In situ EPR studies of electron transfer across a polarised liquid/liquid interface

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The design and operation of the first ever *in situ* EPR cell for studying charge-transfer processes accompanying polarisation of the liquid/liquid interface is presented as well as EPR absorption data obtained from the reduction of TCNQ (to TCNQ·⁻) and the oxidation of TTF (to TTF·⁺) by the ferro–ferri-cyanide redox couple at the water/1,2-dichloroethane interface.

The liquid/liquid interface has attracted increasing attention, both from a theoretical and experimental standpoint, due to its potential relevance to fields as diverse as analytical chemistry, hydrometallurgy and membrane science.[1] Imposition of an external potential difference across this interface has allowed charge-transfer processes to be studied voltammetrically, but interpretations are frequently plagued by controversy because of the difficulty in conclusively identifying the participating species and, crucially, resolving ion- and electron-transfer processes from one another.[2] The latter is of particular interest as it involves bimolecular electron exchange which can be controlled through the potential difference imposed on the water/organic interface. Spectroscopic experiments, including EPR spectroscopy,[3,4] have been used successfully to clarify processes at the metal/electrolyte and semiconductor/electrolyte interfaces. To date spectroscopic reports of liquid/liquid processes have been confined to UV–VIS absorption and emission spectroscopy,[5,6] whereas *in situ* EPR spectroscopy is an ideal way to detect and identify paramagnetic participants, which has not been hitherto applied.

The cell used to perform the interfacial polarisation-EPR experiments is shown in Fig. 1 and is essentially a conventional silica flat cell[7] modified so that a counter and reference electrode can be inserted into either end. The cell was assembled by first filling the higher density solvent through the capillary at the base of the cell [Fig. 1(*f*)] using silicone tubing and a syringe, so that the solvent reached the midpoint of the flat portion of the cell [Fig. 1(*a*)], and then sealing the silicone tubing with a Hoffman clamp. The upper, less dense phase, was then introduced into the cell from the top using a Pasteur pipette. Using this filling method a liquid/liquid interface could be generated and maintained in the mid-portion of the flat part of the cell.

The EPR cell has two counter electrodes of coiled 0.5 mm diameter platinum wire located outside the thin layer section [Fig. 1(*b*) and (*d*)]. The two reference electrodes are 0.5 mm diameter silver wires, flattened at one end to a thickness which enabled their insertion into the flat part of the cell [Fig. 1(*c*) and (*e*)]. Both silver pseudo-reference electrodes were positioned to within 5 mm of the liquid/liquid interface. To obtain optimal control of the potential difference applied between the liquid phases, the portions of the reference electrodes outside the flat part of the cell were jacketed in Teflon tubing [Fig. 1(*h*)] and sealed with silicone rubber so that they were only in contact with the solutions inside the flat part of the cell. The inherent high resistivity of a flat cell combined with low relative permittivity solvents (*e.g.* 1,2-dichloroethane, DCE) can be partially overcome using this arrangement, and reasonable linear sweep voltammetry can be obtained using a four-electrode (two counter and two reference electrodes) potentiostat.

The use of the cell shown in Fig. 1 enabled EPR spectra to be obtained for both the interfacial reduction of TCNQ and
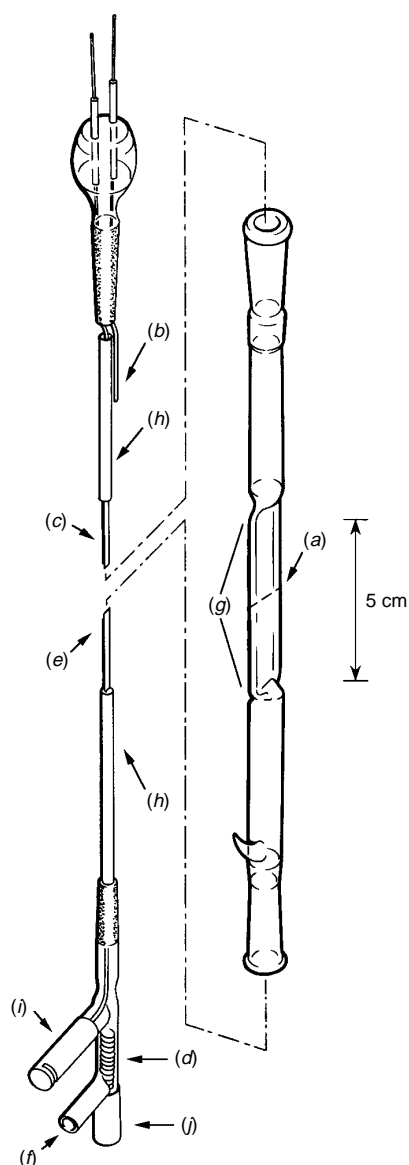

Fig. 1 Silica cell for performing liquid/liquid electrochemical-EPR experiments: (*a*) interface between two immiscible liquids, (*b*) platinum wire counter electrode 1, (*c*) silver wire reference electrode 1, (*d*) platinum wire counter electrode 2, (*e*) silver wire reference electrode 2, (*f*) capillary to fill lower portion of cell, (*g*) thin layer portion of cell, (*h*) Teflon/silicone rubber sleeves surrounding lower portions of reference electrodes, (*i*) electrical contact to reference electrode 2 and (*j*) electrical contact to counter electrode 2

oxidation of TTF (dissolved in DCE) by the aqueous phase ferri–ferro-cyanide couple, following application of a potential difference directly to the liquid/liquid interface. The TCNQ–ferrocyanide system has been previously investigated using both external polarisation with a four-electrode potentiostat and the scanning electrochemical microscope, both techniques indicating that the charge-transfer process observed at the liquid/liquid interface is due to heterogeneous reduction of TCNQ by the aqueous couple[8,9] [eqn. (1)].

$$TCNQ(DCE) + Fe(CN)_6^{4-}(aq) \rightleftharpoons TCNQ^{\cdot-}(DCE) + Fe(CN)_6^{3-}(aq) \quad (1)$$
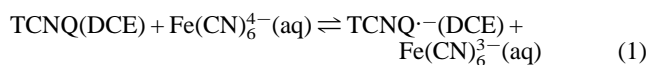
A similar mechanism can be written for the oxidation of TTF [eqn. (2)], where in each case an appropriate potential difference (oxidising or reducing), relative to the two reference electrodes used, can be imposed across the water/DCE interface to drive the reaction in either the forward or reverse direction.

$$TTF(DCE) + Fe(CN)_6^{3-}(aq) \rightleftharpoons TTF^{\cdot+}(DCE) + Fe(CN)_6^{4-}(aq) \quad (2)$$
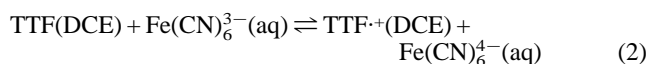
The presence of the organic radicals, and hence the occurrence of an electron-transfer process, was verified using EPR spectroscopy. The EPR spectra obtained for $TCNQ^{\cdot-}$ and $TTF^{\cdot+}$ in DCE at room temperature consisted of single broad lines with peak-to-peak line widths of 5.2 and 3.0 G, respectively. It is unlikely that the line broadening observed is due to the $TCNQ^{\cdot-}$ and $TTF^{\cdot+}$ radicals interacting with the iron complexes in the aqueous phase as broad EPR spectra were also obtained from $TCNQ^{\cdot-}$ and $TTF^{\cdot+}$ radicals which had been generated electrochemically in the appropriate single-phase three-electrode cell[7] using DCE and the same supporting electrolyte, bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate ($BTPPA^+TCPB^-$). The broadening of the EPR spectra is probably caused by the strong ion pairs formed between the product radicals and the organic phase electrolyte cation ($BTPPA^+$) or anion ($TCPB^-$) respectively,
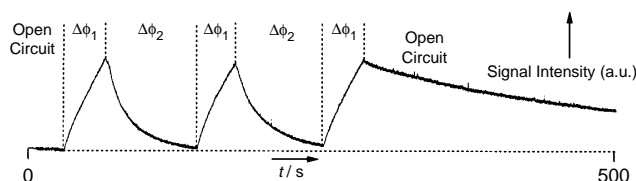
undergoing fast electron exchange with neutral TCNQ or TTF.[10]

An EPR time-sweep experiment for the oxidation of TTF, where the magnetic field was held at a constant value corresponding to the maximum absorption, is shown in Fig. 2. The time-sweep EPR experiments were performed by applying a potential difference, between the silver pseudo-reference electrodes located in each liquid phase, which was sufficient to cause an electron to be transferred across the water/DCE interface from TTF to $[Fe(CN)_6]^{3-}$. The resulting increase in $TTF^{\cdot+}$ in the organic phase caused an increase in signal intensity of the absorption spectrum (Fig. 2), which displayed a square-root temporal dependence as expected for a potential-step occurring under conditions of one-dimensional diffusion.[11] Jumping to a potential difference sufficiently negative to drive the back reaction immediately caused a decrease in the intensity of the absorption signal (also Fig. 2) due to $TTF^{\cdot+}$ being reduced back to neutral TTF. The time-sweep EPR data obtained for the reduction of TCNQ was very similar to that reported for the oxidation of TTF. The spectrum in Fig. 2 also shows that when the potentiostat is open-circuited after generating $TTF^{\cdot+}$ the signal intensity decreases with time. $TTF^{\cdot+}$ is stable in DCE, therefore, the decay in signal intensity can be attributed to the radical diffusing away from the most sensitive part of the EPR cavity since the sensitivity shows a cosine squared dependence on distance, its maximum lying at the cavity centre.[3] Steps are currently in progress to enable accurate kinetic measurements to be made using this cell.

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Fig. 2 Time-sweep first derivative EPR spectrum of $TTF^{\cdot+}$ recorded at constant magnetic field using a liquid/liquid electrochemical-EPR cell. The organic phase (DCE) contained 5 m**m** TTF and 36 m**m** $BTPPA^+$ $TCPB^-$. The aqueous phase contained 25 m**m** $K_4[Fe(CN)_6]$, 25 m**m** $K_3[Fe(CN)_6]$ and 0.1 **m** Li_2SO_4. EPR sweep time = 500 s, sweep width = 0 G, modulation amplitude = 2.0 G and time constant = 10×10^{-2} ms. $\Delta\phi_1$ = oxidising potential, $\Delta\phi_2$ = reducing potential. The potential difference imposed to induce oxidation of the TTF was +0.7 V, whilst this process was reversed using a potential difference of −0.1 V (*vs.* the Ag pseudo-reference electrodes used). See text for further details.