\{Fe(bpy)_3(AsF_6)_2\} = 9.1$ mM, $c\{TEAAsF_6\} = 0.17$ M; (d) $T = 138°C$, $P = 89$ bar, $c\{Fe(bpy)_3(AsF_6)_2\} = 7.6$ mM, $c\{TEAAsF_6\} = 0.14$ M; (e) $T = 174°C$, $P = 112$ bar, $c\{Fe(bpy)_3(AsF_6)_2\} = 7.0$ mM, $c\{TEAAsF_6\} = 0.13$ M. Potential scans start at 0 V and the initial potential sweeps are toward positive potentials.

The counter electrode was Pt gauze and the reference electrode was a silver wire quasi-reference electrode (AgQRE) immersed directly into the test solution.

The test compound, $Fe(bpy)_3^{2+}$, was selected because previous studies [5,6] indicated that the $2 + /3 +$ couple shows well-defined electrochemical behavior in SO_2 at its usual liquid temperature range (-70 to $-15°C$). Typical cyclic voltammograms of $Fe(bpy)_3^{2+}$ at a 25 μm Pt electrode over the temperature range $25°C$ to $174°C$ (supercritical) at a scan rate of 10 V/s are shown in Fig. 1. The waves at all temperatures, including supercritical conditions, are well-defined and nernstian, when compensation for the resistance drop between the working and reference electrodes is applied. The apparent shifts in the absolute peak potentials of the waves are probably not meaningful under the conditions of these experiments, since a shift in the potential of the AgQRE could easily occur.

An interesting aspect of the CV waves is the clear change in shape from linear diffusion-controlled behavior at $25°C$ to a steady-state limited appearance as the temperature is increased, with the same electrode at a given scan rate, v. This change is a reflection of the large increase in the diffusion coefficient of $Fe(bpy)_3^{2+}$ with increasing temperature. As is well known for ultramicroelectrodes [7], the current (i)–time (t) or i–v behavior follows approximately that of a hemispherical electrode, where the ratio of the planar to the spherical components of i are given by [8]

$$\frac{i_{sphere}}{i_{plane}} = 1 + \frac{(\pi Dt)^{1/2}}{r}$$

where r is the electrode radius. Such changes are usually reflections of changes in t (or v); here, they represent a change in D. To demonstrate this change in D/r, D
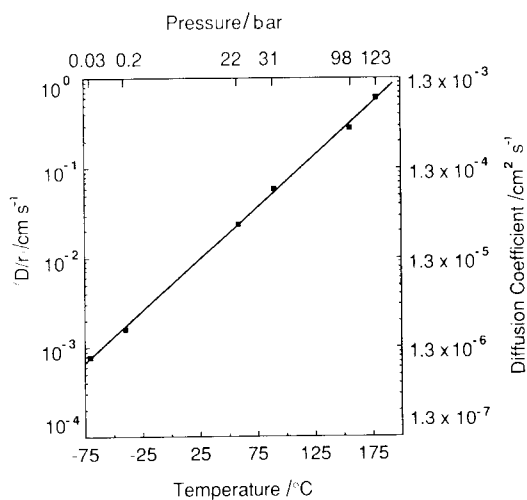

Fig. 2. Plot of D/r and D vs. temperature.

was measured at each temperature by chronoamperometry at the 25 μm diameter electrode over a time range of 0 to 0.1 s. A plot of D/r and D at different temperatures is given in Fig. 2. The typically large value of D found under near-critical and supercritical conditions [1–4] implies that spherical diffusion effects will be important, even with electrodes of larger diameter, especially at lower scan rates.

The results given here demonstrate for the first time that electrochemical studies in SO_2 at high temperatures under near-critical and supercritical conditions are possible and that the metal apparatus used previously for studies in NH_3 and MeCN is apparently stable in SO_2 under these conditions. The application of SO_2 to studies of strongly oxidizing species under these conditions is still to be demonstrated, since preliminary studies suggest that the positive range is decreased greatly at higher temperatures.

ACKNOWLEDGEMENT

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