Communication

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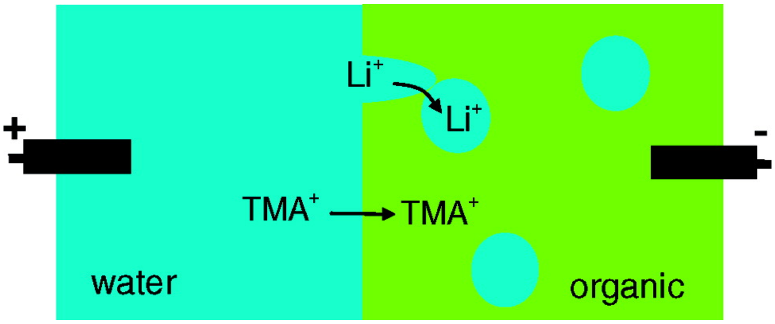

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Role of Trace Amounts of Water in Transfers of Hydrophilic and Hydrophobic Ions to Low-Polarity Organic Solvents

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A detailed knowledge of ion transfer (IT) mechanisms between water and low-polarity media is crucial for many areas of chemistry and biochemistry such as phase transfer catalysis, separations, and biomembranes.[1,2] Recent theoretical and experimental studies and molecular dynamics simulations of IT at the interface between two immiscible electrolyte solutions (ITIES)[3−12] and water/lipid membrane interface[13−15] improved our understanding of thermodynamics, kinetics, and ion distribution at the phase boundary in these systems. IT experiments at nanometer-sized ITIES[16] revealed mechanistic differences between the transfers of relatively hydrophobic and strongly hydrophilic ions: the former can be viewed as unassisted, one-step reactions, while the latter processes have to be facilitated by hydrophobic counterions present in organic phase (shuttling mechanism[16b]). Here we show another important mechanistic difference between the two classes of ITs: relatively hydrophobic ions are transferred into neat organic solvents (e.g., 1,2-dichloroethane, DCE), but hydrophilic ions can only be transferred to water clusters dispersed in organic phase.

Cyclic voltammograms (CVs) of alkali metal ions and tetramethylammonium cation transfers (Figure 1) were obtained using a nanopipet filled with 0.1 M XCl ($X^+ = Li^+$, Na^+, Cs^+ or TMA^+) aqueous solution and immersed in DCE containing no added electrolyte.[17] With no water added to neat DCE, no current of Li^+ or Na^+ transfer can be seen in Figure 1 panels A and B (green curves) at any interfacial voltage (E) up to $E = 3$ V. In contrast, all alkali metal ions (the data for K^+ is not shown) readily transferred to water-saturated DCE (black curves in Figure 1 panels A and B; the concentration of water, ∼0.13 M at 25 °C[18]). These ions could also be transferred to DCE containing much less water (e.g., 130 μM; pink curve in Figure 1A). The same trend can be seen in Figure 1 panels A and B: the higher the water concentration the lower the interfacial voltage required to drive the IT reaction.[19]

Somewhat less hydrophilic Cs^+ ions could be transferred to neat DCE with no added water at $E \geq 2$ V (green curve in Figure 1C). This process is greatly facilitated by the addition of water. In contrast, much less hydrophilic tetramethylammonium (TMA^+) ions readily transfer to neat DCE at low interfacial voltages, and the effect of water concentration in DCE on this process is small (Figure 1D).

Since only strongly hydrophobic organic counterions (e.g., tetrakis(4-chlorophenyl)borate) can assist the transfers of metal cations to neat organic solvents,[16] the facilitation of this reaction by added water cannot be explained by its ionization in DCE.

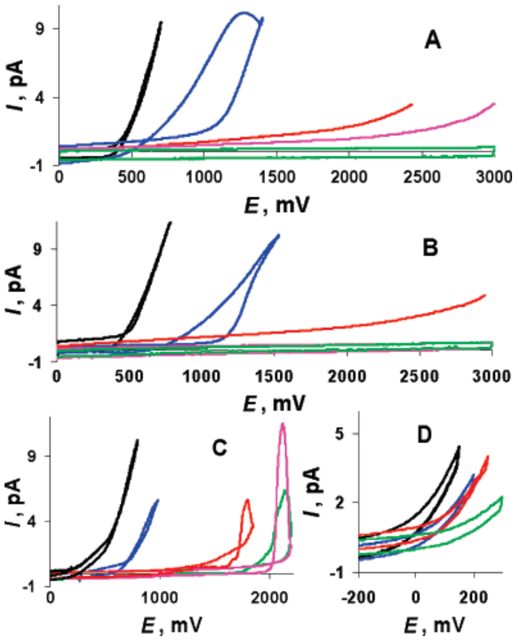

Figure 1. Voltammograms of Li^+ (A), Na^+ (B), Cs^+ (C), and TMA^+ (D) transfers from water to DCE containing the following amounts of water: 130 mM H_2O (black curve), 13 mM (blue curve), 1.3 mM (red curve), 130 μM (pink curve), and 0 (green curve). The radius of nanopipet orifice was ∼150 nm. The potential scan rate was 50 mV/s.

The effect of added water on conductivity of DCE can be seen from admittance versus frequency curves (Figure 2). The conductivity of neat (i.e., triply distilled) DCE corresponds to an effective concentration of ionic impurities of ∼80 nM.[16b] In Figure 2, the admittance at high frequencies is determined by the cell capacitance. It is proportional to the frequency of excitation and independent of water concentration in DCE. In the low-frequency plateau region, the cell admittance is essentially equal to the solution conductance. Surprisingly, the conductance *decreases* with increasing concentration of water in DCE. The conductivity of water-saturated DCE (orange curve in Figure 2) is five times lower than that of essentially dry DCE (green curve). The linear plot of conductance versus log([H_2O]) is shown in Figure 2 (inset).

A significant variation in solution conductivity is due to the change either in viscosity or in the total concentration of charges. Since the addition of 0.1 mM of water could not have caused a major increase in DCE viscosity, the data in Figure 2 suggests that the effective concentration of charges in DCE decreases significantly with increasing [H_2O]. This effect cannot be attributed to the extraction of ionic impurities from DCE during its equilibration with water because only a small fraction of water-saturated DCE was used to prepare most solutions in Figure 2 (e.g., 0.1% of the total solution volume for the black curve).

The diminished effective concentration of charges in water-equilibrated DCE can be attributed to the formation of water clusters into which the ionic species are extracted. The existence of such clusters in nitrobenzene and their role in solvation of ions were revealed by NMR studies.[21] DCE is less polar and less miscible with water than nitrobenzene, and so even more extensive extraction of ions from DCE to water clusters dispersed in it can be expected.

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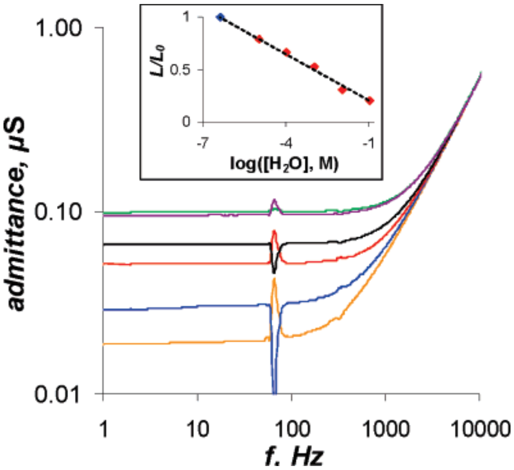

Figure 2. Frequency dependences of the conductometric cell admittance for different concentrations of water in DCE and a plot of normalized conductance (L/L_0) versus water concentration in DCE (inset). L_0 is the conductance of the cell filled with neat DCE. A spike at $f = 60$ Hz is an instrumental artifact. The blue point in the inset was obtained by extrapolation of the experimental plot to the conductance of neat DCE ($L_0 = 95$ nS). The concentration of water added to DCE (from bottom to top), mM: 130, 13, 1.3, 0.13, 0.013, and 0.

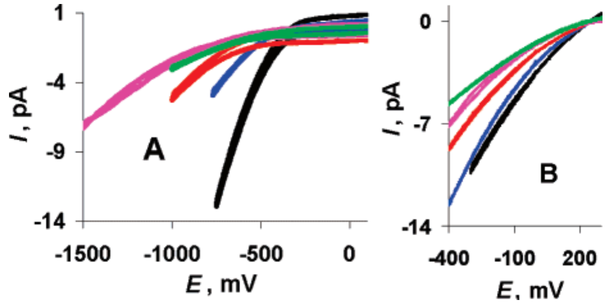

Figure 3. Voltammograms of Cl^- (A) and TPB^- (B) transfers from water to DCE containing the following amounts of water: 130 mM H_2O (black curve), 13 mM (blue curve), 1.3 mM (red curve), 130 μM (pink curve), and 0 (green curve). The radius of nanopipet orifice was ~150 nm. Aqueous solution contained 0.1 M NaCl (A) or NaTPB (B).

A strong catalytic effect of trace amounts of water on IT suggests that hydrophilic metal ions (and protons; see Supporting Information) are actually transferred to water clusters dispersed in DCE rather than to the bulk organic solvent. Although the detailed mechanism of such a transfer has yet to be elucidated, it probably occurs when an aqueous cluster comes close to the phase boundary and interacts with a water "finger" that forms during the IT reaction.[11] Although water molecules continuously egress from the pipet to neat DCE, they diffuse rapidly from the nanointerface into bulk DCE and therefore cannot induce IT processes.

This model explains why the transfers of strongly hydrophilic metal ions to water-saturated DCE occur at modest interfacial voltages. It is also clear that the behavior of more hydrophobic cations (e.g., TMA^+), which can be readily transferred to neat DCE, is almost unaffected by $[H_2O]$ in organic phase.

The transfers of anions (Figure 3) exhibit similar trends. Relatively hydrophilic Cl^- can be transferred to neat DCE only at high negative voltages (Figure 3A). Although the effect of water addition on this process is less pronounced than it is for stronger hydrated Li^+ and Na^+, the shift of the Cl^- wave between the green (neat DCE) and black (water-saturated DCE) curves is ~1 V. In contrast, the onset of transfer of hydrophobic tetraphenylborate (TPB^-; Figure 3B) is almost independent of $[H_2O]$ in DCE.

In summary, our results point to significant mechanistic differences between the transfers of hydrophilic and hydrophobic ions to low-polarity solvents. Hydrophobic ions undergo simple transfers from water to the organic solvents. Such reactions do not require the presence of organic electrolyte,[16] and they are essentially unaffected by concentration of water in organic solvent. In contrast, strongly hydrophilic ions are transferred from the aqueous phase to water clusters dispersed in organic phase. Therefore, the more hydrophilic the ion the more significant the increase in its transfer rate with increasing concentration of water in organic phase. The reported results may be relevant to passive ion permeation through biomembranes.[13,14]

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Supporting Information Available: Voltammograms of proton transfer. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) "Neat" DCE was obtained by distilling HPLC grade DCE (Sigma-Aldrich) three times. The nanopipet preparation was described previously.[16] Briefly, a Model P-2000 laser puller (Sutter Instrument Co.) was used to prepare the pipets from quartz capillaries. 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 the pipet. A 0.25-mm-radius Ag wire was used as a quasi-reference electrode in DCE. Voltammograms were obtained with a BAS-100B potentiostat. To prepare water-saturated DCE, a portion of thrice distilled DCE was equilibrated with an equal amount of pure water in a closed Erlenmeyer flask for 48 h, while the flask was shaken periodically. Water-saturated DCE was diluted by neat DCE to obtain the desired concentration of water. Conductivity measurements were made using a home-built trans-impedance amplifier and a SR-850 lock-in amplifier. For experimental details and data analysis see ref 16b.
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