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Anion Recognition at the Liquid−Liquid Interface. Sulfate Transfer across the 1,2-Dichloroethane−Water Interface Facilitated by Hydrogen-Bonding Ionophores

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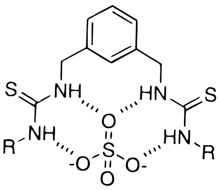
We report here the first observation of facilitated anion transfer across the interface between two immiscible electrolyte solutions (ITIES). Complexation behavior between anions and neutral receptors via hydrogen bonding at the 1,2-dichloroethane (DCE)−water interface is investigated.

Complexation reactions at liquid−liquid interfaces play a fundamental role in biochemical systems such as transmembrane signaling[1] and enzymatic reactions[2] in biological membranes. They are also important in many technological systems from separation chemistry[3] to chemical sensors.[4] To analyze such interfacial complexation mechanisms, electrochemical ion transfer across ITIES facilitated by various ionophores is a useful technique and has been extensively investigated for cations.[5] However, no studies have been reported for anions despite their important role in vivo.

Recently, a variety of neutral hydrogen-bonding receptors have been developed,[6] in mimicry of the binding structure of phosphate-recognition membrane proteins.[7] These artificial receptors, however, have been used only in bulk organic solvents except for some application studies.[6b,8]

In this report hydrogen-bonding receptors, **1** and **2**,[6e] are used to study facilitated anion transfer across the DCE−water interface by electrolyte ascending electrode polarography.[9] Examination of interfacial complexation between anions and receptors can provide further insight not only into the complexation-induced selective anion transport across biological membranes[1,7] but also into a rational design strategy of new receptors for specific sensing and separation systems.



1 R = Bu
2 R = Ph

Ion transfer polarograms for SO_4^{2-} with cell (1)[10a] are shown in Figure 1. The aqueous phase is 0.5 M (1 M = 1 mol dm^{-3}) Na_2SO_4. The DCE phase is 0.05 M tetraheptylammonium tetraphenylborate (THATPB, supporting electrolyte) without (a) and with (b) 0.5 mM **2**. The potential difference at the interface between aqueous and organic phases ($\Delta\phi$) was controlled by a conventional four-electrode potentiostat, and is expressed by

$$\Delta\phi = E - \Delta\phi_{\mathrm{ref}} \tag{1}$$

where E is the potential difference between two reference electrodes and $\Delta\phi_{\mathrm{ref}}$ is the sum of all potential differences involved in the cell.

Although only a wave connected with the transfer of SO_4^{2-} from the aqueous phase to the DCE phase was observed in the absence of **2** (Figure 1a), a new wave appeared on addition of 0.5 mM of **2** to the DCE phase (Figure 1b). This implies that complexation between **2** and SO_4^{2-} successfully takes place at the DCE−water interface.

When ionophore L and anion A^{z-} ($z > 0$) form a 1:1 complex ($L-A^{z-}$) and the ion transfer is controlled by diffusion of L from bulk DCE phase to the interface, as shown in Figure 1, the following equations are applicable:[5c]

$$i_l \propto v^{1/2}\,[\mathrm{L}]_o \tag{2}$$

$$E = E_{1/2} - \frac{2.303RT}{zF}\log\frac{i}{i_l - i} \tag{3}$$

where i_l (μA) is the limiting current, v (mg s^{-1}) is the flow rate of the aqueous solution, and $E_{1/2}$ (mV) is the half-wave potential for the complex $L-A^{z-}$. The half-wave potential can be expressed by the following equation:[5e]

$$E_{1/2} = E^{\circ\prime}_{A^{z-}} - \frac{RT}{2zF}\ln\frac{D_L}{D_{L-A^{z-}}} + \frac{RT}{zF}\ln\,(K[A^{z-}]_w) \tag{4}$$

where $E^{\circ\prime}_{A^{z-}}$ (mV) is the ion transfer formal potential for A^{z-}, D (m^2 s^{-1}) is the diffusion coefficient in the DCE phase, and K (M^{-1}) is the stability constant in the organic phase close to the interface. On the assumption that D_L is nearly equal to $D_{L-A^{z-}}$ in eq 4,[5f] K is expressed as follows:

$$K = \frac{1}{[A^{z-}]_w}\exp\frac{zF(E_{1/2} - E^{\circ\prime}_{A^{z-}})}{RT} \tag{5}$$

The limiting current i_l was measured for different concentrations of **2**, and plotted against $v^{1/2}$ in Figure 2. Linear regression curves are obtained, and the ratio of the line slopes (8.6/5.7 = 1.5) corresponds to the ratio of the concentrations of **2** (0.51/0.32 = 1.6), as a consequence of eq 2. This indicates that the kinetics of the facilitated ion transfer is diffusion-controlled.

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[10] Polarographic cells (1) and (2) are schematically expressed as follows: (a) cell (1) Ag/Ag_2SO_4/0.5 M Na_2SO_4//0.5 M Na_2SO_4 (*aqueous phase*)/*x*mM **1** (**2**) + 0.05 M THATPB (*DCE phase*)/0.05 M NaTPB + 0.5 M Na_2SO_4//0.5 M Na_2SO_4/Ag_2SO_4/Ag; (b) cell (2) Ag/AgCl/0.5 M LiCl//0.5 M electrolytes (*aqueous phase*)/*x*mM **1** (**2**) + 0.05 M THATPB (*DCE phase*)/0.05 M NaTPB + 0.5 M LiCl//0.5 M LiCl/AgCl/Ag. The aqueous solution rises into the DCE phase from a PTFE capillary (0.7 mm i.d.) in the flow-rate range of 2.8−6.3 mg s^{-1}. Negative current flows when anions are transferred from the aqueous phase to the DCE phase.

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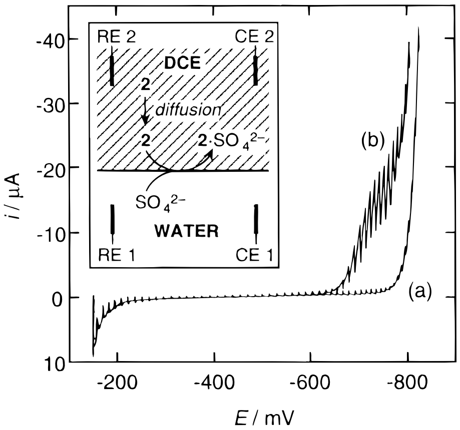

Figure 1. Ion transfer polarograms for SO_4^{2-}. Aqueous phase: 0.5 M Na_2SO_4. DCE phase: 0.05 M THATPB and 0 mM (a) or 0.5 mM (b) **2**. Flow rate: 4.8 mg s^{-1}. Scan rate: 2.5 mV s^{-1}.

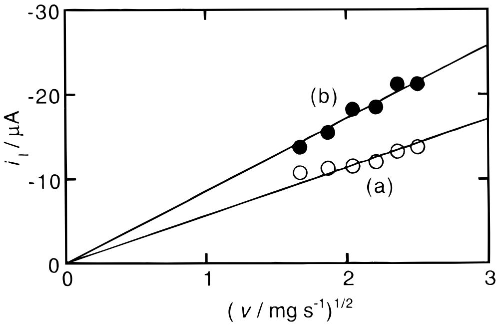

Figure 2. Relationship between limiting current and square root of flow rate. Aqueous phase: 0.5 M Na_2SO_4. DCE phase: 0.05 M THATPB and 0.32 mM (a) or 0.51 mM (b) **2**. Line slopes estimated: -5.7 μA $mg^{-1/2}$ $s^{1/2}$ (a) and -8.6 μA $mg^{-1/2}$ $s^{1/2}$ (b).

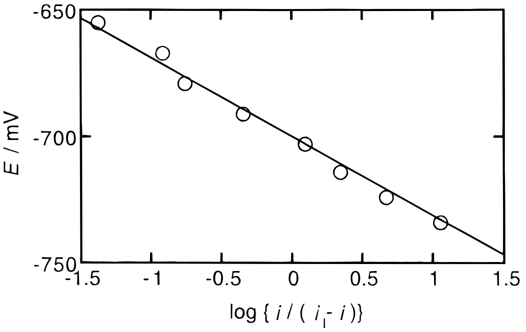

Figure 3. Relationship between E and log $\{i/(i_l - i)\}$. Aqueous phase: 0.5 M Na_2SO_4. DCE phase: 0.05 M THATPB + 0.5 mM **2**. A linear relationship is obtained with a slope of -30 mV, indicating the transfer of divalent anion species from the aqueous phase to the DCE phase.

There is also a linear relationship between E and log $\{i/(i_l - i)\}$, as shown in Figure 3, with a slope of about -30 mV. From eq 3 the complex is shown to be a divalent anion, that is **2**$-SO_4^{2-}$. The half-wave potential for the ion transfer of **2**$-SO_4^{2-}$ is obtained as -700 mV from the intercept of the regression curve in Figure 3. The $E^{\circ\prime}$ value for SO_4^{2-} at the DCE$-$water interface can be estimated as about -880 mV from Figure 1a.[11] These values are used to calculate K as 2.5×10^6 M^{-1} from eq 5.

As for receptor **1**, no clear wave was observed on adding 0.5 mM of **1** to the DCE phase.[12] The positive shift observed was less than about 150 mV, and the K value for **1** was estimated to be less than 2.4×10^5 M^{-1}, which is smaller than that for **2** (Table 1). This difference can be attributed to the strong binding ability of thiourea groups in **2**, which results from the electron-withdrawing effect of phenyl groups.[6e]

Table 1. Potential Shift and Stability Constants

	potential shift/mV		K/M^{-1}	
anion	**1**	**2**	**1**	**2**
SO_4^{2-}	<+150	+180	$<2.4 \times 10^5$	2.5×10^6
Cl^- [a]		<+160		$<1.0 \times 10^3$
CH_3COO^- [b]		<+180		$<2.2 \times 10^3$

[a] Aqueous phase: 0.5 M LiCl (pH 5.0). [b] Aqueous phase: 0.5 M CH_3COONa (pH 8.2).

Other anions, Cl^- and CH_3COO^-,were also examined by using cell (2).[10b] Similarly to the result for **1**$-SO_4^{2-}$ system, only the positive shift was observed for each anion by addition of 0.5 mM of **2** to the DCE phase.[12] The K values estimated from the potential shift are listed in Table 1. It is worth noting that the stability constants obtained from the polarographic waves for Cl^- and CH_3COO^- (Table 1) are about 10 times smaller than those in bulk DCE phase (K_{11} (M^{-1}): **2**$-Cl^-$:1.6×10^4; **2**$-CH_3COO^-$: 1.4×10^4).[13] The smaller stability constants can be explained by the fact that the interface is a more hydrophilic environment than the bulk DCE phase;[14] the complexation takes place not in the DCE phase far from the interface, but at the layer just neighboring to the interface.

It can also be seen from Table 1 that the K value for SO_4^{2-} is remarkably large as compared to those for other anions ($SO_4^{2-} > CH_3COO^- > Cl^-$). Generally, the smaller the dehydration energy and the larger the binding energy in the DCE phase, the larger the potential shift for an ion transfer wave which is observed. Considering the large dehydration energy of SO_4^{2-} (the Hofmeister series: $Cl^- < CH_3COO^- < SO_4^{2-}$) and its relatively weak basicity ($CH_3COO^- > SO_4^{2-} > Cl^-$), sulfate should be less responsive. The high selectivity for SO_4^{2-} over Cl^- and CH_3COO^- can be ascribed to the higher charge number of SO_4^{2-} which results in substantially higher stability of the SO_4^{2-} complex than those of Cl^- and CH_3COO^- complexes.

In conclusion, we have observed, for the first time, the facilitated anion transfer across ITIES using hydrogen-bonding ionophores. Especially, sulfate was remarkably facilitated, although it is one of the most hydrophilic anions and is poorly transferred to the organic phase in comparison with other anions. We found that the hydrogen bonding between hosts and guests works effectively at the DCE$-$water interface as well as at the air$-$water interface[15] although such interaction does not occur in aqueous solutions. The intermediate polarity of the liquid$-$liquid interface and, probably, the orientational effect at the interface[15,16] enhance the host$-$guest hydrogen bonding; further investigation is in progress with dynamic interfacial tensiometry[16] to clarify the effect of these factors on the interfacial complexation mechanisms.

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Supporting Information Available: Polarograms for (a) **1**$-SO_4^{2-}$ and (b) **2**$-$anions (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[11] In polarography, $E^{\circ\prime}$ is nearly equal to $E_{1/2}$. The half-wave potential for SO_4^{2-} can be approximately estimated from theoretical fitting of the polarogram (Figure 1a) using eq 3.

[12] Results given in the Supporting Information.

[13] Determined by UV$-$vis absorption spectrometry.

[14] It has been found by time-resolved total internal reflection fluorescence spectroscopy that the heptane$-$water interface is a layer having intermediate polarity between those of organic and aqueous phases (Bessho, K.; Uchida, T.; Yamauchi, A.; Shioya, T.; Teramae, N. *Chem. Phys. Lett.* **1997**, *264*, 381.), which was predicted by computer simulation studies ((a) Carpenter, I. L.; Hehre, W. J. *J. Phys. Chem.* **1990**, *94*, 531. (b) Benjamin, I. *Science* **1993**, *261*, 1558.).

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