SUPPORTING INFORMATION.

Solvated Structure of Cellulose

in a Phosphonate-based Ionic Liquid.

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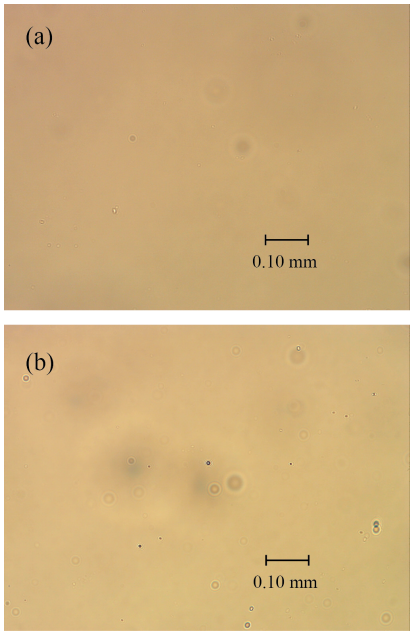
Section S1: Microscope Observation of Cellulose in [C_2mIm][CH_3HPO_3] Solutions.

Droplets of the prepared cellulose in [C_2mIm][CH_3HPO_3] solutions are observed by an optical microscope (BX51N-33P-O-SP, Olympus Co.). Figure S1 shows optical microscope images of neat [C_2mIm][CH_3HPO_3] and cellulose in [C_2mIm][CH_3HPO_3] solution of $\phi = 0.047$, which is the highest concentration examined. The cellulose solution looked almost the same as that of neat [C_2mIm][CH_3HPO_3]. It indicated that undissolved cellulose powder granules did not exist in all the cellulose solutions examined in the present study.

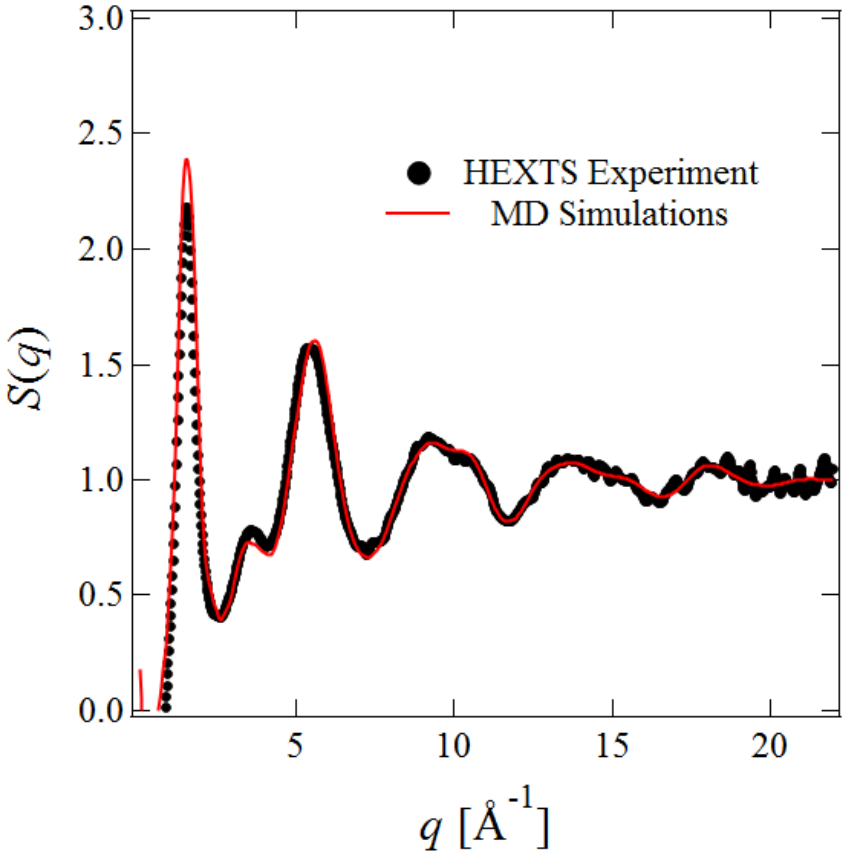
Figure S1.



Optical microscope images of (a) neat [C_2mIm][CH_3HPO_3] and (b) cellulose in [C_2mIm][CH_3HPO_3] solution of $\phi = 0.047$. A scale bar of 0.10 mm is also shown in the images.

Section S2: X-ray Structure Factor, $S(q)$ at Whole q-Range.

Figure S2.



X-ray structure factors, $S(q)$ obtained from HEXTS experiments (filled circles) and MD simulations (red solid line) for 30 wt% cellobiose in $[C_2mIm][CH_3HPO_3]$ solution, at the whole q-range examined.

Section S3: Estimation of the Abundance Ratio of the Intramolecular Hydrogen Bonds within Cellobiose to the Intermolecular Ones between Cellobiose and $CH_3HPO_3^-$.

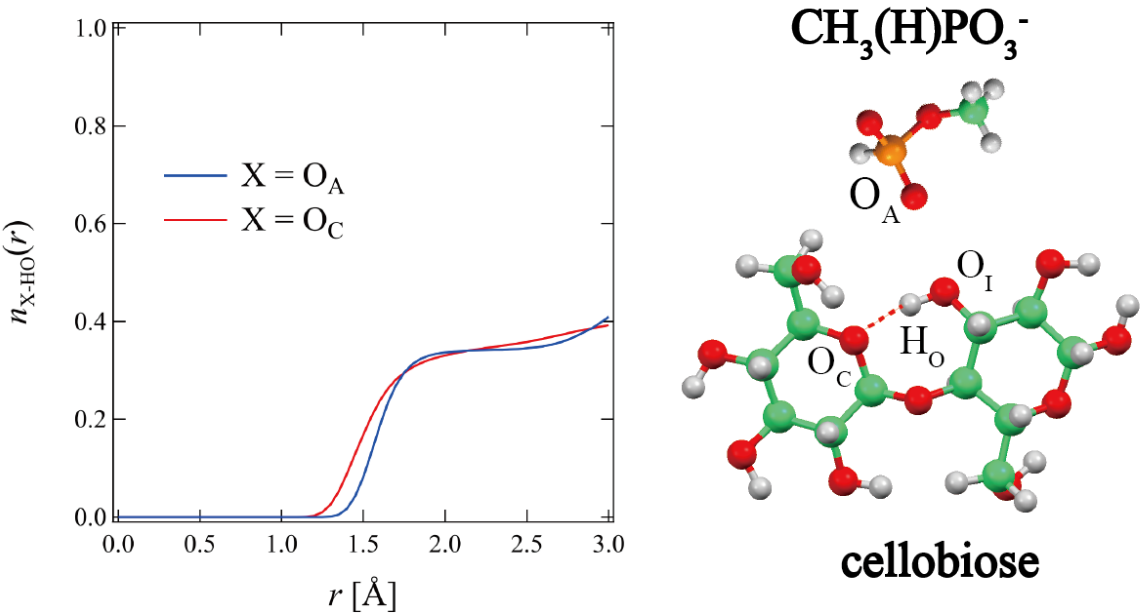
The atom-atom pair correlation function between *i*-atoms and *j*-atoms, $g^{MD}_{i\text{-}j}(r)$ is calculated from the MD simulation trajectory according to the following equations:

$$g_{i-j}^{\mathrm{MD}}(r) = \frac{1}{4\pi r^2 \Delta r} \frac{V}{N_i N_j} \left\langle \sum_{m=1}^{n_i} \Delta N_m^{ij}(r) \right\rangle \qquad \text{(Intermolecular correlations)} \qquad \text{(S1)}$$

$$g_{i-j}^{\mathrm{MD}}(r) = \frac{1}{4\pi r^2 \Delta r} \frac{V}{N_i} \left\langle \sum_{m=1}^{n_i} \Delta N_m^{ij}(r) \right\rangle \qquad \text{(Intramolecular correlations)} \qquad \text{(S2)}$$

Here, N_i (N_j) and V denote the total number of *i*-atoms (*j*-atoms) and the volume of the MD cell, respectively. $\Delta N^{ij}_{\mathrm{m}}(r)$ is the number of *j*-atoms in the spherical shell of radius r and thickness Δr centered on a m th *i*-atom.

Figure S3.



The coordination number of the atoms around Ho, $n_{X\text{-}HO}(r)$ (X = O_A, O_c).

As mentioned in the main text, the intramolecular hydrogen bonds $O_C \cdots H_O\text{-}O_I$ exist in cellobiose molecules dissolved in $[C_2mIm][CH_3HPO_3^-]$. Here, we estimated the abundance ratio of the intramolecular hydrogen bonds, $O_C \cdots H_O\text{-}O_I$ to the intermolecular hydrogen bonds, $O_A \cdots H_O\text{-}O_I$ from the viewpoint of the coordination number. The coordination number of *i*-atoms around *j*-atom is calculated by the following equation;

$$n_{i-j}(r) = \int_0^r \left[\frac{N_i}{V} g_{i-j}^{\mathrm{MD}}(r') \right] 4\pi r'^2 \mathrm{d}r' \qquad \text{(S3)}$$

The abundance ratio can be estimated from the ratio of $n_{OA\text{-}HO}(r)$ to $n_{OC\text{-}HO}(r)$ at the first coordination shell. As shown in Figure S3, both of $n_{OA\text{-}HO}(r)$ and $n_{OC\text{-}HO}(r)$ reached a plateau at r = 2.0 Å; thus we decided that the outer limit of the first coordination shell is r = 2.0 Å. The value of $n_{OA\text{-}HO}(r)$

and $n_{OC\text{-}HO}(r)$ at r = 2.0 Å was 0.34 and 0.33, respectively. Hence, the abundance ratio was found to be 0.33:0.34 = 0.97:1.00.

Section S4: Calculation of the Collective Diffusion Coefficient: A Partial-heterodyne Method.

A "partial-heterodyne" method in dynamic light scattering analysis has been established for scattering medias which contain frozen heterogeneity, such as polymer gels.[1] The analytical procedures are summarized below. According to the main manuscript, the time correlation function of light scattering intensity at a given measurement point, $g_p^{(2)}(\tau) - 1$ can be approximated as follows:

$$g_p^{(2)}(\tau) - 1 = \beta\sigma_{\mathrm{I}}^2 \left[A \exp\left(-D_{\mathrm{A,fast},p} q^2 \tau\right) + (1 - A) \exp\left(-D_{\mathrm{A,slow},p} q^2 \tau\right)\right]^2 \qquad \text{(S4)}$$

where β is the coherence factor. σ_{I}^2 is related to the fraction of time-averaged scattering intensity originating from thermal fluctuation, $\langle I_{\mathrm{F}} \rangle$ in the total scattering intensity, $\langle I \rangle_p$ as follows:

$$\sigma_{\mathrm{I}}^2 = X_p(2 - X_p) \qquad \text{(S5)}$$

$$X_p = \frac{\langle I_{\mathrm{F}} \rangle}{\langle I \rangle_p} \qquad \text{(S6)}$$

When light scattering intensity of sample is comparable with scattering intensity from solvent (I_{back}), we need to subtract I_{back} from $\langle I \rangle_p$ and $\langle I_{\mathrm{F}} \rangle$ in eq. (S6). Then eq. (S6) should be revised as follows:

$$X_p = \frac{\langle I_{\mathrm{F}} \rangle - I_{\mathrm{back}}}{\langle I \rangle_p - I_{\mathrm{back}}} \qquad \text{(S7)}$$

The apparent diffusion coefficient $D_{\mathrm{A,fast},p}$ is affected by the value of X_p and thus $D_{\mathrm{A,fast},p}$ depends on position. The true collective diffusion coefficient D_{fast} can be estimated from $D_{\mathrm{A,fast},p}$ using the following relationship.

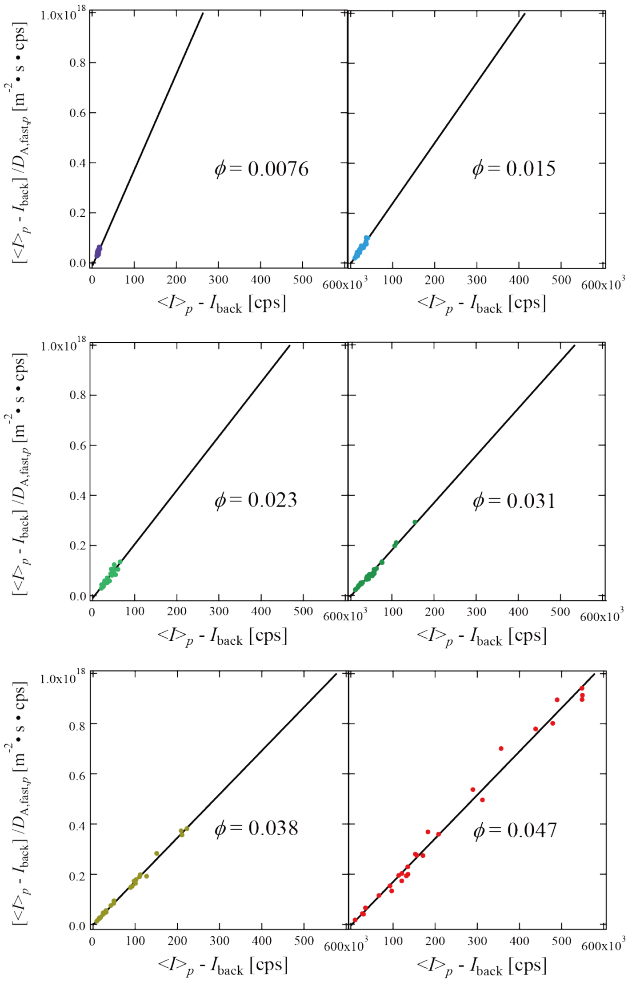
$$D_{\mathrm{fast}} = \left(2 - X_p\right) D_{\mathrm{A,fast},p} \qquad \text{(S8)}$$

Based on eq. (S7) and eq. (S8), one can derive the following equation.

$$\frac{\langle I \rangle_p - I_{\mathrm{back}}}{D_{\mathrm{A,fast},p}} = \frac{2}{D_{\mathrm{fast}}} \left(\langle I \rangle_p - I_{\mathrm{back}}\right) - \frac{\langle I_{\mathrm{F}} \rangle - I_{\mathrm{back}}}{D_{\mathrm{fast}}} . \qquad \text{(S9)}$$

Eq. (S9) indicates that D_{fast} can be obtained from the slope of the plot of $(\langle I \rangle_p - I_{\mathrm{back}})/D_{\mathrm{A,fast},p}$ vs $(\langle I \rangle_p - I_{\mathrm{back}})$.

Figure S4.



$(<I>_p - I_{back})/D_{A,fast,p}$ vs $(<I>_p - I_{back})$ plots for cellulose in $[C_2mIm][CH_3HPO_3]$ solutions of various volume fractions.

Figure S4 shows the plots of $(<I>_p - I_{back})/D_{A,fast,p}$ vs $(<I>_p - I_{back})$ for cellulose in $[C_2mIm][CH_3HPO_3]$ solutions of various volume fractions. Eventually, the correlation length, ξ was estimated from D_{fast} using Einstein-Stokes equation shown in eq. (9) in the main text.

1. Shibayama, M., Universality and Specificity of Polymer Gels Viewed by Scattering Methods. *Bull. Chem. Soc. Jpn.* **2006,** 79, 1799-1819.