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Electronic Supplementary Information

Initial dissolution of D_2O at the gas-liquid interface of ionic liquid $[C_4min][NTf2]$ associated with hydrogen-bond network formation

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1 Experimental details

1-1. Generation and characterization of a flowing jet sheet beam (FJSB) of ionic liquid (IL) $[C_4min]$ [NTf2]

In order to study the initial dissolution process at the gas-liquid interface, we generated a flowing jet sheet beam (FJSB) of ionic liquid (IL) $[C_4min]$ [NTf2] under vacuum. Fig. S1 shows the home-made nozzle tip having a trapezoidally-shaped groove on the inside and a conically-shaped hole on the outside, which can provide a FJSB of $[C_4min]$ [NTf2] with high optical quality as excellent as an interference pattern can be observed. The circulation of IL was operated by a vacuum compliant magnetic coupled gear pump with a flowmeter. Because the viscosity of IL is sensitive to temperature, a temperature-controlled water circulating system was used in order to keep the IL beam condition constant. The temperature of IL is variable within the range of 278 - 323 K.

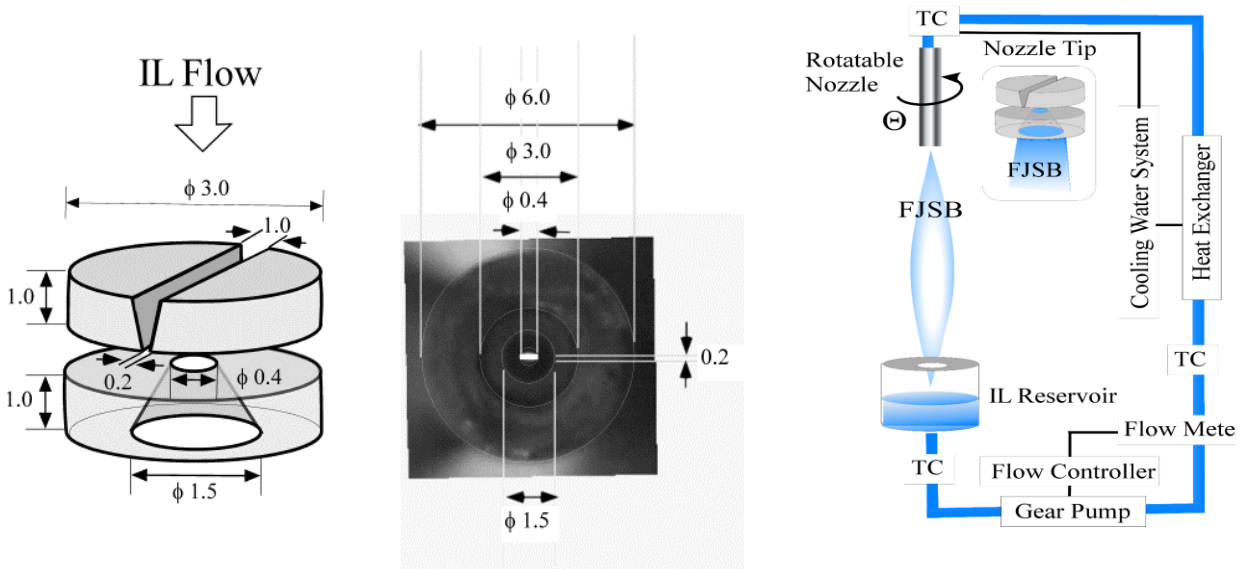

Fig. S1 (left) Schematic view and photograph of the nozzle tip, which consists of a trapezoidally-shaped groove on the inside and a conically-shaped hole on the outside, and (right) the experimental setup of FJSB generation.

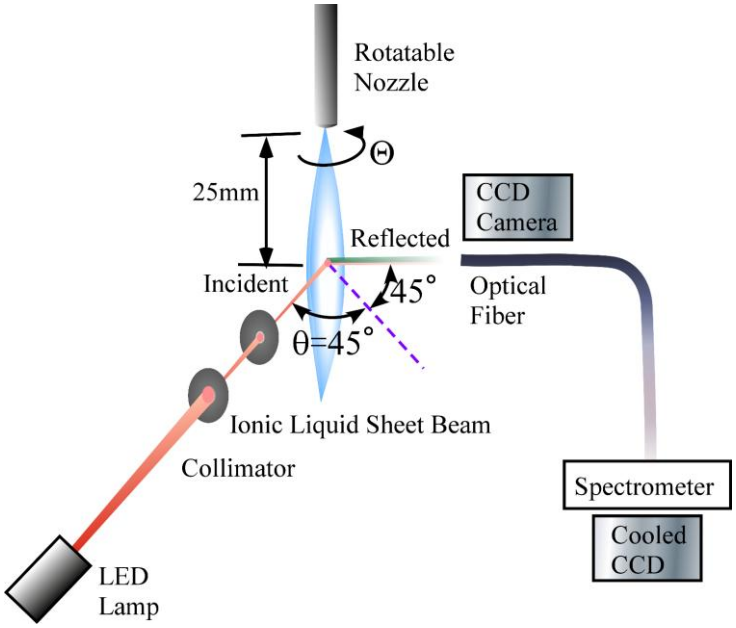

Fig. S2 Experimental setup for measuring an interferometric reflection spectrum.

Fig. S2 shows the experimental setup for measuring an interferometric reflection spectrum for which collimated white LED light is irradiated on FJSB with a spot diameter of ~ 1 mm at an incident angle of 45 deg.. The reflection spectrum was measured by a TE cooled CCD spectrometer coupled with a fiber optics (Glacier X, Konica Minolta). The characterization of FJSB of IL was carried out by observing an interferometric reflection spectrum (see Fig. S3) from the surface of FJS. The thickness of FJS can be determined from the reflectance spectrum using the following relationship.

$$d = \frac{\Delta m}{2\sqrt{n^2 - \sin^2\theta}} \times \frac{1}{\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)} \qquad (1)$$

where d is the thickness of FJS, Δm is the number of peaks (and/or valleys) in fringe pattern within the measurement wavelength range, n is the refractive index of IL [C_4min] [NTf2] (1.42), θ is the incident angle of the light against surface normal (45˚), λ_1 and λ_2 is the initial and final wavelength at the peaks observed in the fringe pattern, respectively. Fig. S3 shows the observed $(1/\lambda_2 - 1/\lambda_1)$ term as a function of Δm. As can be seen in Fig. S3, a linear relationship between $(1/\lambda_2 - 1/\lambda_1)$ and Δm is recognized as with eq. (1). Therefore, the thickness of FJS can be determined from the gradient of straight line. The FJSB of IL [C_4min] [NTf2] operated with a flow rate of 1.10 mLs^{-1} at a temperature of 298 ± 1 K is characterized as a thickness of 3.4 ± 0.1 μm, width of 11 mm at 25 mm downstream from the nozzle. According to the thickness and the flow rate of FJS, the flow velocity is estimated to be ~10 ms^{-1}, which corresponds to a contact time of ~100 μs with D_2O molecular beam.

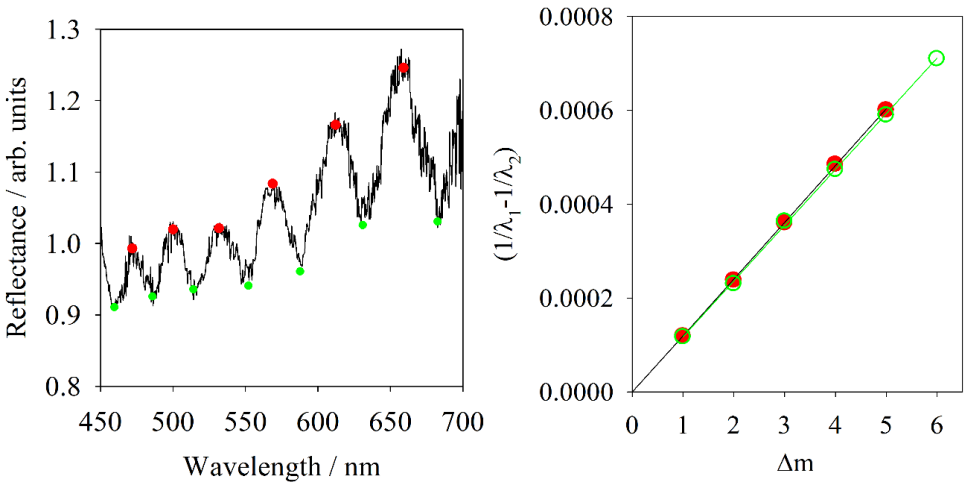

Fig. S3 (left) A typical reflectance spectrum of the FJSB of [C_4min] [NTf2] observed with a flow rate of 1.10 mLs^{-1} at a temperature of 298 ± 1 K. (right) The observed $(1/\lambda_2 - 1/\lambda_1)$ term as a function of Δm, characterizing a thickness of 3.4 ± 0.1 μm, width of 11 mm at 25 mm downstream from the nozzle.

1-2 Characterization of D_2O molecular beam

In order to change the collision energy, the seeding of D_2O by Rg was performed by the bubbling of Rg into D_2O reservoir. The velocity distribution of D_2O molecular beams were determined by using a conventional time-of-flight method with a flight length of 2080mm. The time-of-flight spectra and the resultant velocity distributions are shown in Fig. S4. They are characterized by a shifted-Maxwell-Boltzmann distribution with two parameters, v_s and α_s, summarizing in table 1 with collision energy (E_{col}). The pulsed D_2O molecular beam with a pulse duration of 0.3 ms (FWHM) is operated at a stagnation pressure of 250 Torr with a repetition rate of 10 Hz. The stagnation pressure of D_2O molecular beam is automatically regulated within a fluctuation of less than 0.5 % by using a gas reservoir which is equipped with an electric on-off valve operated by the output from a pressure gauge for the regulation of gas flow rate from Rg cylinder.

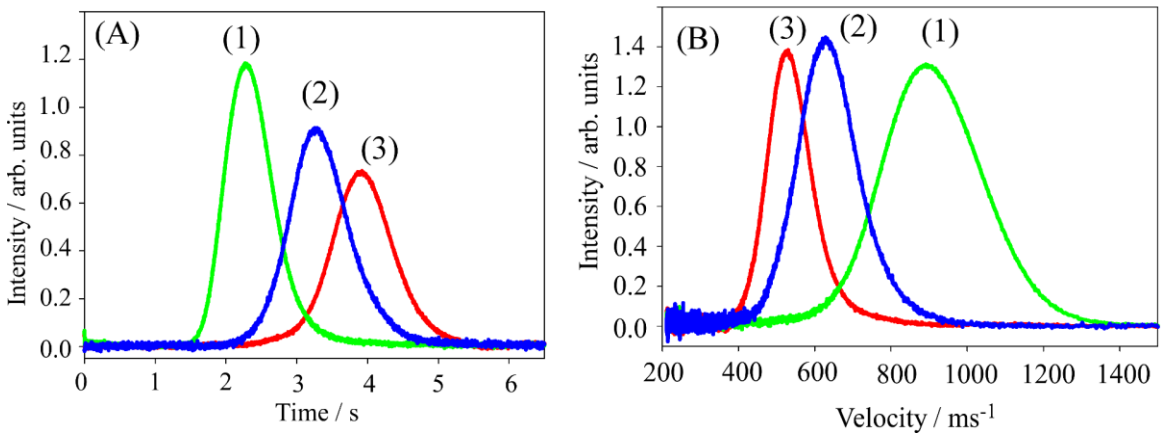

Fig.S4 (A) Time-of-flight spectra of D_2O molecular beams seeded in rare gas (Rg), and (B) the velocity distributions at three beam conditions

Table 1 Velocity distribution of D_2O molecular beams seeded in rare gas (Rg)

Rg	v_s /ms^{-1}	α_s /ms^{-1}	E_{col}/ eV
(1) He	895	299	0.083
(2) He + Ar(1:1)	636	181	0.042
(3) Ar	529	133	0.029

1-3. Experimental apparatus for the King and Wells (K-W) method.

The experimental setup for the King and Wells (K-W) method is shown in Fig. S5. The apparatus consists of four chambers: The D_2O molecular beam source chamber, first buffer chamber, second buffer chamber in which beam-stop (BS) is mounted, the ionic liquid (IL) chamber in which beam-flag (BF) and a quadrupole mass spectrometer (QMS) is mounted for the dissolution analysis by KW method. By using FJSB, the contact time of D_2O beam on IL is reduced to be ~ 100 μs and the exposure time can be reduced to be ~ 2 ms after collision as a travelling time of FJSB to the IL reservoir lying downstream. Therefore, the initial dissolution is defined as the process in which D_2O molecules can't desorb from IL interface within an exposure time of 2 ms after the collision. The experiments were performed by using a FJSB of [C_4min] [NTf2] and a pulsed D_2O molecular beam seeded in rare gas (Rg), and the measurement of the dissolution probability (S) by using the King and Wells (K-W) method.[25] The introduction of D_2O molecular beam into IL chamber was modulated by the beam-stop (BS). The introduction of D_2O molecular beam onto FJSB is modulated by the beam-Flag (BF). After 3-stage differential pumping, the D_2O molecular beam introduces into the IL chamber. The surface of FJSB is rotatable against the D_2O molecular beam axis by rotating the IL nozzle. The incident angle (Θ) is defined as the angle between the surface normal of FJSB and the D_2O molecular beam axis. The pulsed D_2O molecular beam with pulse duration of 0.3 ms (FWHM) is operated at a stagnation pressure of 250 Torr with a repetition rate of 10 Hz. The base pressure of the IL chamber under the operation of the FJS of IL is below 5×10^{-5} Pa.

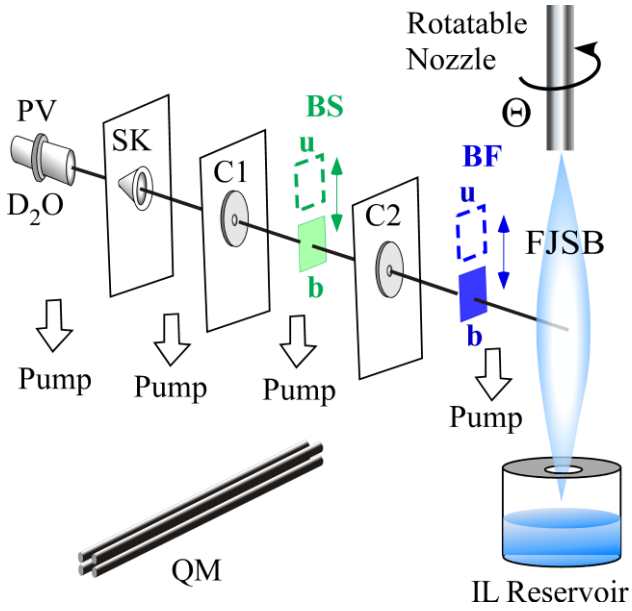

Fig.S5 Experimental setup for measuring the initial gas dissolution by the King and Wells (K-W) method.

2. Physical properties (viscosity, density, surface tension) of the IL [C_4min] [NTf2]

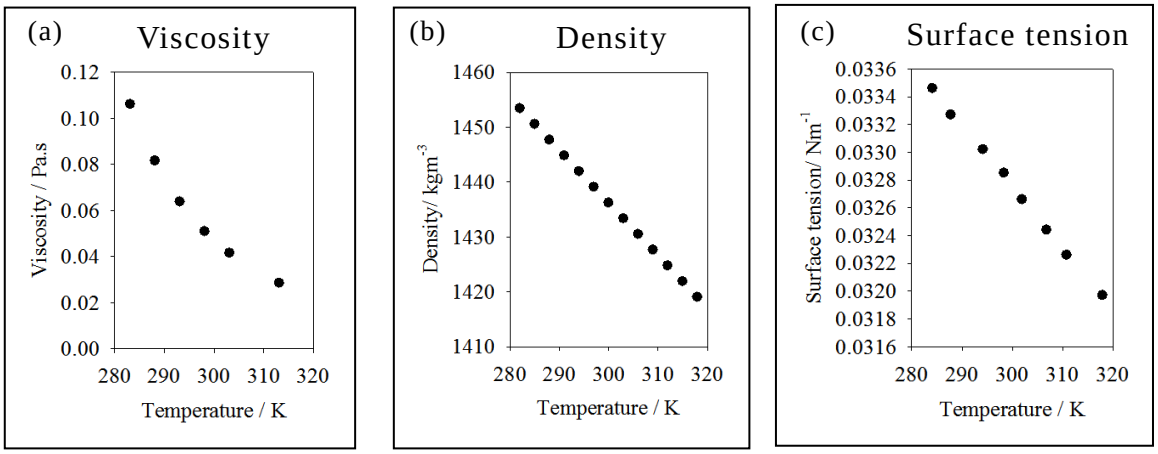

Fig. S6 The literature data on physical properties (viscosity, density, surface tension) of the IL [C_4min] [NTf2]: (a) Viscosity from ref. S1, (b)Density from ref. S2, (c)Surface tension from ref. S3.

References

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