

Lipophilicity of ions electrogenerated at a Pt coated micropipette supported liquid–liquid interface

Peter Liljeroth, Bernadette M. Quinn*, Kyösti Kontturi

Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, P.O. Box 6100, HUT 02150, Finland

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Abstract

A novel method to readily determine the lipophilicity of electrogenerated charged species is reported. This is achieved by local electrolysis at a Pt coated micropipette and, subsequently, driving the electrogenerated species to transfer across the liquid–liquid interface supported at the tip of the micropipette under potential control. The formal potential of ion transfer can then be used to give a measure of its relative lipophilicity. The method proposed is facile and enables the study of potentially unstable charged products of electron transfer reactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lipophilicity; Electron transfer; Ion transfer; Liquid–liquid interfaces; Micropipette; Generator-collector electrodes

1. Introduction

Heterogeneous electron transfer (ET) at liquid–liquid interfaces between reactants located in opposing phases has become an active research area in recent years. Techniques most commonly used to study ET include cyclic voltammetry (CV) [1–5], scanning electrochemical microscopy (SECM) [6–8] and spectroelectrochemical methods [9]. To avoid possible homogeneous ET pathways, which would complicate analysis, highly hydrophobic organic and hydrophilic aqueous redox species are chosen as the reactants [4,10]. If the lipophilicity of all reactants and products are known, experimental conditions and redox species can be chosen judiciously [11]. The organic phase redox reactants considered are generally neutral species whereby the charged species is generated by the heterogeneous ET reaction from an aqueous phase reactant. Such organic charged products are not generally commercially available and thus their lipophilicity has not been readily accessible. It has been probed indirectly by such techniques as double potential-step chronoamperometry SECM [12]. The charged species can be also generated by ex situ bulk electrolysis

of the neutral species [13]. However, this is problematic in highly resistive organic solvents such as 1,2-dichloroethane (DCE) without the addition of large quantities of supporting electrolyte. Chemical oxidation/reduction methods [2,14] are also possible, though lability and purification of the resulting species have to be considered.

Here, we propose a very simple means of determining the lipophilicity of the charged species by in situ localised electrolysis of the neutral species in the vicinity of a polarised liquid–liquid interface supported at the tip of a micropipette. As the species of interest is generated in situ, its potential lability does not pose a problem. Also, very small volumes of each phase are required. This is demonstrated for some of the most commonly studied organic redox species; decamethylferrocene (DcFc), dimethylferrocene (DmFc), ferrocene (Fc), ferrocene methanol (FcMeOH), tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ).

The addition of salting-out agents [15,16] such as lithium sulphate to the aqueous phase has become standard practice in studies concerning heterogeneous ET at liquid–liquid interfaces in an attempt to avoid complications due to coupled ion transfer at the electron transfer potential ($\Delta_o^w \phi_{ET}^0$) [2,3,13,17–21]. The Pt coated micropipette assembly described here offers a convenient and simple means of determining the extent

*Corresponding author. Tel.: +358-9-451-2579; fax: +358-9-451-2580.

E-mail address: bquinn@cc.hut.fi (B.M. Quinn).

the salting-out agent shifts the formal ion transfer potential ($\Delta_o^w \phi_i^{o'}$) and its dependence on the concentration of the agent used. Once the values of $\Delta_o^w \phi_i^{o'}$ are known, the extent to which coupled ion transfer interferes with the heterogeneous ET under study can be assessed [11].

2. Experimental

2.1. Chemicals

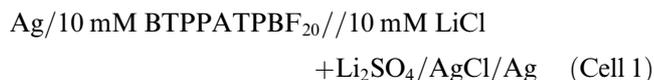
Bis(triphenylphosphoranylidene) ammonium tetrakis pentafluoroborate (BTTPATPBF₂₀) was prepared as in [22]. All other chemicals were of the highest commercially available purity and were used as received. Aqueous solutions were prepared using MQ (Millipore, US) treated water.

2.2. Preparation of the Pt coated micropipettes

Robust micropipettes suitable for liquid–liquid electrochemistry were prepared as described by Evans et al. [23]. A coned silver ultra-microelectrode was painted with Bright Platinum paint (PBC11611, Johnson Matthey, UK) using a small brush, fired at 600°C for 15 min. The resulting Pt coated tip was then polished with 0.3 μm alumina grinding paper (Buehler, US) to expose the silver wire. The silver wire was etched completely with concentrated nitric acid resulting in a Pt coated micropipette with a 25 μm inner diameter. Electrical connection was made to the Pt coat. A schematic is given in Fig. 1.

2.3. Experimental arrangement

The cell used was as follows:



where // refers the polarisable water/DCE interface. The neutral redox species were added to the DCE phase typically at a concentration of 0.5 mM. The cell potential scale was referenced to the absolute scale using the transfer of tetramethylammonium (TMA⁺), tetraethylammonium (TEA⁺) or perchlorate (ClO₄⁻) as an internal reference [13]. The transfer potential on the cell scale was correlated with its literature value on the absolute galvanic scale ($\Delta_o^w \phi_{\text{TMA}^+}^{o'} = 0.160 \text{ V}$, $\Delta_o^w \phi_{\text{TEA}^+}^{o'} = 0.044 \text{ V}$, $\Delta_o^w \phi_{\text{ClO}_4^-}^{o'} = -0.160 \text{ V}$ [24]). The transfer potentials of the reference ions were thus fixed and possible effects of the salting-out agent on their transfer was not considered [21]. The potential was taken as that of the water phase with respect to organic phase, $\Delta_o^w \phi = \phi^w - \phi^o$.

The pipette was filled with the aqueous phase and dipped into the organic phase. A bipotentiostatic

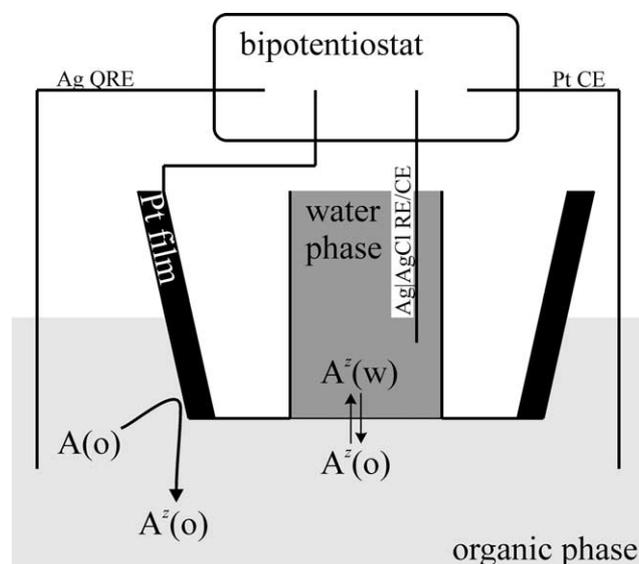


Fig. 1. Schematic of the Pt coated micropipette assembly.

arrangement (CHI 900 potentiostat, CH Instruments, Austin, TX) was used to polarise both the liquid–liquid interface and the Pt outer surface of the pipette. The arrangement is illustrated in the schematic given in Fig. 1.

3. Results and discussion

The micropipette supported liquid–liquid interface has an asymmetric diffusion regime as mass transfer inside the pipette is controlled by linear diffusion (aqueous phase) and by approximately spherical diffusion outside the pipette (organic phase) [25]. Thus, the CV response is asymmetric. The transfer of neutral species across the liquid–liquid interface is independent of $\Delta_o^w \phi$ and does not induce current flow. The CV response given in Fig. 2 (dashed line) does not change with addition of Fc to the organic phase. Applying a suitable potential (E_{Pt}) to the Pt coated electrode generates the charged redox species in the vicinity of the polarised water/DCE interface. In Fig. 2, CV responses for the polarised liquid–liquid interface for different applied electrode potentials are compared; (i) in the absence of applied potential to the Pt electrode, (ii) $E_{\text{Pt}} \ll E_{\text{Fc}/\text{Fc}^+}^0$ and (iii) $E_{\text{Pt}} > E_{\text{Fc}/\text{Fc}^+}^0$. In the first two cases, the CV response remains unchanged (dashed line), as the electrode potential is not sufficient to oxidise Fc. In the latter case, $\text{Fc}(\text{DCE}) - e^- \rightarrow \text{Fc}^+(\text{DCE})$ at the Pt electrode surface and ferricenium transfer across the liquid–liquid interface can be visualised by the appearance of an additional wave ($\text{Fc}^+(\text{DCE}) \rightarrow \text{Fc}^+(\text{w})$) and a peak ($\text{Fc}^+(\text{w}) \rightarrow \text{Fc}^+(\text{DCE})$) in the CV response (solid line). The formal transfer potential of ferricenium is obtained from the cell half-wave potential $E_{1/2}$

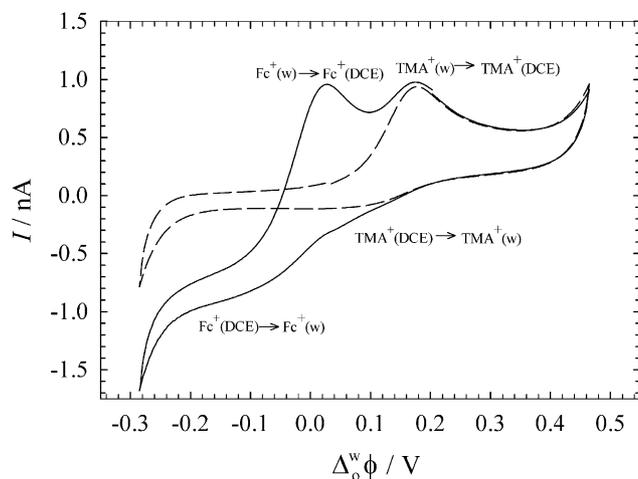


Fig. 2. CV response at the micropipette supported water/DCE interface for $E_{\text{Pt}} = \text{OCP}$ (---) and for $E_{\text{Pt}} > E_{\text{Fc}/\text{Fc}^+}^0$ (—) in the presence of aqueous TMA^+ . Scan rate = 100 mV s^{-1} .

referenced against the transfer potential of the reference ion (TMA^+) to obtain $\Delta_0^w \phi_i^{1/2}$, [21] assuming $\Delta_0^w \phi_i^{0'} \cong \Delta_0^w \phi_i^{1/2}$.

This was repeated for the other redox species considered. For example, typical CVs obtained for the transfer of TCNQ^- across the pipette supported water/DCE interface in the presence of 0, 10, 100, 1000 and 1500 mM Li_2SO_4 (top to bottom) are given in Fig. 3. Values for $\Delta_0^w \phi_i^{0'}$ determined are tabulated in Table 1. For Fc and DmFc, they are comparable to previous reports [2] both in the absence (Fc – 0.021 V, DmFc – 0.090 V) and presence of 1.5 M Li_2SO_4 (Fc – 0.063 V, DmFc – 0.145 V). The slight differences may be due to the means of correcting the cell scale to the Galvani scale. Different values have been reported for $\Delta_0^w \phi_{\text{TCNQ}^-}^{0'}$ (0.021 V [20] and 0.140 V [26]). These discrepancies can be attributed to the known ion pairing between TCNQ^- and the cation of the organic base electrolyte [19]. The present method would also be a convenient means of studying this phenomenon in more detail.

$\Delta_0^w \phi_i^{0'}$ values determined give an indication of the relative lipophilicity of the ions. Hydrophobic cations and anions are characterised by $\Delta_0^w \phi_i^{0'} \ll 0$ and $\gg 0$, respectively and vice versa for hydrophilic ions [10]. From Table 1, the anion TCNQ^- can be classified as hydrophobic and its transfer is salted out by ca. 70

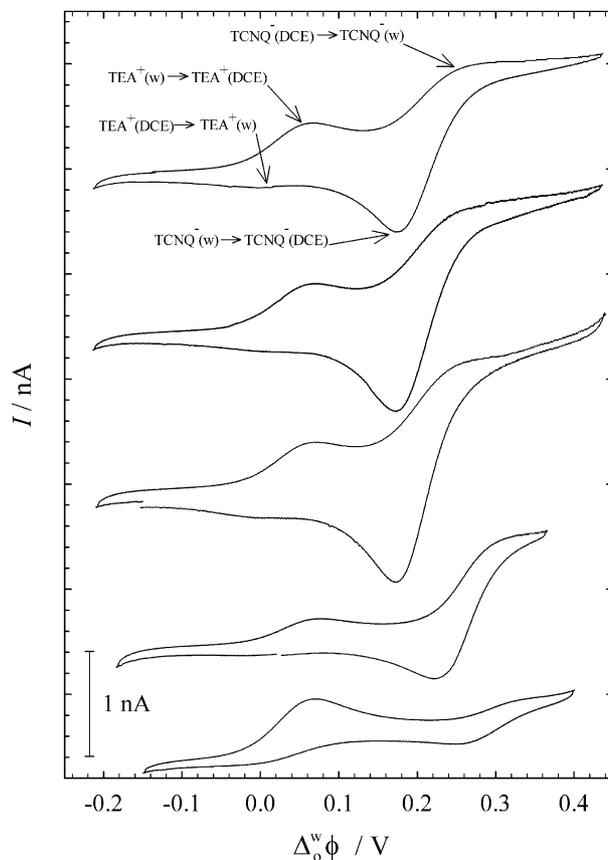


Fig. 3. CVs for TCNQ^- transfer at the micropipette supported water/DCE interface in the presence of increasing aqueous Li_2SO_4 concentration (top to bottom: 0, 0.01, 0.1, 1 and 1.5 M) for $E_{\text{Pt}} < E_{\text{TCNQ}^-/\text{TCNQ}^{\cdot-}}^0$, where TEA^+ transfer was used to set the potential scale. Scan rate = 100 mV s^{-1} .

mV as the concentration of Li_2SO_4 is increased from 0.1 to 1.5 M. DmFc^+ , Fc^+ and FcMeOH^+ are significantly less hydrophobic and hydrophobicity increases in the following order; $\text{DmFc}^+ > \text{Fc}^+ > \text{FcMeOH}^+$ as expected [4]. The transfer was salted out as the concentration of Li_2SO_4 increased from 0.1 to 1.5 M by ca. 60 (FcMeOH^+), 45 (DmFc^+) and 35 (Fc^+) mV. The hydrophobicity of TTF^+ is intermediate between DmFc^+ and Fc^+ , however in this case, the addition high concentrations of Li_2SO_4 induced a slight salting-in effect on ion transfer. From Table 1, it can be concluded that the effect of the salting-out agent on

Table 1

Formal transfer potentials $\Delta_0^w \phi_i^{0'}$ for the charged components of commonly used neutral organic redox species

$[\text{Li}_2\text{SO}_4]$ (M)	^a FcMeOH^+ (mV)	^b Fc^+ (mV)	^b DmFc^+ (mV)	^b TTF^+ (mV)	^c TCNQ^- (mV)
0	30	8	-64	-21	202
0.01	25	6	-71	-19	200
0.1	21	11	-68	-19	200
1	-7	-7	-98	-20	247
1.5	-30	-27	-107	-13	274

Values determined based on the transfer of internal reference ions: ^a ClO_4^- ; ^b TMA^+ ; ^c TEA^+ .

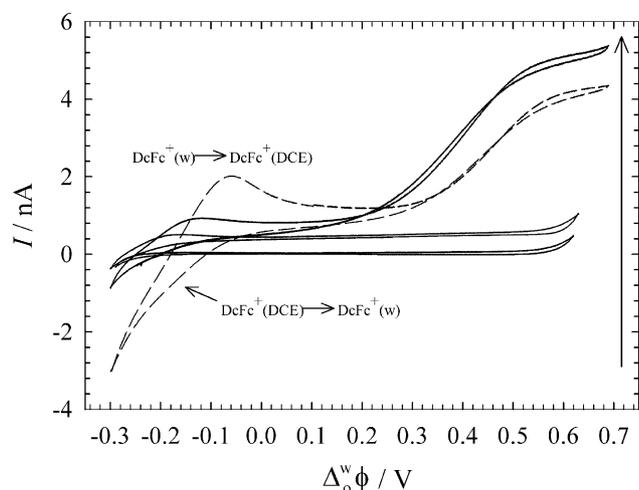


Fig. 4. Micropipette CV response in the presence of increasing concentrations of DcFc in the DCE phase (0, 0.15, and 1.8 mM), with $E_{\text{Pt}} = \text{OCP}$ (—) and the effect of $E_{\text{Pt}} > E_{\text{DcFc/DcFc}^+}^0$ (---) with 1.8 mM DcFc. Scan rate = 100 mV s⁻¹.

the determined transfer potentials is negligible at concentrations below 0.1 M Li₂SO₄ for the ions considered.

DcFc differed from the other redox species considered in that its addition introduced both offset in the CV response and DcFc⁺ transfer was apparent in the absence of applied potential at the Pt electrode. Increasing the concentration of DcFc resulted in the appearance of a wave in the positive portion of the window (Fig. 4). In situ oxidation of DcFc to DcFc⁺ at the Pt electrode resulted in a decrease in the wave current and an increase in the current associated with DcFc⁺ transfer across the interface (dashed line in Fig. 4).

DcFc⁺ is the most hydrophobic ($\Delta_0^w \phi_{\text{DcFc}^+}^0 < -0.15$ V) of the ferrocene derivatives studied here. However, DcFc is easily reduced ($E^0 \approx 0.06$ V vs. NHE [2]) and CVs obtained here at the water/DCE interface indicate interfacial reactivity with either aqueous phase dissolved oxygen or water.

The Pt coat electrode current is dependent on the extent to which the assembly is immersed in the DCE phase and therefore is difficult to control. The current flowing is typically in the μA range and thus the voltage loss due to IR drop may be considerable. However, as demonstrated here for reactions involving single electron transfer, this limitation does not pose a problem, as sufficient charged species is electrogenerated in the vicinity of the liquid–liquid interface to enable study of its lipophilicity.

4. Conclusions

In this report, a very simple means of determining the lipophilicity of the charged products of an electron

transfer reaction was introduced. This was achieved by in situ localised electrolysis of the reactant in the vicinity of a polarised liquid–liquid interface supported at the tip of a micropipette. The lipophilicity of the generated species is then probed by measuring its transfer potential across the liquid–liquid interface. The proposed method is facile, requires only very small volumes (< 100 μl) of both phases, and enables the study of potentially unstable charged products of electron transfer reactions.

All the ions studied here, with the exception of TCNQ⁻, could be classified as relatively hydrophilic as they transfer readily within the available potential window. In most studies concerning heterogeneous ET, the possibility of coupled ion transfer has not been generally considered. In light of this study, coupled charge transfer should not be discounted a priori.

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