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Reverse (Uphill) Electron Transfer at the Liquid/Liquid Interface

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Reverse electron transfer, in which an electron is transferred uphill from a redox couple with a higher standard reduction potential in one phase to another redox couple having a lower standard reduction potential in a second immiscible phase, is demonstrated using the system TCNQ (in 1,2-dichloroethane)/ferrocyanide (in water). The driving force for the reverse electron transfer is the presence of appropriate potential-determining ions that govern the interfacial potential difference, which in turn determines the position of equilibrium in the two-phase redox reaction. The occurrence of reverse electron transfer was monitored by scanning electrochemical microscopy.

Introduction

We use the term "reverse electron transfer" to describe a redox reaction in which an electron is transferred in an apparently "uphill" direction from the reduced form (R_1) of a couple with a more positive standard reduction potential to the oxidized form (O_2) of one with a lower reduction potential (Figure 1A). Such thermodynamically unfavorable reactions are common in living systems and have been known for over 35 years.[1-3] Thus, although the redox potentials for the succinate/fumarate and NAD/NADH couples are 0.031 and −0.320 V, respectively, at pH 7, succinate is known to reduce NAD. The driving force for such reverse electron flow is believed to be a proton electrochemical potential gradient across a membrane, which, according to Mitchell's chemiosmotic hypothesis,[4,5] is responsible for the coupling of the electron-transfer chain of mitochondria, chloroplasts, or bacteria to the synthesis of ATP. Thus, reverse electron flow may be induced by generating a proton electrochemical potential gradient by the hydrolysis of ATP.

The purpose of the present letter is to provide an alternative perspective to the phenomenon of reverse electron transfer by demonstrating it in a system that can be regarded as a simple model of a biological membrane, namely, the interface between two immiscible electrolyte solutions (ITIES). The driving force for the reverse electron transfer in the system to be demonstrated is the presence in the system of potential-determining ions that govern the potential difference across the two-phase system, which in turn determines the position of equilibrium in the two-phase redox reaction. The principle behind the use of ionic potential gradients to drive redox reactions has been presented previously,[6] and reference should be made to this work for further details. The potential-determining ions can also be used to inhibit a downhill redox reaction. In the present paper, the reverse electron flow is detected by generating the reductant R_1 at a microelectrode tip in a scanning electrochemical microscope[7] (Figure 1B).

Theory

One of the simplest models for the study of redox reactions across biological membranes is the ITIES, which can be regarded as one half of a biological membrane. Several electron-transfer reactions at the ITIES have been reported during the past few years.[6,8-13] In most of these studies, an electrical potential difference imposed externally using standard electrochemical instrumentation was used to drive the redox reaction:

$$n_2\mathrm{O}_1(\mathrm{w}) + n_1\mathrm{R}_2(\mathrm{o}) = n_2\mathrm{R}_1(\mathrm{w}) + n_1\mathrm{O}_2(\mathrm{o}) \qquad (1\mathrm{a})$$

$$\Delta G^\circ = -(n_1 n_2)F(E^\circ{}_1 - E^\circ{}_2) \qquad (1\mathrm{b})$$

between an aqueous redox couple (w)

$$\mathrm{O}_1(\mathrm{w}) + n_1 e = \mathrm{R}_1(\mathrm{w}) \qquad E^\circ{}_1 \qquad (2)$$

and a redox couple in an organic phase (o)

$$\mathrm{O}_2(\mathrm{o}) + n_2 e = \mathrm{R}_2(\mathrm{o}) \qquad E^\circ{}_2 \qquad (3)$$

The equilibrium condition for eq 1 is[6,14]

$$\Delta_{\mathrm{o}}^{\mathrm{w}}\varphi = (E^\circ{}_2 - E^\circ{}_1) + (RT/n_1 n_2 F)\ln\left[\frac{a_{\mathrm{R}_1}a_{\mathrm{O}_2}}{a_{\mathrm{O}_1}a_{\mathrm{R}_2}}\right] \qquad (4)$$

where $\Delta_{\mathrm{o}}^{\mathrm{w}}\varphi = \varphi^{\mathrm{w}} - \varphi^{\mathrm{o}}$ is the potential drop across the interface and $E^\circ{}_1$ and $E^\circ{}_2$ are the standard potentials of the aqueous and organic couples, respectively, each in its respective phase, with respect to a reference electrode in one phase, e.g., the standard hydrogen electrode (SHE), correcting for the potential drop $\Delta_{\mathrm{o}}^{\mathrm{w}}\varphi$. In most of the studies reported so far, redox couples with nearly the same redox potentials were chosen and $\Delta_{\mathrm{o}}^{\mathrm{w}}\varphi$ was varied cyclically by imposing a potential between electrodes in each phase to observe electron transfer in either direction in the voltammogram corresponding to the reaction in eq 1. The choice of appropriate redox couples has so far been a stumbling block in such investigations, since if the E°'s of the couples are too far apart, the potential corresponding to electron transfer would interfere with (or may even lie beyond) the potential corresponding to the transfer of ions of the supporting electrolyte across the interface.

The possibility of varying $\Delta_{\mathrm{o}}^{\mathrm{w}}\varphi$ using potential-determining ions has been demonstrated in only one study reported so far.[6] The oxidation of tin(II) phthalocyanine ($E^\circ = 0.460$ V) by ferricyanide ($E^\circ = 0.565$ V), using tetraethylammonium and tetrapropylammonium ions as the ions that partitioned between aqueous and 1,2-dichloroethane phases, was demonstrated from

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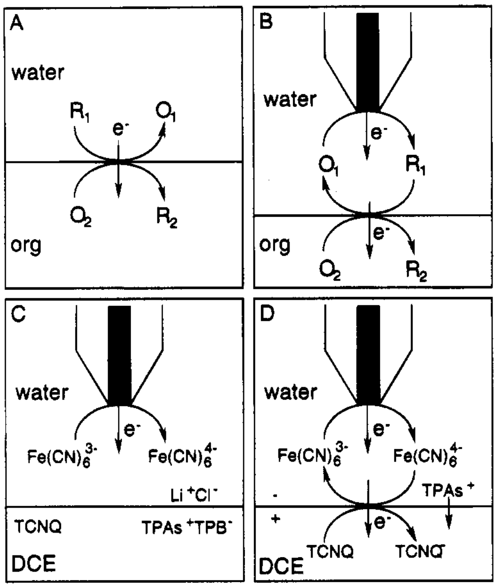

Figure 1. (A) Schematic diagram of a two-phase water/organic system. The reaction shown is a reverse electron transfer when $E^\circ_1 > E^\circ_2$, where E°_i refers to the half-reaction $O_i + e = R_i$. (B) Application of SECM to the study of electron transfer at an ITIES. (C) SECM experiment where $\Delta_o^w\varphi \geq 0$ and electron transfer does not occur (negative feedback observed). (D) SECM experiment where $\Delta_o^w\varphi \ll 0$ and drives reverse electron transfer (positive feedback observed).

the absorption spectra of the phthalocyanine for different interfacial potentials imposed by varying the concentrations of the partitioning ions. The interfacial potential difference generated by the partitioning ions follows the Nernst–Donnan equation:

$$\Delta_o^w\varphi = \Delta_o^w\varphi^\circ + (RT/nF)\ln(a_i(\text{o})/a_i(\text{w})) \qquad (5)$$

Since $\Delta_o^w\varphi^\circ$ values for several ions in water/organic systems can be obtained, with certain extrathermodynamic assumptions, and are well documented (see, for example, ref 15 and references therein), the appropriate choice of ions with suitable $\Delta_o^w\varphi^\circ$ values (and proper adjustment of the concentration ratio) can yield the desired $\Delta_o^w\varphi$ to drive eq 1 in either the forward direction or in reverse. It is this aspect of the control of a redox reaction by an ionic gradient in a two-phase system that will be emphasized in this letter.

Suppose we wish to drive the reverse electron-transfer reaction in eq 1a (where $E^\circ_1 > E^\circ_2$). A typical example is the redox reaction between Fe(CN)_6^{4-} and TCNQ:

$$\text{TCNQ} + \text{Fe(CN)}_6^{4-} = \text{TCNQ}^{\bullet -} + \text{Fe(CN)}_6^{3-} \qquad (6)$$

with

$$\text{Fe(CN)}_6^{3-}(\text{w}) + \text{e} = \text{Fe(CN)}_6^{4-}(\text{w}) \qquad E^\circ_2 = 0.41\ \text{V vs SHE}^{16} \qquad (7)$$

$$\text{TCNQ(o)} + \text{e} = \text{TCNQ}^{\bullet -}(\text{o}) \qquad E^\circ_1 = 0.22\ \text{V vs SHE}^{13} \qquad (8)$$

If the position of equilibrium for the reverse electron-transfer is to lie toward the products O_1(w) and R_2(o), then according to eq 4, the interfacial Galvani potential difference, $\Delta_o^w\varphi$, must be set to a magnitude larger than the difference in E° values, i.e., $\Delta_o^w\varphi \ll E^\circ_2 - E^\circ_1$. $\Delta_o^w\varphi$ can be adjusted to an appropriate value by choosing the nature and concentration of the electrolytes in the two phases. In particular, one selects potential-determining ions that are present in both liquid phases so that the interfacial potential can be calculated via eq 5. (This function should be distinguished from the role of supporting electrolyte in each phase which is to provide ions for charge transport within a phase.) For example, the electrolytes LiCl in water and tetraphenylarsonium tetraphenylborate (TPAsTPB) in dichloroethane (DCE) are essentially confined to the respective phases, since LiCl is insoluble in DCE and TPAsTPB is insoluble in water. The interfacial potential in this case is undefined. However, if an ion (TPAs^+) is present in both phases, e.g., when TPAsCl is in the electrolyte in water and TPAsTPB is in DCE, the partitioning TPAs^+ serves to set the Galvani potential difference across the interface. From eq 5, if (ignoring activity coefficients and ion association) $[\text{TPAs}^+(\text{w})] = [\text{TPAs}^+(\text{o})]$, then $\Delta_o^w\varphi = -364$ mV.[17] This potential difference is large enough to overcome the unfavorable ΔE° (−190 mV) in the Fe(CN)_6^{4-}/TCNQ reaction, so that reverse electron transfer across the interface can be readily induced.

In the SECM mode of monitoring electron transfer, electrolysis is carried out at a microelectrode in one of the phases (the less dense, usually aqueous, phase), which is placed above the other (usually the organic) phase (Figure 1B). The purpose of the microelectrode probe is to generate one of the reactants of the heterogeneous electron-transfer reaction and then to detect or monitor the flow of electrons. No electrode or other sensing device is placed in the lower phase, which acts as the SECM substrate.

Consider the redox reaction in eq 6 with the aqueous solution being the upper phase. In this aqueous phase is a solution containing only Fe(CN)_6^{3-} which is electrochemically reduced to Fe(CN)_6^{4-} at a microelectrode. The potential of the electrode is set to the limiting current region so that a steady-state current, i_{ss}, is reached:

$$i_{\text{ss}} = 4nFDca \qquad (9)$$

where n is the number of electrons transferred, D is the diffusion coefficient, c is the concentration of Fe(CN)_6^{3-}, and a is the radius of the microelectrode. The electrode is then lowered gradually towards the organic phase. As it approaches the interface, the Fe(CN)_6^{4-} generated at the microelectrode tip will react with TCNQ, provided the interfacial potential difference has been set appropriately by potential-determining ions as discussed above (i.e., $\Delta_o^w\varphi = -364$ mV). An additional contribution to the steady-state current is detected as R_1 is generated by the heterogeneous electron transfer in addition to that which reaches the electrode surface by diffusion. This positive feedback is an indication that interfacial electron transfer has taken place.[7] The interference of ion transfer in monitoring the limiting current is thus minimal when the supporting electrolyte concentrations are high.[18]

In the absence of potential-determining ions, i.e., with only supporting electrolytes such as LiCl(w) and tetraphenylarsonium tetraphenylborate(o) present and with none of the ions partitioning into the adjoining phase at open circuit, no electron transfer, and hence no positive feedback, would be observed. In fact, the steady-state current decreases when the electrode approaches the interface, because the interfacial potential difference is not at a level for the interfacial electron-transfer reaction to proceed, and diffusion of Fe(CN)_6^{3-} to the electrode surface is hindered as the electrode approaches the interface. Thus, negative feedback is observed, just as in SECM with an electrically insulating substrate.[7]

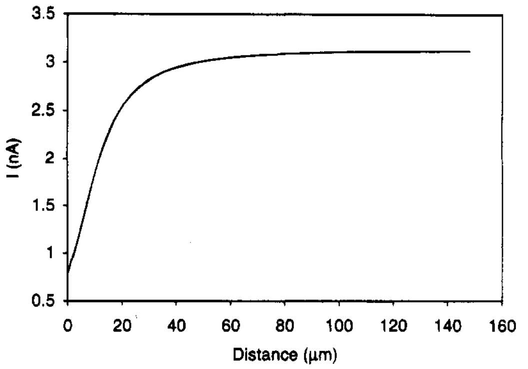

Figure 2. Approach curve for the system: DCE, 10 mM TCNQ, 1 mM TPAsTPB||H_2O, 1 mM Fe(CN)$_6^{3-}$, 0.1 M LiCl, showing the absence of electron transfer across the liquid/liquid interface. A 25-μm-diameter Pt microelectrode was used to generate Fe(CN)$_6^{4-}$ at the electrode tip from the Fe(CN)$_6^{3-}$. Tip potential, −0.4 V vs Ag/AgCl.

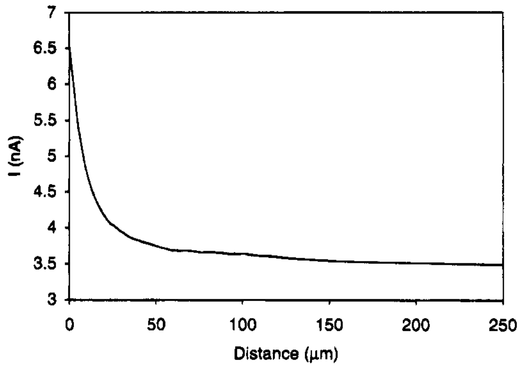

Figure 3. Approach curve for the system: DCE, 10 mM TCNQ, 1 mM TPAsTPB||H_2O, 1 mM Fe(CN)$_6^{3-}$, 0.1 M LiCl; 1 mM TPAsCl, showing reverse electron transfer driven by the phase transfer catalyst $TPAs^+$. $\Delta_o^w\varphi = -364$ mV (see Figure 1D). Tip potential, −0.4 V vs Ag/AgCl.

Experimental Section

The TCNQ (Aldrich) solution was 10 mM in 1,2-dichloroethane (Aldrich) with either 1 mM tetramethylammonium perchlorate ($TMA^+ClO_4^-$, Fluka), or 1 mM tetraphenylarsonium tetraphenylborate as supporting electrolyte. The latter was prepared by precipitation from tetraphenylarsonium chloride (TPAsCl, Aldrich) and sodium tetraphenylborate (Aldrich) followed by recrystallization from acetone.

Fe(CN)$_6^{4-}$ was generated at a 25-μm-diameter Pt microelectrode tip from an aqueous $K_3Fe(CN)_6$ (Aldrich) solution (1 mM) containing 0.1 M LiCl and either 1 mM tetramethylammonium perchlorate or 1 mM TPAsCl. Pt counter and Ag/AgCl reference electrodes were used in a three-electrode arrangement. The SECM setup was the same as that described previously.[19] The zero distance point in the approach curves was determined by noting the sharp drop or rise in current as the tip contacted the interface.

Results and Discussion

Figure 2 shows the curve obtained as the microelectrode approaches the interface when the system contains Fe(CN)$_6^{3-}$ in the aqueous phase, TCNQ in the DCE, and only supporting electrolytes with no partitioning ions. When Fe(CN)$_6^{4-}$ is generated at the tip, negative feedback is observed, showing that the equilibrium represented in eq 6 lies toward the reactant side and there is no redox reaction at the water/DCE interface. However, the reverse electron flow for the same redox reaction can be induced by employing $TPAs^+$ as a potential-determining ion as shown in Figure 3. The driving force for this reverse electron transfer is the imposition of an interfacial potential difference by the presence in solution of $TPAs^+$ in both phases ($\Delta_o^w\varphi = -364$ mV, eq 4) as indicated in Figure 1D. Note that the detection of reverse electron flow in this case could not be done using the method commonly employed for studies of the ITIES, cyclic voltammetry. Since the ITIES is not polarizable in the presence of $TPAs^+$ in both phases, any attempt to impose externally a potential across the interface with electrodes in the water and DCE phases would result in interfacial ion transfer and a current flow. The SECM approach does not suffer from this interference.

The above results clearly demonstrate the applicability of the concepts discussed in ref 6 in studying a wide range of heterogeneous electron-transfer reactions, including the possibility of biochemically interesting reverse electron transfer. Because electron-transfer reactions in biological systems take place without any external imposition of potential, the possibility of inducing, or even inhibiting, two-phase redox reactions by using potential-determining ions should be relevant in the area of bioenergetics.

One important concept that follows from the above discussion is that ion and electron transfer are strongly coupled. What has been demonstrated above is electron transfer induced by potential-determining ions. The reverse process, a key premise of the chemiosmotic hypothesis, is ion (particularly, proton) transport induced by electron transfer. However, as discussed here, electron transfer at the liquid/liquid interface itself requires a $\Delta_o^w\varphi$ that is either externally imposed or set internally by potential-determining ions. No matter how $\Delta_o^w\varphi$ is imposed, this potential will then determine either electron transfer or the transfer of specific ions.

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