Heterogeneous electron transfer at the polarised water/1,2-dichloroethane interface studied by *in situ* UV–VIS spectroscopy and differential cyclic voltabsorptometry

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The heterogeneous electron transfer reaction between the redox couple ferricyanide–ferrocyanide in water and 7,7,8,8-tetracyanoquinodimethane (TCNQ) in 1,2-dichloroethane (DCE) is studied by combining conventional electrochemical measurements and UV–VIS absorption spectroscopy in total internal reflection (TIR) geometry.

Heterogeneous electron transfer reactions are of biological interest, and polarised liquid/liquid interfaces represent a rather simple model system to study this type of reactions where reactants and products are located in their respective adjacent phases.[1–6] However, there is a paucity of reliable experimental data as electrochemical methods suffer from the difficulty of differentiating between currents originating from electron- and ion-transfer reactions occurring across the interface.[7–9] To circumvent the limitations of electrochemical studies, we have developed a novel spectroelectrochemical methodology.

Very few reports of spectroelectrochemical studies on electron transfer at liquid/liquid interfaces have been published.[10,11] *In situ* EPR has been used to study the product formation for the reduction of TCNQ and the oxidation of tetrathiofulvalene (TTF) by the ferro–ferricyanide redox couple at the water/DCE interface.[10] Time-resolved laser-induced fluorescence spectroscopy in TIR mode has been used to study photoinduced electron transfer between europium(III) in water and anthracene in DCE.[11] TIR fluorescence spectroscopy[12–14] and TIR UV–VIS spectroscopy[15] have recently been applied to the field of ion-transfer reactions across the water/DCE interface. The work outlined here shows that UV–VIS spectroscopy in TIR geometry can be used to detect interfacial changes of the products of electron-transfer processes at liquid/liquid interfaces.

The spectroscopic measurements involved the use of a 150 W xenon arc lamp (Applied Photophysics) which supplied white light within the UV–VIS spectral range. The output of the lamp was directed to the bottom face of the interface between water and DCE. The use of a 250 mm focal length lens and several aluminium mirrors then ensured that the light was focused on the interface in TIR mode and also allowed accurate adjustment of the light path to guarantee the optimum conditions for the spectroscopic measurements. An angle of approximately 75° was maintained in all of the experiments which allowed clear observation of the reflected beam at the opposite wall of the cell.[15] The spectroelectrochemical cell which held the solutions was a conventional four-electrode liquid–liquid electrochemistry cell modified to allow unhindered passage of the light beam. The reflected beam was either collected using a optical fibre of 400 μm in diameter attached to a spectrophotometer (Ocean Optics, Inc.) for *in situ* measurement of the whole spectrum, or collected using a water-filled optical waveguide of 1 cm in diameter attached to a high-voltage photomultiplier tube (PMT) *via* a monochromator (Applied Photophysics) equipped with a wavelength stepping motor for voltabsorptometry. The signal measured by either the fibre optic spectrophotometer or the PMT was then sampled and recorded directly on a microcomputer where further processing took place. The cell chosen for the simultaneous investigation of the electrochemistry and the absorptometry was cell 1,[5] where BTPPA represents bis(triphenylphosphoranylidene)ammonium, TPBCl represents tetrakis(4-chlorophenyl)borate. For the experiments conducted here the product of the electron-transfer reaction was $TCNQ^{\cdot -}$ in the DCE phase and was monitored spectroscopically. The potential difference imposed on the water/DCE interface and the whole data acquisition process were driven by LabView(Version 4, National Instruments). Using this set-up, the data acquisition program allowed the straightforward measurement of the whole absorption spectrum from the fibre optic spectrometer at frequencies up to 10 Hz or the signal intensity from the PMT, together with the applied interfacial potential and the corresponding electrochemical current at frequencies up to 20 kHz.

Cyclic voltammograms were recorded using a four-electrode potentiostat[16] which uses the positive feedback method for the compensation of potential drop due to solution resistance. All the potentials are absolute values obtained by comparison of the formal transfer potential of the tetramethylammonium cation: $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{0}_{\mathrm{TMA^+}}$, 0.160 V.

To obtain a whole spectrum, the raw data were processed in the following way. Since the data were in transmittance form which is effectively the final intensity incident at the fibre optic spectrometer, taking the negative logarithm of the ratio of signal data over the reference data at the beginning applied potential where there is no electron-transfer reaction gave the corresponding absorption spectrum directly. Fig. 1 shows the interfacial absorption spectra of the product *i.e.* $TCNQ^{\cdot -}$ in DCE following the application of a potential to the water/DCE interface, which drives the reduction of TCNQ in DCE by ferrocyanide in the aqueous phase. The acquisition frequency of a whole spectrum is 1 Hz. The electronic absorption spectrum of the $TCNQ^{\cdot -}$ following electroreduction of the parent TCNQ (the absorption maximum at 390 nm) by a platinum electrode in DCE exhibits clearly major absorption bands at 842, 744, 760,

$$\mathrm{Ag}\ \Big|\ \mathrm{Ag_2SO_4}\ \Big|\ \begin{array}{c} 0.4/0.01\ \mathrm{M}\ \mathrm{Fe(CN)_6^{4-/3-}} \\ 0.5\ \mathrm{M}\ \mathrm{Li_2SO_4} \end{array}\ (\mathrm{aq.})\ \Big\|\ \begin{array}{c} 10\ \mathrm{mM}\ \mathrm{BTPPATPBCl} \\ 0.6\ \mathrm{mM}\ \mathrm{TCNQ} \\ (\mathrm{DCE}) \end{array}\ \Big|\ \begin{array}{c} 0.001\ \mathrm{M}\ \mathrm{BTPPACl} \\ 0.01\ \mathrm{M}\ \mathrm{LiCl} \end{array}\ (\mathrm{aq.})\ \Big|\ \mathrm{Ag'Cl}\ \Big|\ \mathrm{Ag'}$$

cell 1

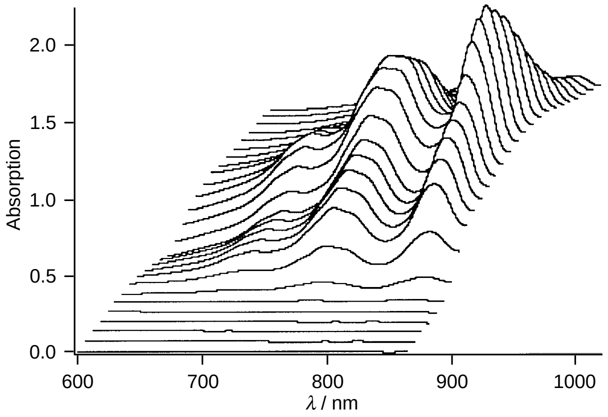

Fig. 1 *In-situ* absorption spectra measured in TIR mode when the applied potential is scanned at 25 mV s^{-1}. From bottom to top, the applied potential $\Delta_O^W\phi$ varies from 0.187 to −0.26 V (forward scan) and from −0.26 to 0.187 V (backward scan) with a potential difference of *ca.* 40 mV between two spectra.

670 and 650 nm. This is similar to the spectrum reported for TCNQ$^{\cdot-}$ in acetonitrile.[17] The spectra shown in Fig. 1 can be attributed to the heterogeneous reduction of TCNQ to TCNQ$^{\cdot-}$ on forward sweep as the water phase becomes increasingly negative and the re-oxidation of the TCNQ$^{\cdot-}$ on the reverse sweep as the water becomes more positive relative to the DCE phase. TCNQ is totally water insoluble. The appearance and disappearance of the TCNQ$^{\cdot-}$ proves without any doubt that a heterogeneous electron-transfer process does take place at the water/DCE interface. The success of the experiment relies on the choice of the redox couple which must have distinct absorption spectra in the two oxidation states. The resolution of the experiment depends on the molar absorption coefficient of the product. A background spectrum was measured before and after addition of 0.6 mM TCNQ to the DCE phase and no absorption could be measured at any wavelength between 600 and 900 nm when the applied interfacial potential was held at a potential (0.258 V for example) far away from the formal electron transfer potential($\Delta_O^W\phi^0 = -0.105$ V).

The dependence of the absorbance waveform on scan rate has been established for the system in Fig. 2(*a*). By monitoring the absorbance of the TCNQ$^{\cdot-}$ species at 670 nm during a potential sweep, an increase in absorbance until the zero current point and then a decrease in absorbance is observed at applied potentials corresponding to those of the electron-transfer voltammogram. Following the theory we have described elsewhere,[15] the shape is similar to that of an integrated voltammogram. The slower the scan rate, the larger the absorbance, because the absorption represents the amount of electron-transfer product which is formed during the electron-transfer reaction or the charge which has passed across the interface. Then differentiation of the absorbance data against time gave a voltammetric shape when plotted against applied potential. The results shown in Fig. 2(*b*) for several different scan rates corresponding to Fig. 2(*a*) are analogous to the measured electrochemical voltammograms with the observed peak height exhibiting a linear response as a function of the square root of scan rate. Because the concentration of ferrocyanide is very high in this case, the water phase acted analogously to a solid electrode and the electron-transfer rate was mainly controlled by the diffusion of TCNQ in DCE.

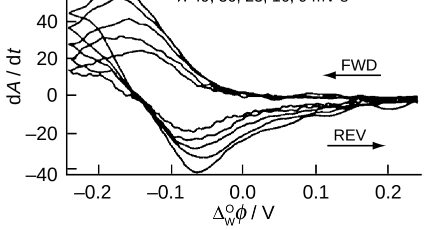

Fig. 2 (*a*) Absorption data for cell 1 measured simultaneously during the voltammetry, and (*b*) corresponding differential cyclic voltabsorptograms. The monochromator was set to 670 nm and the scan rates (from top to bottom) are indicated.

This study confirms the ability of *in situ* TIR UV–VIS spectroscopy to follow heterogeneous electron transfer at the liquid/liquid interface. The technique provides more information than conventional electrochemical techniques in mechanistic and kinetic studies. The kinetics of electron transfer for this system is currently under investigation based on spectroscopic approaches, such as chronoabsorptometry[15] and potential modulated reflectance spectroscopy.[18]

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Footnote and References

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1 H. H. Girault and D. J. Schiffrin, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1989, vol. 15, p. 1.
2 Z. Samec, V. Marecek and J. Weber, *J. Electroanal. Chem.*, 1979, **103**, 11.
3 G. Geblewicz and D. J. Schiffrin, *J. Electroanal. Chem.*, 1988, **244**, 27.
4 V. J. Cunnane, D. J. Schiffrin, C. Beltran, G. Geblewicz and T. Solomon, *J. Electroanal. Chem.*, 1988, **247**, 203.
5 Y. Cheng and D. J. Schiffrin, *J. Electroanal. Chem.*, 1991, **314**, 153.
6 Y. F. Cheng and D. J. Schiffrin, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2517.
7 J. Hanzlik, Z. Samec and J. Hovorka, *J. Electroanal. Chem.*, 1987, **216**, 303.
8 V. J. Cunnane, G. Geblewicz and D. J. Schiffrin, *Electrochim. Acta*, 1995, **40**, 3005.
9 K. Maeda, S. Kihara, M. Suzuki and M. Matsui, *J. Electroanal. Chem.*, 1991, **303**, 171.
10 R. A. W. Dryfe, R. D. Webster, B. A. Coles and R. G. Compton, *Chem. Commun.*, 1997, 779.
11 R. A. W. Dryfe, Z. F. Ding, R. G. Wellington, P. F. Brevet, A. M. Kuznetzov and H. H. Girault, *J. Phys. Chem. A*, 1997, **101**, 2519.
12 T. Kakiuchi, Y. Takasu and M. Senda, *Anal. Chem.*, 1992, **64**, 3096.
13 T. Kakiuchi and Y. Takasu, *Anal. Chem.*, 1994, **66**, 1853.
14 Z. F. Ding, R. G. Wellington, P. F. Brevet and H. H. Girault, *J. Phys. Chem.*, 1996, **100**, 10 658.
15 Z. F. Ding, R. G. Wellington, P.-F. Brevet and H. H. Girault, *J. Electroanal. Chem.*, 1997, **420**, 35.
16 Z. Samec, V. Marecek and J. Weber, *J. Electroanal. Chem.*, 1979, **100**, 841.
17 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.
18 D. J. Fermin, Z. Ding, P.-F. Brevet and H. H. Girault, *J. Electroanal. Chem.* in press.

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