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The voltammetry of decamethylferrocene and coboltacene in supercritical difluoromethane (R32)

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ABSTRACT

The voltammetry of decamethylferrocene, cobaltocene and decamethylcobaltocene at micro and macrodisc electrodes in supercritical difluoromethane at 360 K and 17.6 MPa has been studied. In all cases the voltammetry is distorted to some degree by the effects of random convection but these can be suppressed by adding a baffle around the electrode. The voltammetry of decamethylferrocene is well behaved with fast electrode kinetics at Pt microdisc electrodes. The limiting currents, corrected for random convection, obey the normal microdisc equation and are linear in electrode radius for decamethylferrocene up to the highest concentration (11 mM) used in this study. Based on the microelectrode studies, we find that the diffusion coefficient of decamethylferrocene in supercritical difluoromethane containing 20 mM $[NBu^n{}_4][BF_4]$ at 360 K and 17.6 MPa is 8.3×10^{-5} cm^2 s^{-1}. Finally we have briefly investigated the voltammetry of cobaltocene and decamethylcobaltocene in supercritical difluoromethane under the same conditions. We find that reduction of the cobaltocenium cation leads to fouling of the Pt microdisc electrode which limits its use as a model redox system and that reduction of the decamethylcobaltocenium cation was not observed before electrolyte reduction at around −1.6 V *vs.* Pt.

1. Introduction

Supercritical fluids are interesting solvents in which to carry out electrochemistry because of their unique combination of properties that fall between those of liquids and those of gases. However because of the difficulties of working at elevated pressures they have not been that widely studied or used in electrochemistry [1,2]. Recent studies have shown that supercritical fluids are of interest for electrodeposition [3–7], electrosynthesis [8–10], and as media for the electrochemical reduction of carbon dioxide [11–13]. This interest arises because of the combination of low viscosity, high mass transport rates, the absence of surface tension and the wide potential window that supercritical electrolytes can offer combined with the opportunity to tune their solvent properties by control of the temperature and pressure.

Metallocenes are obvious choices as model redox probe species for studies of electrochemistry in supercritical fluids since they are available as neutral, and thus soluble in low dielectric solvent, fairly volatile species and are expected to undergo one electron outer-sphere redox reactions. For non-aqueous solutions the International Union of Pure and Applied Chemistry (IUPAC) recommends the use of the ferrocene/ferrocenium (Fc/Fc^+) redox couple [14–16] as an internal reference system. However this has been questioned [17] as some studies have shown that the Fc^+ ion can react with nucleophiles in some solutions and the decamethylferrocene/decamethylferrocenium ($DMFc/DMFc^+$) couple has been proposed [16] as a better choice. Here the bulky methyl groups on the two cyclopenadienyl rings are expected to sterically hinder specific and nonspecific interactions between solute and solvent molecules [17]. The electrochemistry of the $DMFc/DMFc^+$ couple has been studied by a number of groups under a range of conditions: the couple exhibits a reversible one electron redox process at the electrode with facile electron transfer kinetics [16–23]. Noviandri et al. [17] extensively studied the solvent dependences of the formal redox potential of the Fc/Fc^+, $DMFc/DMFc^+$ and 1,2,3,4,5-pentamethyl-ferrocene (Me_5Fc) couples in 29 solvents and concluded that $DMFc/DMFc^+$ satisfied the criteria required for a redox standard for use in non-aqueous solvents that complied with all of the IUPAC requirements.

The first studies of the electrochemistry of metallocenes in supercritical fluid were by Crooks and Bard [24] who investigated the electrochemistry of ferrocene in near-critical and supercritical acetonitrile ($scCH_3CN$) between 298 and 573 K. They found a reversible, or nearly reversible, one-electron oxidation wave for ferrocene at low scan rates over the entire temperature range studied. At subcritical temperatures a simple one electron oxidation of Fc to Fc^+ was observed [24] but in experiments above T_C (the critical temperature for the solvent) there was evidence of mild filming of the electrode. Subsequently Cabrera and Bard [21] studied the electrochemistry of other organometallic complexes, including decamethylferrocene, in near and supercritical CH_3CN. Decamethylferrocene was found to show reversible or quasi-reversible behaviour from 298 to 555 K (into the supercritical region), and as the temperature increased the peak to peak potential separation increased due to increasing uncompensated resistance in the cell.

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Other studies of ferrocene electrochemistry at 25 μm Pt microdisc electrodes in supercritical chlorodifluoromethane (scCHClF$_2$; $T_C = 369.15$ K and $p_C = 4.97$ MPa, $\varepsilon = 2.31$ at the critical point) by Olsen and Tallman [25] showed a typical microelectrode response very similar to that found in the liquid solvent at 299 K, although they did see some evidence for passivation of the electrode surface. Subsequently the same authors also investigated the voltammetry of ferrocene and cobaltocenium in liquid and scCHClF$_2$[26]. They concluded that ferrocene and colbaltocenium were excellent choices as potential references in scCHClF$_2$ since the difference in their half-wave potentials was independent of pressure over a considerable range and only slightly, but predictably, dependent on temperature. Voltammetry of ferrocene was also performed in supercritical trifluoromethane (scCHF$_3$) where reversible Nernstian behaviour was observed [26]. Goldfarb and Corti [27,28] studied the electrochemistry of DMFc and decamethylferrocenium hexafluorophosphate (DMFc$^+$) in scCHF$_3$ using linear sweep voltammetry at 25 μm platinum microelectrodes at 323 K at several densities with and without supporting electrolyte (tetrabutylammonium hexafluorophosphate). It was found that DMFc$^+$ voltammetry was strongly influenced by the concentration of supporting electrolyte — with a decrease in concentration of supporting electrolyte causing an increase in the limiting current for DMFc$^+$ reduction due to the effects of migration [27].

Decamethylferrocene (DMFc) has also been used as a probe redox couple in supercritical carbon dioxide with acetonitrile co-solvent (scCO$_2$/CH$_3$CN). Toghill et al. [11] using up to 0.41 mol fraction CH$_3$CN and tetradecylammounium tetrakis(pentafluorophenyl)borate (TDATFPB, a room temperature ionic liquid) as the supporting electrolyte suggested that the electrochemistry occurred in a liquid-like CH$_3$CN phase formed at the electrode surface. In contrast, we [29] found well behaved voltammetry for the same redox couple in scCO$_2$/MeCN containing around 15 wt% (0.17 mol fraction) CH$_3$CN with no evidence for a liquid film at the electrode surface.

The cobaltocenium, CoCp$^+$, couple is isoelectronic with ferrocene and also expected to show ideal reversible, one-electron electrochemistry [15]. The cobaltocenium (CoCp$^+$/CoCp$_2$) redox couple has a formal redox potential that is sufficiently separated from DMFc/DMFc$^+$ to allow the two couples to be investigated in the same solution without interference. Stojanovic and Bond [30] examined the CoCp$_2^+$/CoCp$_2$ couple with respect to the Fc/Fc$^+$ couple and found that the measured half-wave potential separation between the two couples was essentially independent of electrode material, electrolyte and solvent [30]. In contrast, the half-wave potential for the CoCp$_2^+$/CoCp$_2$ couple when used in isolation was found to be considerably more solvent dependent and could not always be accurately measured at 25 °C because of overlap with the "solvent" response and for "a range of other reasons" [30]. To overcome this problem, the fully methylated version of the compound decamethylcobaltocene (DMCc$^+$) has been investigated. Aranzaes et al. [31] made measurements of the redox potential ($E_{1/2}$) of a variety of metallocenes (including DMFc and DMCc$^+$) in a range of solvents (including acetonitrile and dichloromethane). They found that the difference in $E_{1/2}$ values between DMFc and DMCc$^+$ was solvent independent [31].

In this paper we describe the results of experiments performed using DMFc as a model redox system in supercritical difluoromethane (scR32) at both micro and macro electrodes and compare the results to those of our earlier work in scCO$_2$/MeCN [29]. We also report preliminary results for the electrochemistry of cobaltocene and decamethylcobaltocene in scR32.

2. Experimental

2.1. Reagents

Difluoromethane (CH$_2$F$_2$, Apollo Scientific Ltd., 99%) was used as received with no further purification. The supporting electrolyte tetrabutylammonium tetrafluoroborate ([NBu$^n{}_4$][BF$_4$], Aldrich, 99%) was used as received. Decamethylferrocene (DMFc, C$_{20}$H$_{30}$Fe, Aldrich, 97%), decamethylcobaltocene (C$_{20}$H$_{30}$Co, Aldrich) and decamethylcobaltocenium hexafluorophosphate ([C$_{20}$H$_{30}$Co]$^+$[PF$_6$]$^-$, Aldrich, 98%) were all sublimed prior to use. Cobaltocenium hexafluorophosphate ([C$_{10}$H$_{10}$Co]$^+$[PF$_6$]$^-$, Aldrich, 98%) was used as received.

2.2. Electrodes for supercritical fluids

The working electrodes were platinum wires of varying size (10–500 μm diameter, Goodfellow, Advent Research Materials Ltd.) and gold macrodiscs which were either sealed in glass or in polyether-ether ketone (PEEK, Supelco, Thames Restek, Upchurch Scientific, Vici) 1/16″ tubing. All electrodes were polished prior to each experiment on a polishing cloth (12″ microcloth, Buehler) with alumina paste (1 μm followed by 0.3 μm average particle diameter). All electrodes were sealed in PEEK (1.6 mm diameter OD, 0.5–1 mm ID, Supelco.) tubing with bisphenol A epoxy resin (EpoFix kit, Struers). Gold (0.5 mm Ø) macrodiscs along with platinum (10–50 μm Ø) microdiscs were used as working electrodes. For supercritical experiments using microwires, the microwires were directly contacted to a 250 μm diameter NiCr wire in a soda glass capillary, the whole section was then sealed further in PEEK. Platinum wires (0.5 mm Ø) were used for both counter and pseudo reference electrodes; these were sealed in PEEK as previously described.

2.3. Cell design

All the high pressure electrochemical experiments were carried out with the use of a 316L stainless steel reactor. This cell is specially designed and has been described in the literature [32]. The steel cell consists of two parts, the top part contains seven 1/16 in. female SSI type fittings through which a thermocouple, a CO$_2$/R32 feeding line and the 5 electrodes could be fed and sealed. The last port is used for the safety key which makes the final seal. The bottom part contains an 8.65 ml working volume where the solution is confined after pressurisation, along with an area for the O-ring to be placed. The two parts of the cell were held together with a belt clamp and safety seal, Figs. 1 and 2.

2.4. Procedure

Electrolytes and metallocenes were introduced into the cell as dry powders. This loading step was carried out in a dry, dinitrogen purged

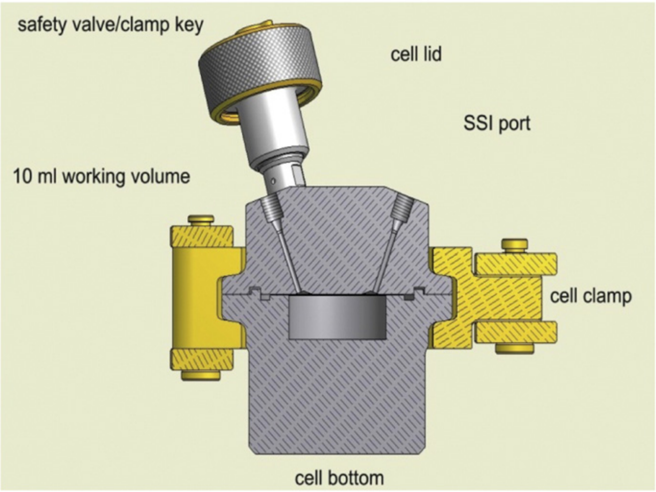

Fig. 1. Schematic of the high pressure reactor. Courtesy of the Engineering workshop of the School of Physics and Astronomy, University of Southampton, UK.