Supplementary Materials
for

Ionic Liquids and water: hydrophobicity *vs* hydrophilicity

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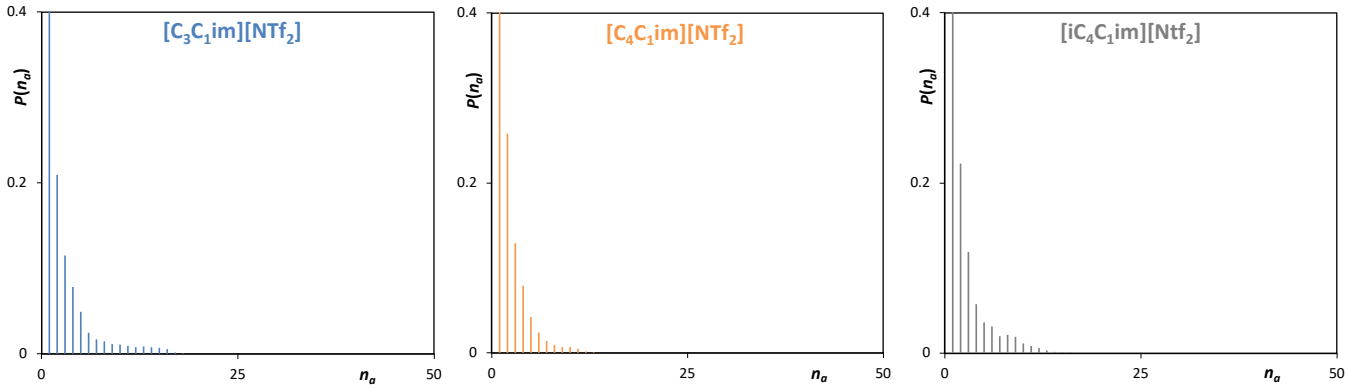

Figure S1. Discrete probability distribution of aggregate sizes, $P(n_a)$, as a function of aggregate size number, n_a, for water-water aggregates found in aqueous solutions of $[C_3C_1im][NTf_2]$, $[C_4C_1im][NTf_2]$ and $[iC_4C_1im][NTf_2]$ with $X_{IL} = 0.70$ at 320 K.

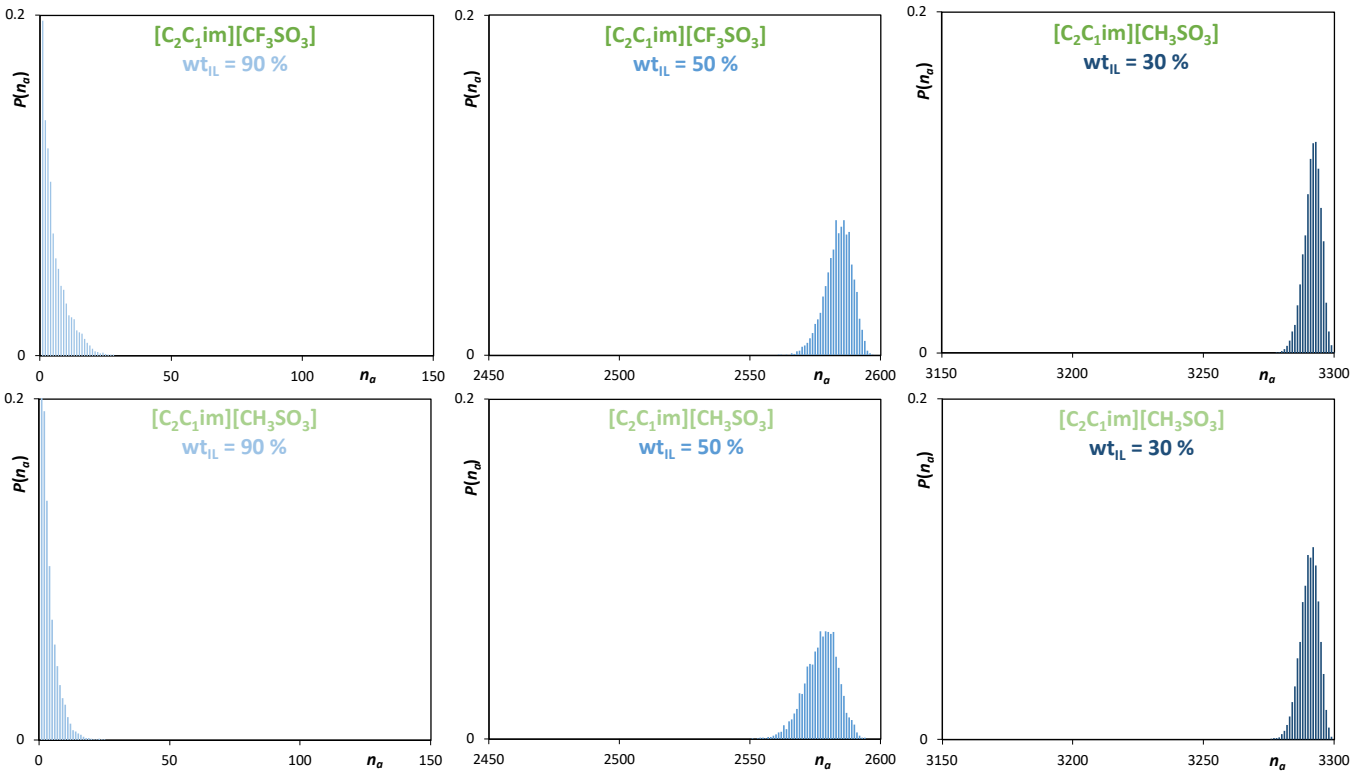

Figure S2. Discrete probability distribution of aggregate sizes, $P(n_a)$, as a function of aggregate size number, n_a, for water-water aggregates found in aqueous solutions of $[C_2C_1im][CF_3SO_3]$ and $[C_2C_1im][CH_3SO_3]$ at 300 K.

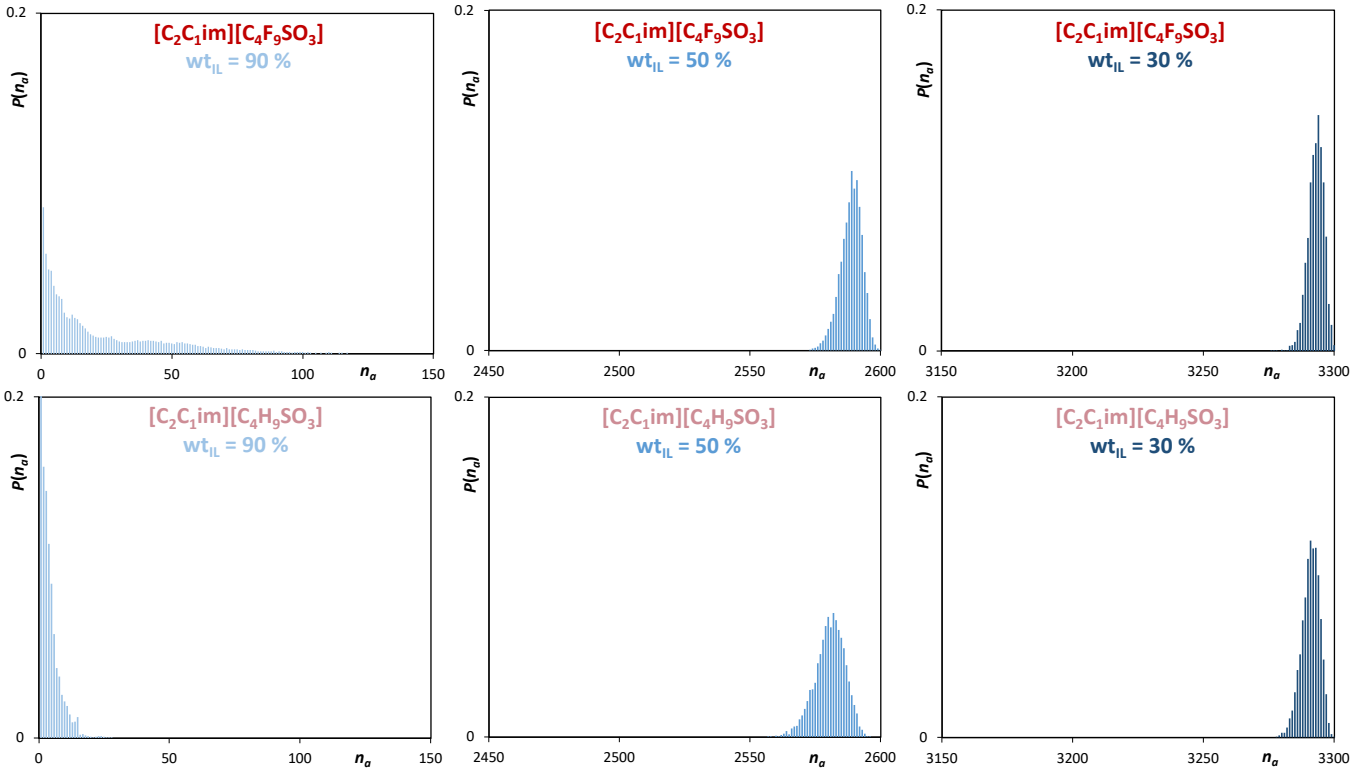

Figure S3. Discrete probability distribution of aggregate sizes, $P(n_a)$, as a function of aggregate size number, n_a, for water-water aggregates found in aqueous solutions of $[C_2C_1im][C_4F_9SO_3]$ and $[C_2C_1im][C_4H_9SO_3]$ at 300 K.

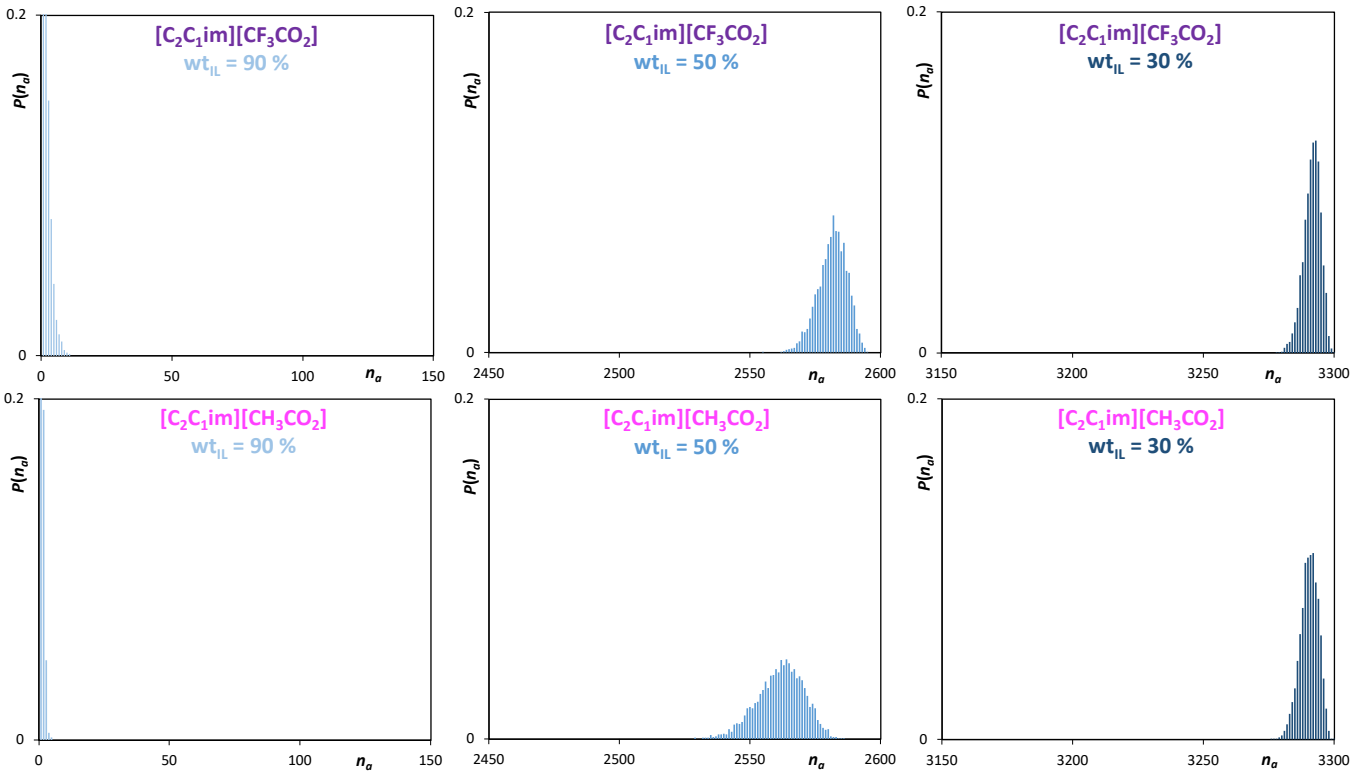

Figure S4. Discrete probability distribution of aggregate sizes, $P(n_a)$, as a function of aggregate size number, n_a, for water-water aggregates found in aqueous solutions of $[C_2C_1im][CF_3CO_2]$ and $[C_2C_1im][CH_3CO_2]$ at 300 K.

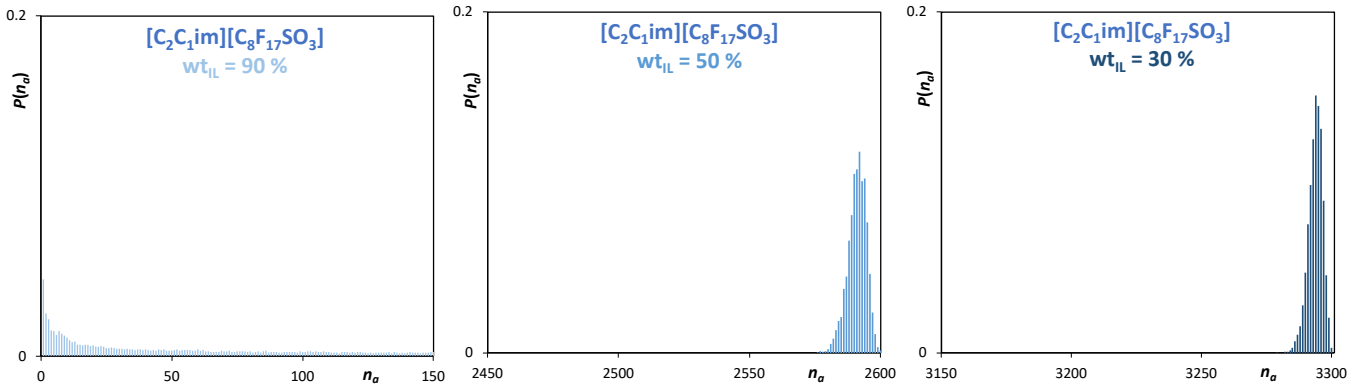

Figure S5. Discrete probability distribution of aggregate sizes, $P(n_a)$, as a function of aggregate size number, n_a, for water-water aggregates found in aqueous solutions of $[C_2C_1im][C_8F_{17}SO_3]$ at 300 K.

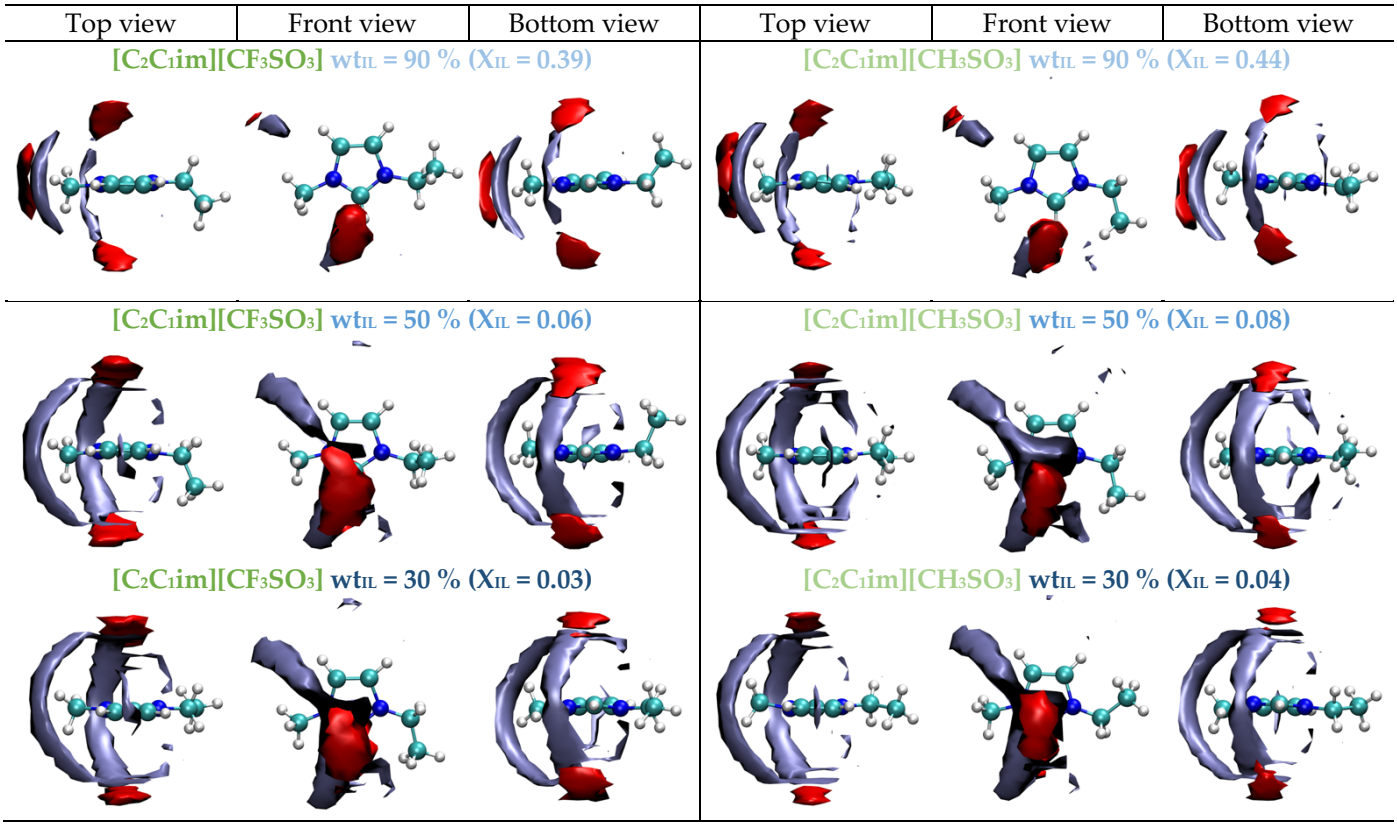

Figure S6. Selected Spatial Distribution Functions around the $[C_2C_1im]^+$ cation in aqueous mixtures of $[C_2C_1im][CF_3SO_3]$ and $[C_2C_1im][CH_3SO_3]$ at 300 K. The red and light blue colours represent S (-$\underline{S}O_3$) atom of anion and water O atom, respectively. The isosurface value is 70% of the maximum number density.

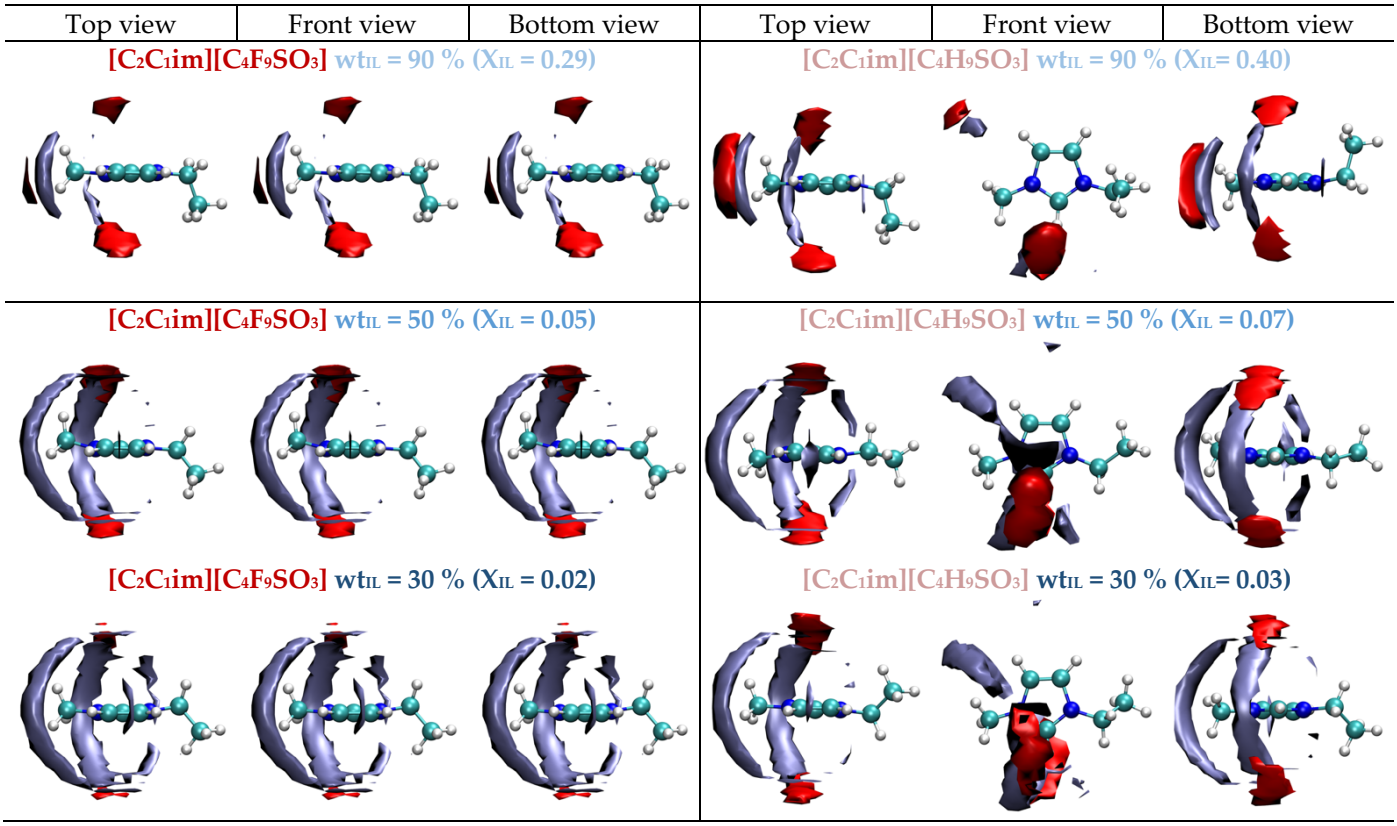

Figure S7. Selected Spatial Distribution Functions around the $[C_2C_1im]^+$ cation in aqueous mixtures of $[C_2C_1im][C_4F_9SO_3]$ and $[C_2C_1im][C_4H_9SO_3]$ at 300 K. The red and and light blue colours represent S (-$\underline{S}O_3$) atom of anion and water O atom, respectively. The isosurface value is 70% of the maximum number density.

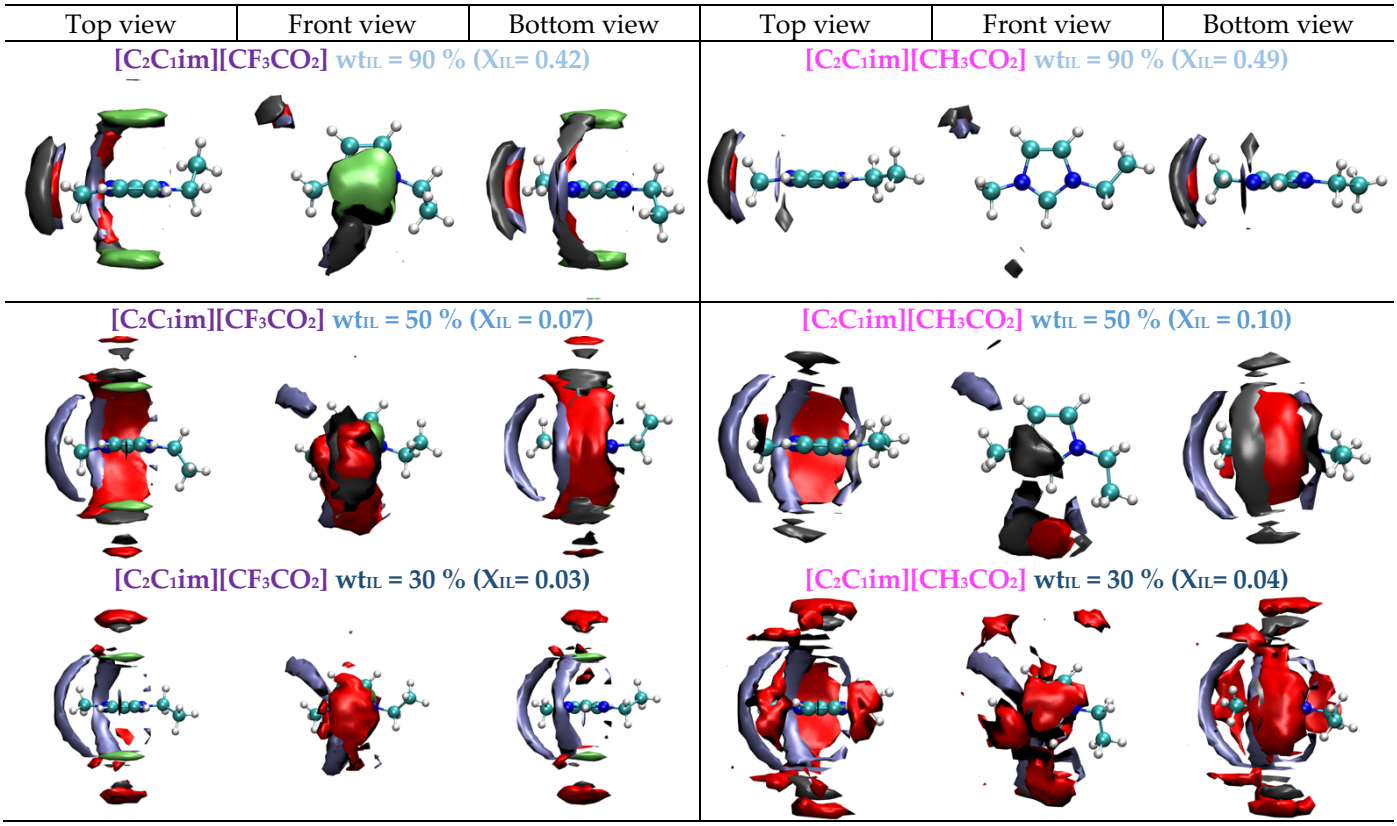

Figure S8. Selected Spatial Distribution Functions around the $[C_2C_1im]^+$ cation in aqueous mixtures of $[C_2C_1im][CF_3CO_2]$ and $[C_2C_1im][CH_3CO_2]$ at 300 K. The grey, red and green colours represent C, O (-$C\underline{O}_2$) and F atoms of anion, respectively, and light blue depicts water O atom. The isosurface value is 70% of the maximum number density.

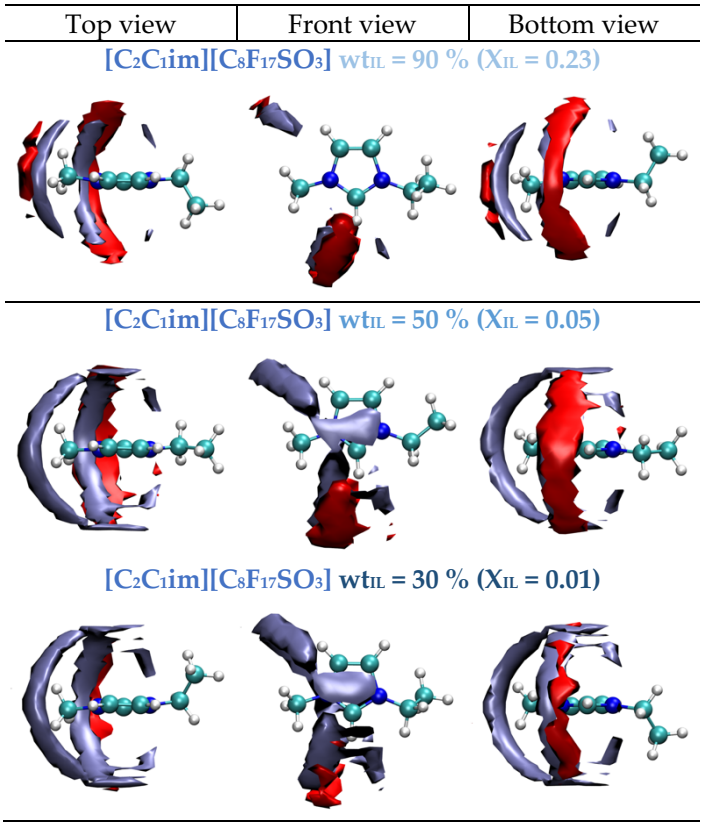

Figure S9. Selected Spatial Distribution Functions around the $[C_2C_1im]^+$ cation in aqueous mixtures of $[C_2C_1im][C_8F_{17}SO_3]$ at 300 K. The red colour represent S (-$\underline{S}O_3$) atom of anion and light blue depicts water O atom. The isosurface value is 70% of the maximum number density.

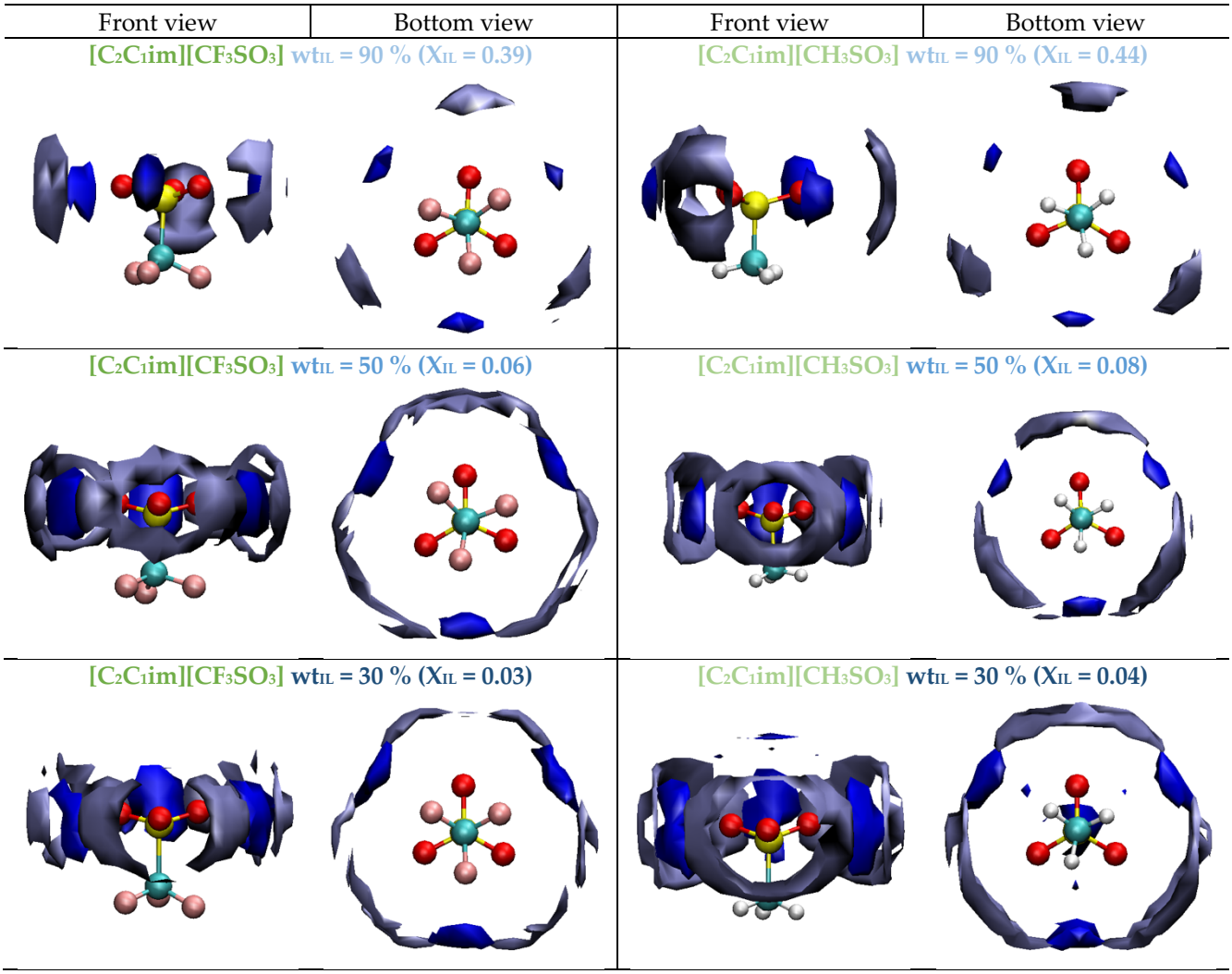

Figure S10. Selected Spatial Distribution Functions around the $[CF_3SO_3]^-$ and $[CH_3SO_3]^-$ anions in aqueous mixtures of $[C_2C_1im][CF_3SO_3]$ and $[C_2C_1im][CH_3SO_3]$ at 300 K. The blue colour represents H atom of cations attached to the carbon between nitrogen atoms of the imidazolium ring and light blue depicts water O atom. The isosurface value is 70% of the maximum number density.

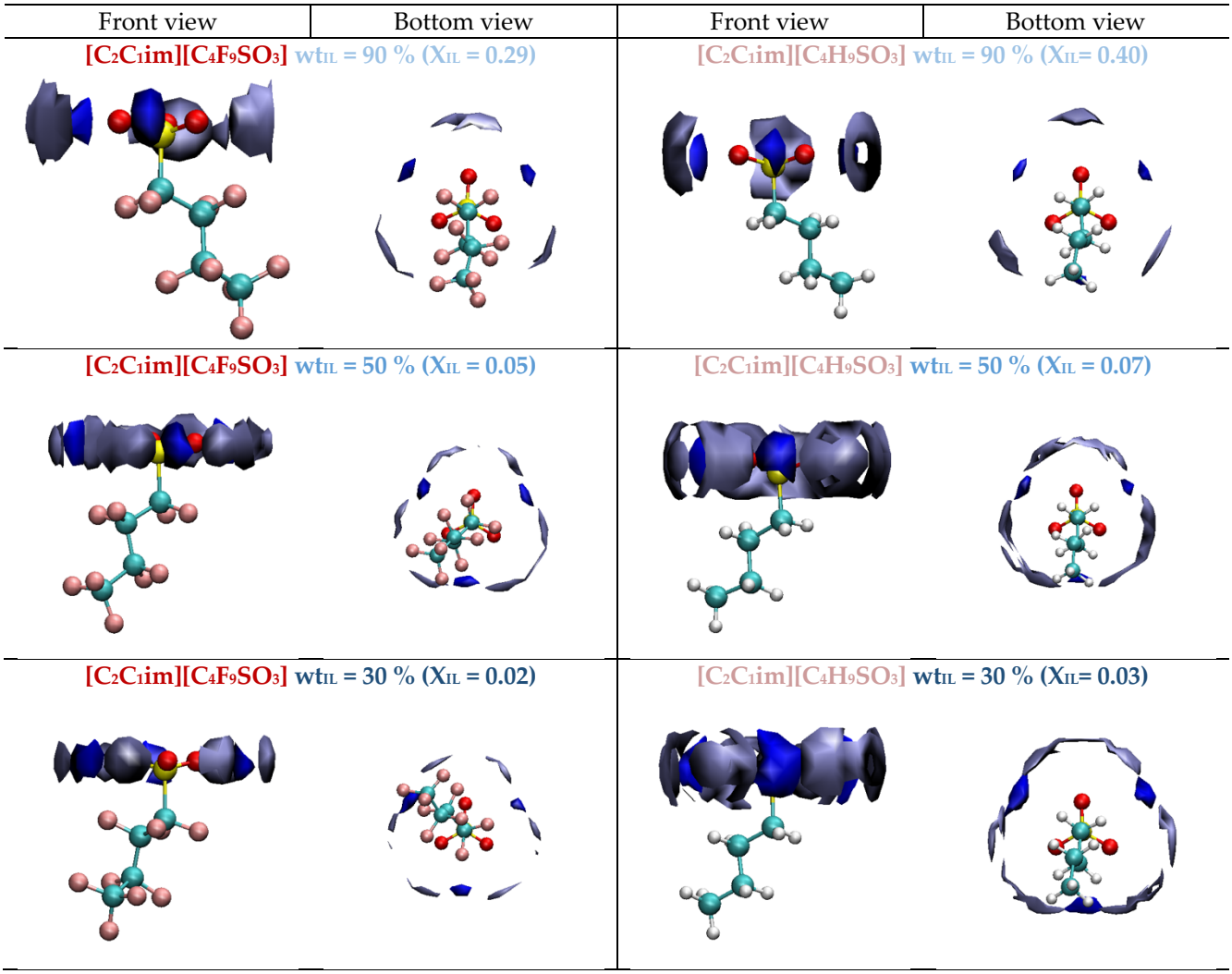

Figure S11. Selected Spatial Distribution Functions around the $[C_4F_9SO_3]^-$ and $[C_4H_9SO_3]^-$ anions in aqueous mixtures of $[C_2C_1im][C_4F_9SO_3]$ and $[C_2C_1im][C_4H_9SO_3]$ at 300 K. The blue colour represents H atom of cations attached to the carbon between nitrogen atoms of the imidazolium ring and light blue depicts water O atom. The isosurface value is 70% of the maximum number density.

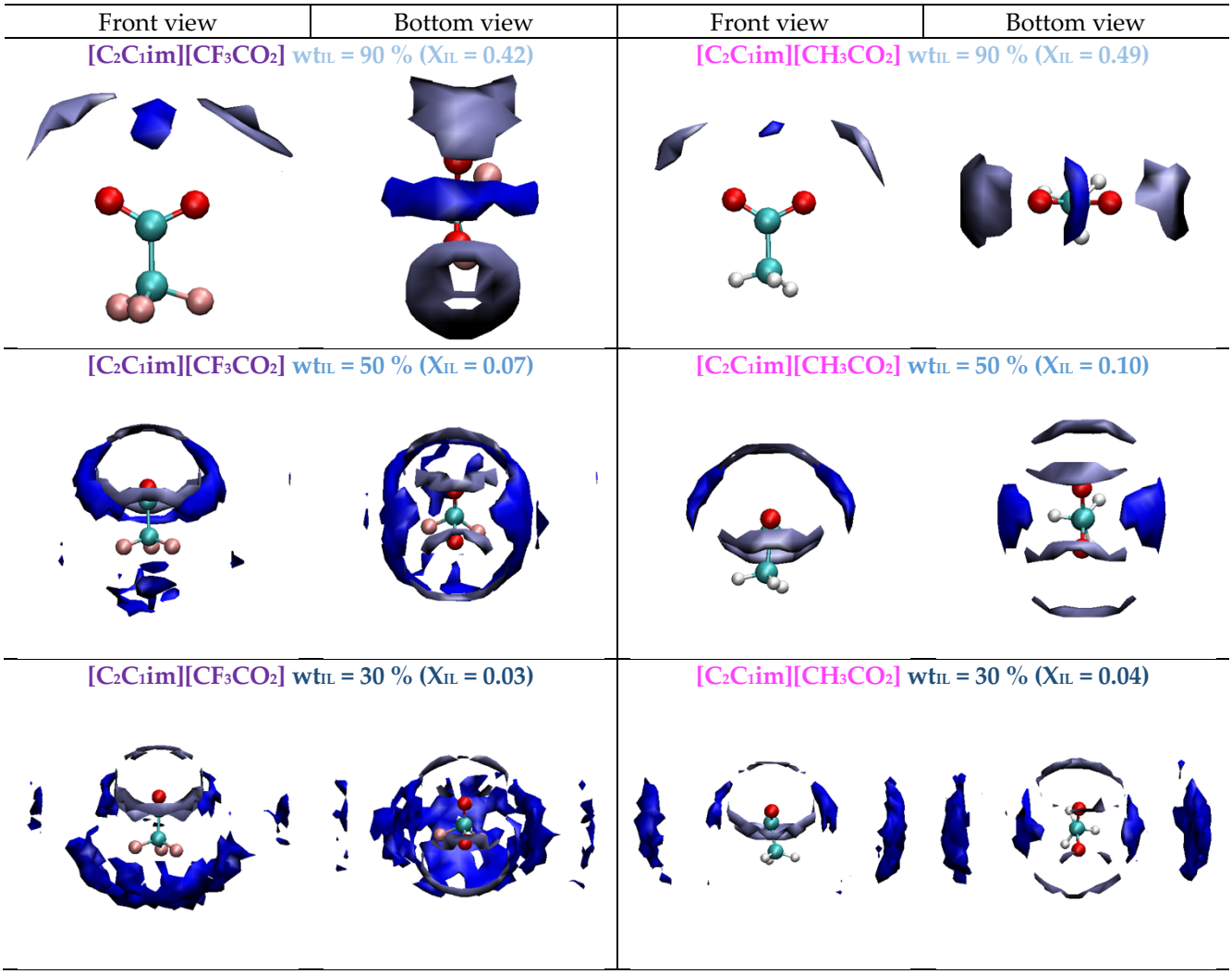

Figure S12. Selected Spatial Distribution Functions around the $[CF_3CO_2]^-$ and $[CH_3CO_2]^-$ anions in aqueous mixtures of $[C_2C_1im][CF_3CO_2]$ and $[C_2C_1im][CH_3CO_2]$ at 300 K. The blue colour represents H atom of cations attached to the carbon between nitrogen atoms of the imidazolium ring and light blue depicts water O atom. The isosurface value is 70% of the maximum number density.

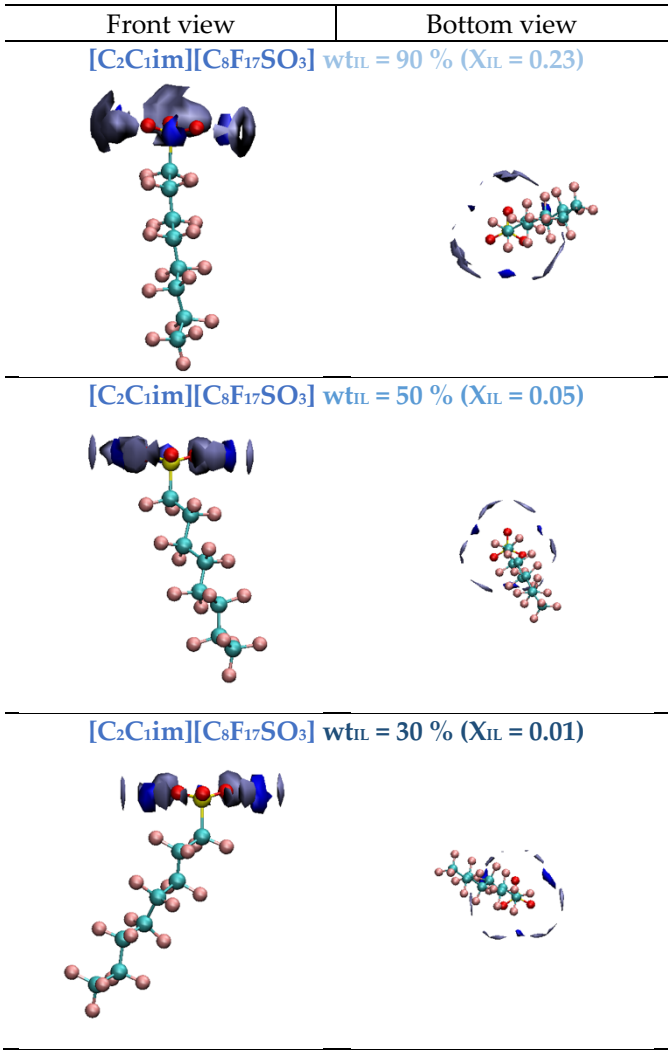

Figure S13. Selected Spatial Distribution Functions around the $[C_8F_{17}SO_3]^-$ anion in aqueous mixtures of $[C_2C_1im][C_8F_{17}SO_3]$ at 300 K. The blue colour represents H atom of cations attached to the carbon between nitrogen atoms of the imidazolium ring and light blue depicts water O atom. The isosurface value is 70% of the maximum number density.

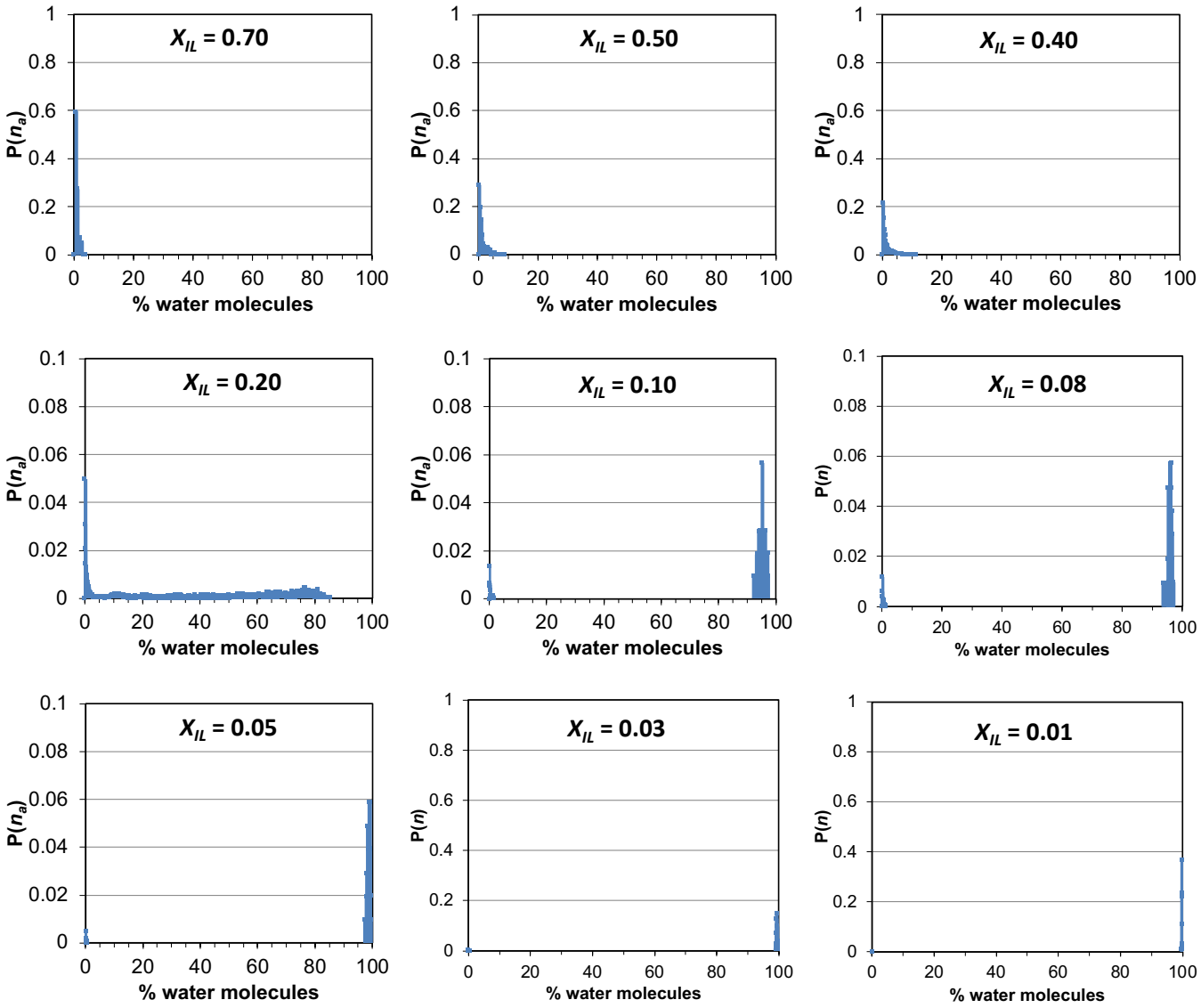

Figure S14. Discrete probability distribution of aggregate sizes, $P(n_a)$, as a function of aggregate size number, n_a, for water-water aggregates found in aqueous solutions of [$N_{1\,2OH\,2OH\,2OH}$][NTf_2] at 300 K.