Photocurrent Measurements at the Interface between Two Immiscible Electrolyte Solutions

Fiona L. Thomson, Lesley J. Yellowlees, and Hubert H. Girault*

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

The electrochemical measurement of a photocurrent has been successfully achieved using the $[Ru(bpy)_3]^{2+}|C_7V^{2+}$ system (bpy = 2,2′-bipyridine, C_7V = heptyl-4,4′-bipyridinium) across a liquid/liquid interface.

A major problem in the study of photoinduced electron transfer reactions has been the separation of the products (D^+ and A^-) in order to prevent back electron transfer (step iii)

$$D \xrightarrow{h\nu} D^* \qquad \text{(i)}$$

$$D^* + A \longrightarrow D^+ + A^- \qquad \text{(ii)}$$

$$D^+ + A^- \longrightarrow D + A \qquad \text{(iii)}$$

In 1979, Calvin has shown that the change in the hydrophobicity or hydrophilicity of an acceptor, or quencher, following electron transfer, which is located in the vicinity of a water/toluene interface leads to a separation of the photoproducts by transfer of the reduced quencher across the interface.[1] The two reactions studied were (1) and (2).

$$^*Ru(bpy)_3{}^{2+}{}_{water} + C_{16}V^{2+}{}_{interface} \longrightarrow Ru(bpy)_3{}^{3+}{}_{water} + C_{16}V^{+}{}_{toluene} \qquad (1)$$

$$^*Ru(bpy)_3{}^{2+}{}_{water} + BNA^{+}{}_{interface} \longrightarrow Ru(bpy)_3{}^{3+}{}_{water} + BNA_{toluene} \qquad (2)$$

The donor or sensitizer tris(2,2′-bipyridine)ruthenium(II) chloride $[Ru(bpy)_3]Cl_2$ and the quenchers hexadecyl-4,4′-bipyridinium chloride ($C_{16}VCl_2$) or benzylnicotinamide chloride (BNACl) were dissolved in the aqueous phase. However the amphiphilic nature of the quenchers in their oxidised state ($C_{16}V^{2+}$ or BNA^+) is such that they were adsorbed at the water/toluene interface. The increase of their hydrophobicity as a result of the photoreaction was sufficient for their transfer across the interface into the toluene layer, thus ensuring a physical separation of the photoproducts. This

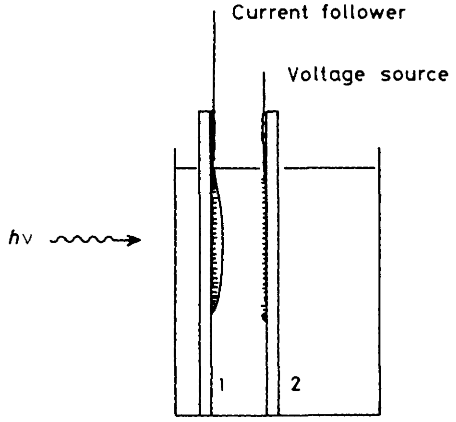

Figure 1. Electrochemical cell used. The organic phase is a film supported by the Pt electrode mounted on microscope slide 1.

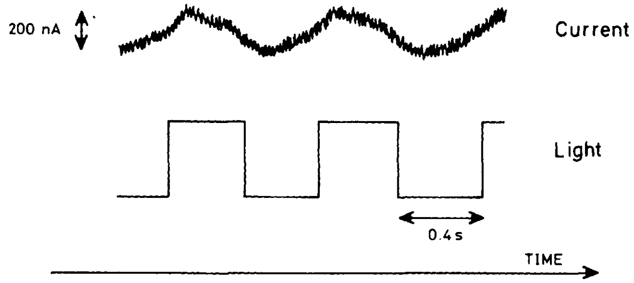

Figure 2. A.C. photocurrent measured, showing signal to noise ratio.

experiment was an early example of a photoinduced ion transfer reaction across a liquid/liquid interface.

The recent developments of the electrochemistry of liquid/liquid interfaces[2] and in particular the study of interfacial electron transfer reactions of the type (3)[3] have permitted the electrochemical study of interfacial photoreactions. We now report the measurement of the photocurrent for the photoreactions (4).

$$\mathrm{Ox1_{water}} + \mathrm{Red2_{oil}} \leftrightarrows \mathrm{Red1_{water}} + \mathrm{Ox2_{oil}} \quad (3)$$

$$\mathrm{Ru(bpy)_3{}^{2+}{}_{water}} + \mathrm{C_7V^{2+}{}_{oil}} \rightarrow \mathrm{Ru(bpy)_3{}^{3+}{}_{water}} + \mathrm{C_7V^{+}{}_{oil}} \quad (4)$$

The electrochemical cell was made of two platinum gauze electrodes fixed onto microscope slides with a fluorosilicon sealent. The electrodes measured 15 × 23 mm and 7 × 23 mm for the aqueous and organic slides respectively. The organic phase was supported as a thin film on the Pt gauze and the slide made hydrophobic by silylation with trimethylchlorosilane. This method thus ensured that the organic electrolyte wetted the glass and covered the Pt gauze. The two electrodes were placed face to face in a spectroscopic cuvette filled with the aqueous solution. Once immersed in the cuvette, the interfacial tension (oil/water) held the organic film on the assembly. The interface was renewed before each experiment.

The aqueous solution contained 4×10^{-4} M $[\mathrm{Ru(bpy)_3}]\mathrm{Cl_2}$ (Aldrich). The organic phase contained 4×10^{-3} M $\mathrm{C_7V(TPB)_2}$ (TPB = 1,1′-diheptyl-4,4′-bipyridinium tetraphenylborate) and 10^{-3} M TBATPB (tetrabutylammonium tetraphenyl borate) in 1,2-dichloroethane (Analar BDH). Both phases were deoxygenated with nitrogen prior to use. The $\mathrm{C_7V(TPB)_2}$ salt was prepared by metathesis from $\mathrm{C_7VBr_2}$ (Aldrich) and NaTPB (Aldrich). The orange precipitate obtained was filtered and dried under vacuum.

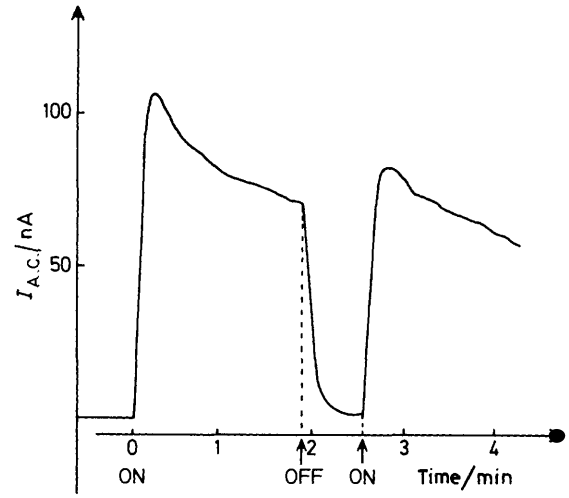

Figure 3. Photocurrent as a function of time.

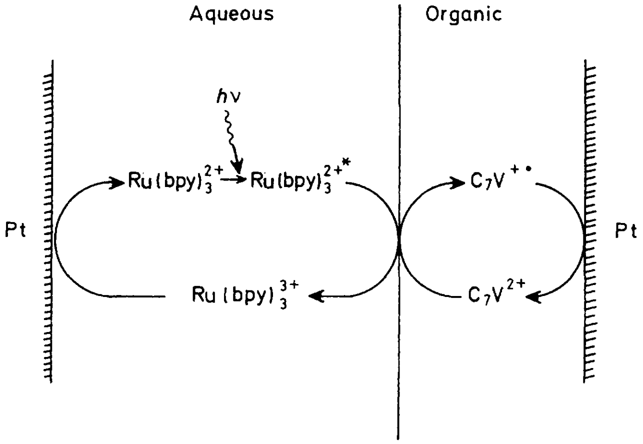

Figure 4. Electron transfer cycle.

The heptylviologen cation $\mathrm{C_7V^{2+}}$ is more hydrophobic than $[\mathrm{Ru(bpy)_3}]^{2+}$ and no cation exchange was observed by equilibrating an aqueous solution of $[\mathrm{Ru(bpy)_3}]\mathrm{Cl_2}$ and $\mathrm{C_7V(TPB)_2}$ in 1,2-dichloroethane. The higher hydrophobicity of $\mathrm{C_7V^{2+}}$ compared to that of $\mathrm{Ru(bpy)_3{}^{2+}}$ was confirmed by cyclic voltammetry of ion transfer at a liquid/liquid interface where it was observed that $\mathrm{C_7V^{2+}}$ transferred at a higher potential (oil *vs.* water) than $[\mathrm{Ru(bpy)_3}]^{2+}$. Because the two ions $\mathrm{C_7V^{2+}}$ and $[\mathrm{Ru(bpy)_3}]^{2+}$ have rather close Gibbs energy of transfer, the interface used for the photochemical experiment was not polarisable. If a potential difference $\Delta_w^o\Phi$ higher than the equilibrium value is applied then $\mathrm{C_7V^{2+}}$ is transferred from the oil phase to the aqueous layer whereas a lower applied potential difference results in the transfer of $[\mathrm{Ru(bpy)_3}]^{2+}$ from the water to the dichloroethane.

Prior to illumination, the equilibrium value of the applied potential was measured and then applied. The dark current measured was thus equal to zero. The cuvette was illuminated as shown in Figure 1 with a 150 W Xenon arc lamp (Applied Photophysics, U.K.). The photocurrents were measured using a light chopper (Bentham, U.K.) together with a high accuracy current follower connected to a lock-in amplifier (EG & G, U.S.A.).

The A.C. photocurrent observed during illumination chopped at a frequency of 2.5 Hz is shown in Figure 2 and the output of the lock-in amplifier is shown in Figure 3. The results obtained show that photoinduced interfacial electron transfer across an ITIES has indeed been observed and measured and corresponds to the cycle shown in Figure 4. Because the aqueous photoproduct $[Ru(bpy)_3]^{3+}$ is more hydrophilic than the aqueous reactant $[Ru(bpy)_3]^{2+}$ and the organic photoproduct $C_7V^{+\cdot}$ is more hydrophilic than the organic reactant C_7V^{2+}, it is certain that the photocurrent observed is not due to an ion transfer reaction but an interfacial electron transfer of the type described in reaction (3). Obviously, no photocurrent was observed when either the sensitizer or quencher was absent.

Therefore, it has been shown that the measurement of photocurrents is not limited to the quenching of an excited sensitizer by a semiconductor electrode and the liquid/liquid interface can provide a new tool for the electrochemical study of photoinduced charge transfer reactions.

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