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Measurement of rapid electron transfer across a liquid/liquid interface from 7,7,8,8-tetracyanoquinodimethane radical anion in 1,2-dichloroethane to aqueous tris(2,2-bipyridyl)-ruthenium (III)

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Abstract

Rate constants for the reduction of tris(2,2-bipyridyl)-dichlororuthenium (III) ($Ru(bipy)_3^{3+}$) in water by 7,7,8,8-tetracyanoquinodimethane radical anion ($TCNQ^{\cdot-}$) in 1,2-dichloroethane (DCE) have been measured as a function of the Galvani potential across an ideally non-polarizable interface using scanning electrochemical microscopy (SECM). The Galvani potential was varied by changing the concentration of tetrabutylammonium chloride in the aqueous phase, with a fixed concentration of the organic electrolyte, tetrabutylammonium tetrakis(penta-fluoro)phenylborate, employed in the DCE phase. By selecting appropriate concentration ratios of the reactants in the two phases, fast electron transfer (ET) rate constants were measured which were found to increase with increasing driving force. The experimentally obtained ET rate constants have been compared to the corresponding theoretical values calculated from the sharp boundary and thick layer models of Marcus. The results are consistent with the sharp boundary model, providing further evidence for the applicability of this model for the description of simple ET processes across liquid/liquid interfaces.

Keywords: SECM; Interface between two immiscible electrolyte solutions; Galvani potential; Electron transfer; Marcus theory

1. Introduction

The study of electron transfer (ET) processes across the interface between two immiscible electrolyte solutions (ITIES) is an area of considerable research activity, for both fundamental reasons and possible applications [1,2]. As a consequence, many new electrochemical techniques have been developed to measure the kinetics of ET processes which were previously difficult to study [3–19].

A fundamental question addressed in these studies concerns the dependence of ET rate constants on the Galvani potential across the ITIES. Scanning electrochemical microscopy (SECM) [20] has proven a powerful tool for addressing this question and the advantages of SECM over alternative methods have been pointed out [4–6]. Since the initial studies of Soloman and Bard [21], SECM has provided significant information on the effect of driving force on ET kinetics across the ITIES [4–6,22–34]. Most of the previous reports have described potential-dependent ET rate constants at the ITIES [4–6,26–31], although some ET systems appear to be characterized by potential-independent ET rate constants [32,33]. Significantly, there is a growing body of evidence that the kinetics of the most simple ET reactions at the ITIES follow Butler–Volmer (B–V) theory at low overpotentials [3–5], with an inverted region at high driving force as predicted by Marcus theory [3–5,9,31,35–41].

Photoinduced ET, recognized as a model system for natural photosynthesis and heterogeneous photocatalysis [1,42,43], is an interesting approach for investigating the rates of ET reactions across the ITIES. In this context, the reaction between the photoexcited sensitizer tris(2,2-bipyridyl)-ruthenium (II) ($Ru(bipy)_3^{2+}$), dissolved in an

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aqueous phase, with the quenching species 7,7,8,8-tetracyanoquinodimethane (TCNQ), located in an immiscible organic phase, has been studied with electrochemical and spectroelectrochemical techniques [44,45]. A key aspect of photoelectrochemical technologies based on this type of process is to enhance the efficiency of product separation by diminishing the probability of back electron transfer processes. Consequently, knowledge of the kinetics of back electron transfer reactions is important [41,46–48], but the rate of such processes is usually treated as a fitting parameter within a more complex photoelectrochemical scheme. Furthermore, to the best of our knowledge, the reaction between $\mathrm{Ru(bipy)}_3^{3+}$ and $\mathrm{TCNQ}^{\cdot -}$ has not been studied previously.

A feature of photoinduced ET studies of the type mentioned is that the driving force for back ET is usually large, which places demands on the techniques used to elucidate the kinetics. We have shown that by using a small concentration ratio of the reactants in the two liquid phases, it is possible to use SECM to measure rapid dark ET reactions across the ITIES that are inaccessible to other techniques [9]. This approach has also been used by others to measure large ET rate constants [31].

In this paper, we investigate the rate of oxidation of $\mathrm{TCNQ}^{\cdot -}$ in 1,2-dichloroethane (DCE) by aqueous $\mathrm{Ru(bipy)}_3^{3+}$. We establish that ET is fast and the rate depends on the Galvani potential across the ITIES. The rate constants measured have been compared with the theoretical values arising from the sharp boundary and thick layer models of Marcus [35–39]. The studies of ET at high driving force presented in this paper provide evidence that the sharp boundary model, which has been shown to apply at relatively low driving forces [49,50], also applies to dark ET reactions at high driving force.

2. Experimental

2.1. Chemicals

$\mathrm{Ru(bipy)_3Cl_2}$ (99.95%, Aldrich), TCNQ ($\geqslant$98%, Fluka), tetrabutylammonium chloride (TBACl, $\geqslant$97%, Fluka), lithium tetrakis(penta-fluoro)phenylborate ethyl etherate (LiTPBF, Fluka), sodium chloride (A.R., Fisher) and DCE (HPLC grade, Sigma–Aldrich) were used as received. The organic salt, tetrabutylammonium tetrakis(penta-fluoro)phenylborate ($\mathrm{TBA^+TPBF^-}$), was prepared by metathesis of TBACl and LiTPBF in a 2:1 mixture of methanol and water. The product was filtered and desiccated overnight. Aqueous and organic solutions were prepared, respectively, from Milli-Q reagent water (Millipore Corp.) and water-saturated DCE.

2.2. Apparatus and procedures

The SECM setup and experimental method used to measure the ET rate constants were similar to those reported previously [49]: a layer of DCE covered an inverted glassy carbon electrode (GCE) (3 mm diameter) by depositing a 35 μL drop of DCE solution containing 2 mM TCNQ and 0.05 M TBATPBF on the surface. A schematic of the SECM arrangement is shown in Fig. 1. The cell was filled with aqueous electrolyte containing 1–4 mM $\mathrm{Ru(bipy)}_3^{2+}$, 0.1 M NaCl and 0.01–0.1 M TBACl.

Prior to SECM experiments, a three-electrode system was employed to generate $\mathrm{TCNQ}^{\cdot -}$ by electrolyzing TCNQ in the DCE phase on the GCE working electrode with a saturated calomel electrode (SCE) and a Pt mesh as the reference and counter electrodes, respectively. The electrolysis procedure is described as follows: TCNQ in the DCE droplet on the GCE was exhaustively reduced to $\mathrm{TCNQ}^{\cdot -}$ in the absence of O_2 by biasing the potential of the GCE at 0 V vs. SCE in the aqueous phase with a Pt mesh counter electrode, such that the reduction of TCNQ to $\mathrm{TCNQ}^{\cdot -}$ was diffusion-controlled. The electrolysis process was deemed to be complete when the recorded charge approached a limiting value (as shown in Fig. 2), consistent with the quantity of TCNQ in the droplet. The extent of electrolysis and concentration of $\mathrm{TCNQ}^{\cdot -}$ in the DCE phase was also confirmed by dipping an ultramicroelectrode (UME) into the organic layer and measuring the concentration of $\mathrm{TCNQ}^{\cdot -}$ from the steady-state diffusion-limited current.

To ensure that the generated $\mathrm{TCNQ}^{\cdot -}$ was stable, the whole system was thoroughly deaerated throughout all experiments. The stability of $\mathrm{TCNQ}^{\cdot -}$ was checked by recording a voltammogram before and after the SECM measurements, with the UME dipped into the organic drop. The change in the diffusion limited current for $\mathrm{TCNQ}^{\cdot -}$ oxidation to TCNQ was negligible (<2%), indicating that $\mathrm{TCNQ}^{\cdot -}$ is stable under these conditions. After the electrolysis process, the GCE was disconnected. It should be noted that the SECM process itself barely converts any of the $\mathrm{TCNQ}^{\cdot -}$ compared to the total amount

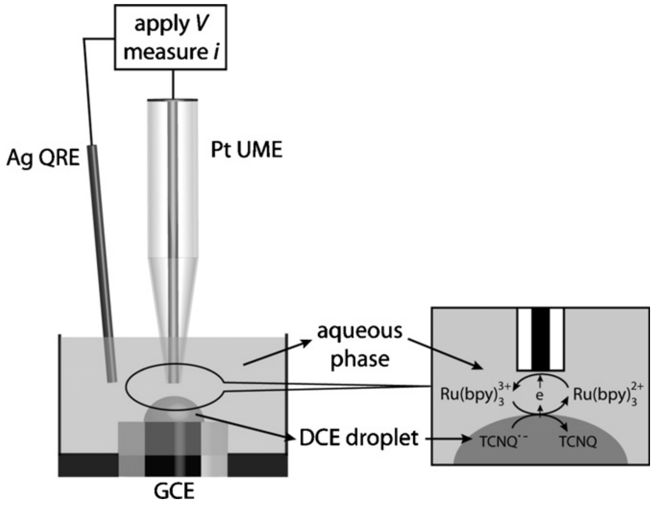

Fig. 1. Schematic of the SECM setup for the measurement of ET rate constants at the aqueous/DCE interface.