**Table S1a:** Radial Distribution Function and Coordination Number (CN) Calculation between cation (polar) and anion.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN |
| S1a | 3.65 | 2.462 | 4.75 | 1.65 | S1b | 3.65 | 2.470 | 4.75 | 1.65 | S1c | 3.65 | 2.458 | 4.75 | 1.64 |
| S2a | 3.85 | 1.987 | 4.75 | 1.15 | S2b | 3.85 | 1.985 | 4.75 | 1.15 | S2c | 3.85 | 1.953 | 4.75 | 1.12 |
| S3a | 3.85 | 1.469 | 4.65 | 0.50 | S3b | 3.85 | 1.460 | 4.65 | 0.50 | S3c | 3.85 | 1.457 | 4.65 | 0.50 |
| S4a | 3.95 | 1.318 | 4.55 | 0.16 | S4b | 3.95 | 1.319 | 4.55 | 0.16 | S4c | 3.95 | 1.317 | 4.55 | 0.16 |

**Table S1b:** Radial Distribution Function and Coordination Number (CN) Calculation between cation (non-polar) and cation (non-polar).

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN |
| S1a | 4.05 | 1.425 | 6.05 | 2.52 | S1b | 4.05 | 1.420 | 6.05 | 2.50 | S1c | 4.05 | 1.415 | 6.05 | 2.50 |
| S2a | 4.05 | 1.327 | 6.05 | 1.85 | S2b | 4.05 | 1.326 | 6.05 | 1.85 | S2c | 4.05 | 1.319 | 6.05 | 1.83 |
| S3a | 4.15 | 1.089 | 6.05 | 0.92 | S3b | 4.15 | 1.080 | 6.05 | 0.91 | S3c | 4.15 | 1.076 | 6.05 | 0.90 |
| S4a | 4.15 | 0.825 | 5.85 | 0.23 | S4b | 4.15 | 0.820 | 5.95 | 0.25 | S4c | 4.15 | 0.811 | 5.85 | 0.23 |

**Table S1c:** Radial Distribution Function and Coordination Number (CN) Calculation between Water and anion.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN |
| S2a | 3.55 | 4.130 | 4.35 | 3.33 | S2b | 3.55 | 4.127 | 4.35 | 3.33 | S2c | 3.55 | 4.080 | 4.35 | 3.38 |
| S3a | 3.45 | 2.973 | 4.25 | 5.73 | S3b | 3.45 | 2.962 | 4.25 | 5.70 | S3c | 3.45 | 2.950 | 4.25 | 5.68 |
| S4a | 3.45 | 2.449 | 4.25 | 7.08 | S4b | 3.45 | 2.450 | 4.25 | 7.08 | S4c | 3.45 | 2.401 | 4.25 | 6.95 |

**Table S1d:** Radial Distribution Function and Coordination Number (CN) Calculation between Water and cation (polar).

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN |
| S2a | 3.35 | 1.74 | 4.25 | 1.85 | S2b | 3.35 | 1.74 | 4.25 | 1.85 | S2c | 3.35 | 1.71 | 4.25 | 1.87 |
| S3a | 3.35 | 1.21 | 4.15 | 2.94 | S3b | 3.35 | 1.20 | 4.15 | 2.93 | S3c | 3.35 | 1.20 | 4.15 | 2.91 |
| S4a | 3.35 | 0.96 | 4.05 | 3.17 | S4b | 3.35 | 0.96 | 4.05 | 3.17 | S4c | 3.35 | 0.94 | 4.05 | 3.12 |

**Table S1e:** Radial Distribution Function and Coordination Number (CN) Calculation between Water-Water.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN |
| S2a | 2.75 | 3.438 | 4.75 | 3.27 | S2b | 2.75 | 3.442 | 4.75 | 3.27 | S2c | 2.75 | 3.415 | 4.75 | 3.33 |
| S3a | 2.85 | 3.008 | 4.65 | 7.15 | S3b | 2.85 | 3.005 | 4.65 | 7.13 | S3c | 2.85 | 2.998 | 4.65 | 7.10 |
| S4a | 2.85 | 2.551 | 4.15 | 7.06 | S4b | 2.85 | 2.550 | 4.15 | 7.05 | S4c | 2.85 | 2.537 | 4.15 | 7.02 |
| S5 | 2.85 | 2.327 | 4.05 | 7.21 | S5 | 2.85 | 2.327 | 4.05 | 7.21 | S5 | 2.85 | 2.327 | 4.05 | 7.21 |

**Table S1f:** Radial Distribution Function and Coordination Number (CN) Calculation between Cellulose and anion.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN |
| S1a | 2.65 | 4.564 | 3.35 | 1.02 | S1b | 2.65 | 4.511 | 3.35 | 1.00 | S1c | 2.65 | 4.682 | 3.35 | 1.05 |
| S2a | 2.65 | 4.721 | 3.35 | 0.84 | S2b | 2.65 | 4.783 | 3.35 | 0.85 | S2c | 2.65 | 4.870 | 3.35 | 0.87 |
| S3a | 2.65 | 3.870 | 3.35 | 0.47 | S3b | 2.65 | 4.104 | 3.35 | 0.45 | S3c | 2.65 | 4.304 | 3.35 | 0.47 |
| S4a | 2.65 | 2.705 | 3.35 | 0.11 | S4b | 2.65 | 2.722 | 3.35 | 0.11 | S4c | 2.65 | 3.881 | 3.35 | 0.16 |

**Table S1g:** Radial Distribution Function and Coordination Number (CN) Calculation between Cellulose and cation (polar).

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN |
| S1a | 3.25 | 1.056 | 4.15 | 0.53 | S1b | 3.35 | 1.027 | 4.15 | 0.52 | S1c | 3.25 | 1.076 | 4.15 | 0.55 |
| S2a | 3.35 | 1.037 | 4.15 | 0.41 | S2b | 3.35 | 1.039 | 4.15 | 0.41 | S2c | 3.35 | 1.087 | 4.15 | 0.45 |
| S3a | 3.35 | 0.805 | 4.05 | 0.18 | S3b | 3.35 | 0.856 | 4.05 | 0.19 | S3c | 3.35 | 0.897 | 4.05 | 0.20 |
| S4a | 3.35 | 0.506 | 4.05 | 0.04 | S4b | 3.35 | 0.517 | 4.05 | 0.04 | S4c | 3.35 | 0.734 | 4.05 | 0.06 |

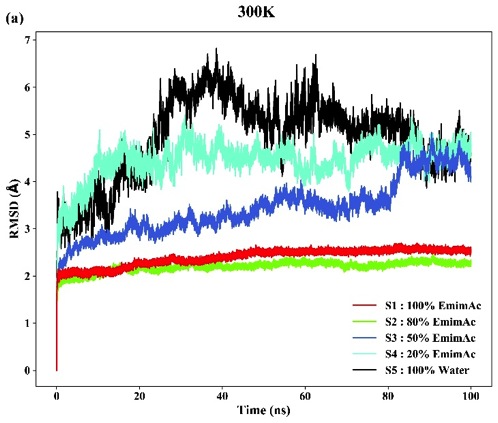
**Table S1h:** Radial Distribution Function and Coordination Number (CN) Calculation between Cellulose and Water.

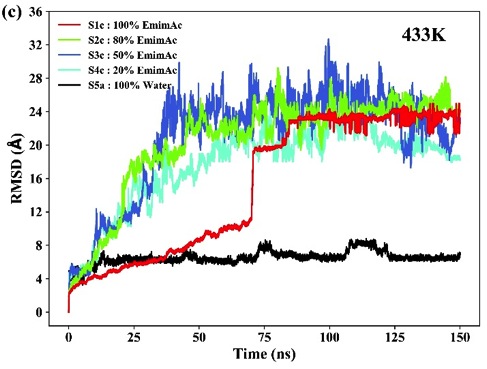
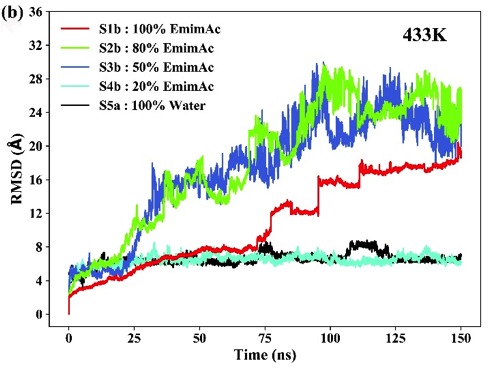
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN | System | rpeak | g (r) | r min | CN |
| S2a | 2.85 | 0.841 | 3.75 | 0.55 | S2b | 2.85 | 0.848 | 3.75 | 0.56 | S2c | 2.85 | 0.931 | 3.75 | 0.63 |
| S3a | 2.85 | 0.977 | 3.75 | 1.37 | S3b | 2.85 | 1.019 | 3.75 | 1.44 | S3c | 2.85 | 1.081 | 3.75 | 1.54 |
| S4a | 2.85 | 0.699 | 3.75 | 1.44 | S4b | 2.85 | 0.721 | 3.75 | 1.48 | S4c | 2.85 | 0.894 | 3.75 | 1.86 |
| S5 | 2.85 | 0.715 | 3.75 | 1.76 | S5 | 2.85 | 0.715 | 3.75 | 1.76 | S5 | 2.85 | 0.715 | 3.75 | 1.76 |

**Figure S1.** Three distinct rotameric conformers of the glucose hydroxymethyl group (C6-OH) based on the omega dihedral angle (O5-C5-C6-O6), are presented i.e. gauche-gauche (gg ~-60◦), gauche-trans (gt ~ +60◦) and trans-gauche (tg ~ ± 180◦).

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**Figure S2.** Root-mean-square deviation (RMSD) of cellulose (Iβ) with reference to the minimized crystal structure for five MD trajectories. The trajectories correspond to the simulations on five systems are: 100% EmimAc (red), 80% EmimAc (green), 50% EmimAc (blue), 20% EmimAc (cyan) and 100% Water (black) for (a) 300K and (b) set b at 433K and (c) set c at 433K.

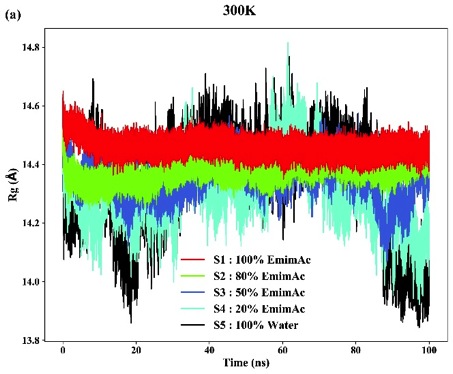
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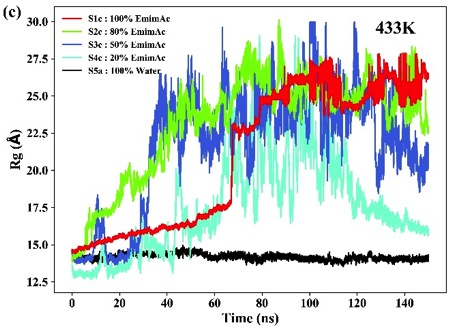
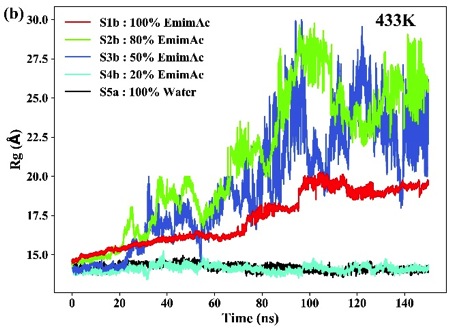
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**Figure S3.** Final snapshots of the cellulose structures after 100 ns MD simulation in 100% EmimAc (S1), 80% EmimAc (S2), 50% EmimAc (S3), 20% EmimAc (S4) and 100% Water (S5) systems at 300K. The cellulose chains mostly remain in an aggregated bunch form that suggests no dissolution.

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**Figure S4.** Radius of gyration (Rg) of cellulose (Iβ) correspond to the simulations on five systems are: 100% EmimAc (red), 80% EmimAc (green), 50% EmimAc (blue), 20% EmimAc (cyan) and 100% Water (black) for (a) 300K and (b) set b at 433K and (c) set c at 433K.

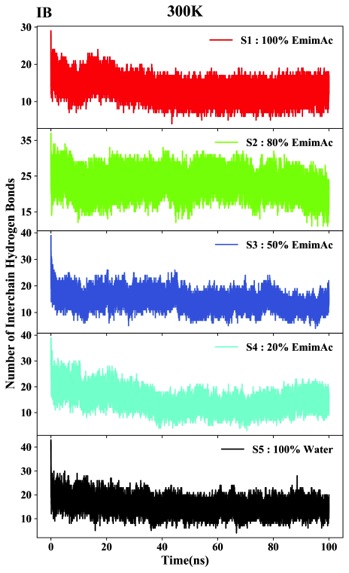
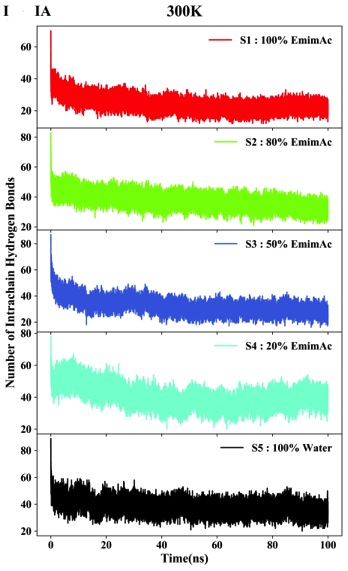
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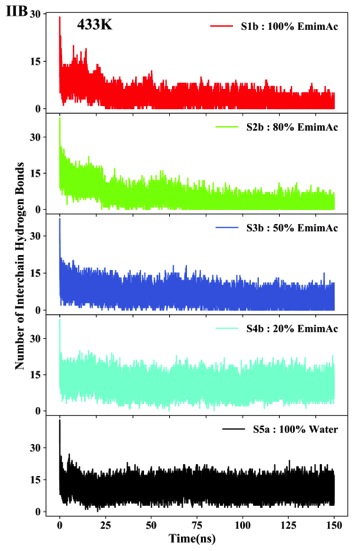
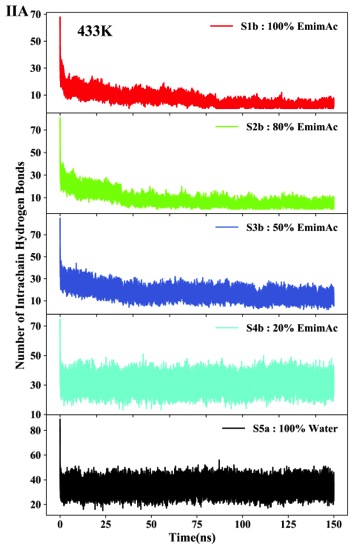
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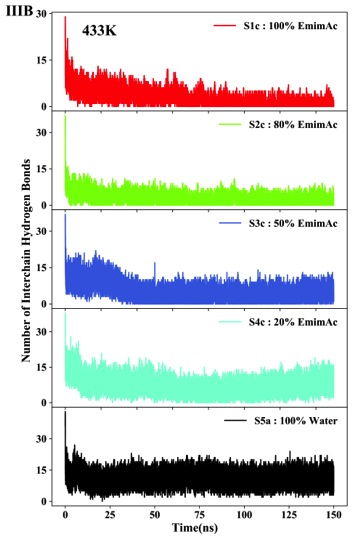
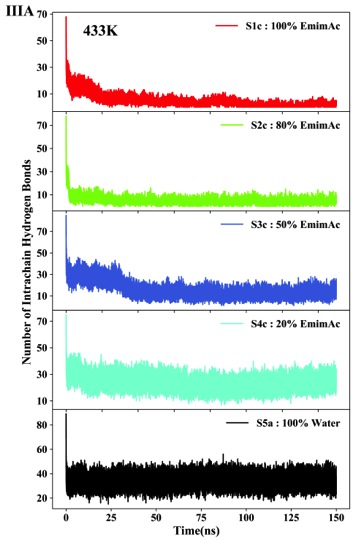
**Figure S5.** The major intrachain (O3−H3...O5 and O2−H2...O6) and interchain (O6−H6...O2 and O6−H6...O3) hydrogen bonds between two octamer glucan chains are presented. The carbon, oxygen and hydrogen atoms are colored in green, red and white respectively.



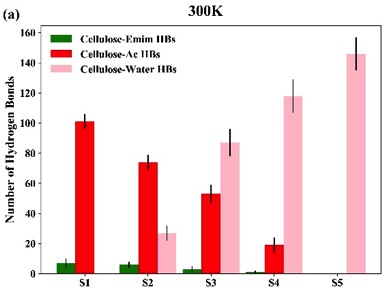
**Figure S6.** Number of cellulose hydrogen bonds as present in simulation trajectory for 100% EmimAc (S1a) (red), 80% EmimAc (S2a) (green), 50% EmimAc (S3a) (blue), 20% EmimAc (S4a) (cyan) and 100% Water (S5a) (black) systems at 300K: I(A) intrachain hydrogen bond, I(B) interchain hydrogen bond; set b at 433K: II(A) intrachain hydrogen bond, II(B) interchain hydrogen bond; set c at 433K: III(A) intrachain hydrogen bond, III(B) interchain hydrogen bond.

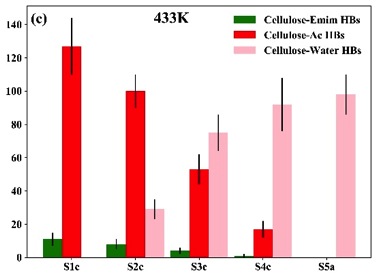
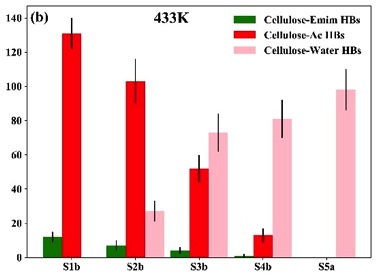
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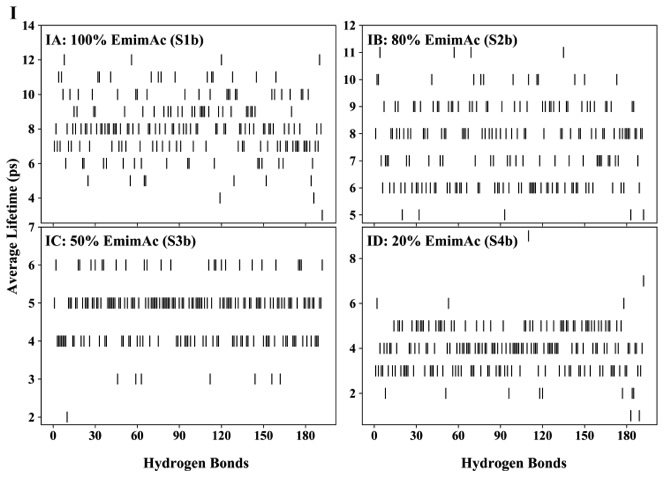
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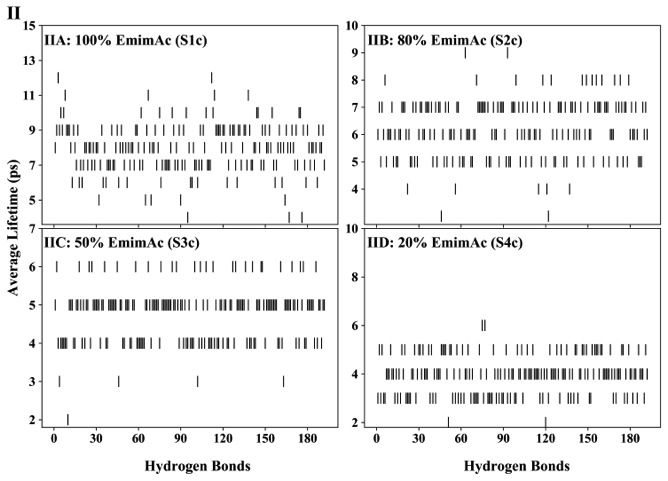
**Figure S7.** Histogram plot of the average number of hydrogen bonds between cellulose hydroxyl groups and cations (green), anions (red) and water (pink) are represented in the 100% EmimAc, 80% EmimAc, 50% EmimAc, 20% EmimAc and 100% Water systems: (a) at 300K, (b) set b at 433K and (c) set c at 433K.

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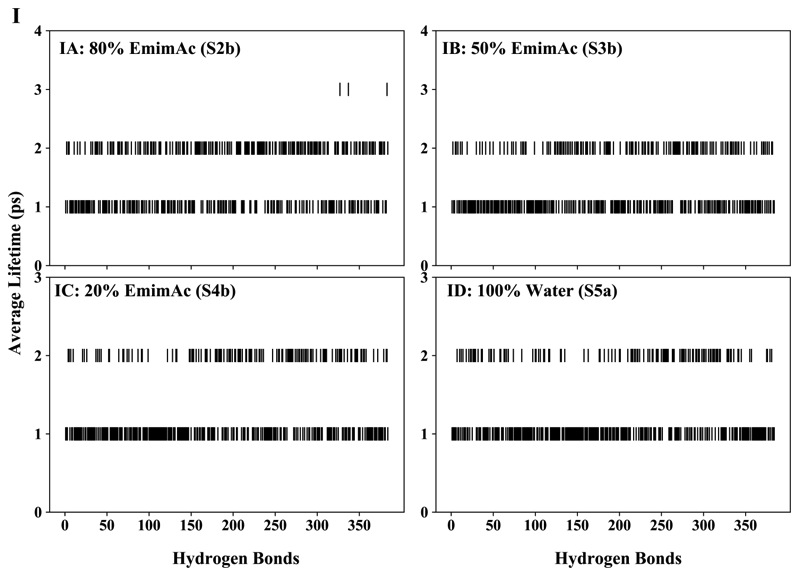
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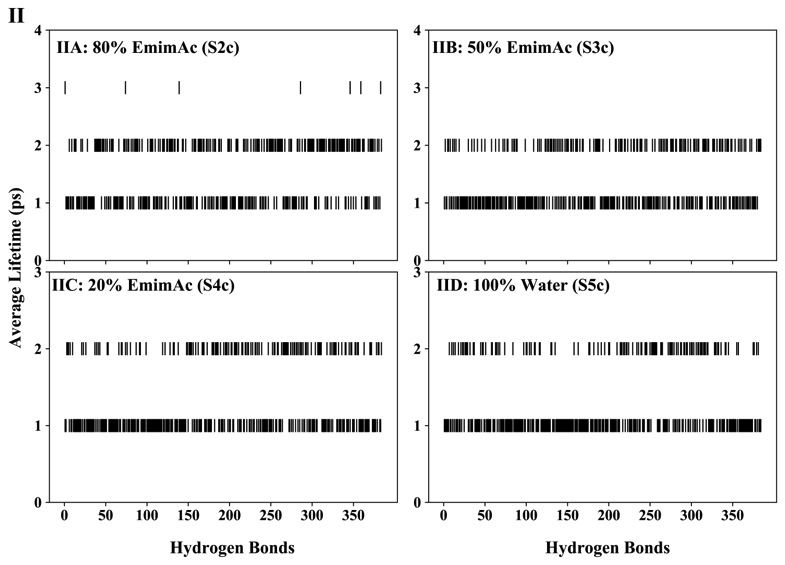
**Figure S8.** Average lifetime (ps) of different cellulose-acetate hydrogen bonds obtained from MD trajectories of set b at 433K: I(A) 100% EmimAc (S1b), I(B) 80% EmimAc (S2b), I(C) 50% EmimAc (S3b), I(D) 20% EmimAc (S4b); and set c at 433K: II(A) 100% EmimAc (S1c), II(B) 80% EmimAc (S2c), II(C) 50% EmimAc (S3c), II(D) 20% EmimAc (S4c).



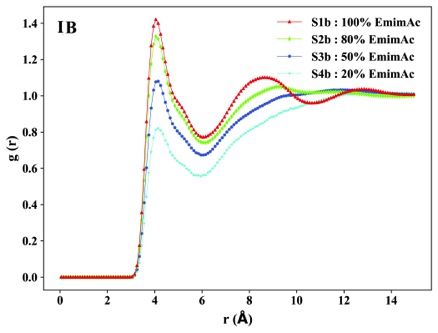
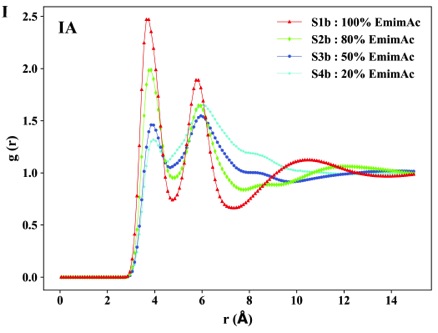


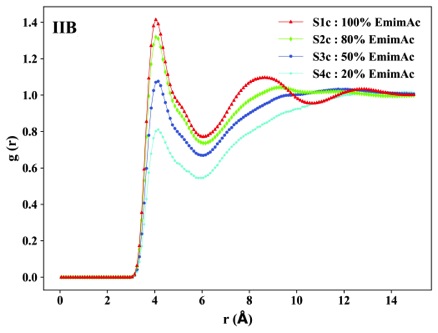
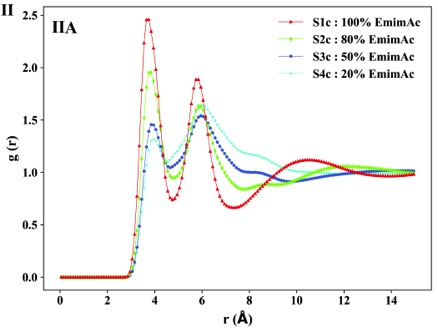
**Figure S9.** Average lifetime (ps) of different cellulose-water hydrogen bonds obtained from MD trajectories of set b at 433K: I(A) 80% EmimAc (S2b), I(B) 50% EmimAc (S3b), I(C) 20% EmimAc (S4b), I(D) 100% Water (S5a); and set c at 433K: II(A) 80% EmimAc (S2c), II(B) 50% EmimAc (S3c), II(C) 20% EmimAc (S4c), II(D) 100% Water (S5a).

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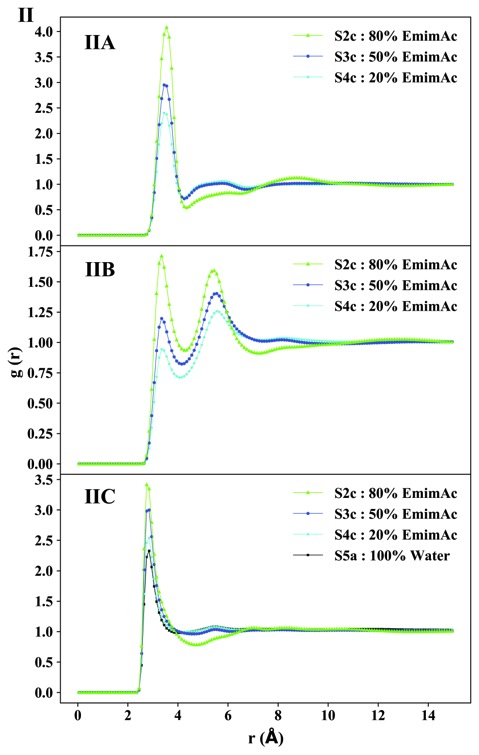
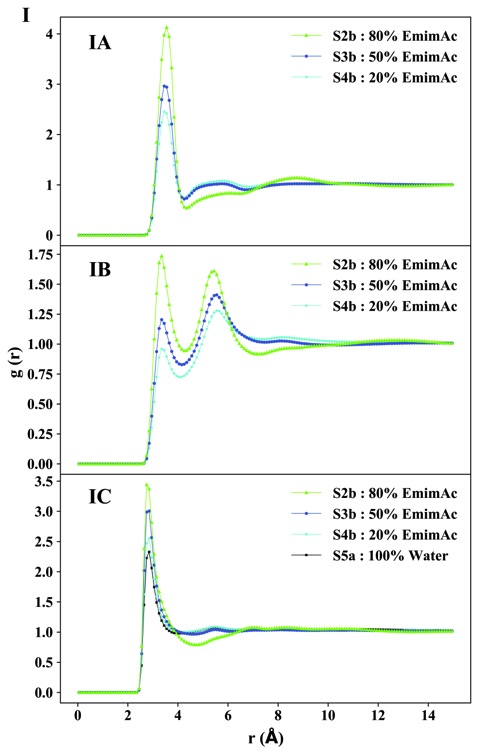
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**Figure S10.** Radial distribution function (RDF) obtained from MD trajectories of 100% EmimAc (red), 80% EmimAc (green), 50% EmimAc (blue) and 20% EmimAc (cyan) systems for set b at 433K: I(A) cation-anion polar interaction, I(B) cation-cation nonpolar interaction; and set c at 433K: II(A) cation-anion polar interaction, II(B) cation-cation nonpolar interaction.

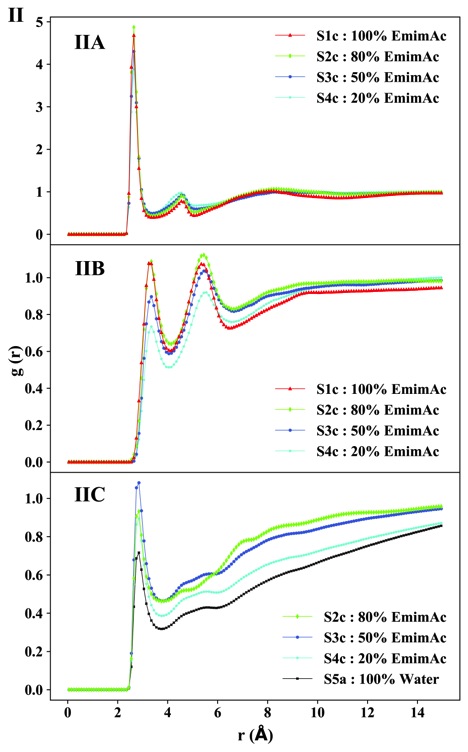
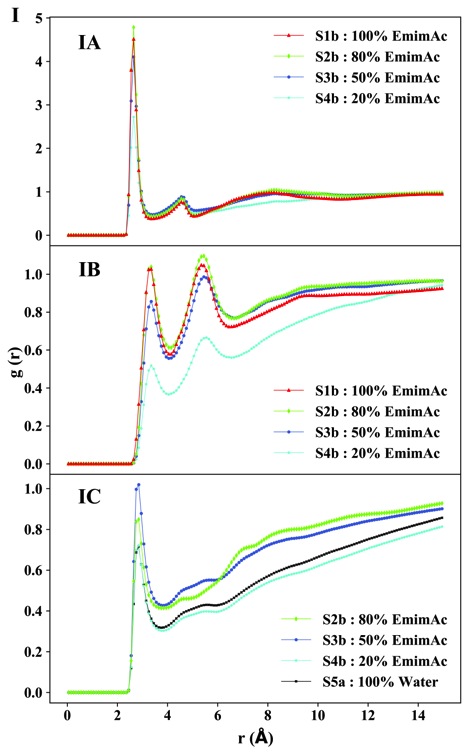
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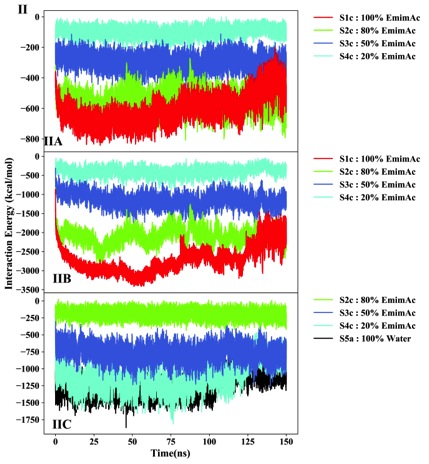
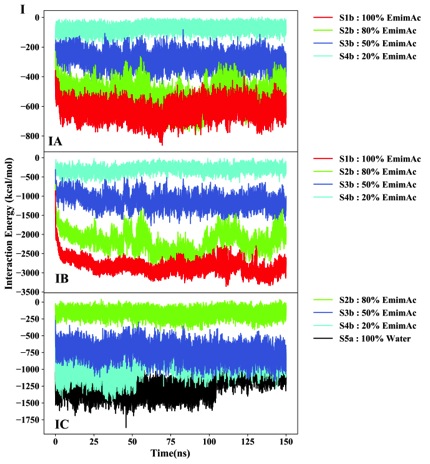
**Figure S11.** Radial distribution function (RDF) obtained from MD trajectories of 80% EmimAc (green), 50% EmimAc (blue), 20% EmimAc (cyan) and 100% Water (black) systems for set b at 433K: I(A) water-anion, I(B) water-cation and I(C) water -water interactions; and set c at 433K: II(A) water-anion, II(B) water-cation and II(C) water -water interactions.

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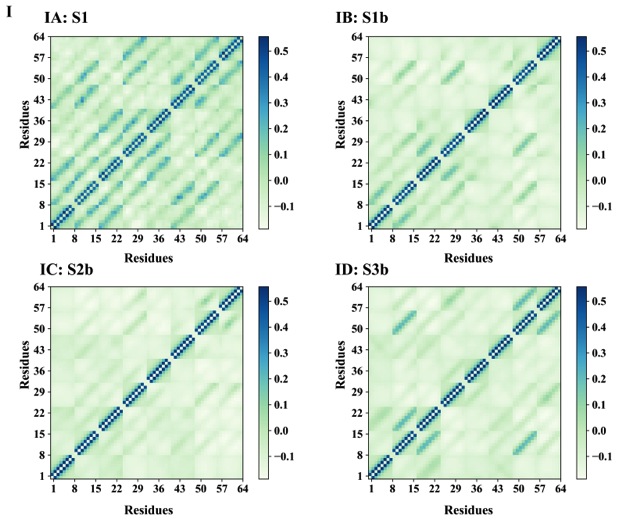
**Figure S12.** Radial distribution function (RDF) of cellulose (O2, O3, O6) interacting with specific regions of anion (C2), cation (C4) and water (O) molecules in 100% EmimAc (red), 80% EmimAc (green), 50% EmimAc (blue), 20% EmimAc (cyan) and 100% Water (black) systems for set b at 433K: I(A) cellulose-anion, I(B) cellulose-cation and I(C) cellulose-water interaction; and set c at 433K: II(A) cellulose-anion, II(B) cellulose-cation and II(C) cellulose-water interaction.

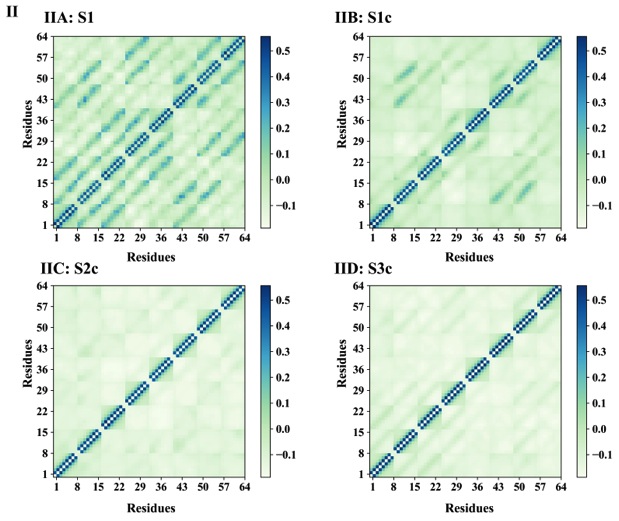
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**Figure S13:** The Cellulose-solvent electrostatic interaction energy has been calculated from MD trajectories of 100% EmimAc (red), 80% EmimAc (green), 50% EmimAc (blue), 20% EmimAc (cyan) and 100% Water (black) systems for set b at 433K: I(A) cellulose-cation, I(B) cellulose-anion and I(C) cellulose-water interactions; and set c at 433K: II(A) cellulose-cation, II(B) cellulose-anion and II(C) cellulose -water interactions.

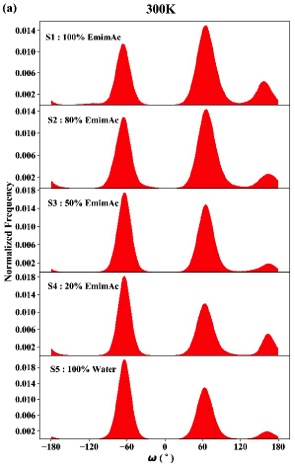


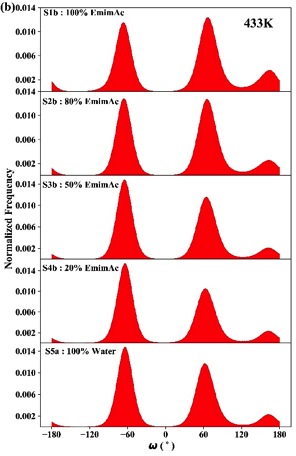
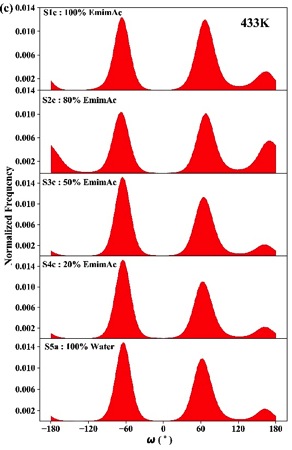
**Figure S14:** The correlated motion of the cellulose chains is framed in different solvent systems from MD trajectories of 100% EmimAc, 80% EmimAc and 50% EmimAc systems for : I(A) 100% EmimAc (S1) at 300K; II(A) 100% EmimAc (S1) at 300K; set b at 433K: I(B) 100% EmimAc (S1b), I(C) 80% EmimAc (S2b) and I(D) 50% EmimAc (S3b) systems; set c at 433K: II(B) 100% EmimAc (S1c), II(C) 80% EmimAc (S2c) and II(D) 50% EmimAc (S3c) systems.

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**Figure S15.** Distribution of the omega (ω) dihedral angles of the glucose residues in the cellulose chains in 100% EmimAc, 80% EmimAc, 50% EmimAc, 20% EmimAc and 100% Water systems: (a) at 300K, (b) set b at 433K and (c) set c at 433K. The histograms of the rotameric conformers obtained from the MD simulation were divided based on the range of normal distribution as gg = (−120◦ to 0◦), gt = (0◦ to 120◦), tg = (−180◦ to −120◦) and (120◦ to 180◦) for simplicity.



**Figure S16.** Snapshots of the simulation boxes, displaying the last 100ps ensemble of the system trajectories which show gradual disappearance of nanostructured water-clusters and even distribution of water molecules from (A) 50% EmimAc (S3a) to (B) 20% EmimAc (S4a). Thus, with the rising water concentration the systems transform more into an aqueous like system than IL-water mixture. The oxygen and hydrogen atoms in water molecules are colored in red and white respectively. The rest of the solvents are denoted in sea-green for easy discrimination.

