Ultrafast dynamics of ionic liquids in colloidal dispersion Supplemental Information

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Dynamic light scattering data

The dynamic light scattering (DLS) experiments have been conducted on two different instruments. One is a commercial Malvern ZS90 Zetasizer; the other one is a home-built Brookhaven DLS instrument. Both DLS instruments operate at 633 nm.

Through out the DLS experiments, the angle between the incident light and the detector is kept at 90 degrees, and the temperature is stabilized at room temperature. The data acquisition time is 300 seconds.

We have tried with different surfactant concentrations. For concentrations lower than 100 mM, no readable signal is presence for both instruments. When the concentration is above 100 mM, there are minor reproducible features, but the signal is still too weak to yield unambiguous size information.



Figure 1: The correlation plot with Brookhaven and Malvern instruments. The sample is [BMIM][SCN] with AOT in chlorobenzene, with W = 0.5 and the surfactant concentration is 400mM.

Figure 2: fig:DLS

It is possible to fit the feature from the Brookhaven instrument to get an estimation of the size. The diameter is estimated to be ~ 1 nm, which is similar than the estimation given by DOSY experiments, but is systematically smaller. The fitting is highly dependent on the acquisition time range and the fitting model.

Previous literature has utilized DLS with 488 nm laser source to characterize the size of $[BMIM][Tf_2N]/surfactant systems$. Since the probability for scattering event to happen is proportional to the wavelength to the fourth power, it is reasonable to suspect that our 633 nm laser is too long to characterize clusters of one nanometer. In the future, we could try DLS instruments with shorter wavelengths.

Anisotropy decay in ionic liquid-surfactant complexes

The anisotropy for each time point is obtained from the 2D-IR spectra. The resolved 2D-IR spectra are fitted with two two-dimensional Gaussians with opposite signs. The shape parameter (diagonal and antidiagonal width) are used to calculate the ellipticity, and the intensity parameter (amplitude of the peak, I) is used to calculate the anisotropy.

Representative anisotropy decay curves show that the anisotropy experiences a fast decay for all three IL/surfactant systems. By ~ 20 ps, the anisotropy decays to near zero and stays constant for the rest of the waiting time. The fitting with single exponential plus a constant has good agreement with the overall trend, which suggests diffusive reorientation.



Figure 3: The anisotropy decay of thiocyanate in BHDC (red), AOT (blue) and TX-100 (black) systems. The solvent is chlorobenzene, and W = 0.5.

It is worth noting that the anisotropy decays to negative for some systems. This is possibly because the pump intensities are not perfectly equal for the two polarization configurations in our experiments. It is possible that there is a constant offset for anisotropy, due to the non-isotropic orientation distribution. Based on the quality of our data, however, it is not possible to distinguish the offset.

Reorientation and structural dynamics of [BMIM][SCN] in pure TX-100

The TX-100 is liquid at room temperature, and therefore it is possible to obtain the dynamics of [BMIM][SCN] in pure TX-100. This system provides us an important data point to compare with the IL-surfactant complex systems. When the W value is very small, one could think that each particle is constructed with only one [BMIM][SCN] ion-pair, and many TX-100 molecules. If the ionic liquid was surrounded by TX-100, then one would expect the dynamics observed should be similar to the dynamics in the bulk TX-100. If the ionic liquid is not very well surrounded, then the overall dynamics should be significantly different.

The dynamics, regardless of reorientation or structural, are much slower for pure TX-100 compared to the IL-surfactant complex.



Figure 4: The anisotropy decay (a) and the FFCF in ZZZZ configuration (b) of [BMIM][SCN] in pure TX-100.

The anisotropy of thiocyanate decays gradually within the waiting time, but it is not fully resolved within our experimental waiting time, indicating a much longer reorientation time. Indeed, the single exponential fit is capable of capturing major features, and the resolved timescale is ~ 100 ps (Table 1). The reorientation time is almost an order of magnitude slower than that in the complex system.

The structural dynamics of thiocyanate in pure TX-100 is also significantly slower than the bulk dynamics. From the FFCF curve, one could see that for almost all the data points, the pure TX-100 system yields a higher correlation, indicating slower dynamics. Since the FFCF is not fully resolved within our experimental time, the fitting gives a relatively big offset. Nonetheless, the resolved timescales are still slower than the IL-surfactant complex systems.

Parameter	Value
$\overline{ au_1(\mathrm{ps})}$	5.4 ± 0.6
$ au_2(\mathrm{ps})$	109 ± 17
A	0.11 ± 0.01
В	0.62 ± 0.05
C	0.09 ± 0.06
$ au_{or}$	105

Table 1: Fitting result for pure TX-100 systems