

Published in final edited form as:

J Am Chem Soc. 2008 November 5; 130(44): 14364–14365. doi:10.1021/ja804631p.

Anion Transfer at a Micro-Water/1,2-Dichloroethane Interface Facilitated by β -Octafluoro-*meso*-octamethylcalix[4]pyrrole

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Due to its potential importance in drug delivery and value in understanding ion transport across biomembranes, facilitated ion transfer (FIT) at liquid/liquid (L/L) interfaces has been widely investigated since the pioneering work of Koryta in 1979.¹ To date, most reports in this area have focused on facilitated cation transfer (FCT).² In fact, in spite of great advances in the area of anion recognition chemistry,³ few studies involving facilitated anion transfer (FAT) at L/L interfaces have been published,⁴ and even fewer reports regarding a kinetic analysis of the underlying phenomenon have appeared.^{4j} Given this lack of available dynamic information, we have used electrochemical methods to study the thermodynamic and kinetic transfer behavior of several monovalent anions at a micropipet-supported micro-water/1,2-dichloroethane (μ -W/DCE) interface. As detailed below, little effective transfer is observed in the absence of an additive or when calix[4]pyrrole **1** is used as a potential transfer agent (cf. Fig. 1A for structures). On the other hand, in the presence of β -octafluoro-*meso*-octamethylcalix[4]pyrrole **2** effective transfer of Cl⁻, Br⁻, NO₂⁻ and CH₃CO₂⁻ (Ac⁻) at the μ -W/DCE interface is observed. However, the kinetic rate constants are 1-2 orders of magnitude smaller than those for analogous FCT processes involving crown ethers as the ion receptor.²

In simplified terms, FAT at a μ -W/DCE interface involves the following process:



where A⁻ and R represent a monovalent anion and the putative facilitating anion transfer agent (e.g., receptors **1** or **2**, respectively). Key goals of the present study were therefore to i) find a receptor that would allow for facilitated anion transfer and ii) determine the transfer kinetics of anion transport in the event that such a transfer agent is identified.

By their nature, anions are relatively challenging substrates for FIT studies. They are usually larger than isoelectronic cations.^{3,5,6} They thus have lower charge densities and are less prone to bind strongly to potential transfer agents through electrostatic interactions. Compared to cations, inorganic anions also have larger Gibbs energies of transfer.⁴ Therefore, transfer of

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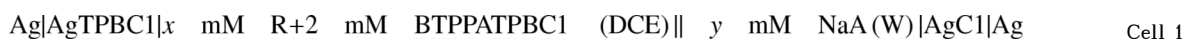
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Supporting Information Available: Details of experiments and electrochemical measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

most free inorganic anions occurs at the negative limit or outside of the potential window accessible using typical μ -W/DCE setups. This means that it is inherently harder to find a receptor for FAT than it is for FCT.² In fact, to date, only a limited number of systems have been used to effect FAT and only when relatively large L/L interfaces (on the order of cm^2) were employed.⁴ We thus sought to explore whether FAT could be achieved in a μ -W/DCE setup using a calix[4]pyrrole as the receptor.⁷

Calix[4]pyrroles, such as **1**, have attracted much attention as anion receptors over the past decade.⁵ In organic solution and in solid phase, calix[4]pyrroles can bind anions such as F^- , Cl^- , Br^- , I^- , and H_2PO_4^- effectively.⁵ β -Octafluorocalix[4]pyrrole **2** was shown to have an increased anion binding affinity relative to the parent system **1** due to the presence of electron withdrawing fluorine substituents.⁸ To date, calix[4]pyrroles have been studied in a number of applications, including as response elements in ion-selective electrodes.⁹ In this work, the FAT of small anions at the μ -W/DCE interface was studied electrochemically using both **1** and **2** as the possible receptors.

The μ -W/DCE electrochemical cell (Cell 1) employed for the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements (see SI for experimental detail) is as follows:



Of the anions tested, four (Cl^- , Br^- , NO_2^- , and Ac^-) displayed reasonable steady-state voltammograms within the potential window when **2** was used as the receptor (Fig. 1B). The negative current reflects the transfer of anions from the aqueous to the DCE phase.¹⁰ In the case of F^- , which has the strongest interaction with **2** in organic media,⁵ no wave corresponding to its facilitated transfer can be observed within the potential window. This finding likely reflects the fact that F^- is very hydrophilic and retained in the aqueous phase. From the CV and DPV curves, the thermodynamic parameters (such as the diffusion coefficient D_{R} , the stoichiometric ratio $m:n$, and the association constant $\log \beta_{\text{AR}^-}^{\circ}$) can be easily obtained (see the SI for experimental details); these values are listed in Table 1.

Bard *et al.* have developed a three-point method to determine the kinetic parameters of a heterogeneous electron transfer reaction from a quasi-steady state voltammogram.¹² Three parameters, namely the half-wave potential, $E_{1/2}$, and the quartile potentials $E_{1/4}$ and $E_{3/4}$, which can be obtained experimentally, are used to determine the transfer coefficient (α) and the standard rate constant (k°).¹³ However, it is subject to several caveats, including the need for well-defined steady state voltammograms. In the particular case of the reaction shown in Eq. 1, if the three potentials obtained at a W/DCE interface cannot satisfy the conditions that i) $|\Delta E_{1/4} = E_{1/2} - E_{1/4}| \geq 30.5 \text{ mV}$, ii) $|\Delta E_{3/4} = E_{3/4} - E_{1/2}| \geq 31.0 \text{ mV}$, and iii) $|\Delta E_{3/4}| \geq |\Delta E_{1/4}|$, then the reaction at the μ -W/DCE interface is reversible and no kinetic data can be obtained using this method. Reversibility depends on k° and the mass transport rate (k_{d}); therefore, it is useful to increase the k_{d} , e.g., by using a smaller nano-L/L interface, to determine even larger k° values. This is what has been done for the previously reported FCT studies.¹³ In accord with what would be expected based on Eq. S1 (see SI), the $E_{1/2}$ was found to shift to a more positive potential as the anion concentration increased. Using this approach, well-defined steady state voltammograms for Cl^- and Ac^- could be observed (cf. Fig. 2 for Cl^-). This allowed k° values of 2.11 ± 0.90 and 0.75 ± 0.50 ($\times 10^{-2} \text{ cm/s}$), as well as α values of 0.57 ± 0.07 and 0.62 ± 0.04 for Cl^- and Ac^- , respectively, to be determined (see Table T1 in the SI). Efforts to extend this analysis to Br^- and NO_2^- failed since their waves proved too close to the negative end of potential window.

From the above results it is clear that the FAT at the W/DCE interface mediated by **2** is much slower than analogous FCT processes observed for alkali metal cations using crown ether as receptors.¹³ While too many differences exist to allow for direct comparisons, there are a number of likely explanations for this apparent dichotomy. First, as noted above, most anion binding agents, including **2**, generally display lower affinities for their targeted anions than do receptors for similarly sized cations. While an obvious oversimplification, such a thermodynamic disadvantage is likely to translate into slower ion transfer kinetics.¹⁴ Second, anions of similar charge and size are usually characterized by higher hydration energies (ΔG_{hyd}); cf. e.g., F^- -465/ Na^+ -365 kJ mol^{-1} , Cl^- -340/ K^+ -295 kJ mol^{-1} .¹⁵ According to the Marcus theory,¹⁶ an ion transfer reaction at a L/L interface involves initial desolvation of an ion from the first phase and then concerted solvation by the second phase. The higher the hydration energy, the harder it is to overcome this barrier. As above, this thermodynamic “penalty” (in the case of anions) is likely to be reflected in slower facilitated ion transfer kinetics. Anions also usually display shorter solvation times than cations (on the order of picoseconds and nanoseconds, respectively);¹⁷ however, the effect of this difference on the FIT kinetics is unclear. Nevertheless, this clear difference between cation and anion behavior is of inherent interest and could be useful in the design of ion sensors.

In summary, we have demonstrated the facilitated ion transfer of four anions, namely Cl^- , Br^- , NO_2^- , and Ac^- , by receptor **2** at a μ -W/DCE interface. We have also shown for the first time that the dynamics of this process can be studied by micropipet-voltammetry. Studies such as these are expected to be useful in understanding the mechanism of anion transport at soft interfaces and for the design of yet-improved anion receptors and carriers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (20735001, 20628506, 20525518, 20775005), the Foundation of Doctoral Programs of the Ministry of Education of China, and the special 985 project of Peking University. The work in Austin was supported by the National Institutes of Health (Grant No. 58907 to J.L.S.) and the INEST Group of Philip Morris USA.

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- (14). In simplified terms, the binding energy (ΔG_{bind}) associated with the interaction between an ion and a receptor in two phases can be described as $\Delta G_{\text{bind}} = G_{\text{int}} - G_{\text{hyd}}$, where ΔG_{int} is the complexing energy between the ion and receptor and ΔG_{hyd} is the energy of hydration.¹⁸ Under interfacial conditions, the situation is more complex, making it difficult to compare directly the energetics of anion vs. cation binding, let alone the underlying kinetics of ion transfer
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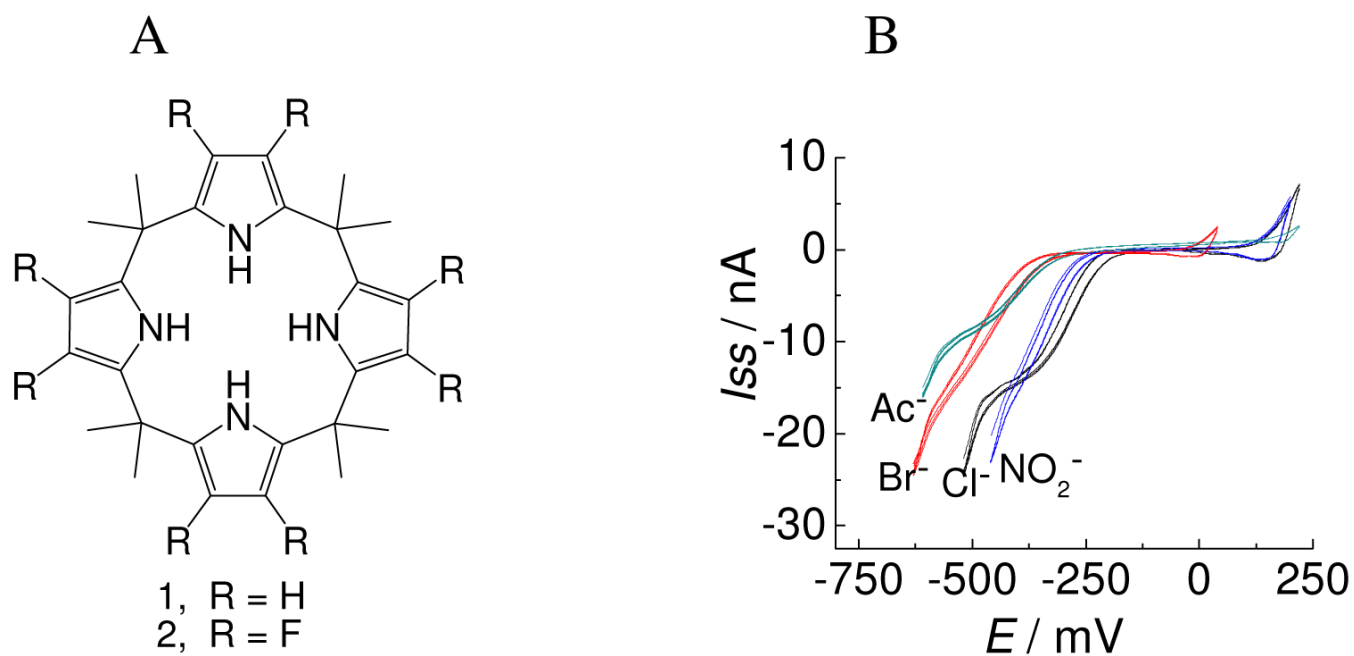


Figure 1.

A) Structures of calix[4]pyrroles, **1** and **2**. B) Cyclic voltammograms for the transfer of Cl⁻, Br⁻, NO₂⁻ and Ac⁻ at a μ -W/DCE interface facilitated by **2** using Cell 1 ($x = 2$, $y = 100$) and a pipet radius, r , of 20, 20, 22, and 10 μm , respectively. The scan rate is 50 mV/s.

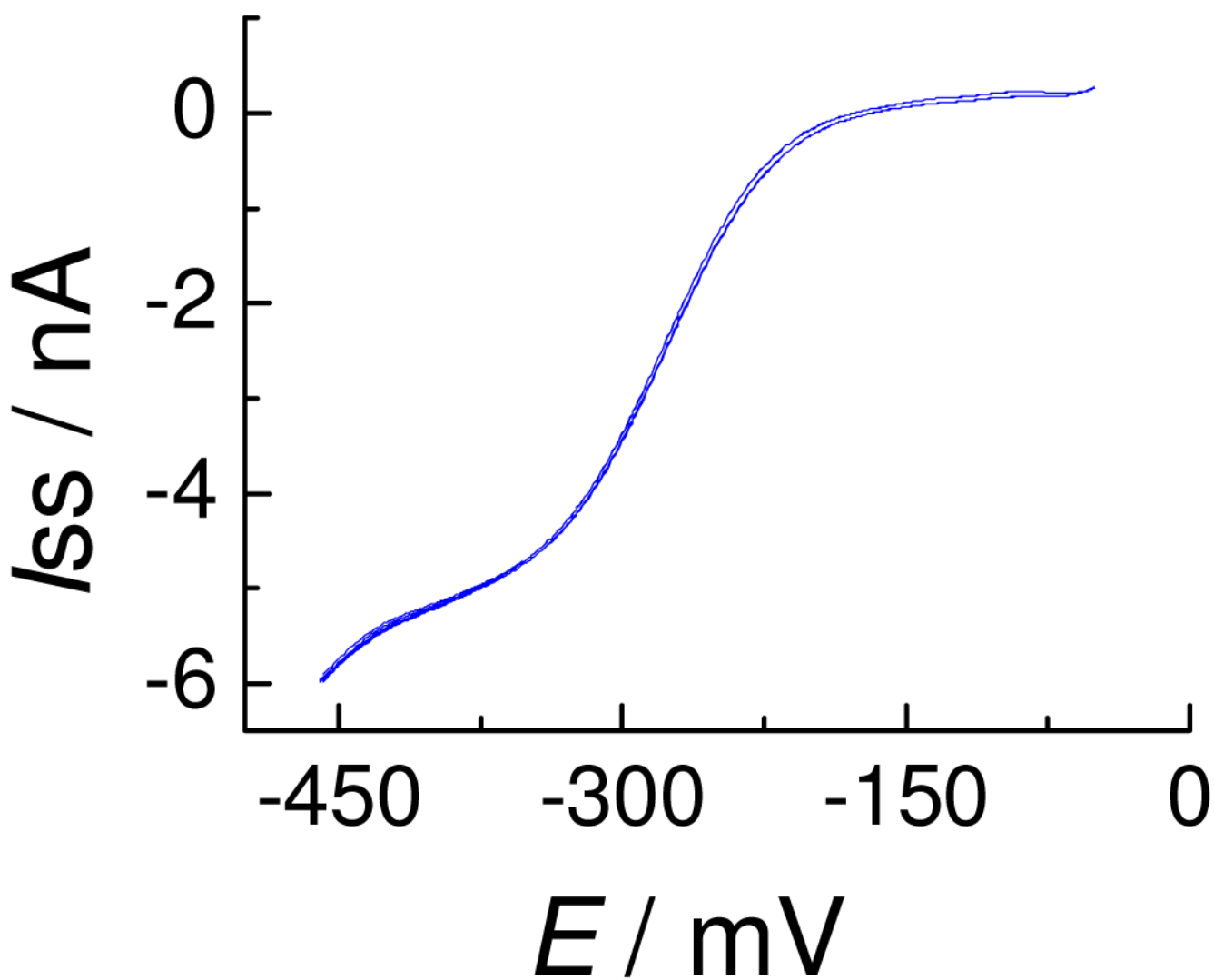


Figure 2. Steady-state voltammogram of Cl^- transfer at a $\mu\text{-W/DCE}$ interface facilitated by **2** using Cell 1, where $x = 2$, $y = 5000$. The scan rate is 50 mV/s and $r = 7 \mu\text{m}$.

Table 1
Thermodynamic Data for Anion Transfer Facilitated by **2**

Anion	$\Delta_o^w \phi_A^{\ominus}$ (mV)	<i>m</i> : <i>n</i>	$\log \beta_{AR}^{\ominus}$	D_R (cm ² /s)
Cl ⁻	-514 ^{11a}	1:1	8.26	4.2×10 ⁻⁶
Br ⁻	-405 ^{11a}	1:1	6.52	3.6×10 ⁻⁶
NO ₂ ⁻	-332 ^{11b}	1:1	3.28	3.2×10 ⁻⁶
CH ₃ CO ₂ ⁻	-560 ^{11c}	1:1	5.77	3.0×10 ⁻⁶
Mean				(3.5±0.5)×10 ⁻⁶