Supporting Information for:

Experimental Insight into the Thermodynamics of the Dissolution of Electrolytes in Room-Temperature Ionic Liquids: From the Mass Action Law to the Absolute Standard Chemical Potential of a Proton

Yasuo Matsubara,*† David C. Grills*‡, Yoshihiro Koide†

†Department of Material and Life Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan
‡Chemistry Division, Brookhaven National Laboratory, P.O. Box 5000, Upton, NY 11973-5000, United States

To whom correspondence should be addressed.
Email: ft101936fb@kanagawa-u.ac.jp (Y.M.); dcgrills@bnl.gov (D.C.G.)

Contents

A. Calorimetric measurement on mixing two IL solutions ........................................... S2
B. Estimation of Gibbs energy change upon transfer of “Ag” from [emim][NTf₂]............ S3
C. Control experiment for estimation of a diffusion potential difference ..................... S6
D. The intrinsic standard Gibbs transfer energy of H⁺ from CH₃CN to [emim][NTf₂]........ S7
E. Potential differences of electrochemical cells at high temperatures ........................ S9
F. Derivation of transfer energies of “pseudo-single” ions .......................................... S12
G. Estimation of conditional liquid junction potential differences ............................... S15
H. Derivations of Eqs S10 and 17 ................................................................................ S18
I. Conversion of potentials at different standard states ............................................... S20
J. Complete versions of references 7, 49, and 102 in the main text ............................. S22
K. Supporting information references ......................................................................... S23

http://dx.doi.org/10.1021/acsomega.6b00129
A. Calorimetric measurement upon mixing two IL solutions containing TP$^+$NTf$_2^-$ and emim$^+$TB$^-$, respectively

Figure S1. Heats (●) produced upon titration (40 μL aliquots) of a TP$^+$NTf$_2^-$ solution (20 mM in [emim$^+$][NTf$_2^-$]) into an emim$^+$TB$^-$ solution (2.0 mM in [emim$^+$][NTf$_2^-$]) at 25.00 °C. The negative values indicate that this titration was exothermic. Heats (○) produced upon titration (40 μL aliquots) of [emim$^+$][NTf$_2^-$] with a TP$^+$NTf$_2^-$ solution (20 mM in [emim$^+$][NTf$_2^-$]), i.e., a simple dilution of the TP$^+$ solution. Frictional heats (□) produced upon mixing of [emim$^+$][NTf$_2^-$] (40 μL aliquots) in a syringe with [emim$^+$][NTf$_2^-$] in the reaction cell are also shown at positions of the horizontal axis corresponding to volumes of the TP$^+$ solution added.

http://dx.doi.org/10.1021/acsomega.6b00129
B. Estimation of the Gibbs energy change upon transfer of a silver cation from [emim$^+$][NTf$_2^-$] IL to a neutral molecular solvent denoted by “S”

\[
\text{Ag} | \text{AgNTf}_2 \text{(IL, ca. 1 mM)} | \text{AgNTf}_2 \text{ (IL)}^+ \text{emim$^+$TB$^-$(IL)} | \text{Ag} \quad \text{(Cell S1)}
\]

Determination of the Gibbs transfer energies of TP$^+$ and TB$^-$ as pseudo-single ions enabled us to measure the Gibbs transfer energy of Ag$^+$ that we used as a probe for the activity measurement. The Gibbs transfer energies of Ag$^+$ as a probe cation from various common solvents to [emim$^+$][NTf$_2^-$] were deduced by measuring the solubility of Ag$^+$TB$^-$ in [emim$^+$][NTf$_2^-$] together with its solubility in a solvent reported previously. Figure S2 shows a potentiometric titration of a solution of Ag$^+$NTf$_2^-$ in [emim$^+$][NTf$_2^-$] with a solution of emim$^+$TB$^-$ in [emim$^+$][NTf$_2^-$] as the titrant by using a cell as shown in Cell S1. Least squares-fitting of the theoretical response curve based on the Nernst equation (Eq 9 in the main text), and an equilibrium (Eq S1) where $K_{sp}(\text{AgTB})$ is defined by Eq S2, to this titration curve yielded a $pK_{sp}$ of 12.4±0.2. As mentioned in the main text, the Ag$^+$ cation exists in the form of a complex, i.e., [emim$^+$][Ag(NTf$_2$)$_2$] in [emim$^+$][NTf$_2^-$], and therefore, this transfer energy reflects a transfer reaction as shown in Eq S3. In combination with the $pK_{sp}$ in methanol (Table 1 in the main text), the Gibbs transfer energy of Ag$^+$ from [emim$^+$][NTf$_2^-$] to methanol was determined to be $-0.3\pm3.0$ kJ/mol (Eq S4, where “M” denotes methanol; a detailed derivation of Eq S4 is shown in Scheme S1 based on a thermodynamic cycle). In the same manner, the Gibbs transfer energies of Ag$^+$ from [emim$^+$][NTf$_2^-$] to acetonitrile and water were determined to be $-31.5\pm3.0$ and $-7.4\pm3.0$ kJ/mol by using Gibbs transfer energies of Ag$^+$ from methanol to water and from water to acetonitrile ($-7.1$ and $-24.1$ kJ/mol, respectively; see Table 2 in the main text).
\[
\text{AgTB}_\text{(s)} + 2 \text{[emim}^+\text{][NTf}_2^-\text{]}_{\text{IL, x}} \xrightarrow{K_{\text{sp} \text{[AgTB]}}^{\text{IL}}} \text{[emim}^+\text{][Ag(NTf}_2^-\text{)}_2\text{]}_{\text{IL}} + \text{[emim}^+\text{][TB}^-\text{]}_{\text{IL}} \quad (S1)
\]

\[
K_{\text{sp} \text{[AgTB]}}^{\text{IL}} = \frac{C(\text{[emim}^+\text{][Ag(NTf}_2^-\text{)}_2\text{]}_{\text{IL}})C(\text{[emim}^+\text{][TB}^-\text{]}_{\text{IL}})}{x_{\text{IL}}^2} \quad (S2)
\]

\[
\text{[emim}^+\text{][Ag(NTf}_2^-\text{)}_2\text{]}_{\text{IL}} - \text{[emim}^+\text{][NTf}_2^-\text{]}_{\text{IL, x}} - \text{[NTf}_2^-\text{]}_{\text{IL, x}} \xrightarrow{\Delta_{\text{tr}}^{\text{IL} \rightarrow \text{M} \text{G}^{\circ}(\text{Ag})}} \text{Ag}^+\text{(M)} \quad (S3)
\]

\[
\Delta_{\text{tr}}^{\text{IL} \rightarrow \text{M} \text{G}^{\circ}(\text{Ag})} = \Delta_{\text{tr}}^{\text{IL} \rightarrow \text{M} \text{G}^{\circ}(\text{AgTB})} - \Delta_{\text{tr}}^{\text{IL} \rightarrow \text{M} \text{G}^{\circ}(\text{TB}^-)} \quad (S4)
\]

Figure S2. Potentiometric titration of a Ag\(^{+}\)NTf\(^{-}\) solution (0.97 mM in [emim\(^{+}\)][NTf\(^{-}\)], 1.05 mL) with a emim\(^{-}\)TB\(^{-}\) solution (0.96 mM in [emim\(^{+}\)][NTf\(^{-}\)], 2.00 mL) at 25±1°C under N\(_2\) atmosphere in the dark. The potential was measured by using a Ag wire vs a AgNTf\(_2\)/Ag electrode (\(C_0(\text{AgNTf}_2)\) is ca.1 mM in [emim\(^{+}\)][NTf\(^{-}\)] and then converted to the values vs the half-wave electrode potential of Fe\(^{3+}/\text{Fc}\) in [emim\(^{+}\)][NTf\(^{-}\)]. A theoretical response curve based on Eq 9 (in the main text) and Eq S2 is also shown by a red line where precipitation of Ag\(^{+}\)TB\(^{-}\) (Eq S1) was assumed to take place during the titration.

http://dx.doi.org/10.1021/acsomega.6b00129
Scheme S1. A thermodynamic cycle to derive Eq S4 on the molarity scale, unless otherwise noted by “x”, which refers to the mole fraction scale. Emim$^+$NTf$_2^-$ is denoted by “IL”, the molecular solvent is denoted by “sol”, and species in the solid state are denoted by “s”.

\[
\begin{align*}
\text{emim}^+\text{Ag(NTf}_2^-\text{)}_2^{(l,l)} & \rightarrow \text{Ag}^+_{(s,1)} \quad \Delta_{\text{tr} \rightarrow \text{sol}} G^o \\
\text{emim}^+\text{TB}^{(l,l)} - \text{emim}^+_{(l,x=1)} & \rightarrow \text{TB}^-_{(s,1)} \quad \Delta_{\text{tr} \rightarrow \text{sol}} G^o\text{(TB)} \\
\text{AgTB}_{(s,x=1)} + 2\text{emim}^+\text{NTf}_2^-_{(l,l)} & \rightarrow \text{emim}^+\text{Ag(NTf}_2^-\text{)}_2^{(l,l)} \quad 2.303RTpK_{sp}^{ll}(\text{AgTB}) \\
\text{emim}^+\text{NTf}_2^-_{(l,l)} & \rightarrow \text{emim}^+_{(l,x=1)} + \text{NTf}_2^-_{(l,l)} \quad 0 \quad \text{(Eq 4d)}
\end{align*}
\]
C. Control experiment for estimation of the diffusion potential difference developed in a sintered glass frit separating two IL solutions

|        | AgNTf₂ (30.5 mM) in IL ($\chi_{\text{IL}} = 0.984$) | AgNTf₂ (25.3 mM) + Bu₄N⁺NTf₂⁻ (418 mM) in IL ($\chi_{\text{IL}} = 0.871$) | Ag (Cell S2) |
|--------|--------------------------------------------------|-------------------------------------------------|-------------|

To estimate the diffusion potential difference developed by mutual diffusion of constituent ions in two IL ([emim⁺][NTf₂⁻]) solutions separated by a sintered glass frit with a porosity of 5 μm, the electrochemical cell shown in Cell S2 was constructed, where a high concentration (418 mM) of an NTf₂⁻ salt of tetrabutylammonium (Bu₄N⁺) was employed in the right hand side of the cell and the liquid junction was formed by the glass frit. The potential difference of the cell was measured as −0.5 mV (referring to the left hand side of the cell) at 25±1°C. This value is in good agreement with −1.4 mV calculated by Eq 9 in the main text with the experimental concentration and mole ratio of AgNTf₂ and the IL, respectively, indicating that the diffusion potential difference can be up to 1 mV, which is roughly estimated by the Henderson equation.
D. The intrinsic standard Gibbs transfer energy of a proton from acetonitrile to [emim$^+$][NTf$_2^-$] IL

$$H^+_{(CH_3CN)} \rightarrow [emim^+][H(NTf_2)_2]_{(IL)} - [emim^+][NTf_2^-]_{(IL,s)} - [NTf_2^-]_{(IL,s)}$$  \hspace{1cm} (S5)

The intrinsic standard Gibbs transfer energy of a proton from acetonitrile to [emim$^+$][NTf$_2^-$] IL can be estimated to be $-8.0 \pm 3.3$ kJ/mol (Eq S5) from the standard Gibbs energy change for the reaction shown in Eq S6 because the Gibbs energy changes of formation of dihydrogen in the IL and acetonitrile at the standard state of 1 bar are defined to be equal.

$$H^+_{(CH_3CN)} + \frac{1}{2}H_{(2g,bar)} + [emim^+][NTf_2^-]_{(IL,s)} + [NTf_2^-]_{(IL,s)}$$

$$\rightarrow [emim^+][H(NTf_2)_2]_{(IL)} + \frac{1}{2}H_{(2g,bar)} + [emim^+][NTf_2^-]_{(IL,s)} + [NTf_2^-]_{(IL,s)}$$  \hspace{1cm} (S6)

Eq S6 consists of two electrode reactions (Eqs S7 and S8). For Eq S7, the standard electrode potential is estimated to be $-26 \pm 2$ mV vs the formal electrode potential of Fe$^+/Fe$ in acetonitrile at $I = 0.10$ M, which is calculated from the standard electrode potential of H$^+/0.5H_2$ ($-44 \pm 2$ mV) vs the standard electrode potential of Fe$^+/Fe$, both in acetonitrile at zero ionic strength, and a correction.$^1$ For Eq S8, the standard electrode potential is calculated to be $+7 \pm 5$ mV vs Fe$^+/Fe$ in the IL at the standard states of 1 bar of gases and 1 M solute, as described in the main text and section I of the Supporting Information.

$$H^+_{(CH_3CN)} + e^- \rightleftharpoons \frac{1}{2}H_{(2g,bar)}$$  \hspace{1cm} (S7)

$$[emim^+][H(NTf_2)_2]_{(IL)} + e^- \rightleftharpoons \frac{1}{2}H_{(2g,bar)} + [emim^+][NTf_2^-]_{(IL,s)} + [NTf_2^-]_{(IL,s)}$$  \hspace{1cm} (S8)

$^1$ The standard electrode potentials of Fe$^+/Fe$ and H$^+/0.5H_2$ in acetonitrile were reported to be +74 and +30 mV vs a Ag$^+/Ag$ electrode, respectively, by Kolthoff and Thomas (Kolthoff, I. M. et al. J. Phys. Chem. 1965, 69, 3049-3058). The formal electrode potential of Fe$^+/Fe$ depends on the ionic strength of the tested solution, and its dependence was also reported in their work, from which the extent of the correction is calculated to be +18.2 mV from zero ionic strength to $I = 0.10$ M at 25 °C, since the potentials at zero ionic strength and $I = 0.10$ M were reported as 344.2 and 326.0 mV vs SCE, respectively. Note that the positive sign for +18.2 mV is due to a correction for the potential (Fe$^+/Fe$) referenced by the potential of interest (H$^+/0.5H_2$).

http://dx.doi.org/10.1021/acsomega.6b00129
Finally, the transfer energy (−8.8±3.3 kJ/mol) is obtained by a correction of the potential difference (−124±33 mV) between these two electrode reactions (Fc⁺/Fc) as clarified in Cell 3b and Cell 4 (in the main text). A diagram for the calculation procedure above is shown in Scheme S2, which also includes a relationship to the potential of SHE as described in the main text.

**Scheme S2.** A potential diagram (in units of mV) for the calculation procedure in Section D
E. Potential differences of electrochemical cells (Cell S3) at high temperatures

Following the potential difference measurements in [emim⁺][NTf₂⁻] at 25±1°C, we conducted a series of measurements in ILs having the same and longer alkyl chains in the imidazolium ring by using Cell S3 at higher temperatures, where \( c_1 \) of FcNTf₂ was a molar concentration typically in the range from 20 to 800 mM, and \( c_2 \) was the molar concentration of ferrocene, typically in the range from 15 to 10 mM.

![Figure S3. Dependence of the potential of a Fc⁺/Fc redox couple at a Pt electrode in an IL (1-ethyl-3-methylimidazolium, [emim⁺][NTf₂⁻]) on a function of the concentration of Fc⁺NTf₂⁻ in the IL at 39±1 °C under a N₂ atmosphere. The potential was measured by using an electrochemical cell (Cell S3) consisting of the IL solution vs a Ag⁺/Ag electrode in the IL \((C_0(\text{Ag}^+\text{NTf}_2^-) \approx 1 \text{ mM})\), with the electrode isolated by a sintered glass frit with a porosity of 5 μm, and then converted to values versus the standard electrode potential of Fc⁺/Fc in the IL at the same temperature, which was determined by the method described in the Experimental Section. The effect of the thermal junction on the potential was corrected. The red line indicates a linear correlation between the potential and the function, i.e., \(\ln\left(\frac{C[\text{Fc}^+\text{NTf}_2^-]}{C(\text{Fc}) \times x_{\text{IL}}}\right)\), where \(C = \text{concentration}\), acquired by a linear least squares fitting method.](http://dx.doi.org/10.1021/acsomega.6b00129)
Figure S4. Dependence of the potential of a Fc⁺/Fc redox couple at a Pt electrode in an IL (1-butyl-3-methylimidazolium, [bmim][NTf₂⁻]) on a function of the concentration of Fc⁺NTf₂⁻ in the IL at (a) 25±1 °C and (b) 39±1 °C under a N₂ atmosphere. The potential was measured by using an electrochemical cell (Cell S3) consisting of the IL solution vs a Ag⁺/Ag electrode in the IL (C₀(Ag⁺NTf₂⁻) ≈ 1 mM, with the electrode isolated by a sintered glass frit with a porosity of 5 μm), and then converted to values versus (a) the standard electrode potential of Fc⁺/Fc in the IL at 25±1 °C, which was determined by the method described in the Experimental Section, and (b) the half-wave potential of Fc⁺/Fc in the IL at 39±1 °C. The effect of the thermal junction on the potential was corrected. The red lines indicate linear correlations between the potentials and the functions, i.e., ln(C([Fc⁺][NTf₂⁻]) / (C(Fc) × xIL)), where C = (concentration), acquired by a linear least squares fitting method.
Figure S5. Dependence of the potential of a Fc⁺/Fc redox couple at a Pt electrode in an IL (1-octyl-3-methylimidazolium, [omim⁺][NTf₂⁻]) on a function of the concentration of Fc⁺NTf₂⁻ in the IL at (a) 25±1 °C and (b) 67±1 °C under a N₂ atmosphere. The potential was measured by using an electrochemical cell (Cell S3) consisting of the IL solution vs a Ag⁺/Ag electrode in the IL ($C_0(\text{Ag}^+\text{NTf}_2^-) \approx 1 \text{ mM}$, with the electrode isolated by a sintered glass frit with a porosity of 5μm), and then converted to values versus (a) the half-wave potential of Fc⁺/Fc in the IL at 25±1 °C, and (b) the half-wave potential of Fc⁺/Fc in the IL at 67±1 °C. The effect of the thermal junction on the potential was corrected. The red lines indicate linear correlations between the potentials and the functions, i.e., $\ln(C([\text{Fc}^+][\text{NTf}_2^-]) / (C(\text{Fc}) \times x_{\text{IL}}))$, where $C = \text{(concentration)}$, acquired by a linear least squares fitting method.
F. Derivation of transfer energies of “pseudo-single” ions

The necessity to define a “pseudo-single” ion is highlighted when two interesting salts, TP⁺NTf₂⁻ and emim⁺TB⁻, that contain anionic and cationic constituents of the IL, respectively, are dissolved into the IL yielding only [TP⁺][NTf₂⁻] and [emim⁺][TB⁻] in the IL as shown in Eqs S9a and S9b, for which values of pK_{sp} were calculated to be 1.04 and 1.36, respectively (see Table 1 in the main text).

\[
\begin{align*}
\text{TP}^+ \text{NTf}_2^- & \rightleftharpoons [\text{TP}^+][\text{NTf}_2^-]_{\text{IL}} \\
\text{emim}^+ \text{TB}^- & \rightleftharpoons [\text{emim}^+][\text{TB}^-]_{\text{IL}}
\end{align*}
\]

(S9a) (S9b)

In fact, we have confirmed that titration of an [emim⁺][NTf₂⁻] solution of TP⁺NTf₂⁻ to an [emim⁺][NTf₂⁻] solution of emim⁺TB⁻ did not produce any heat (or <0.1 kJ/mol) other than frictional heat upon mixing of the two solutions. This pure entropic mixing indicates that there is no enthalpic interaction between TP⁺ and TB⁻ (see Figure S1).

This situation is different from that in a molecular solvent of high permittivity where each ionic constituent of a salt is completely solvated by the solvent molecules. It is also different from molecular solvents with low permittivity where, due to the absence of a salt as a solvent, it is theoretically possible to reach the thermodynamic properties at infinite dilution. Meanwhile, in an IL, it is theoretically impossible to reach the thermodynamic properties of TP⁺ (or TB⁻) as a single ion by infinite dilution unless the (thermodynamically-virtual) ion dissociation energies of these species (TP⁺NTf₂⁻ or emim⁺TB⁻) are known. However, an estimation of the Gibbs

---

ii Conceptually, it is possible to define a dissociation energy that determines the concentration of "free" ions, by treating ILs as a traditional electrolyte solution (see Israelachvili, J. N. et al. *PNAS* 2015, *112*, 7432-7437). Although this solution model is attractive to explain our results, there has been some controversy in the literature over such an electrolyte solution model and, therefore, this problem has been discussed as a central matter in the ionics of ILs (see Fedorov, M. V. and Kornyshev, A. A. *Chem. Rev.* 2014, *114*, 2978-3036 and references therein).

http://dx.doi.org/10.1021/acsomega.6b00129
transfer energies of single ions is still possible as shown below when the transfer energies of so-called pseudo-single ions are considered.

The transfer reaction of TP’TB⁻ from [emim⁺][NTf₂⁻] IL to a neutral molecular solvent (sol) can be represented by Eq S9c.\textsuperscript{iii}

\[ [\text{TP}^+] [\text{NTf}_2^-](\text{IL}) + [\text{emim}^+][\text{TB}^-](\text{IL}) \rightarrow \text{TP}^+_{(\text{sol})} + \text{TB}^-_{(\text{sol})} + \text{NTf}_2^-_{(\text{IL, x})} + \text{emim}^+_{(\text{IL, x})} \] (S9c)

Accordingly, the Gibbs energy change of this transfer is formulated by using chemical potentials as shown in Eq S9d, where Eq 4d (in the main text) has been applied for [emim⁺][NTf₂⁻]. Thus, the transfer energy was calculated to be +23.4 kJ/mol when “sol” is methanol, by using values tabulated in Table 1 and Scheme 1 in the main text.

\[
\Delta_{\text{tr}}^{\text{IL-sol}} G^O(\text{TP}^+\text{TB}^-) = (\mu_{\text{TP}^+}^{\text{sol}} + \mu_{\text{TB}^-}^{\text{sol}} + \mu_{\text{NTf}_2^-}^{\text{IL, x}} + \mu_{\text{emim}^+}^{\text{IL, x}}) - \left(\mu_{\text{TP}^+}^{\text{IL}} + \mu_{\text{TB}^-}^{\text{IL}} + \mu_{\text{NTf}_2^-}^{\text{IL}} + \mu_{\text{emim}^+}^{\text{IL}}\right) \\
= \mu_{\text{TP}^+}^{\text{sol}} + \mu_{\text{TB}^-}^{\text{sol}} - \mu_{\text{TP}^+\text{TB}^-}^{\text{IL}} \\
- \left\{ \left(\mu_{\text{TP}^+}^{\text{IL}} + \mu_{\text{NTf}_2^-}^{\text{IL}}\right) + \left(\mu_{\text{emim}^+}^{\text{IL}} + \mu_{\text{emim}^+}^{\text{IL}}\right) \right\} \\
= 2.303RTpK_{\text{sp}}^{\text{sol}} - \left\{ 2.303RTpK_{\text{sp}}^{\text{IL}} + \left(\mu_{\text{emim}^+}^{\text{IL}} + \mu_{\text{emim}^+}^{\text{IL}}\right) \right\} \\
= +23.4 \text{ kJ/mol}
\] (S9d)

When the terms relating to the IL phase are bundled together as shown in Eq S9e, the Gibbs energy changes for the transfer reactions (Eqs S9f and S9g) of so-called pseudo-single ions can be defined as shown in Eqs S9h and S9i (analogous to Eqs 13c and 13d in the main text). One can then treat the Gibbs energy change for the transfer of TP’TB⁻ from the IL to a conventional neutral molecular solvent as the sum of Eqs S9h and S9i (i.e., Eq S9j), in the same way that it is treated for the transfer between two conventional neutral molecular solvents (Eq 13e in the main text).

\[ A\text{ transfer reaction represented by } [\text{TP}^+] [\text{NTf}_2^-](\text{IL}) + [\text{emim}^+][\text{TB}^-](\text{IL}) \rightarrow \text{TP}^+_{(\text{sol})} + \text{TB}^-_{(\text{sol})} + \text{NTf}_2^-_{(\text{sol})} + \text{emim}^+_{(\text{sol})} \text{ is also possible. However, experimentally, this is not appropriate when it comes to discussing “single-ion transfer” unless the Gibbs formation energy of either NTf}_2^-_{(sol)} or emim}^+_{(sol)} \text{ which are usually difficult to obtain) is known.}

http://dx.doi.org/10.1021/acsomega.6b00129
\[ \Delta_{\text{tr}}^{\text{IL} \rightarrow \text{sol}} \Omega(G^\circ(TP^+TB^-)) \equiv (\mu_{\text{TP}^+}^{\text{sol}} + \mu_{\text{TB}^-}^{\text{sol}}) - (\mu_{\text{TP}^+}^{\text{IL}} - \mu_{\text{TB}^-}^{\text{IL}}) = (\mu_{[\text{TP}^+][\text{NTf}_2^-]}^{\text{IL}} - \mu_{[\text{NTf}_2^-]}^{\text{IL}} + \mu_{[\text{emim}^+][TB^-]}^{\text{IL}} - \mu_{[\text{emim}^+]}^{\text{IL}}) \]  

(S9e)

\[ [\text{TP}^+][\text{NTf}_2^-]_{(\text{IL})} - [\text{NTf}_2^-]_{(\text{IL},x)} \rightarrow \text{TP}^+ \quad (\text{sol}) \]  

(S9f)

\[ [\text{emim}^+][\text{TB}^-]_{(\text{IL})} - [\text{emim}^+]_{(\text{IL},x)} \rightarrow \text{TB}^- \quad (\text{sol}) \]  

(S9g)

\[ \Delta_{\text{tr}}^{\text{IL} \rightarrow \text{sol}} \Omega(G^\circ(\text{TP}^+)) \equiv \mu_{\text{TP}}^{\text{IL}} - (\mu_{\text{TP}^+}^{\text{IL}} - \mu_{\text{[NTf}_2^-]}^{\text{IL}}) \]  

(S9h)

\[ \Delta_{\text{tr}}^{\text{IL} \rightarrow \text{sol}} \Omega(G^\circ(\text{TB}^-)) \equiv \mu_{\text{TB}}^{\text{IL}} - (\mu_{\text{[emim}^+][TB^-]}^{\text{IL}} - \mu_{\text{[emim}^+]^{\text{IL}}) \]  

(S9i)

\[ \Delta_{\text{tr}}^{\text{IL} \rightarrow \text{sol}} \Omega(G^\circ(\text{TP}^+TB^-)) = \Delta_{\text{tr}}^{\text{IL} \rightarrow \text{sol}} \Omega(G^\circ(\text{TP}^+)) + \Delta_{\text{tr}}^{\text{IL} \rightarrow \text{sol}} \Omega(G^\circ(\text{TB}^-)) \]  

(S9j)
G. Estimation of conditional liquid junction potential differences ($\Delta_{LJ}E$)

In order to estimate $\Delta_{LJ}E$, the electrochemical cells shown in Cells S4a and S4b ("IL" denotes [emim$^+$][NTf$_2^-$], “sol” denotes methanol or acetonitrile as a solvent in Cell S4a, and “aq” denotes water as a solvent in Cell S4b)$^\text{iv}$ were constructed, where the liquid junction was formed by a Vycor glass frit. The potential differences of the cells ($E_{\text{Cell S4a}}$ and $E_{\text{Cell S4b}}$) were measured as $-152\pm10$ and $-431\pm5$ mV at $25\pm1^\circ\mathrm{C}$ for Cell S4a where “sol” was methanol and acetonitrile, respectively, and $-596\pm5$ mV at $25\pm1^\circ\mathrm{C}$ for Cell S4b. By the addition of $+564$ mV for the standard electrode potential of Ag$^+/\text{Ag}$ in water ($+0.799$ V vs SHE$^2$) referring to the electrode potential of Ag/AgCl ($+0.235$ V vs SHE$^3$) when [KCl] = 1.00 M, the potential difference of Cell S4b was converted to $-32$ mV for Cell S4c with a silver electrode, with Ag$^+$ at unit activity.

$^\text{iv}$ Typically, an electrochemical cell is composed of multiple phases in series forming interfaces where junction potential differences that are developed or eliminated (or are negligible) are denoted by “|” or “||”, respectively. Silver metal at both ends is used for potential difference measurements referring to the left hand side as a reference potential.

$^\text{v}$ When a sintered glass disc with a porosity of 5 $\mu$m was used as the frit material in Cell S4a (Cell 2a in the main text) and Cell S4b (Cell 2b in the main text), the potential differences of the cells were measured as $-444$ mV for Cell S4a using acetonitrile as “sol”, and $-602$ mV for Cell S4b. Although these values are different from those measured when a Vycor glass frit was used, our conclusions are not affected by this difference as long as the potential differences developed in a frit made of the same material are measured throughout our discussion.

http://dx.doi.org/10.1021/acsomega.6b00129
The potential difference can be expressed by Eq S10 where, in the right hand side, the first term contains the activities of “Ag\(^{+}\)” in [emim\(^{+}\)][NTf\(_{2}^{-}\)] (denoted by “IL”) and “sol”, the second term is the Gibbs transfer energy of Ag\(^{+}\) from IL to “sol”, as reported in Table 2 (in the main text), and the third term contains the conditional liquid junction potential difference, \(\Delta_{LJ}E\), which is ideally equal to the inner potential difference at the interface between [emim\(^{+}\)][NTf\(_{2}^{-}\)] and “sol”, but on a practical level, additionally contains a potential difference caused by diffusion of Et\(_4\)N\(^{+}\)ClO\(_4^{-}\) as a spectator electrolyte at the interface\(^{vi}\) (a detailed derivation of Eq S10 is provided in Scheme S3 based on a thermodynamic cycle). The activity of “Ag\(^{+}\)” in the IL was calculated to be 1.0 \times 10^{-2} by using Eq 9 (in the main text). The activity of Ag\(^{+}\) in both methanol and acetonitrile was calculated to be 3.6 \times 10^{-3} by using Eq S11a, where \(\gamma_\pm\) is the mean activity coefficient of Ag\(^{+}\), \(C_0\) is the analytical concentration of AgNO\(_3\) (10 mM in both methanol and acetonitrile), and \(\alpha\) is the degree of dissociation of AgNO\(_3\) to Ag\(^{+}\) and NO\(_3^{-}\) in methanol and acetonitrile, of which the permittivities are moderate. In Eq S11a, values of \(\gamma_\pm\) were estimated to be 0.40 and 0.39 in methanol and acetonitrile, respectively, by using the Davies equation\(^5\) (Eq S11b), which is one of the extended Debye-Hückel equations, where \(I\) is the ionic strength (0.10 M), \(\varepsilon_r\) is the relative permittivity (32.6 and 37.5 for methanol and acetonitrile, respectively), and \(T\) is the temperature (298.15 K). Values of \(\alpha\) were calculated to be 0.90 and 0.91 in methanol and acetonitrile, respectively by using Eq S11c,\(^6\) where \(K_A\) is the association constant of AgNO\(_3\) (78 and 71 M\(^{-1}\),\(^7\) respectively). The activity of Ag\(^{+}\) in water for Cell S4c is defined to be unity. Thus, 

\(^{vi}\) Strictly speaking, there is one more region where a spectator electrolyte in “sol” and constituent ions of the IL diffuse to outer Helmholtz planes on the silver metal from the bulk. Potential differences caused by this diffusion are also involved in the conditional liquid junction potential difference estimated in this study, which is a practical quantity determined by the particular experimental conditions.
using the activities discussed above and the transfer energies listed in Table 2, values of $\Delta_{\text{LJ}}E$

were calculated from Eq S10 and reported in the main text.

$$
-FE = RT \ln \frac{a_{\text{II}}^{\text{IL}}(\text{Ag}^+)}{a_{\text{sol}}^{\text{IL}}(\text{Ag}^+)} - \Delta_{\text{II} \rightarrow \text{sol}}^{\text{IL}} G^0(\text{Ag}^+) - F \Delta_{\text{LJ}}^{\text{II} \rightarrow \text{sol}} E
$$

(S10)

$$
\ln a_{\text{sol}}^{\text{IL}}(\text{Ag}^+) = \ln (\gamma_+ C_0 \alpha)
$$

(S11a)

$$
\ln \gamma_+ \equiv -\frac{4.198 \times 10^6}{(\varepsilon_i T)^{3/2}} \left[ \frac{\sqrt{I}}{1 + \sqrt{I}} - \frac{1}{3} \right]
$$

(S11b)

$$
\alpha \equiv \frac{-1 + (1 + 4K_A \gamma_+^2 C_0)^{1/2}}{2K_A \gamma_+^2 C_0}
$$

(S11c)
H. Derivations of Eqs S10 and 17

| Ag | emim$^+$Ag(NTf$_2$)$_2$ (a$_1$) in IL (x$_1$) | Ag$^+$ (a$_2$) in sol | Ag | (Cell S5) |
|----|-------------------------------------|-----------------------|----|----------------|

Potential differences developed in Cells S4a-c are comprised of activity terms of the silver cation ($a_1$ and $a_2$), the standard Gibbs transfer energy of silver cation ($\Delta_{It} G^\circ$), and a conditional liquid junction potential difference ($\Delta_{LJ} E$) as expressed by Eq S10. When Cells S4a-c are generalized to a form of Cell S5, where $a$ denotes the activity (in the molarity scale) of the species indicated and $x$ denotes the mole fraction of the species indicated, Eq S10 is derived by using a thermodynamic cycle as shown Scheme S3 where $\phi_{\text{sol}}$ and $\phi_{\text{IL}}$ denote inner (Galvani) potentials of the molecular solvent and the IL as media, respectively, so that Ag$^+$ (sol at $\phi_{\text{IL}}, 1$) denotes silver cation with unit activity solvated in “sol” at an inner potential of $\phi_{\text{IL}}$, for example.

**Scheme S3.** A thermodynamic cycle to derive Eq S10 on the molarity scale, unless otherwise noted by “$x$”, which refers to the mole fraction scale. Emim$^+$NTf$_2^-$ is denoted by “IL” and the molecular solvent is denoted by “sol”.

\[
\begin{align*}
\text{Ag}^+_{(\text{sol at } \phi_{\text{sol}}, a_2)} & + \text{emim}^+\text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) + \text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) \rightarrow \text{emim}^+\text{Ag(NTf}_2^-)_{2(\text{IL at } \phi_{\text{IL}}, a_1)} - F E_{\text{Cell S5}} \\
\text{emim}^+\text{Ag(NTf}_2^-)_{2(\text{IL at } \phi_{\text{IL}}, x_1)} + e^- & \rightarrow \text{emim}^+\text{Ag(NTf}_2^-)_{2(\text{IL at } \phi_{\text{IL}}, x_1)} + \text{emim}^+\text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) + \text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) - F E_1 \\
\text{emim}^+\text{Ag(NTf}_2^-)_{2(\text{IL at } \phi_{\text{IL}}, x_1)} - \text{emim}^+\text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) - \text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) & \rightarrow \text{emim}^+\text{Ag(NTf}_2^-)_{2(\text{IL at } \phi_{\text{IL}}, x_1)} - \text{emim}^+\text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) - \text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) - RT \ln a_1 \\
\text{emim}^+\text{Ag(NTf}_2^-)_{2(\text{IL at } \phi_{\text{IL}}, x_1)} - \text{emim}^+\text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) - \text{NTf}_2^- (\text{IL at } \phi_{\text{IL}}, x_1) & \rightarrow \text{Ag}^+_{(\text{sol at } \phi_{\text{IL}}, 1)} - \text{rt}_{\text{sol}} G^\circ \\
\text{Ag}^+_{(\text{sol at } \phi_{\text{sol}}, 1)} & \rightarrow \text{Ag}^+_{(\text{sol at } \phi_{\text{sol}}, 1)} - F \Delta_{LJ}^{\text{IL} \rightarrow \text{sol}} E \\
\text{Ag}^+_{(\text{sol at } \phi_{\text{sol}}, 1)} & \rightarrow \text{Ag}^+_{(\text{sol at } \phi_{\text{sol}}, a_2)} - RT \ln a_2
\end{align*}
\]

http://dx.doi.org/10.1021/acsomega.6b00129
Scheme S4. A thermodynamic cycle to derive Eq 17 in the main text on the molarity scale, unless otherwise noted by “x”, which refers to the mole fraction scale. Emim”NTf$_2^-$ is denoted by “IL” and the molecular solvent is denoted by “sol”. The potential difference of Cell 3a, $E_{\text{Cell 3a}}$ is defined as the difference between $E_1$ and $E_2$, i.e., $E_1 - E_2$.

\[
\begin{align*}
\text{Fc}^+ \text{NTf}_2^- (\text{IL at } \phi^{\text{IL}}) + \text{Ag} & \rightarrow \text{Fc} (\text{IL at } \phi^{\text{IL}}) + \text{NTf}_2^- (\text{IL at } \phi^{\text{IL}}) + \text{Ag}^+ (\text{sol at } \phi^{\text{IL}}) & -FE_{\text{Cell 3b}} \\
\text{Fc}^+ \text{NTf}_2^- (\text{IL at } \phi^{\text{IL}}) + e^- & \rightarrow \text{Fc} (\text{IL at } \phi^{\text{IL}}) + \text{NTf}_2^- (\text{IL at } \phi^{\text{IL}}) & -FE_1 \\
\text{Ag}^+ (\text{sol at } \phi^{\text{IL}}) + e^- & \rightarrow \text{Ag} & -FE_2 \\
\text{Ag}^+ (\text{sol at } \phi^{\text{IL}}) & \rightarrow \text{Ag}^+ (\text{sol at } \phi^{\text{IL}}) & F\Delta_{\text{IL} \rightarrow \text{sol}} E
\end{align*}
\]
I. Conversion of potentials at different standard states

The chemical potential, $\mu$, of hydrogen gas at a temperature, $T = 298.15$ K, and a pressure, $p$ (in bar) is defined as a function of $T$ and $p$ as shown in Eq S12, where $R$ is the gas constant, $p^o$ is defined as 1 bar, and $\varphi$ is a fugacity coefficient. In the case of hydrogen gas in [emim$^+$][NTf$_2^-$], $\varphi$ is assumed to be unity because the standard solubility (or the Henry constant) of H$_2$ gas in [emim$^+$][NTf$_2^-$] was found to be almost independent of H$_2$ pressure.$^{8,9}$

$$\mu_{H_2}(T, p) = \mu_{H_2}^o(T, p^o) + RT \ln \frac{\varphi p}{p^o}$$  \hspace{1cm} (S12)

The chemical potential of hydrogen gas at 1 M concentration ($c = 1$ M) is defined to be equal to the chemical potential of hydrogen gas at 278 bar in the gas phase, as shown in Eq S13, since the equilibrium solubility of hydrogen gas at 1 bar and 298.15 K is estimated to be 3.6 mM, as an average of two reported values (2.6$^8$ and 4.6$^{10}$ mM).

$$\mu_{H_2}(T, c = 1$ M) $= \mu_{H_2}(T, p = 278$ bar) $= \mu_{H_2}^o(T, p^o) + RT \ln \frac{278}{p^o}$$  \hspace{1cm} (S13)

Thus, the standard chemical potential of hydrogen gas at the standard state of 1 bar H$_2$ is given by Eq S14.

$$\mu_{H_2}^o(T, p^o) = \mu_{H_2}(T, p = 278$ bar) $- RT \ln \frac{278}{p^o}$$  \hspace{1cm} (S14)

Meanwhile, the standard potential of a hydrogen electrode at the standard states of 1 M H(NTf$_2$)$_2^-$ and 1 bar H$_2$ is defined by the second line of Eq S15. Substitution of the second line with Eq S14 gives the third line of Eq S15. Since the first term in the fourth line is equal to the potential of a hydrogen electrode at states of 1 M H(NTf$_2$)$_2^-$ and H$_2$, $+7$ mV vs Fe$^+/Fe$ is then obtained as the standard potential of a hydrogen electrode at the standard states of 1 M H(NTf$_2$)$_2^-$ and 1 bar H$_2$, based on the formal potential of a hydrogen electrode in [emim$^+$][NTf$_2^-$] ($-65\pm5$ mV$^{10}$ vs Fe$^+/Fc$ at the standard states of 1 M of H(NTf$_2$)$_2^-$ and H$_2$).

http://dx.doi.org/10.1021/acsomega.6b00129
\[ E^\circ (1 \text{ M H(NTf}_2)_2, 1 \text{ bar H}_2) \text{ vs. Fe}^+/\text{Fe} \]

\[ = -\frac{1}{F} \left[ \frac{1}{2} \mu_{\text{H}_2}^\circ (T, p^\circ) - \mu_{\text{H(NTf}_2)_2}^\circ (T, c^\circ = 1 \text{ M}) \right] \]

\[ = -\frac{1}{F} \left[ \frac{1}{2} \mu_{\text{H}_2}^\circ (T, p = 278 \text{ bar}) - \mu_{\text{H(NTf}_2)_2}^\circ (T, c^\circ = 1 \text{ M}) \right] + \frac{RT}{2F} \ln \frac{278}{p^\circ} \]

\[ = -\frac{1}{F} \left[ \frac{1}{2} \mu_{\text{H}_2}^\circ (T, c = 1 \text{ M}) - \mu_{\text{H(NTf}_2)_2}^\circ (T, c^\circ = 1 \text{ M}) \right] + \frac{RT}{2F} \ln \frac{278}{p^\circ} \]

\[ = \left[ E(1 \text{ M H(NTf}_2)_2, 1 \text{ M H}_2) \text{ vs. Fe}^+/\text{Fe} \right] + \frac{RT}{2F} \ln \frac{278}{p^\circ} \]

\[ = -0.065 + 0.072 \text{ V vs. Fe}^+/\text{Fe} \]

\[ = +0.007 \text{ V vs. Fe}^+/\text{Fe} \]
J. Complete versions of references 7, 49, and 102 in the main text

(7) Kobayashi, Y.; Hernandez, O. J.; Sakaguchi, T.; Yajima, T.; Roisnel, T.; Tsujimoto, Y.; Morita, M.; Noda, Y.; Mogami, Y.; Kitada, A.; Ohkura, M.; Hosokawa, S.; Li, Z.; Hayashi, K.; Kusano, Y.; Kim, J. e.; Tsuji, N.; Fujiwara, A.; Matsushita, Y.; Yoshimura, K.; Takegoshi, K.; Inoue, M.; Takano, M.; Kageyama, H. An Oxyhydride of BaTiO$_3$ Exhibiting Hydride Exchange and Electronic Conductivity. *Nat. Mater.* **2012**, *11*, 507-511.

(49) Chen, S.; Itoh, Y.; Masuda, T.; Shimizu, S.; Zhao, J.; Ma, J.; Nakamura, S.; Okuro, K.; Noguchi, H.; Uosaki, K.; Aida, T. Subnanoscale Hydrophobic Modulation of Salt Bridges in Aqueous Media. *Science* **2015**, *348*, 555-559.

(102) Deyko, A.; Lovelock, K. R. J.; Corfield, J.-A.; Taylor, A. W.; Gooden, P. N.; Villar-Garcia, I. J.; Licence, P.; Jones, R. G.; Krasovskiy, V. G.; Chernikova, E. A.; Kustov, L. M. Measuring and Predicting $\Delta_{vap}H_{298}$ Values of Ionic Liquids. *PCCP* **2009**, *11*, 8544-8555.

http://dx.doi.org/10.1021/acsomega.6b00129
K. Supporting information references

(1) Kolthoff, I. M.; Thomas, F. G. Electrode Potentials in Acetonitrile. Estimation of the Liquid Junction Potential Between Acetonitrile Solutions and the Aqueous Saturated Calomel Electrode. *J. Phys. Chem.* 1965, *69*, 3049-3058.

(2) Bratsch, S. G. Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K. *J. Phys. Chem. Ref. Data* 1989, *18*, 1-21.

(3) deBethune, A. J.; Licht, T. S.; Swendeman, N. The Temperature Coefficients of Electrode Potentials: The Isothermal and Thermal Coefficients—The Standard Ionic Entropy of Electrochemical Transport of the Hydrogen Ion. *J. Electrochem. Soc.* 1959, *106*, 616-625.

(4) Bates, R. G.; Macaskill, J. B. Standard Potential of the Silver-Silver Chloride Electrode. *Pure Appl. Chem.* 1978, *50*, 1701-1706.

(5) Davies, C. W. Activity measurements. In Ion Association; Butterworths: Washington, 1962, pp 34-54.

(6) Berne, D. H.; Popovych, O. Solubility Products of Tetrphenylarsonium and Tetrphenylphosphonium Picrates in Ethanol-Water Solvents at 25°C. *J. Chem. Eng. Data* 1972, *17*, 178-180.

(7) Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. Solvation of Ions. XVI. Solvent Activity Coefficients of Single Ions. Recommended Extrathermodynamic Assumption *J. Am. Chem. Soc.* 1972, *94*, 1148-1158.

http://dx.doi.org/10.1021/acsomega.6b00129
(8) Jacquemin, J.; Husson, P.; Majer, V.; Costa Gomes, M. F. Influence of the Cation on the Solubility of CO₂ and H₂ in Ionic Liquids Based on the Bis(trifluoromethylsulfonyl)imide Anion. *J. Sol. Chem.* **2007**, *36*, 967-979.

(9) Raeissi, S.; Schilderman, A. M.; Peters, C. J. High Pressure Phase Behaviour of Mixtures of Hydrogen and the Ionic Liquid Family [enmim][Tf₂N]. *J. Supercrit. Fluids* **2013**, *73*, 126-129.

(10) Meng, Y.; Aldous, L.; Belding, S. R.; Compton, R. G. The Hydrogen Evolution Reaction in a Room Temperature Ionic Liquid: Mechanism and Electrocatalyst Trends. *PCCP* **2012**, *14*, 5222-5228.

http://dx.doi.org/10.1021/acsomega.6b00129