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Shuttling Mechanism of Ion Transfer at the Interface between Two Immiscible Liquids

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Abstract: The transfers of hydrophilic ions between aqueous and organic phases are ubiquitous in biological and technological systems. These energetically unfavorable processes can be facilitated either by small molecules (ionophores) or by ion-transport proteins. In absence of a facilitating agent, ion-transfer reactions are assumed to be “simple”, one-step processes. Our experiments at the nanometer-sized interfaces between water and neat organic solvents showed that the generally accepted one-step mechanism cannot explain important features of transfer processes for a wide class of ions including metal cations, protons, and hydrophilic anions. The proposed new mechanism of ion transfer involves transient interfacial ion paring and shuttling of a hydrophilic ion across the mixed-solvent layer.

Introduction

The transfer of ions from water to organic phases is, in most cases, energetically unfavorable. This property is essential for many biological and technological systems. For example, living cell membranes, whose interior can be compared to hexadecane,[1] inhibit ion crossing,[2] thus enabling selective transport through pores and ion channels.[3] In separation systems, the differences in energetics and kinetics of transfer across the liquid/liquid interface determine the efficiency of the extraction of a particular ionic species.[4,5]

Ion-transfer (IT) reactions at the water/organic solvent interface have been the subject of numerous experimental and theoretical studies.[6−10] Two substantially different classes of IT reactions are distinguished in the current literature: facilitated (or assisted) and simple (or unassisted) IT.[6] In the former case, an organic solution contains a ligand L that can react with ion X to form a complex, XL (the stoichiometry of complexation can be different). Such a reaction can assist the transfer of an ion:

$$X^{n+}(aq) + L^{m-}(org) \rightleftarrows XL^{n-m}(org) \qquad (1)$$

Although facilitated IT of cations is more common, assisted transfers of anions have also been reported.[11]

Simple IT processes are one-step reactions not involving any facilitating agent:

$$X^{n+}(aq) \rightleftarrows X^{n+}(org) \qquad (2)$$

This large group includes practically important transfers of metal cations, tetraalkylammonium ions, and various inorganic and organic anions. Among several contentious points in the theory of simple IT is the nature of its rate-limiting step. One model attributes the finite IT rate to slow diffusion of the transferred species through the interfacial layer,[12,13] while another treatment considers activation-controlled changes in ion solvation.[9,10]

In most previous studies of IT at the liquid/liquid interface, the organic solution contained a supporting electrolyte, i.e., a hydrophobic salt whose role was to increase the organic phase's conductivity without directly participating in the interfacial reaction. A few experiments with no (or very little) electrolyte added to either the aqueous or organic phase have been reported by us[14] and by other groups.[15] Recently, electrochemical measurements were carried out at the interface between an aqueous solution and a neat organic solvent formed at the tip of a nanopipet.[14] The transfer of an ion between the aqueous filling solution and the external organic phase was induced by applying a voltage between the internal and external reference electrodes. In those experiments, alkali metal cations could not

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be transferred from water to less polar organic solvents containing no supporting electrolyte, even at very high interfacial voltages (e.g., up to 9 V). This observation could not be explained either by low conductivity of the neat organic solvent or by slow charge transfer at the organic reference electrode because relatively hydrophobic cations (e.g., tetraalkylammonium ions) were readily transferred from water to neat 1,2-dichloroethane (DCE). Moreover, the addition of a very low concentration of organic supporting electrolyte induced the transfer of alkali metal cations to DCE. These findings are inconsistent with the generally accepted mechanism of simple IT reactions. Here we report IT experiments at the water/neat DCE interface for a wide class of hydrophilic ions, including metal cations, protons, and some anions. The transfer behavior of these species turned out to be similar to that of alkali metal cations. A model is proposed that can explain how these IT reactions are facilitated by hydrophobic counterions added to the organic phase.

The main technique employed in our experiments—nanopipet voltammetry—offers a powerful combination of the high mass-transfer rate and very straightforward data analysis with the negligibly small effects of the resistive potential drop and double-layer charging current, which is essential for investigations of simple and facilitated IT reactions at the interface between two immiscible electrolyte solutions. The resistance of the pipets filled with 0.1 M KCl solution was shown to be sufficiently low for the maximum iR drop of <1 mV.[16a] The orifice radius, a, and the ratio of the glass wall radius to the orifice radius, RG, were verified by scanning electrochemical microscopy (SECM) and shown to be consistent with the values obtained from steady-state voltammetry.[16b]

To obtain further information about the nature of ions transferred across the water/neat DCE interface, we carried out generation/collection experiments with θ-pipets. A θ-pipet is a device in which two closely spaced coplanar pipet orifices are separated by a thin line of glass.[17,18] One of the two pipets (generator) can be filled with an aqueous solution containing an ion of interest (e.g., a cation) and immersed in DCE. When the generator pipet is biased at a sufficiently positive potential with respect to an external reference electrode, cations are expected to transfer from it to DCE. Some fraction of these ions will then diffuse to the orifice of the water-filled collector pipet (biased at a more negative potential) and transfer into it. The previously developed theory[17] allows one to verify that the generator current is produced by cation transfer from water to DCE rather than the transfer of some anionic species from DCE to the aqueous phase.

Experimental Section

Chemicals. $MgCl_2$ from Fisher (Fair Lawn, NJ), HCl and $CaCl_2$ from J.T. Baker (Phillipsburg, NJ), and tetrabutylammonium chloride, tetrahexylammonium chloride, potassium tetrakis[4-chlorophenyl]borate (KTPBCl), trimethylchlorosilane, LiCl, NaCl, NaOH, $Fe_2(SO_4)_3$, and KCl from Aldrich (Milwaukee, WI) were used as received. Tetrahexylammonium tetrakis[4-chlorophenyl]borate (THATPBCl) and tetrahexylammonium perchlorate were prepared as described previously.[19] All aqueous solutions were prepared from deionized water (Milli-Q, Millipore Corp.).

The high solvent purity was essential for IT experiments in the absence of organic supporting electrolyte. HPLC grade (99.8%) 1,2-dichloroethane was purchased from Sigma-Aldrich and distilled at least thrice before use. The distillation apparatus was washed by starting a distillation and discarding the first few milliliters of distillate. The distillation was performed until ~5% of DCE remained in the boiling flask. The remainder was discarded each time prior to a new distillation. The triply distilled DCE was kept in a sealed container.

Preparation of Single-Barrel Nanopipets and θ-Pipets. A model P-2000 laser puller (Sutter Instrument Co.) was used to prepare the pipets from capillaries, as described previously.[16] Quartz capillaries of 1 mm outer diameter, 0.58 mm inner diameter were used for regular pipet preparation, and borosilicate θ-tubing, OD = 1.5 mm (Sutter), was used to produce θ-pipets. The aqueous solution was filled from the back using a 10-μL syringe, and then a 0.125-mm-radius Ag/AgCl wire was inserted in each pipet. The pipets were checked using an Olympus BX-60 optical microscope prior to each measurement. The outer glass wall of the θ-pipet was silanized to prevent the formation of an aqueous film between the two orifices. This was done by dipping the pipet tip into trimethylchlorosilane for 1−2 min while the flow of argon (sufficiently fast to produce small bubbles) was passed through the pipet from the back to avoid silanization of the inner pipet wall. This was crucial because the outer organic solvent gets drawn inside a pipet if its inner surface is hydrophobic.

Instrumentation and Electrochemical Cells. Nanopipet voltammograms were obtained using a BAS 100B electrochemical workstation (Bioanalytical Systems, West Lafayette, IN). Using an EI-400 bipotentiostat (Ensman Instruments, Bloomington, IN), the voltage was applied between the reference electrode inside each barrel of the θ-pipet and the reference electrode in the outer solution. Voltammetric experiments were carried out in a 5-mL vial inside a Faraday cage.

Conductivity measurements were carried out in a Beckman conductivity cell with two Pt black parallel disk electrodes (5 cm^2 geometric area; 0.4 cm separation distance). Before measurements, the cell was washed with Milli-Q water and dried, washed with HPLC-grade DCE, and then rinsed with triple-distilled DCE. The resistance measurements over the range of frequencies from 10 Hz to 100 kHz were made using a home-built trans-impedance amplifier (R_{ampl} = 20 kΩ, 20 MHz bandwidth) and an SR-850 lock-in amplifier. An alternating current signal (100 mV$_{rms}$) was applied to the conductometric cell, and the current returned to ground via the trans-impedance amplifier, whose output was fed to the lock-in amplifier and filtered (time constant 1 s).

Results and Discussion

Ion-Transfer Voltammetry at the Water/Neat DCE Interface. Figure 1 shows steady-state voltammograms of various IT processes at the water/DCE interface formed at the tip of a nanopipet ($a \approx 150$ nm). As discussed earlier, Li^+ cannot be transferred to neat DCE at any experimentally achievable voltage (curve 1 in Figure 1A). The addition of just a 1 nM concentration of THATPBCl, shown in Figure 1A, curve 2, was sufficient to produce a well-defined IT wave of Li^+. On the other hand, the addition of a much higher concentration of a less hydrophobic counterion (e.g., 100 nM ClO_4^- in Figure 1A, curve 3) did not result in any noticeable cation transfer. This indicates that the transfer of a hydrophilic cation is made possible by interaction with a hydrophobic organic anion ($TPBCl^-$) rather than by the increase in concentration of ionic species in the organic phase.

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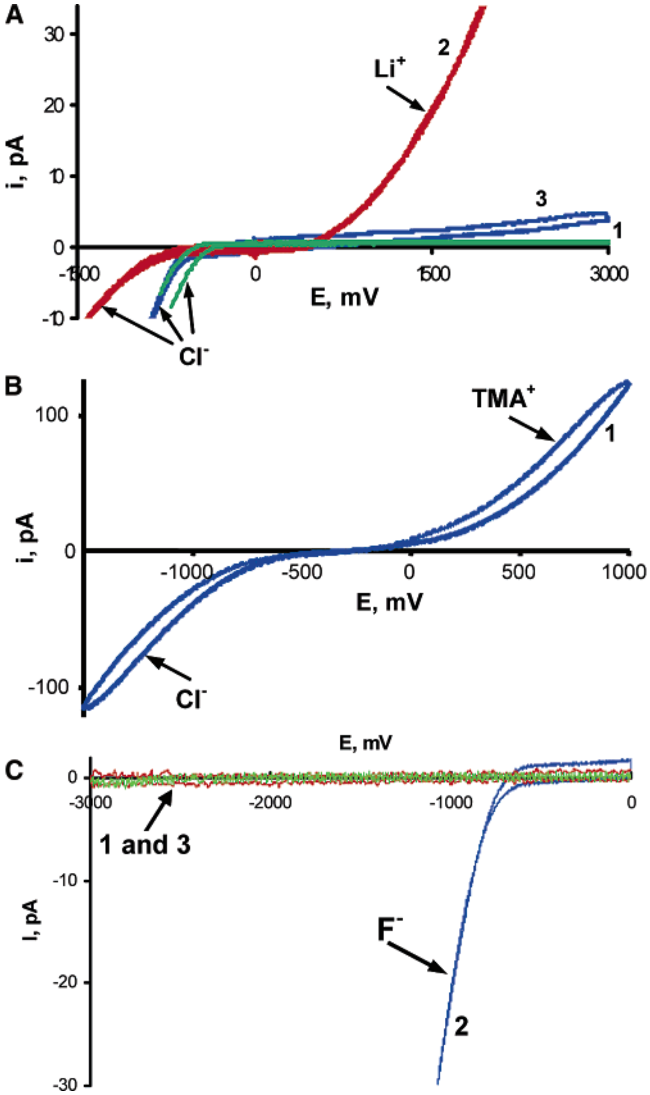

Figure 1. Transfers of cations and anions from aqueous solution inside an ~150 nm nanopipet to external DCE solution. Filling solution: (A) 0.1 M LiCl, (B) 0.1 M TMACl, and (C) 0.01 M LiF. DCE solution: (1) neat DCE; (2) 1 nM THATPBCl in A, or 100 nM THATPBCl in C; (3) 100 nM $TBAClO_4$ in A, or 100 nM KTPBCl in C.

The described phenomenon is quite general: all metal cations we have tested as well as protons could not be transferred to neat DCE (Figure 2A). Fluoride anion exhibits a very similar behavior: it cannot be transferred to neat DCE (curve 1 in Figure 1C), and the transfer occurs in the presence of a very low concentration of a hydrophobic cation in DCE (e.g., THA^+, curve 2 in Figure 1C). However, the same concentration of a hydrophilic cation (e.g., K^+, curve 3 in Figure 1C) added to the organic phase does not induce the transfer of F^-. The addition of tetrabutylammonium (TBA^+) cation, which is less hydrophobic than THA^+, to DCE resulted in a much lower current of F^- transfer (not shown). OH^- also does not transfer to neat DCE (Figure 2B), but this reaction is harder to study because the products of glass dissolution in concentrated NaOH get transferred, producing a small but measurable current.

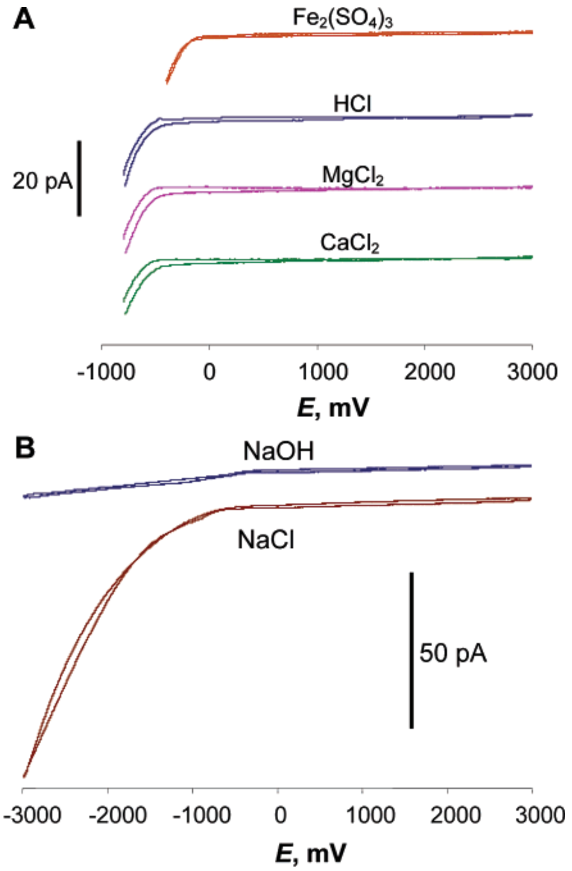

Figure 2. IT voltammograms at the water/neat DCE interface. The transfers of Cl^- and SO_4^{2-} can be seen at negative potentials. The electrolyte concentrations in aqueous filling solutions were (A) 100 and (B) 10 mM. The pipet radii were ~150 nm. The scan rates were (A) 50 and (B) 20 mV/s. The voltammograms are shifted vertically for better clarity.

One should notice that other anions, e.g., Cl^- (Figure 1A,B) and SO_4^{2-} (Figure 2A), and relatively hydrophobic cations, e.g., tetraalkylammonium ions (Figure 1B), readily transfer from water to neat DCE. Thus, the hindrance of transfers of more hydrophilic ions is not related either to low conductivity of neat DCE or to slow charge transfer at the organic reference electrode.

The transfer of a hydrophilic cation can be induced by adding an extremely low concentration of a hydrophobic anion to the organic phase. For example, only 50 pM THATPBCl was required to induce the IT of Ca^{2+} to DCE (Figure 3). From conductivity measurements (see Supporting Information), the

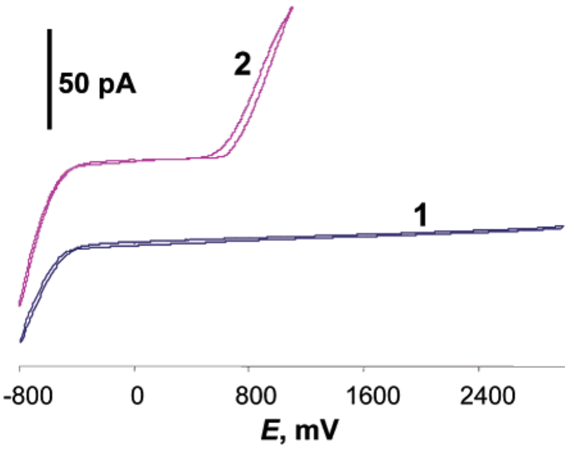

Figure 3. Voltammograms of Ca^{2+} transfer. No transfer of Ca^{2+} occurs without supporting electrolyte in the organic phase (curve 1). Ca^{2+} is transferred by adding 50 pM THATPBCl to neat DCE (curve 2). c_{CaCl_2} = 100 mM; $a \cong 150$ nm. The voltammograms are shifted vertically for better clarity.

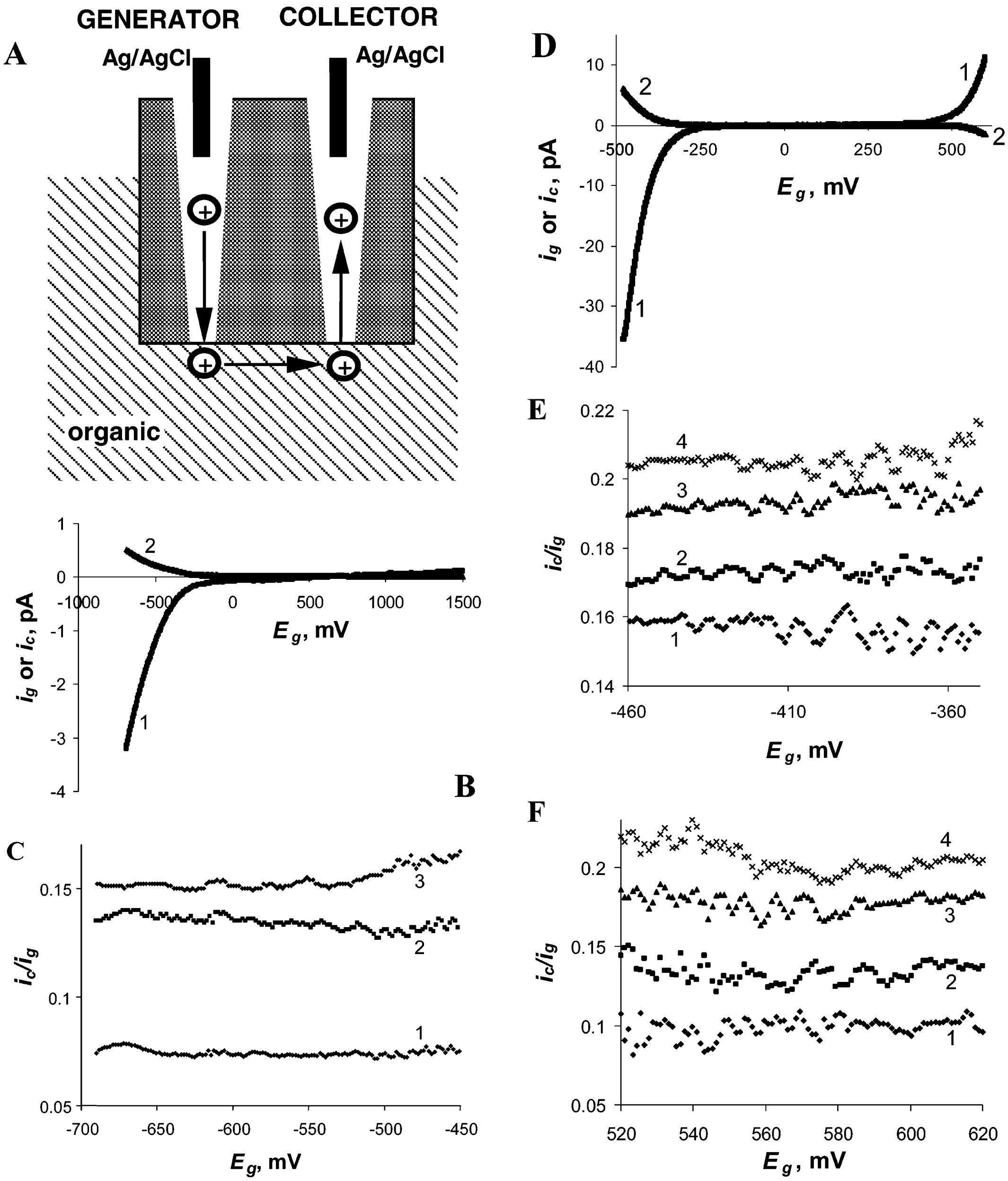

Figure 4. Probing IT with a θ-pipet. (A) Schematic representation of cation transfer from the generator pipet to the external solution and then to the collector pipet. (B,D) Dependencies of the generator (i_g, curve 1) and collector (i_c, curve 2) currents on generator potential (E_g). (C,E,F) Dependecies of collection efficiency (i_c/i_g) on E_g for the transfers of Li^+ (F) and Cl^- (C,E) between water and DCE. Collector potentials (E_c, mV): (B) 500; (C) from curve 1 to curve 3, 0, 500, and 1000; (D) −200; (E) from curve 1 to curve 4, −200, 0, 200, and 400; and (F) from curve 1 to curve 4, 400, 200, 0, and −200. DCE contained no added electrolyte (B,C) or 1 μM THATPBCl (D−F). The generator and collector radii were 420 nm each (B,C) or 680 nm each (D−F).

effective concentration of ionic species in neat (triply distilled) DCE was found to be ~80 nM. Therefore, the addition of ≤1 nM THATPBCl to DCE could not appreciably change its conductivity.

Even with no electrolyte added, a diffuse double layer certainly exists on the organic side of the interface. Moreover, the effective ionic concentration in DCE near the liquid/liquid interface is probably higher than that in the bulk due to the extraction of aqueous electrolyte.[14] The observed transfers of TMA^+ and Cl^- across the water/neat DCE interface also indicate that the interfacial voltage can be established in the absence of added organic electrolyte.

Generation/Collection Experiments with θ-Pipets. We used θ-pipets to further investigate the effect of very low concentrations of organic supporting electrolyte on interfacial IT. Both capillaries of the θ-pipet (Figure 4A) were filled with the same aqueous solution (e.g., 0.1 M LiCl), and the θ-pipet was immersed in DCE containing either no added electrolyte (Figure 4B,C) or 1 μM THATPBCl (Figure 4D−F). When a sufficiently negative voltage was applied between the reference electrode inside the generator pipet and the external reference, Cl^- was transferred from the aqueous filling solution to neat DCE (curve 1 in Figure 4B). Some fraction of chloride ions diffused to the orifice of the second (collector) pipet, which was biased at a more positive potential, and transferred into it. This processes produced the collector current (curve 2 in Figure 4B). In agreement with the previously developed theory,[17] Figure 4C shows that the collection efficiency (i_c/i_g) of Cl^- was essentially independent of the generator potential (E_g) and increased with the increasingly positive value of collector potential (E_c). The results obtained in the presence of 1 μM THATPBCl (Figure 4D,E) are very similar, except that the transfer of Cl^- occurred at slightly less negative voltages.

In contrast, the curves obtained for the transfer of Li^+ with and without organic supporting electrolyte are strikingly different. In the former case, the generator and collector voltammograms (curves 1 and 2 in Figure 4D at positive E_g) as well as the i_c/i_g dependences vs E_g and E_c (Figure 4F) are in agreement with conventional theory.[17] Essentially flat generator and collector voltammograms (curves 1 and 2 at positive E_g) in Figure 4B confirm that no Li^+ transfer occurs in the absence of $TPBCl^-$.

Shuttling Model of IT. The above data suggest that the transfers of hydrophilic cations and anions to organic solvents have to be facilitated by hydrophobic organic counterions. The mechanism of these reactions is, however, completely different from that of conventional facilitated IT (eq 1). Unlike transition metals,[20] alkali metal ions and protons do not form stable complexes with organic anions. Moreover, nanomolar counterion concentrations are too low to produce measurable facilitated IT current. In the case of conventional facilitated IT (reaction 1), the diffusion-limiting current (i_d) must be proportional to the concentration of the facilitating agent (c_L), as long as it is smaller than the concentration of the ion of interest in water (c_{X^+}):[21]

$$i_d = 3.35\pi nFaD_L c_L \tag{3}$$

where F is the Faraday constant, D_L is the diffusion coefficient of L in DCE, a is the pipet radius, and n is the charge of the transferred ion. According to eq 3, the diffusion-limiting current corresponding to $a = 150$ nm and $c_L = 1$ nM would be $\sim 10^{-15}$ A, i.e., 4 orders of magnitude lower than the current in curve 2 (Figure 1A). To further prove this point, we carried out constant-potential electrolysis of Li^+ transfer from a ~150-nm-radius pipet into 1.5 mL of DCE containing 10 nM THATPBCl. The current was almost constant during 120 min of electrolysis, and the amount of Li^+ transferred (36 pmol) was more than twice the amount of $TPBCl^-$ dissolved in DCE (15 pmol). Therefore, the observed effect cannot be explained by a conventional facilitation mechanism (eq 1) that involves the formation of a stable XL species.

Figure 5 shows the scheme of the shuttling mechanism that explains how a miniscule amount of a hydrophobic counterion can produce measurable IT current. (The process in Figure 5 is cation transfer, but the extension of this model to anion transfer is straightforward.) The aqueous and organic phases in Figure 5 are separated by ~1 nm-thick mixed-solvent layer.[6,22] An ion pair ("$-+$") formed by a hydrophilic cation ("$+$") and a hydrophobic organic anion ("$-$") at the outer boundary of the aqueous phase diffuses across the mixed-solvent layer toward the organic phase and dissociates. The released cation is driven into the bulk of the organic phase by the electric field, while the anion travels (via diffusion/migration) across the mixed-solvent layer and assists the transfer of the next cation. Besides the interfacial voltage, which carries the cation and the anion in opposite directions, the shuttling process is driven by the gradient of the cation concentration across the mixed layer, which is high (e.g., $c_{X^+} = 0.1$ M) on the aqueous side of the interface and low on the organic side.

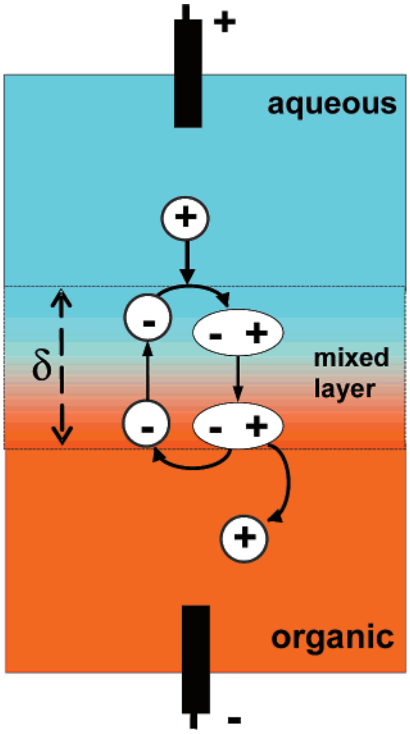

Figure 5. Scheme of the shuttling mechanism of IT. Transfer of a cation from water to the organic phase involves the formation of a short-lived ion pair with a hydrophobic anion.

Determination of the Ion Association Constant of KTPBCl in DCE. To quantitatively describe the formation and decomposition of an ion pair, one needs to know the value of the ion association constant,

$$K_A = \frac{c_{\mathrm{pair}}}{c_{X^+}c_-} \tag{4}$$

where c_{pair} and c_- are the concentrations of the ion pair and the hydrophobic counterion, respectively. Although interfacial ion pairing has been studied,[23] the association constants for this process are difficult to measure. We carried out conductometric experiments to determine the association constant for K^+ and $TPBCl^-$ in DCE. This value can be used as a rough approximation for the interfacial association constant, which may actually be somewhat smaller because the polarity of the interfacial region is the arithmetic average of the polarities of water and DCE.[24] A saturated solution of potassium tetrakis(4-chlorophenyl)borate in DCE was prepared and allowed to equilibrate with solid KTPBCl overnight. Conductivity measurements (see Supporting Information) were made by diluting the filtered stock solution with pure, triply distilled DCE. The dilution shifted equilibrium (5) to the left:

$$K^+ + TPBCl^- \overset{K_A}{\rightleftharpoons} K^+\,TPBCl^- \tag{5}$$

The combination of the mass action expression for reaction (5)

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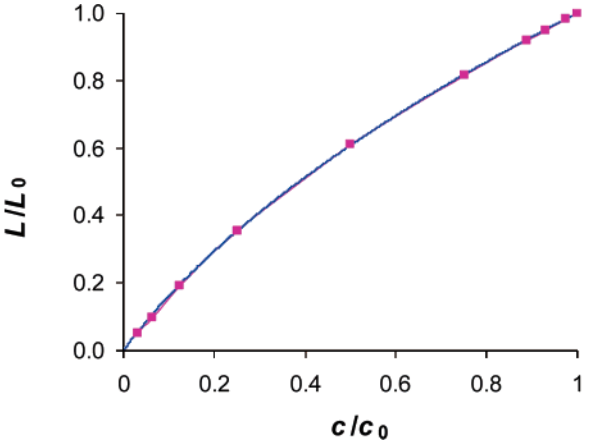

Figure 6. Experimental (squares) and theoretical (solid line) dependences of DCE solution conductivity on KTPBCl concentration.

with the electroneutrality and conservation of mass equations gives

$$[\mathrm{K}^+] = [\mathrm{TPBCl}^-] = \frac{\sqrt{1 + 4K_A c_{\mathrm{KTPBCl}}} - 1}{2K_A} \tag{6}$$

where K_A is the association constant and c_{KTPBCl} is the total concentration of dissolved salt at the given dilution. Since the solution conductance, L, is proportional to the concentration of dissociated salt in solution,

$$\frac{L}{L_0} = \frac{\sqrt{1 + 4K_A c_{\mathrm{KTPBCl}}} - 1}{\sqrt{1 + 4K_A c_0} - 1} \tag{7}$$

where $L_0 = 24.3$ μS is the conductance and $c_0 = 73$ μM is the concentration of salt in the saturated solution before dilution. The fit of the experimental data to eq 7, shown in Figure 6, yields the association constant for K^+ TPBCl^-, $K_A = 2.1 \times 10^4$ M^{-1}.

For the aqueous side of the interface, where $c_{\mathrm{X}^+} = 0.1$ M, one obtains from eq 4

$$\frac{c_{\mathrm{pair}}}{c_-} = K_A c_{\mathrm{X}^+} \cong 2000 \tag{8}$$

Equation 8 indicates that nearly all TPBCl^- ions reaching the aqueous side of the interface get paired with K^+. On the organic side of the interface, the low cation and anion concentrations result in decomposition of an ion pair. Assuming $c_- = 100$ nM,

$$\frac{c_{\mathrm{X}^+}}{c_{\mathrm{pair}}} = 1/K_A c_- \cong 5 \times 10^3 \tag{9}$$

i.e., practically all ion pairs dissociate, releasing K^+ and TPBCl^- ions.

The Rate of Ion Shuttling. The mass-transfer rate for the ion-shuttling mechanism is determined by the transport of the counterions and/or ion pairs across the mixed-solvent layer. The counterion transport, which is accelerated by the interfacial voltage, should be faster than the diffusion of neutral ion pairs. Since almost all counterions reaching the aqueous phase get ion-paired (cf. eq 8), the steady-state diffusion current across the mixed-solvent layer can be expressed as

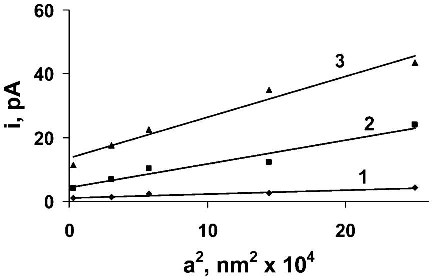

Figure 7. Dependencies of Li^+ transfer current on the square of the pipet radius at different interfacial voltages, $E = 350$ (1), 400 (2), and 450 mV (3). DCE contained 2 μM THATPBCl. For other parameters, see Figure 1A.

$$i = \pi a^2 nFD_{\mathrm{pair}} c^{\mathrm{s}}_-/\delta \tag{10}$$

where D_{pair} is the diffusion coefficient of an ion pair, c^{s}_- is the counterion concentration in the organic phase near the phase boundary, and $\delta \approx 1$ nm is the thickness of the mixed-solvent layer. From eq 10, one can see that the c^{s}_- value has to be ~3 orders of magnitude higher than the 1 nM bulk concentration of TPBCl^- to support the current measured in Figure 1A (curve 2). An accumulation of this magnitude can be expected from both the classical Gouy−Chapman theory[6] and the recent molecular dynamics simulations,[25] since the major portion of the interfacial potential drop (several hundred millivolts) occurs within the thick diffuse layer in DCE. The shuttling mechanism could not be deduced from the published experimental data obtained with the excess supporting electrolyte in the organic phase, where the ion-shuttling process was rapid and did not limit the overall IT rate.

The above model predicts that the rate of ion shuttling should be proportional to the interfacial area, in contrast to the direct proportionality between the steady-state diffusion current and the pipet radius expected from the conventional IT theory (cf. eqs 3 and 10). The experimental verification of this prediction is shown in Figure 7. Each line in Figure 7 has a nonzero intercept whose value increases with increasing E. This behavior can be attributed to the combination of the charging current, small current of organic ion transfer, reference potential instability, and other experimental issues.

The developed model also explains why only hydrophobic counterions can facilitate IT reactions. An aqueous ion is not expected to form an ion pair with a hydrophilic counterion. Moreover, if such a pair were formed, it would be too hydrophilic to partition to the organic phase.

The observed differences in transfer behaviors of two groups of ions (i.e., metal cations, protons, fluoride, and hydroxide vs tetraalkylammonium cations and moderately hydrophilic anions) cannot be attributed to different energetics of those processes. For example, the Gibbs free energy of Cl^- transfer to DCE (51 kJ/mol) is within the range of free energies of K^+, Na^+, and Li^+ transfers (50−57 kJ/mol).[26] The sharp contrast between the transfer of Cl^- to neat DCE at moderate interfacial voltages and the very strong hindrance of metal cation transfers points

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to very slow kinetics of the latter processes. Apparently, the group of IT reactions that do not require the presence of a hydrophobic counterion in the organic phase are low-barrier processes whose rates are determined either by interfacial diffusion/migration alone[12,13] or in combination with interfacial protrusions.[10,27] In contrast, high-barrier IT reactions do not proceed without a facilitating agent. Since most of the applied voltage drops within a thick diffuse layer in the organic phase,[9,28] the fraction of voltage dropping across the interfacial boundary may actually be too small to cross a high barrier.

Conclusions

Two types of ion-transfer behavior were observed in our experiments at liquid/liquid nano-interfaces: while a number of ions can be transferred from water to neat organic solvents, the transfers of a wide class of hydrophilic ions (e.g., metal cations, protons, and some anions) must be facilitated by hydrophobic organic counterions. This finding contradicts the generally accepted notion of those IT reactions as unassisted, one-step processes. A new shuttling mechanism is proposed to describe this class of IT reactions. It involves the formation of a short-lived ion pair at the interface and shuttling of a hydrophilic ion across the mixed-solvent layer. Although the concept of ion shuttling across membranes is well known, it has never been applied to liquid/liquid interfaces. This model explains how a tiny amount of hydrophobic counterions (e.g., <1 nM) can be sufficient to induce measurable IT current. The transfer reactions requiring facilitation by hydrophobic counterions may represent the case of high-barrier, activation-controlled IT,[9,10] while the transfers occurring with no organic counterion can be seen as a low-barrier, diffusion-controlled IT processes.[12,13]

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Supporting Information Available: Additional details of the DCE conductivity measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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