Communication

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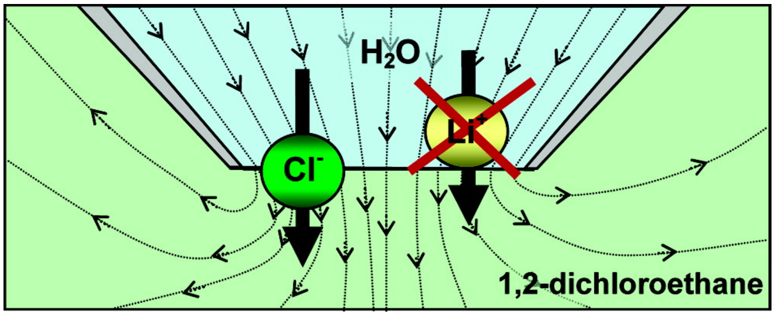

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Ion Transfer at Nanointerfaces between Water and Neat Organic Solvents

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The need for electrolyte to be present in both liquid phases is a major constraint in electrochemistry at the interface between two immiscible electrolyte solutions (ITIES). By narrowing the polarization window, supporting electrolyte prevents one from studying ion transfer (IT) and electron-transfer reactions occurring at high positive (or negative) interfacial voltages. A number of other problems (e.g., impurities, interfacial precipitation, adsorption, and ion paring) associated with the presence of electrolyte often impair electrochemical studies at the ITIES.[1−3] While solid/liquid electrochemistry without supporting electrolyte has been reported,[4] similar experiments at a macroscopic ITIES without organic electrolyte may not be possible because of extremely high resistive potential drop (iR-drop) in the neat solvent. The iR-drop can be minimized by forming an ITIES at the tip of a water-filled micropipet[1b] or a nanopipet.[5] Here, we demonstrate the possibility of electrochemical measurements at the nano-ITIES between an aqueous solution and a neat organic solvent. An intriguing result of these experiments is that metal cations can be transferred from water to less polar organic solvents only in the presence of organic electrolyte.

Cyclic voltammograms (CVs) shown in Figure 1 were obtained at a pipet filled with 0.1 M LiCl solution and immersed in either benzonitrile (BN), nitrobenzene (NB), 1,2-dichloroethane (DCE), or benzene (BZ) containing no added electrolyte.[6]

Ag | organic solvent || 100 mM LiCl | AgCl |Ag (Cell 1)
outer solution nanopipette

While the polarization window in BN (∼750 mV) or NB (∼900 mV) is only slightly wider than the one obtained with commonly used organic electrolytes (e.g., tetrabutylammonium tetrakis(4-chlorophenyl)borate, TBATPBCl), the window obtained in DCE is extremely wide (>9 V). No IT waves could be observed at the water/BZ interface (curve 4). Overall, a much wider polarization window was measured for less polar solvents.

A striking feature in curve 3 (Figure 1A) is the lack of cation transfer wave. While the transfer of Cl^- to DCE was observed at a relatively low interfacial voltage, $E \approx -600$ mV, which is similar to the voltage required to transfer Cl^- to either BN or NB (curves 1 and 2), the wave corresponding to Li^+ transfer was not observed up to $E \approx +10$ V, at which point the interface becomes unstable. Similar voltammograms were obtained with KCl and NaCl filling solutions and also with nano- and micropipets of various radii.

Unlike alkali metal ions, whose transfers were not observed at any applied voltage, differential pulse voltammograms (DPVs) of less hydrophilic cations such as tetramethylammonium (TMA^+) or tetraethylammonium (TEA^+) in Figure 2 show that they are transferred to DCE at modest interfacial voltages (curve 1). The difference between the two peak potentials (∼400 mV) is somewhat larger than that measured in the presence of organic supporting electrolyte. The transfer of Na^+ could also be observed when it was facilitated by addition of dibenzo-18-crown-6 (DB18C6) to DCE (curve 2). One should notice that DB18C6 is a neutral species whose presence does not increase conductivity of DCE.

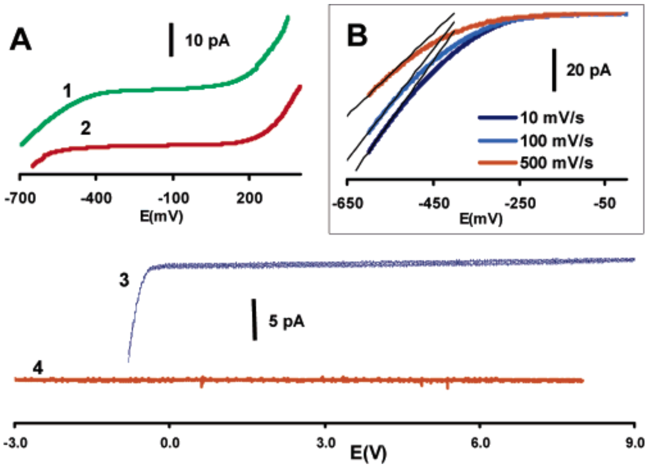

Figure 1. Cyclic voltammograms of IT obtained in Cell 1. The pipet radius was $r = 138$ nm. (A) The solvent was: (1) BN, (2) NB, (3) DCE, and (4) BZ. The scan rate was 50 mV/s. Voltammograms are shifted vertically for better clarity. (B) Linear sweep voltammograms of chloride transfer to DCE at different scan rates.

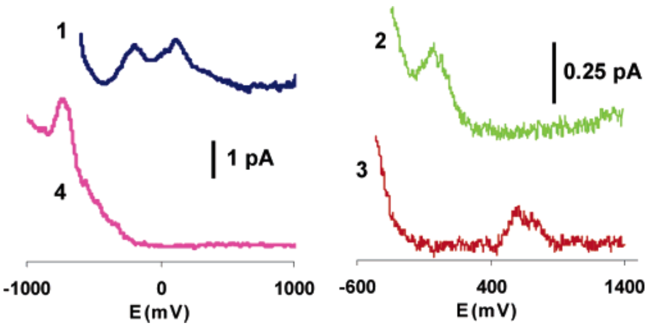

Figure 2. DPVs of cation (1−3) and Cl^- (4) transfers from water-filled nanopipets to DCE obtained in the following cells: (1) Ag/DCE//100 mM LiCl + 1 mM TMACl + 1 mM TEACl/AgCl/Ag, (2) Ag/DCE, 1 mM DB18C6//100 mM NaCl/AgCl/Ag, (3) Ag/DCE//100 mM LiCl + 10 mM HCl + 1 mM L-Ala/AgCl/Ag, and (4) Ag/DCE//100 mM Li_2SO_4 + 1 mM LiCl/AgCl/Ag. The pulse amplitude was +50 mV.

The extreme sluggishness of alkali metal ion transfers to DCE cannot be explained by high Gibbs free energies of those processes because $\Delta G°$ of Cl^- transfer to DCE (51 kJ/mol[7]) is within the range of free energies of K^+, Na^+, and Li^+ transfers (50−57 kJ/mol[7]). The large hydration numbers of metal cations (four for sodium and lithium ions as compared to two for chloride) may be a factor contributing to the apparent slow kinetics of their transfers. Also, the large potential drop (∼9 V in Figure 1, curve 3) occurs mostly within a very thick diffuse double layer in DCE, and the driving force for the interfacial IT may actually be not very high.

Another factor that might hinder IT to neat DCE is its high ohmic resistance, though the well-shaped, curved (i.e., Nernstian rather

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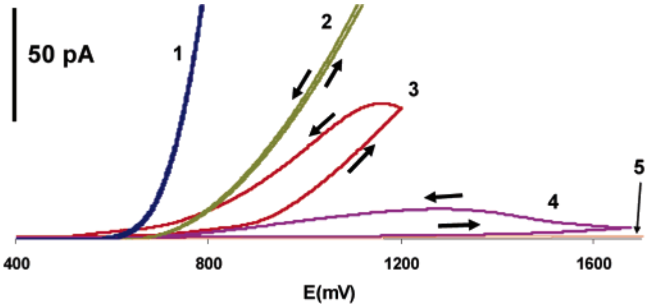

Figure 3. CVs of lithium transfer to DCE with varying electrolyte concentrations: [THATPBCl] = 10 μM (1), 100 nM (2), 1 nM (3), 0.1 nM (4), 0.05 nM (5). The scan rate was 50 mV/s. [LiCl] = 100 mM.

than ohmic) current−potential dependences produced by the transfer of Cl^- (curve 3 in Figure 1) do not support this assumption. The ohmic control of the Cl^- transfer rate becomes apparent at more extreme overpotentials (Figure 1B). The resistance value extracted from the slope of the linear portion of the voltammogram obtained at 10 mV/s is 3.7×10^9 Ω. This value is several orders of magnitude larger than the filling solution resistances measured for pipets with similar radii,[5] and therefore it corresponds to the resistance of the external DCE phase. For comparison, we used a commercial conductimetry cell and a lock-in amplifier to measure the conductivity of neat DCE, $\kappa = 1.07 \times 10^{-8}$ S cm^{-1}.[8] Using this value, one can calculate the expected resistance for a 138-nm-radius pipet in DCE, $R = 1/4\kappa r = 1.7 \times 10^{12}$ Ω.[9] The measured pipet resistance is ~500 times lower than the calculated value based on conductivity of neat DCE. These values are different because the main part of the resistive potential drop occurs within the layer of DCE adjacent to the liquid−liquid interface whose thickness is equivalent to a few pipet radii.[11] The ions expelled from the pipet greatly increase the conductivity of this layer and thus cause a decrease in the effective pipet resistance. As expected, the measured resistance decreases with time. The voltammograms of Cl^- transfer obtained with the scan rates of 10, 100, and 500 mV/s (Figure 1B) yielded the resistance values of 3.7, 4.1, and 5.6 GΩ, respectively. Similar resistance values were obtained from current−potential dependences of TEA^+ transfer. A more detailed analysis of resistance changes and double layer formation in organic solvent that accompany the expulsion of ions from the pipet will be presented elsewhere.[10]

The addition of a small amount of tetrahexylammonium tetrakis-(4-chlorophenyl)borate (THATPBCl) electrolyte to DCE causes dramatic changes in the shape of IT voltammograms (Figure 3). At the 10 μM electrolyte concentration, curve 1 is essentially identical to the voltammogram of Li^+ transfer obtained with excess of THATPBCl in organic phase. A significant resistive effect can be seen at 100 nM electrolyte concentration (curve 2). On the other hand, no Li^+ transfer could be observed with $c_{\mathrm{THATPBCl}} = 0.05$ nM (curve 5), which is a little lower than the threshold concentration value required for this IT reaction to occur. At somewhat higher concentrations (curves 3 and 4), the current begins to rise only at high positive interfacial voltages.

After the turning point, the current continues to increase and exhibits a peak. The peak current increases with *decreasing* scan rate; stopping the potential sweep at a turning point for a few seconds and then changing its direction also results in a higher peak current (not shown). These observations are indicative of an "auto-catalytic" response (i.e., at low concentrations of organic electrolyte, the rate of transfer of alkali metal ions to DCE increases with time). This type of response, which was not observed for Cl^- transfer process, cannot be explained by changes in ohmic resistance.

In summary, the transfers of strongly hydrated alkali metal cations from water to a less polar organic solvent, such as DCE, occur only in the presence of organic supporting electrolyte. Apparently, hydrophobic anions facilitate these processes. It was shown recently that the transfer of Ag^+ to DCE is facilitated by complex formation with $TPBCl^-$;[12] however, the mechanism of alkali metal transfers must be different. One should also notice that the diffusion flux of $TPBCl^-$ to the nanopipet orifice at concentrations as low as ≤10 nM is too small to support a measurable IT current. We are currently working on the model to explain this intriguing phenomenon.

An extremely wide polarization window observed with no electrolyte added to the organic phase allows one to probe simple and facilitated IT reactions, which are not normally accessible by electrochemical techniques. For example, the transfer of Cl^- (curve 4 in Figure 2) is difficult to study at a conventional ITIES.[13] The transfer of L-alaninamide cation (curve 3 in Figure 2) is even more energetic, and to our knowledge, it has not yet been observed electrochemically.

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