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Observations of Probe Dependence in the Solvation Dynamics in Ionic Liquids

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A. Comparisons of Solvation Response Functions from the Literature

Figure S1 compares the solvation response functions of C153 and 4AP from the present work with those reported previously by different groups.[1-5] Due to the fact that the missing components of $S_\nu(t)$ are not always reported in the literature, $S_\nu(t)$ data from these groups are vertically scaled to match our results at their reported instrument response times (FWHM), which are 50 ps in the case of Samanta's group and 80 ps for Petrich's group. The experiments were taken at 293.5 K in this work, and the temperature were 298 K and 293 K in the case of Samanta's group and Petrich's group, respectively. These comparisons all show a relatively good agreement with the exception of "C153/I4B" reported by Samanta and coworkers. We do not know the source of this disagreement.

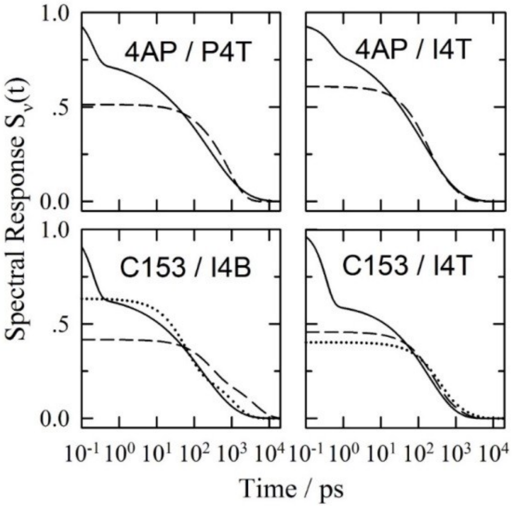

Fig.S1 Spectral response functions (eq.2) of C153 and 4AP measured by our group[1] (solid lines, measured at 293.5 K), Samanta and coworkers (dashed line, measured at 298 K)[2-4] and Petrich and coworkers (dotted lines, measured at 293 K).[5] The latter are normalized to $S_\nu(t)$ obtained by us at t=50 ps and t=80 ps, respectively.

B. Divergence of Anisotropies Measured by FLUPS and TCSPC

Time-resolved fluorescence anitropies r(t) were calculated using the equation

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)}$$

where, G is the correction factor for the polarization sensitivity of the detection system. $I_{\parallel}$(t) and $I_{\perp}$(t) are the fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. For FLUPS measurements, the scattering of the pump pulse is very strong with parallel polarization, which makes the anisotropy unreliable at times less than 1 ps. Due to the fact that FLUPS can only measure up to 800 ps, where orientational relaxation is incomplete , the correction factor G can not be determined properly. As shown in Fig. S2, the $r(t)$ measured with FLUPS are all higher than the TCSPC data, although both data sets represent a nearly identical rotational dynamics after renormalizing the FLUPS data.

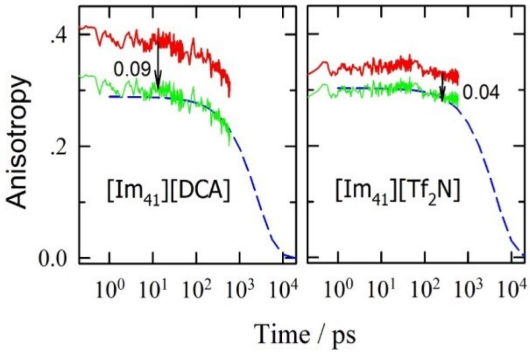

Fig.S2 Anisotropies of 4AP measured by FLUPS (red) and TCSPC (blue). For comparison, the anisotropy decays obtained by FLUPS are shifted to match the TCSPC data (green curves). Due to the large Raman scattering with parallel polarization in FLUPS measurements, anisotropy data are not reliable before 1 ps.

C. Effect of Rotational Correction on $S_v(t)$

Fig. S3 compares the spectral response function $S_v(t)$ of C153 (shown in red) and 4AP (shown in blue). In contrast to C153, $S_v(t)$ of 4AP do not show a clear Gaussian-shaped initial component in the ILs surveyed here. To eliminate the difference in the short time dynamics reported by the two solutes in comparisons of $S_v(t)$, the 4AP data are normalized to those of C153 at t = 2ps, where the inertial dynamics are largely complete. The normalized $S_v(t)$ curves of 4AP are shown in black in Fig. S3. Although this elimination of the difference in fast dynamics brings the responses measured with the two probes into much closer agreement, there is still a systematic difference between the two solutes.

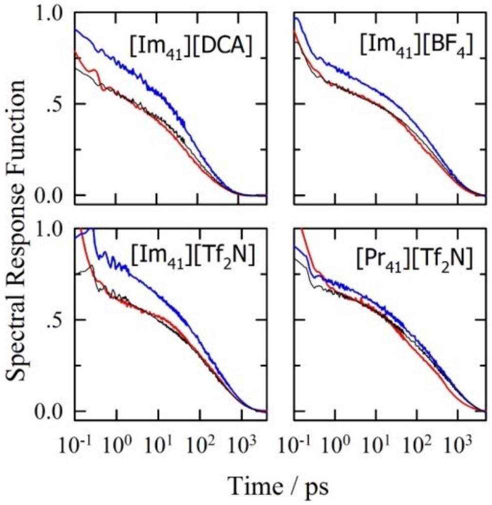

Fig.S3 Spectral response function $S_v(t)$ of C153 (red) and 4AP (blue). Black curves are $S_v(t)$ of 4AP normalized to C153 at t=2ps and used as references.

To examine the effect of solute rotation, the (unscaled) solvation response functions of both solute were rotationally corrected as described in the main text (eqns. 5-6). The rotationally corrected response functions, $S_{RC}(t)$ were also fit to the 4-parameter Guassian + stretched exponential form shown in eqn (2). As listed in Table S1, the fast time was determined from $\langle\tau\rangle_G = (\pi/2)^{1/2}\omega_G^{-1}$ and the slow time by $\langle\tau\rangle_{str} = (\tau_0/\beta\Gamma(1/\beta))$. The integral solvation time was then calculated by $\langle\tau_{solv}\rangle = f_G\langle\tau\rangle_G + (1-f_G)\langle\tau\rangle_{str}$. ΔRC is used to quantify the change of solvation time caused by rotational correction according to eqn. (7). The fractional difference of integral solvation time between C153 and 4AP, Δτ, is quantified with eqn. (3).

Table S1 Parameters Characterizing the Rotationally Corrected Solvation Response Functions[α]

4AP / IL	f_G	ω_G/ps^{-1}	$\langle\tau\rangle_G$/ps	τ/ns	β	$\langle\tau\rangle_{str}$/ns	ΔRC	Δτ
I4D	0.34	15.1	0.08	0.07	0.46	0.16	6%	4%
I4B	0.26	5.3	0.24	0.23	0.47	0.52	6%	24%
I4T	0.15	2.6	0.49	0.16	0.48	0.33	1%	16%
P4T	0.26	7.0	0.18	0.28	0.47	0.61	0%	26%

C153 / IL	f_G	ω_G/ps^{-1}	$\langle\tau\rangle_G$/ps	τ/ns	β	$\langle\tau\rangle_{str}$/ns	ΔRC	Δτ
I4D	0.32	6.8	0.18	0.05	0.43	0.15	23%	-
I4B	0.35	6.8	0.18	0.21	0.47	0.46	23%	-
I4T	0.38	4.0	0.31	0.24	0.57	0.39	36%	-
P4T	0.32	3.3	0.38	0.26	0.50	0.52	41%	-

[α] f_G, ω_G, β and τ are the fit parameters of eqn (2) used to describe S_{RC}(t) data. $\langle\tau\rangle_G$ and $\langle\tau\rangle_{str}$the integral times of Gaussian and stretched exponential components which characterize the time scales of the two components of S_{RC}(t). ΔRC, defined by eqn (7), is used to quantify the change of solvation time caused by RC. Δ calculated with eqn (3) is used for determining the difference of integral solvation times observed by C153 and 4AP.

D. Comparisons with DCS Data

Before numerical comparisons of $S_\nu(t)$ of DCS measured at 298 K can be compared with the data measured in this work at 293.5 K, the temperature dependence behavior of solvation dynamics needs to be considered. Numerous studies have shown that within a single IL, the slow components of solvation vary in proportion to IL viscosity.[6-8] While this scaling should not apply to the inertial component, given our focus on the slower components of solvation we rescale the times observed with DCS by a factor $\eta(293.5\,\mathrm{K})/\eta(298\,\mathrm{K})$ before making these comparisons. Table S2 lists these scale factors (≤1.3), the fits to the scaled data according to eqn. (2). Also shown in Table S2 are the differences in integral solvation times $\langle\tau_{solv}\rangle$ between DCS and C153 calculated according to eqn. (3) (D1=DCS, D2=C153) both without ($\Delta\tau$) and with ($\Delta\tau^{cor}$) rotational correction.

Table S2 Viscosities of ILs and their S_ν(t) Response observed by DCS[α]

IL	$\eta(293)/\eta(298)$	f_1	τ_1/ps	τ_2/ns	τ_2*/ns	β	$\langle\tau_{solv}\rangle$/ns	$\Delta\tau$	$\Delta\tau^{cor}$
I4B	1.27	0.19	0.32	0.13	0.16	0.41	0.42	52%	32%
I4T	1.24	0.10	0.74	0.08	0.09	0.46	0.20	12%	-18%
I4P	1.30	0.19	0.33	0.14	0.18	0.31	1.18	65%	24%
P3T	1.35	0.15	0.15	0.12	0.16	0.48	0.30	41%	0%

[α] η_1 and η_2 are the viscosity of ILs at 298 K and 293.5 K, respectively, obtained from parameterized temperature-dependent data. Fit parameters f_1, τ_1, τ_2 and β are from Ref. 8. τ_2* is viscosity scaled τ_2 according to $\langle \tau_{str} \rangle \propto \eta$. $\Delta\tau$ and $\Delta\tau^{cor}$ defined by eqn (3), is used for determining the difference of integral solvation time observed by DCS and C153, with and without RC applied to $S_v(t)$ of C153 respectively.

As shown in Table S2, the differences in solvation times measured by DCS and C153 are significantly reduced using the rotational correction. Fig. S4 compares the rotationally corrected spectral response functions of DCS (green) and C153 (shown in red) with the viscosity scaled S_v (t) of DCS normalized to it at t=2 ps (shown in green). The red dashed line represents our previous data of C153 which were measured with TCSPC only, showing the reproducibility of our data.

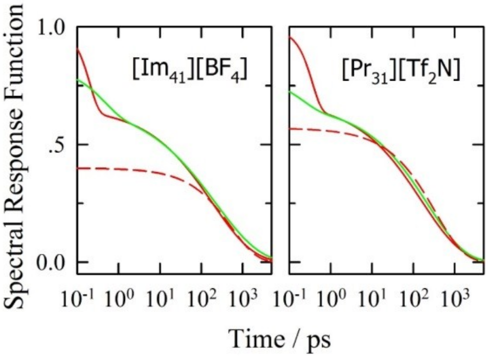

Fig.S4 Comparison of rotationally corrected spectral response function $S_{RC}(t)$ of C153 (Ref. 1) with uncorrected spectral response function $S_v(t)$ of DCS normalized to it at t=2ps. $S_{RC}(t)$ of C153 from our prior study (Ref. 6) is shown in red dashed line as references. All data sets are measured, or rescaled with viscosity to correspond to a temperature of 293.5 K.

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