

Void-Assisted Ion-Paired Proton Transfer at Water–Ionic Liquid Interfaces

Eva Alvarez de Eulate, Debbie S. Silvester, and Damien W. M. Arrigan*

Abstract: At the water–trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ($[P_{14,6,6,6}][FAP]$) ionic liquid interface, the unusual electrochemical transfer behavior of protons (H^+) and deuterium ions (D^+) was identified. Alkali metal cations (such as Li^+ , Na^+ , K^+) did not undergo this transfer. H^+/D^+ transfers were assisted by the hydrophobic counter anion of the ionic liquid, $[FAP]^-$, resulting in the formation of a mixed capacitive layer from the filling of the latent voids within the anisotropic ionic liquid structure. This phenomenon could impact areas such as proton-coupled electron transfers, fuel cells, and hydrogen storage where ionic liquids are used as aprotic solvents.

Proton transfer reactions occur widely in nature and technology. Important energy conversions in nature require coupled reactions involving transfer of electrons and protons (for example, cell respiration and photosynthesis),^[1] which have stimulated the mimicking of these systems in order to achieve highly efficient energy convertors^[2] or energy storage^[3] cells. Recently, room temperature ionic liquids (RTILs) have received intense scrutiny owing to their unique physicochemical properties,^[4] which make them highly attractive for various studies including electrochemistry,^[5] with available potential windows as wide as 7 V at solid electrodes.^[6] Since the pioneering study by Quinn et al.,^[7] electrochemistry at water/RTIL (H_2O /RTIL) interfaces has become a new platform to study interfacial charge transfer processes, including simple^[8] and facilitated ion transfers.^[9] While proton transfers have been of interest at polarized water/oil interfaces,^[10] including proton transfer catalyzed reactions,^[11] proton transfers into ionic liquids have not yet been addressed.

Herein, we explore the behavior of protons at the interface between water and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ($H_2O/[P_{14,6,6,6}][FAP]$), building on previous work on the formation of a H_2O /RTIL microinterface array for organic cation trans-

fer^[12] and protein behavior.^[13] Surprisingly, a remarkable ion transfer process was observed when alkali cation solutions were replaced with an acidic (hydrogen or deuterium cation) aqueous solution. The proton–RTIL interactions are believed to be the result of interfacial transfers into voids in the RTIL phase. These results will be of particular interest in areas where aprotic RTILs are utilized in protonated environments (for example, electrocatalytic reactions, proton-coupled electron transfers, fuel cells, and hydrogen storage).

At an array of microscale H_2O /RTIL interfaces, $[P_{14,6,6,6}][FAP]$ showed the largest potential window compared to the RTILs trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonylethyl)imide $[P_{14,6,6,6}][NTf_2]$, 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate $[C_6mim][FAP]$, and 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate $[C_4mpyr][FAP]$ (Supporting Information, Figure S1). When LiCl was replaced with HCl as the aqueous electrolyte at the $H_2O/[P_{14,6,6,6}][FAP]$ interface (Figure 1), an increase in current at -0.1 V in the forward sweep of the cyclic voltammograms (CVs) was observed. This response to aqueous phase hydrogen cations is quite different than the behavior of acidic aqueous solutions at H_2O /organic solvent interfaces.^[14] Furthermore, this charge transfer process is absent when the aqueous phase consists of LiCl, NaCl, or KCl (Figure 1, inset), but is evident when the aqueous phase contains deuterium ions (D^+); the latter behave similarly to protons. The CVs in Figure 1 are quite different from those expected for a diffusion-controlled ion transfer reaction at microinterface arrays.^[12,15]

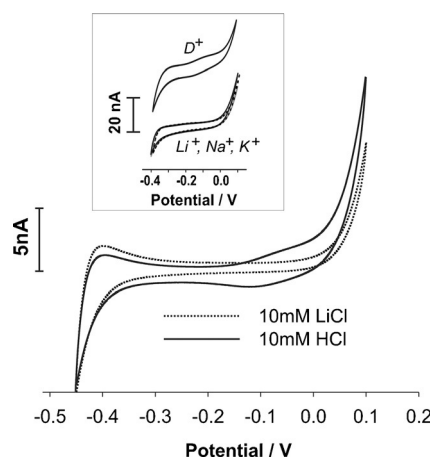


Figure 1. Cyclic voltammograms of the $H_2O/[P_{14,6,6,6}][FAP]$ microinterface array, where the aqueous phase is 0.01 M LiCl (.....) or HCl (—). Inset: 0.1 M LiCl, NaCl, KCl in H_2O or DCl in D_2O . Scan rate: 10 mVs^{-1} .

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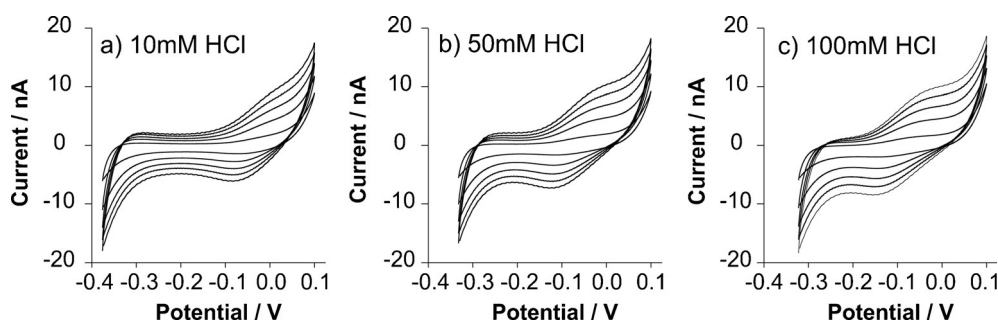


Figure 2. Cyclic voltammetry at the micro-interface array between water and the RTIL [P_{14,6,6}][FAP]. The aqueous phase is a) 10 mM HCl, b) 50 mM HCl, or c) 100 mM HCl. Scan rates: 5, 10, 25, 50, 75, and 100 mVs⁻¹ (inner to outer).

The influence of HCl concentration (in the range 1–500 mM) was investigated (Supporting Information, Figure S2). Although not detectable at 1 mM, at 5 mM a shoulder was evident at the positive end of the CV. Higher concentrations of HCl were easily detected (Figure 2). These voltammograms exhibit some notable features: i) the current on the forward sweep reaches a steady-state, consistent with radial diffusion to microinterfaces, but it increases with the scan rate; ii) the reverse scans exhibit a peak-shaped voltammogram, consistent with linear diffusion or an adsorption/desorption process. The diffusion-limited steady-state current (I_{lim}) at a micro-interface array is described by Equation (1):

$$I_{\text{lim}} = N_p 4 z F D C r \quad (1)$$

where N_p is the number of microinterfaces, z , D , and C are the charge, diffusion coefficient, and bulk concentration of the transferring species, and r is the radius of one interface.

For the diffusion-controlled transfer of protons at a H₂O/RTIL interface array consisting of 30 microinterfaces, taking into account the bulk aqueous diffusion coefficient of protons, $D_{\text{H}^+} \sim 10^{-4} \text{ cm}^2 \text{ s}^{-1}$,^[16] the limiting current is expected to be 13, 65, and 130 μA at each of the concentrations shown in Figure 2 (10–100 mM); the experimental currents are, in fact, several orders of magnitude lower than these predictions. Furthermore, the limiting currents unexpectedly change with scan rate [see Eq. (1)]. Scan rate data for the five cations studied are provided in the Supporting Information (Figure S3). Also, it is notable that the proton transfer potential is dependent on the proton concentration in the aqueous phase (Supporting Information, Figure S4). The half-wave potential for proton transfer varied linearly with the logarithm of proton concentration, with a slope of -64 mV dec^{-1} (Supporting Information, Figure S4), close to the expected -59 mV dec^{-1} for a single-positive charged species. This shift in the potential can be attributed to a facilitated proton transfer mechanism driven by $\text{H}^+ \cdot [\text{FAP}]^-$ ion-pairing. Mirkin and co-workers proposed a facilitated transfer, from water to low permittivity solvents, of hydrophilic ions by hydrophobic counter ions.^[17] This process involves a transient ion-pairing that facilitates the transfer across the interface, which agrees with the phenomenon observed here, although it fails to explain the exclusion of alkali metal cations.

Electrochemical impedance spectroscopy (EIS) was employed to probe the capacitive and resistive properties of the H₂O/RTIL system. Figure 3a shows Nyquist plots of the H₂O/RTIL system, where the aqueous phase is 1 mM LiCl in the absence (solid line) or presence of 50 mM HCl (dotted line) polarized at -0.2 V (no charge transfer). Figure 3b shows the

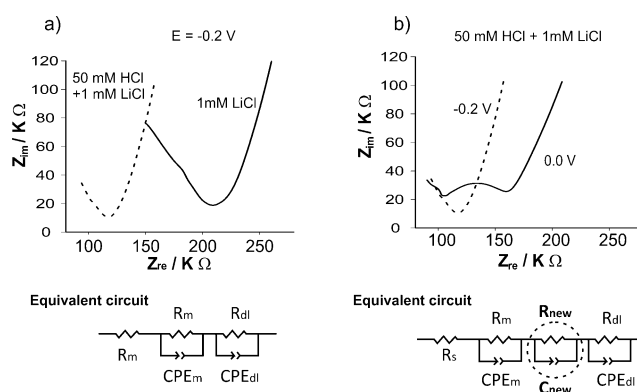


Figure 3. EIS of the H₂O/RTIL system: a) The aqueous phase is 50 mM HCl in 1 mM LiCl (---) or 1 mM LiCl (—), at -0.2 V (no interfacial transfer); b) 50 mM HCl in 1 mM LiCl at -0.2 V (---) or 0.0 V (—). Below the graphs are the corresponding equivalent circuits which fit the experiments with w of 50 mM HCl in 1 mM LiCl at either a) -0.2 V or b) 0.0 V . Frequency range shown: 500 kHz to 80 Hz.

Nyquist plots where the H₂O/RTIL interface with acidic aqueous phase is polarized at -0.2 V (dotted line) or 0.0 V (red solid line): interfacial proton transfer occurs only at the latter potential. The corresponding equivalent circuits, which show the combinations of series and parallel resistances from solution, membrane and diffusion (R_s , R_m , and R_d) and capacitances (non-ideal CPE_m , CPE_d , and ideal C_{new}) that best fit the experimental data, are shown beneath each plot. In these circuits, R_s is the solution resistance, while R_m and CPE_m are attributed to the silicon membrane that supports the H₂O/RTIL microinterfaces and the Ag/AgCl electrodes, since these are constant and independent of the applied potential. R_d and CPE_d correspond to a diffusion process at lower frequencies (right hand side of the Nyquist plot).

EIS reveals a new semi-circle feature between 100 and 160 k Ω (Figure 3b) when implemented at a potential (0.0 V) where the transfer process occurs. This new feature (Figure 3b, R_{new} and C_{new}), reaches an impedance maximum of circa 30 k Ω and occurs at high frequencies. This is an indication of a process two or more orders of magnitude faster than the diffusion process observed at lower frequencies (R_d and CPE_d). Experiments for different HCl concentrations produced similar Nyquist plots (Supporting Informa-

tion, Figure S5). The magnitude of the new semi-circle feature is independent of the proton concentration above 10 mM HCl.

This new feature fits to a circuit with a third capacitor, which suggests a change at the H₂O/RTIL interface owing to the transfer of protons and their interaction with [P_{14,6,6,6}]⁺[FAP][−]. Relative dielectric permittivity (ϵ_r) values reported for a wide range of ionic liquids vary between 8 and 16.^[18] Assuming that the relative dielectric permittivity of [P_{14,6,6,6}]⁺[FAP][−] is within this range and the geometric area (A) of the microinterface array is 1.18×10^{-4} cm², then the thickness of this new capacitor can be estimated by [Eq. (2)].

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (2)$$

where C is the capacitance, ϵ_r is the relative dielectric permittivity, ϵ_0 is the electric constant (8.85×10^{-12} F m^{−1}), d is the thickness, and A is the microinterface array area. The new capacitor value (C) is circa 3.7×10^{-10} F, as obtained from the equivalent circuit fitting (C_{new} , Figure 3b), and corresponds to a new layer of thickness 2.3–4.5 nm at the H₂O/RTIL microinterface array.

Alternating current (AC) voltammetry of the H₂O/RTIL system with either LiCl or HCl as aqueous electrolytes was undertaken at different phase angles (0° and 90°). This analysis presented a negative shift of the potential of zero charge (E_{pzc}) in the presence of the acidic aqueous phase,^[19] which indicates an interaction of positively-charged species with the H₂O/[P_{14,6,6,6}]⁺[FAP][−] microinterface (Supporting Information, Figure S6). Furthermore, similar CV behavior was observed when the RTIL phase was replaced with a solution of RTIL dissolved in an organic solvent (Supporting Information, Figure S7), although the magnitude of the effect was diminished owing to the dilution factor. Conventional electrolytes in organic solvents do not exhibit the effect seen here with [P_{14,6,6,6}]⁺[FAP][−]. Furthermore, ionic effects were investigated in both phases, although the presence of [NTf₂][−], [C₆mim]⁺, and [C₄mpyr]⁺ in the RTIL limited the available potential window (≤ 0.25 V). Nevertheless, when replacing Cl[−] with SO₄^{2−} in the aqueous phase, the same phenomenon was observed in the presence of H⁺ (Supporting Information, Figure S8).

Recent models to explain the electrical double layer (EDL) formed at electrode/RTIL interfaces have taken into account the finite size of the ions,^[20] the concentrated nature of the electrolyte,^[21] as well as steric effects,^[22] which were not addressed in the Gouy–Chapman theory. Fedorov and Kornyshev used the formation of “voids” in the ionic liquid structure to explain the camel-shaped capacitance of the EDL at metal/RTIL interfaces.^[23] It was suggested that ionic liquids may contain voids, owing to the typically anisotropic nature of the bulky ions present, which can accommodate small charged molecules. This effect could provide a cavity for hosting of ions transferred from an adjoining immiscible phase, leading to the formation of a new capacitive layer and a change in capacitive current, as observed here. Such a change explains why the CV currents (Figures 1,2) vary with sweep rate despite having a steady-state form. Further transfer of these ions is hindered by the large non-polar alkyl

groups of the RTIL cation ([P_{14,6,6,6}]⁺), which reduces the mobility of the proton within the ionic liquid. Furthermore, this process is possible only for small cations, either solvated or unsolvated, because H⁺ and D⁺ (radii ~ 0.037 nm and ~ 0.036 nm, respectively,^[24] hydronium radius ~ 0.14 nm) can physically occupy the cavities in the RTIL phase within the EDL because of their dimensions. The RTIL void radii were estimated to be $r \sim 0.17$ – 0.19 nm (see the Supporting Information), which can accommodate hydronium ions, but not hydrated alkali cations (> 0.3 nm). This resembles LaF₃ solid-state membranes where only fluoride can occupy vacancies in the crystal lattice.^[25] It is also known that diffusion of small gas molecules, such as H₂, in RTIL occurs by hopping between RTIL interstices.^[26] In the present studies, no chemical reactions between transferred cation and components of the RTIL were observed, which is in agreement with the reversible solvation of H⁺ by [FAP][−] reported by Silvester et al. in studies of H₂(g) oxidation.^[27]

In conclusion, voltammetry and electrochemical impedance spectroscopy suggests that solvated H⁺ and D⁺ transfer cross the H₂O/[P_{14,6,6,6}]⁺[FAP][−] microinterface, forming a capacitive thin film layer, but larger cations (Li⁺, Na⁺, and K⁺) do not transfer. This new capacitor-like layer is formed as H⁺/D⁺ fill the latent voids within the RTIL, but further transfer into the bulk RTIL is limited by the steric effect of the RTIL cations. This is in agreement with recent theoretical models of the EDL at electrode/RTIL interfaces, where crowding effects, finite size of the ions, and steric effects have been incorporated to expand the Gouy–Chapman model. The ability to transport ions into cavities within a liquid phase may have implications for proton transfer reactions of importance in proton-coupled electron transfers, fuel cells, hydrogen storage, and protein extraction and stabilization.

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- [1] S. Hammes-Schiffer, *Acc. Chem. Res.* **2009**, *42*, 1881–1889.
- [2] S. de Vries, K. Dörner, M. J. F. Strampraad, T. Friedrich, *Angew. Chem. Int. Ed.* **2015**, *54*, 2844–2848; *Angew. Chem.* **2015**, *127*, 2886–2890.
- [3] J. Andrews, S. S. Mohammadi, *Int. J. Hydrogen Energy* **2014**, *39*, 1740–1751.
- [4] L. E. Barrosse-Antle, A. M. Bond, R. G. Compton, A. M. O'Mahony, E. I. Rogers, D. S. Silvester, *Chem. Asian J.* **2010**, *5*, 202–230.
- [5] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* **2009**, *8*, 621–629.
- [6] a) N. V. Ignat'ev, U. Welz-Biermann, A. Kucheryna, G. Bissky, H. Willner, *J. Fluorine Chem.* **2005**, *126*, 1150–1159; b) N. Nishi, S. Imakura, T. Kakiuchi, *Anal. Chem.* **2006**, *78*, 2726–2731.

- [7] B. M. Quinn, Z. F. Ding, R. Moulton, A. J. Bard, *Langmuir* **2002**, *18*, 1734–1742.
- [8] Y. X. Wang, T. Kakiuchi, Y. Yasui, M. V. Mirkin, *J. Am. Chem. Soc.* **2010**, *132*, 16945–16952.
- [9] J. Langmaier, Z. Samec, *Anal. Chem.* **2009**, *81*, 6382–6389.
- [10] A. Sabela, V. Marecek, Z. Samec, R. Fuoco, *Electrochim. Acta* **1992**, *37*, 231–235.
- [11] a) P. Peljo, L. Qiao, L. Murtomaki, C. Johans, H. H. Girault, K. Kontturi, *ChemPhysChem* **2013**, *14*, 311–314; b) R. Partovi-Nia, B. Su, F. Li, C. P. Gros, J. M. Barbe, Z. Samec, H. H. Girault, *Chem. Eur. J.* **2009**, *15*, 2335–2340.
- [12] D. S. Silvester, D. W. M. Arrigan, *Electrochem. Commun.* **2011**, *13*, 477–479.
- [13] E. A. de Eulate, D. S. Silvester, D. W. M. Arrigan, *Chem. Asian J.* **2012**, *7*, 2559–2561.
- [14] M. D. Scanlon, J. Strutwolf, D. W. M. Arrigan, *Phys. Chem. Chem. Phys.* **2010**, *12*, 10040–10047.
- [15] a) J. Strutwolf, M. D. Scanlon, D. W. M. Arrigan, *Analyst* **2009**, *134*, 148–158; b) Y. Shao, H. H. Girault, *J. Electroanal. Chem.* **1991**, *282*, 59–72.
- [16] E. S. Medvedev, A. A. Stuchebrukhov, *J. Phys. Condens. Matter* **2011**, *23*, 234103.
- [17] a) P. Sun, F. O. Laforge, M. V. Mirkin, *J. Am. Chem. Soc.* **2007**, *129*, 12410; b) F. O. Laforge, P. Sun, M. V. Mirkin, *J. Am. Chem. Soc.* **2006**, *128*, 15019–15025.
- [18] a) C. Wakai, A. Oleinikova, M. Ott, H. Weingartner, *J. Phys. Chem. B* **2005**, *109*, 17028–17030; b) C. Daguenet, P. J. Dyson, I. Krossing, A. Oleinikova, J. Slattery, C. Wakai, H. Weingartner, *J. Phys. Chem. B* **2006**, *110*, 12682–12688.
- [19] H. Jensen, D. J. Fermin, J. E. Moser, H. H. Girault, *J. Phys. Chem. B* **2002**, *106*, 10908–10914.
- [20] A. A. Kornyshev, *J. Phys. Chem. B* **2007**, *111*, 5545–5557.
- [21] M. S. Kilic, M. Z. Bazant, A. Ajdari, *Phys. Rev. E* **2007**, *75*, 021502.
- [22] H. Yining, H. Shanghui, Y. Tianying, *J. Phys. Condens. Matter* **2014**, *26*, 284103.
- [23] a) M. V. Fedorov, N. Georgi, A. A. Kornyshev, *Electrochem. Commun.* **2010**, *12*, 296–299; b) N. Georgi, A. A. Kornyshev, M. V. Fedorov, *J. Electroanal. Chem.* **2010**, *649*, 261–267.
- [24] a) P. Choi, N. H. Jalani, R. Datta, *J. Electrochem. Soc.* **2005**, *152*, E123–E130; b) Y. Marcus, *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 2995–2999.
- [25] M. S. Frant, J. W. Ross, *Science* **1966**, *154*, 1553–1555.
- [26] Y. Meng, L. Aldous, R. G. Compton, *J. Phys. Chem. C* **2011**, *115*, 14334–14340.
- [27] D. S. Silvester, K. Ward, L. Aldous, C. Hardacre, R. G. Compton, *J. Electroanal. Chem.* **2008**, *618*, 53–60.

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