

Resolution of coupled electron transfer–ion transfer processes at liquid/liquid interfaces by visualisation of interfacial concentration profiles

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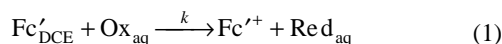
A powerful approach for investigating heterogeneous electron transfer (ET) reactions at liquid/liquid (oil/water) interfaces is described and illustrated with studies of the reactions between IrCl_6^{2-} or $\text{Fe}(\text{CN})_6^{3-}$ in an aqueous phase and decamethylferrocene (DMFc) or ferrocene (Fc) in 1,2-dichloroethane (DCE).

ET reactions that occur at the interface between two immiscible electrolyte solutions (ITIES) are of considerable fundamental and industrial interest,¹ as well as representing a simple, useful analogue of redox processes that occur across cell membranes.^{2,3} Surprisingly, ET kinetics at ITIES are still poorly understood⁴ and difficult to investigate unambiguously, because conventional electrochemical methods measure a total current flow which does not discriminate between ET and coupled ion transfer (IT).^{5–7} To circumvent this problem, differential cyclic voltabsorptometry was recently combined with UV-VIS spectroscopy, to determine whether the products of an ET process crossed the interface.⁸ A similar, earlier approach,^{9,10} employed fluorescence as the spectroscopic probe. An *in-situ* EPR cell has also recently been developed to detect and monitor paramagnetic species produced as a result of ET at ITIES.¹¹

While spectroscopic methods have provided improved insights into ET at liquid/liquid interfaces, they necessarily place demands on the types of reactants and products that can be studied.¹² Here, we describe a novel approach for investigating ET kinetics at ITIES, based on microelectrochemical measurement at expanding droplets (MEMED)^{13,14} which, we show, allows all of the reactant and product distributions adjacent to the interface to be visualised. In this way, not only can the kinetics of the ET reaction be determined, but the extent to which the products are involved in coupled IT processes can readily be identified.

In the MEMED technique,^{13,14} the ITIES is created by flowing a feeder liquid through a fine capillary tip (100–200 μm internal diameter), so that droplets form and grow periodically in a second receptor phase, immiscible with the first, analogous to the dropping mercury electrode¹⁵ or electrolyte dropping electrode.^{16,17} In contrast to these methods, however, MEMED determines the individual concentration profiles of products or reactants extending from the droplet surface into the receptor phase using a probe ultramicroelectrode (UME), positioned adjacent to the capillary. In the studies here, we used a 1 or 0.5 μm radius Pt disc working electrode held at a potential to detect a specific reactant or product by local diffusion-limited electrolysis. The current for the species of interest was recorded as a function of time, as droplets grew towards the tip, and converted to a concentration-distance profile.

We consider the redox reaction between Fc or DMFc (which we denote as Fc') in DCE and either IrCl_6^{2-} or $\text{Fe}(\text{CN})_6^{3-}$ in the aqueous phase (denoted by Ox_{aq}):



where k is a first-order rate constant for the heterogeneous reaction. The objective was to determine k and identify whether the products (particularly Fc'^+) crossed the interface, by recording the concentration profiles for all four species in eqn. (1). This was achieved by expanding a DCE droplet containing

Fc' into an aqueous phase containing Ox and recording the Ox and Red profiles with the UME in the aqueous phase. Subsequently, an aqueous droplet, containing Ox, was expanded into the DCE phase and the profiles for Fc' and Fc'^+ recorded in DCE.

In all experiments, the potential across the interface was established by using the potential-determining ClO_4^- ion in each phase.¹⁸ Fig. 1 and 2 show the concentration profiles for the reactants and products in the receptor phase for the reaction between IrCl_6^{2-} and either Fc or DMFc. The concentrations have been normalised with respect to the bulk reactant concentrations, $[\text{IrCl}_6^{2-}]^*$ or $[\text{Fc}']^*$, and plotted against the separation, d , between the probe and droplet surface. The initial driving force for the reactions is governed by the difference in the formal potentials of the $\text{IrCl}_6^{2-}/\text{IrCl}_6^{3-}$ couple and the Fc'/Fc'^+ couple, ΔE° , and the relative potential drop, $\Delta\phi$, across the ITIES. This was determined by measuring the difference in the half-wave potentials, $\Delta E_{1/2}$, of the reversible couples in the two phases *versus* saturated calomel (SCE) reference electrode in the aqueous phase:

$$\Delta E_{1/2} = \Delta E^\circ + \Delta\phi \quad (2)$$

For the IrCl_6^{2-} –Fc reaction $\Delta E_{1/2}$ was *ca.* 0.40 V, while for the IrCl_6^{2-} –DMFc reaction $\Delta E_{1/2}$ was *ca.* 0.70 V. These are

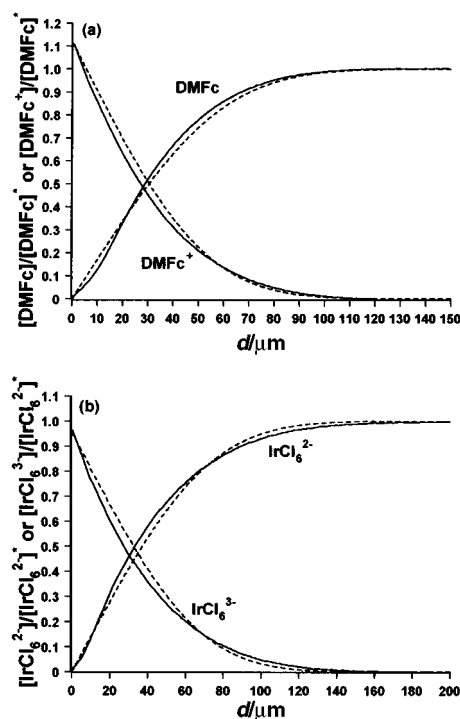


Fig. 1 Normalised concentration profiles (solid lines) of the reactants and products in the DCE (a) and aqueous (b) receptor phases for the reaction between DMFc (DCE) and IrCl_6^{2-} (aqueous). Drop times and final sizes were (a) 5.54 s and 0.96 mm, and (b) 6.32 s and 1.00 mm. The theoretical profiles (dashed lines) are for a transport-controlled reaction, with no transfer of the product ions.

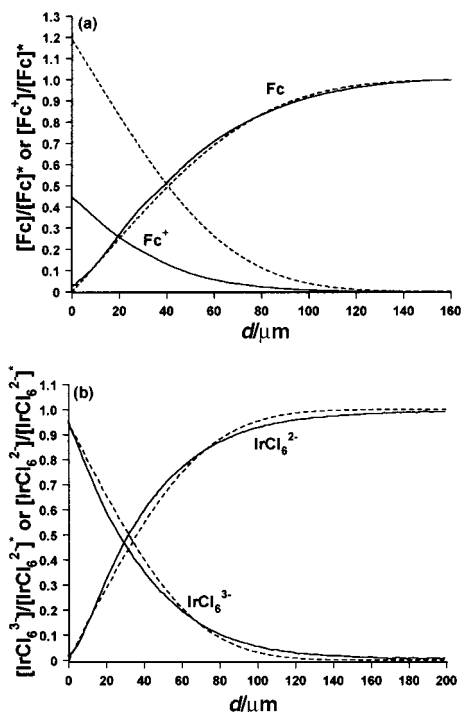


Fig. 2 Normalised concentration profiles (solid lines) of the reactants and products in the DCE (a) or aqueous (b) receptor phase for the reaction between Fc (DCE) and IrCl_6^{2-} (aqueous). Drop times and final sizes were (a) 5.54 s and 0.96 mm, and (b) 6.32 s and 1.00 mm. The theoretical profiles (dashed lines) are for a transport-controlled reaction, with no transfer of the product ions.

relatively large driving forces and consequently the IrCl_6^{2-} and IrCl_6^{3-} profiles in both cases indicate that the reaction is transport-controlled ($k > 0.1 \text{ cm s}^{-1}$), with the concentration of IrCl_6^{2-} falling to zero at the surface of the droplet. There is generally good agreement between the experimental and theoretical profiles, calculated based on the following convective-diffusion equation, which applies close to the interface of the expanding droplet:^{13,14}

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial r^2} - \frac{q}{2\pi} \left(\frac{1}{r^2} - \frac{1}{r_o^2} \right) \frac{\partial c_i}{\partial r} \quad (3)$$

D_i and c_i are the diffusion coefficient and concentration of the reactant, $i = \text{R}$, or product, $i = \text{P}$, in the receptor phase, respectively. The spherical coordinate, starting at the centre of the drop, is denoted by r ; q is the volume flow rate, and r_o is the (time-dependent) drop radius.

The interfacial boundary condition is:

$$r = r_o : -D_R \frac{\partial c_R}{\partial r} = D_P \frac{\partial c_P}{\partial r} = kc_R \quad (4)$$

where R and P are, respectively, IrCl_6^{2-} and IrCl_6^{3-} for the aqueous receptor phase or Fc' and $\text{Fc}^{+'}$ for the DCE receptor phase. Eqn. (4) assumes that neither the product nor the reactant in the receptor phase partition into the droplet. Semi-infinite no-flux boundary conditions apply at a long distance from the ITIES. Measured values of $D_{\text{IrCl}_6^{2-}} = 6.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{IrCl}_6^{3-}} = 7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ were employed to calculate the concentration profiles.

The DMFc and DMFc⁺ profiles (Fig. 1) for the DCE receptor phase also show a good fit to a transport-controlled process, with $k > 0.1 \text{ cm s}^{-1}$, calculated using $D_{\text{DMFc}} = 7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{DMFc}^+} = 6.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The excellent agreement between the DMFc⁺ experimental and theoretical

profiles indicates that DMFc⁺ does not cross the ITIES under the defined experimental conditions, and that charge neutrality must be maintained by ClO_4^- transfer from the aqueous phase to the DCE phase. In contrast, while the Fc profile in Fig. 2 indicates that the IrCl_6^{2-} -Fc reaction is clearly transport-controlled, the Fc⁺ profile indicates a substantial loss of Fc⁺ which can be attributed to transfer across the interface from the DCE to the aqueous phase.⁵

The reaction between $\text{Fe}(\text{CN})_6^{3-}$ and DMFc was also investigated. Although DMFc was proposed as an ideal electron donor for ET studies at ITIES,⁶ earlier investigations concluded that no ET reaction could be observed between DMFc and $\text{Fe}(\text{CN})_6^{3-}$ at the DCE/aqueous interface.⁶ In this study, DMFc and DMFc⁺ were measured in a DCE receptor phase, while forming an aqueous droplet containing $\text{Fe}(\text{CN})_6^{3-}$. The results clearly showed that an ET reaction occur between $\text{Fe}(\text{CN})_6^{3-}$ and DMFc, evidenced by a decrease in DMFc and formation of DMFc⁺ close to the interface. The process was characterised by a first-order heterogeneous reaction rate constant of $(2.0 \pm 0.2) \times 10^{-3} \text{ cm s}^{-1}$. The smaller rate constant with $\text{Fe}(\text{CN})_6^{3-}$ compared to IrCl_6^{2-} as the electron acceptor can be attributed to a lower driving force, $\Delta E_{1/2} = 0.086 \text{ V}$.

In summary, MEMED is a promising technique for studying ET reactions at ITIES. Determining all of the reactant and product distributions adjacent to the ITIES allows interfacial ET kinetics to be determined unambiguously, and the nature of any coupled IT processes is revealed.

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- 18 The aqueous phase contained $0.25 \text{ mol dm}^{-3} \text{ NaClO}_4$ and $0.1 \text{ mol dm}^{-3} \text{ NaCl}$, while the DCE phase contained 0.1 mol dm^{-3} tetra-*n*-hexylammonium perchlorate (THAP). The DCE phase contained either $1 \times 10^{-2} \text{ mol dm}^{-3} \text{ Fc}'$ (droplet) or $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Fc}'$ (receptor), while the aqueous phase contained $1 \times 10^{-2} \text{ mol dm}^{-3} \text{ Ox}$ (droplet) or $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ox}$ (receptor). Constant composition could be assumed for the droplet, and mass transport only had to be considered for the receptor phase.

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