

# The Influence of Mesoscopic Confinement on the Dynamics of Imidazolium-Based Room Temperature Ionic Liquids in Polyether Sulfone Membranes

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## Supplemental Material

### Bulk RTIL Rotational Dynamics

Orientational dynamics experiments were excited at 395 nm and detected at the wavelength corresponding to the emission peak maximum upon the completion of any solvation dynamics ( $v(t = \infty)$ ). These values will be discussed in detail later and can be found in Table 1 of the main text. The fluorescence excitation beam was rotated to collect fluorescence decays at parallel, perpendicular, and magic angle decays. From the parallel and perpendicular decays, denoted below as  $I_{\parallel}(t)$  and  $I_{\perp}(t)$  respectively, the anisotropy decays were calculated.

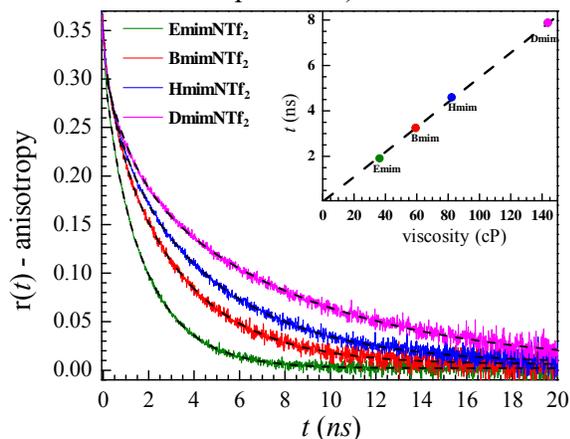
$$I_{\parallel}(t) = P(t)(1 + 0.8C_2(t)) \quad (S1)$$

$$I_{\perp}(t) = P(t)(1 - 0.4C_2(t)), \quad (S2)$$

where  $P(t)$  is the excited state population decay and  $C_2(t)$  is the 2<sup>nd</sup> order Legendre polynomial orientational correlation function. The anisotropy,  $r(t)$ , is given by

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} = 0.4C_2(t). \quad (S3)$$

Therefore,  $r(t)$  reports solely on orientational relaxation with the population component ( $P(t)$ , the denominator in Equation 6) removed. The solvation dynamics present in these measurements



will be captured by the population term,  $P(t)$  (see Figure 4B in the main text), and will not affect  $r(t)$ . The anisotropy decays of bulk  $\text{NTf}_2^-$  ionic liquids are shown in Figure S1 (colored curves). It was determined that a biexponential function gave the best fit to the data (black dashed curves). The time constants from these fits are given in Table S1. Anisotropy experiments could not be performed on RTILs confined in PES 200 membranes because of the extreme light scattering that depolarized the fluorescence.

**Figure S1.** Anisotropy decays of the bulk RTIL samples (colored curves). The black dashed curves are biexponential fits to the data, which are analyzed using the wobbling-in-a-cone model. Inset. The slowest decay components, the time for complete orientational relaxation, plotted vs. viscosity. The dashed black line is the calculated orientational relaxation time vs. viscosity for stick boundary conditions using Equation S6

The lack of a wavelength dependence for the fluorescence lifetime demonstrates that there is a single ensemble of molecules. Then the biexponential decay of the anisotropy can be interpreted in terms of the wobbling-in-a-cone model,<sup>1</sup> in which the chromophore is initially constrained to sample a restricted range of angles, the cone. Looking at Figure S1, it is seen that the anisotropy

decays start at a value of  $\sim 0.35$  rather than the theoretical maximum of 0.4. The observed initial value of 0.35 is caused by ultrafast inertial motions of the chromophore, which are on too short a time scale to be observed. However, the difference between 0.4 and the observed initial values of the data can be used to obtain the inertial cone angle. In the case of an ultrafast inertial cone and then a slower time scale wobbling cone,  $C_2(t)$  can be modelled as

$$C_2(t) = (1 - S_i^2)e^{-t/\tau_m} + S_i^2(S_c^2 + (1 - S_c^2)e^{-t/\tau_c})e^{-t/\tau_m} \quad (\text{S4})$$

In the above equation  $S_i$  and  $S_c$  are order parameters describing the restricted motions experienced by the probe where  $i$  is for inertial, and  $c$  is for the wobbling cone.<sup>2</sup>  $\tau_{in}$  is the time constant of the ultrafast inertial component;  $\tau_c$  is the wobbling time constant; and  $\tau_m$  is the total orientational randomization time constant. Here  $\tau_i$  is too fast to measure, and in the analysis it is set to a very short value. The value does not change the analysis as only the order parameter (cone angle) can be obtained.  $\tau_c$  and  $\tau_m$  are obtained by fitting the anisotropy data to a biexponential function. The slowest component is  $\tau_m$ . The faster component, labeled  $\tau_{r1}$  is in Table 3.  $\tau_c$  (listed in Table S1) is found from  $\tau_m$  and  $\tau_{r1}$  using Equation S4.  $\tau_c$  is slightly slower than  $\tau_{r1}$  because of the contribution to the decay at short time from  $\tau_m$ . The order parameter can be used to obtain the cone angle,

$$S_k^2 = (0.5 \cos \theta_k (1 + \cos \theta_k))^2, \quad (\text{S5})$$

where  $\theta_k$  is the cone angle of the  $k^{\text{th}}$  cone.

The results of the wobbling-in-a-cone analysis are given in Table S1. The data reveal that the inertial cone half angle ranges from  $21.9^\circ$  to  $23.3^\circ$  while the wobbling cone half angle ranges from  $28.5^\circ$  to  $35.9^\circ$ . The inertial cone angles fall within the error bars of each other, but there is a systematic trend in the wobbling cone angles that is outside of the error bars. Simulations by Corcelli demonstrated a preference for the C153 molecule to interact with the imidazolium ions because of the effects of pi-stacking interactions.<sup>3</sup> The trend in the  $\theta_c$  values indicates an increase in the angular space that C153 can sample on a relatively short time scale as the alkyl chain length increases. This increase with chain length may be caused by limitations on the optimal ionic packing necessitated by requirement of accommodating chain-chain packing.

Some information on the nature of the intermolecular interactions of C153 with the RTILs can be obtained by comparing the time constants for complete orientational relaxation to those predicted by hydrodynamic theory.<sup>4,5</sup> There are two limiting boundary conditions, stick and slip. Slip occurs when the principal resistance to rotation is caused by the need for the rotator to sweep out a volume as it rotates without strong restrictions through intermolecular interactions. Stick occurs when there are strong interactions between the rotating molecule and the solvent.

The reorientation time constant for stick boundary conditions is

$$\tau_{stick} = \frac{\eta Vf}{kT} \quad (\text{S6})$$

where  $\eta$  is the dynamic viscosity,  $T$  is the absolute temperature (297.5 K),  $V$  is the volume of the probe ( $223 \text{ \AA}^3$  for C153 using the Connolly solvent excluded volume), and  $f$  is a shape factor for an prolate spheroid obtained from the Perrin equations.<sup>6</sup> The calculated time constants,  $\tau_{stick}$ , are listed in Table 3 along with the ratios  $\tau_{stick}/\tau_m$ .

The inset in Figure S1 shows the values of  $\tau_m$  plotted against viscosity (colored points). In addition, the theoretical orientational relaxation time for a prolate spheroid with the dimensions of C153 as a function of viscosity is shown as the green dashed line in Figure S1. The points fall almost exactly on the line, showing first that hydrodynamic theory is applicable

as the decay time constants are linear in the viscosity. It also shows that C153 rotates with essentially stick boundary conditions independent of the chain lengths. For EmimNTf<sub>2</sub>, BmimNTf<sub>2</sub>, HmimNTf<sub>2</sub>, and DmimNTf<sub>2</sub>, the ratios  $\tau_m/\tau_{stick}$  are 0.97, 1.01, 1.03, and 1.01, respectively (see Table S1).

The ratios  $\tau_m/\tau_{stick}$  and the inset in Figure S1 show that C153 interacts strongly with the surrounding ions yielding the observed stick boundary conditions. As discussed above, the final exponential decay in the OHD-OKE data and the slowest component of the Stokes shift data match for the bulk liquids. This agreement between the two measurements shows that the slowest component of the Stokes shift data arises from complete structural randomization of the RTILs. The stick boundary conditions for the C153 orientational relaxation shows the strong coupling between C153 and the surrounding RTIL. The strong coupling between the C153 dynamics and the RTILs demonstrated by the stick boundary conditions and the need for total RTIL structural relaxation for the Stokes shifts to be complete are consistent.

**Table S1: Orientational Dynamics of C153 in Bulk RTIL Samples**

Sample	$\tau_{r1}$ (ns) <sup>a</sup>	$\tau_m$ (ns) <sup>b</sup>	$\tau_c$ (ns) <sup>h</sup>	$\tau_{stick}$ (ns) <sup>c</sup>	$\tau_m/\tau_{stick}$ <sup>d</sup>	$\eta$ (cP) <sup>e</sup>	$\Theta_i$ (deg) <sup>f</sup>	$\Theta_c$ (deg) <sup>g</sup>
EmimNTf <sub>2</sub>	0.46±0.12	1.91±0.04	0.6±0.2	1.96	0.97	36.3	21.9±1.6	18.7±1.2
BmimNTf <sub>2</sub>	0.60±0.08	3.25±0.04	0.7±0.1	3.22	1.01	59.3	20.8±0.9	21.1±0.6
HmimNTf <sub>2</sub>	0.80±0.07	4.60±0.06	1.0±0.1	4.48	1.03	82.3	22.3±0.7	23.9±0.5
DmimNTf <sub>2</sub>	1.17±0.07	7.88±0.16	1.4±0.1	7.87	1.01	143.6	23.4±0.6	27.9±0.4

<sup>a-b</sup> Rotational decay constants

<sup>c</sup> Theoretical stick boundary condition time constant

<sup>d</sup> Total randomization normalized to stick boundary conditions ( $\tau_m/\tau_{stick}$ )

<sup>e</sup> Dynamic viscosity measured to within ±1%

<sup>f</sup> Inertial cone half angle

<sup>g</sup> Wobbling cone half angle

<sup>h</sup> Wobbling time constant

## References

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