Supporting Information

Improved Coarse-grain Model to Unravel the Phase Behavior of 1-alkyl-3-methylimidazolium-based Ionic Liquids through Molecular Dynamics Simulations

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1. Literature report

1.1. Critical micellar concentration (cmc) of [C$_n$mim][Cl] and [C$_n$mim][Br] salts.

Table S1. CMC data from literature for 1-alkyl-3-methylimidazolium halides.

Cation	Anion	CMC /M	Method	Reference
[C_6mim]	Cl	0.900	ST	1
[C_8mim]	Cl	0.100	ST	2
[C_8mim]	Cl	0.090	C	2
[C_8mim]	Cl	0.220	ST/C	1,3–5
[C_8mim]	Cl	0.200	NMR/C	1,6
[C_8mim]	Cl	0.234	ST	3
[C_{10}mim]	Cl	0.055	ST/NMR	1
[C_{10}mim]	Cl	0.045	F	1
[C_{10}mim]	Cl	0.062	C	6
[C_{10}mim]	Cl	0.060	C	3
[C_{10}mim]	Cl	0.054	ST	3
[C_{10}mim]	Cl	0.040	ST/C/F	7
[C_{10}mim]	Cl	0.057	C	5
[C_{12}mim]	Cl	0.015	ST	1
[C_{12}mim]	Cl	0.007	F	1
[C_{12}mim]	Cl	0.013	NMR/ST/C	1,7
[C_{12}mim]	Cl	0.014	C/F	6,7
[C_{14}mim]	Cl	0.004	ST/NMR/C/F	1,6,7
[C_{14}mim]	Cl	0.003	ST/C	1,3,5,7
[C_{16}mim]	Cl	<0.001	C/ST/F	3,7
[C_6mim]	Br	0.600	ST	8
[C_6mim]	Br	0.797	NMR	9
[C_6mim]	Br	0.400	C	8
[C_8mim]	Br	0.150	ST/C	8
[C_8mim]	Br	0.160	SANS/C	4,8
[C_8mim]	Br	0.190	F	4
[C_8mim]	Br	0.140	NMR	10
[C_9mim]	Br	0.074	C	11
[C_{10}mim]	Br	0.040	P/ST/SANS/C	8,11–13
[C_{10}mim]	Br	0.030	C/NMR	8,9
[C_{12}mim]	Br	0.010	C/ST	10,11,14
[C_{12}mim]	Br	0.011	F/NMR	9,10
[C_{14}mim]	Br	0.002	C	11
[C_{14}mim]	Br	0.003	ST/F/C	10,14
[C_{16}mim]	Br	<0.001	C/ST/F	10,11,14

ST – Surface Tension measurements; C- Conductivity Measurements; NMR – Nuclear Magnetic Resonance; F- Fluorescence; P-Potentiometry

1.2. Average aggregation numbers (N_{agg}) of [C$_n$mim][Cl] and [C$_n$mim][Br] salts.

Table S2. N_{agg} data from literature for 1-alkyl-3-methylimidazolium halides.

Cation	Anion	[IL] /M	*N*	Method	Reference
[C$_8$mim]	Cl	0.380	39	F	4
[C$_{10}$mim]	Cl	0.186	23	DLS	6
[C$_{10}$mim]	Cl	0.041	40	F	7
[C$_{12}$mim]	Cl	0.014	37	DLS	6
[C$_{12}$mim]	Cl	0.014	58	F	7
[C$_{14}$mim]	Cl	0.011	46	DLS	6
[C$_{14}$mim]	Cl	0.004	79	F	7
[C$_{16}$mim]	Cl	0.001	99	F	7
[C$_6$mim]	Br	0.797	18	NMR	9
[C$_8$mim]	Br	0.200	10	SANS	8
[C$_8$mim]	Br	0.250	21	SANS	8
[C$_8$mim]	Br	0.300	23	SANS	8
[C$_8$mim]	Br	0.350	21	SANS	8
[C$_8$mim]	Br	0.400	24	SANS	8
[C$_8$mim]	Br	0.500	23	SANS	8
[C$_8$mim]	Br	0.750	26	SANS	8
[C$_8$mim]	Br	1.000	27	SANS	8
[C$_8$mim]	Br	1.500	24	SANS	8
[C$_8$mim]	Br	0.252	53	F	4
[C$_8$mim]	Br	0.141	25	NMR	9
[C$_9$mim]	Br	0.150	45	F	11
[C$_{10}$mim]	Br	0.040	14	SANS	8
[C$_{10}$mim]	Br	0.050	37	SANS	8
[C$_{10}$mim]	Br	0.060	37	SANS	8
[C$_{10}$mim]	Br	0.080	40	SANS	8
[C$_{10}$mim]	Br	0.100	39	SANS	8
[C$_{10}$mim]	Br	0.130	40	SANS	8
[C$_{10}$mim]	Br	0.170	41	SANS	8
[C$_{10}$mim]	Br	0.200	42	SANS	8
[C$_{10}$mim]	Br	0.300	45	SANS	8
[C$_{10}$mim]	Br	0.400	45	SANS	8
[C$_{10}$mim]	Br	0.600	47	SANS	8
[C$_{10}$mim]	Br	0.150	42	F	11
[C$_{10}$mim]	Br	0.031	27	NMR	9
[C$_{12}$mim]	Br	0.055	44	F	10,11
[C$_{12}$mim]	Br	0.020	37	F	10
[C$_{12}$mim]	Br	0.011	46	NMR	9
[C$_{14}$mim]	Br	0.025	59	F	10,11

[C_{14}mim]	Br	0.010	48	F	[10]
[C_{16}mim]	Br	0.010	66	F	[10,11]
[C_{16}mim]	Br	0.004	64	F	[10]

F- Fluorescence; DLS- Dynamic Light Scattering; SANS – Small Angle Neutron Scattering; NMR – Nuclear Magnetic Resonance

2. MD-Simulations conditions

2.1. All-atom

Table S3. All-atom MD simulations carried in this work.

Run N#	Cation	*T*/K	Ion Pairs	[IL]/%wt.	[IL]/M	Time (ns)
A1	[C_{14}mim]	298	50	1.015	0.032	20
A2	[C_{10}mim]	298	40	15.53	0.600	50

2.2. Coarse-grain

Table S4. Coarse-grain MD simulations carried in this work.

Run	Cation	*T*/K	ILs	[IL]/%wt.	[IL]/M	Time (μs)	IC
C1	[C_4mim]	298	1000	7.65	0.438	3	RP
C2	[C_4mim]	298	1000	17.5	1.000	3	RP
C3	[C_4mim]	298	1000	26.2	1.500	3	RP
C4	[C_4mim]	298	2000	61.8	3.536	3	RP
C5	[C_8mim]	298	2000	10	0.433	3	RP
C6	[C_8mim]	350	2000	10	0.433	3	RP
C7	[C_8mim]	390	2000	10	0.433	3	RP
C8	[C_8mim]	298	2000	25	1.083	3	RP
C9	[C_8mim]	350	2000	25	1.083	3	RP
C10	[C_8mim]	390	2000	25	1.083	3	RP
C11	[C_8mim]	298	2000	37	1.603	3	RP
C12	[C_8mim]	350	2000	37	1.603	3	RP
C13	[C_8mim]	390	2000	37	1.603	3	RP
C14	[C_8mim]	298	2000	50	2.167	3	RP
C15	[C_8mim]	350	2000	50	2.167	3	RP
C16	[C_8mim]	390	2000	50	2.167	3	RP
C17	[C_8mim]	298	2000	68.1	2.951	3	RP
C18	[C_8mim]	350	2000	68.1	2.951	3	RP
C19	[C_8mim]	390	2000	68.1	2.951	3	RP
C20	[C_8mim]	298	2000	50	2.167	3	FP (C16)
C21	[C_8mim]	450	2000	68.1	2.951	3	RP
C22	[C_8mim]	350	2000	68.1	2.951	3	FP (C21)

C23	[C_{10}mim]	298	2000	10	0.386	3	RP
C24	[C_{10}mim]	350	2000	10	0.386	3	RP
C25	[C_{10}mim]	390	2000	10	0.386	3	RP
C26	[C_{10}mim]	298	2000	25	0.966	3	RP
C27	[C_{10}mim]	350	2000	25	0.966	3	RP
C28	[C_{10}mim]	390	2000	25	0.966	3	RP
C29	[C_{10}mim]	298	2000	37	1.430	3	RP
C30	[C_{10}mim]	350	2000	37	1.430	3	RP
C31	[C_{10}mim]	390	2000	37	1.430	3	RP
C32	[C_{10}mim]	298	2000	50	1.932	3	RP
C33	[C_{10}mim]	350	2000	50	1.932	3	RP
C34	[C_{10}mim]	390	2000	50	1.932	3	RP
C35	[C_{10}mim]	298	2000	70	2.704	3	RP
C36	[C_{10}mim]	350	2000	70	2.704	3	RP
C37	[C_{10}mim]	390	2000	70	2.704	3	RP
C38	[C_{10}mim]	298	40	15.5	0.600	0.1	PM
C39	[C_{10}mim]	298	2000	35.3	1.365	0.1	RP
C40	[C_{10}mim]	350	2000	50	1.932	3	FP(C34)
C41	[C_{14}mim]	298	2000	10	0.318	3	RP
C42	[C_{14}mim]	350	2000	10	0.318	3	RP
C43	[C_{14}mim]	390	2000	10	0.318	3	RP
C44	[C_{14}mim]	298	2000	25	0.794	3	RP
C45	[C_{14}mim]	350	2000	25	0.794	3	RP
C46	[C_{14}mim]	390	2000	25	0.794	3	RP
C47	[C_{14}mim]	298	2000	37	1.175	3	RP
C48	[C_{14}mim]	350	2000	37	1.175	3	RP
C49	[C_{14}mim]	390	2000	37	1.175	3	RP
C50	[C_{14}mim]	298	2000	50	1.588	3	RP
C51	[C_{14}mim]	350	2000	50	1.588	3	RP
C52	[C_{14}mim]	390	2000	50	1.588	3	RP
C53	[C_{14}mim]	298	2000	71.4	2.267	3	RP
C54	[C_{14}mim]	350	2000	71.4	2.267	3	RP
C55	[C_{14}mim]	390	2000	71.4	2.267	3	RP
C56	[C_{14}mim]	298	50	1.01	0.032	0.02	PM
C57	[C_{14}mim]	298	50	1.01	0.032	1	RP
C58	[C_{14}mim]	298	1000	2.80	0.089	1	RP
C59	[C_{14}mim]	450	2000	50	1.588	3	RP
C60	[C_{14}mim]	350	2000	50	1.588	3	FP (C59)
C61	[C_{14}mim]	450	2000	71.4	2.267	3	RP
C62	[C_{14}mim]	350	2000	71.4	2.267	3	FP (C61)

IC- Initial Coordinates; RP – Random Positions
FP – Final Positions; PM – Pre-shaped Micelle

3. CG Model development and validation

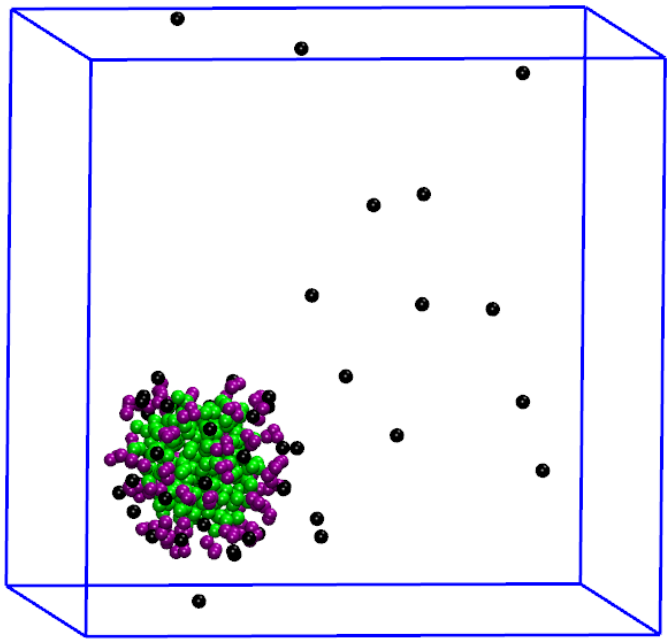

Figure S1. Final snapshot of a CG-MD simulation of [C14mim][Cl] in water at 298 K and an IL concentration of 0.032 M, starting from random positions (run C57). Color code: green for the cation alkyl tails, purple for the surfactant head groups, and black for the chloride anions. Water molecules have been removed for clarity.

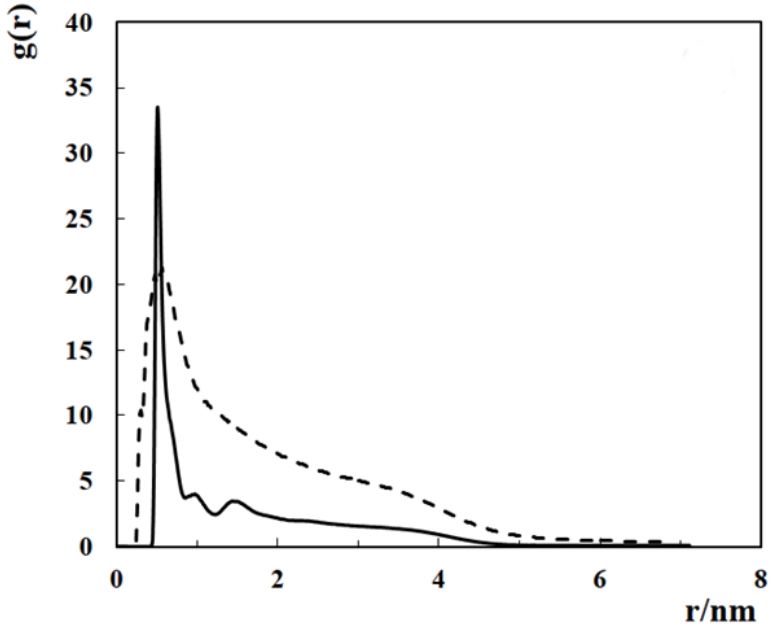

Figure S2. Radial distribution function between the imidazolium ring and the chloride anions for the CG (solid line) and AA (dashed lines) MD simulations of the [C_{14}mim][Cl]/H2O system.

4. MD simulations at low IL concentrations (Micellar regime)

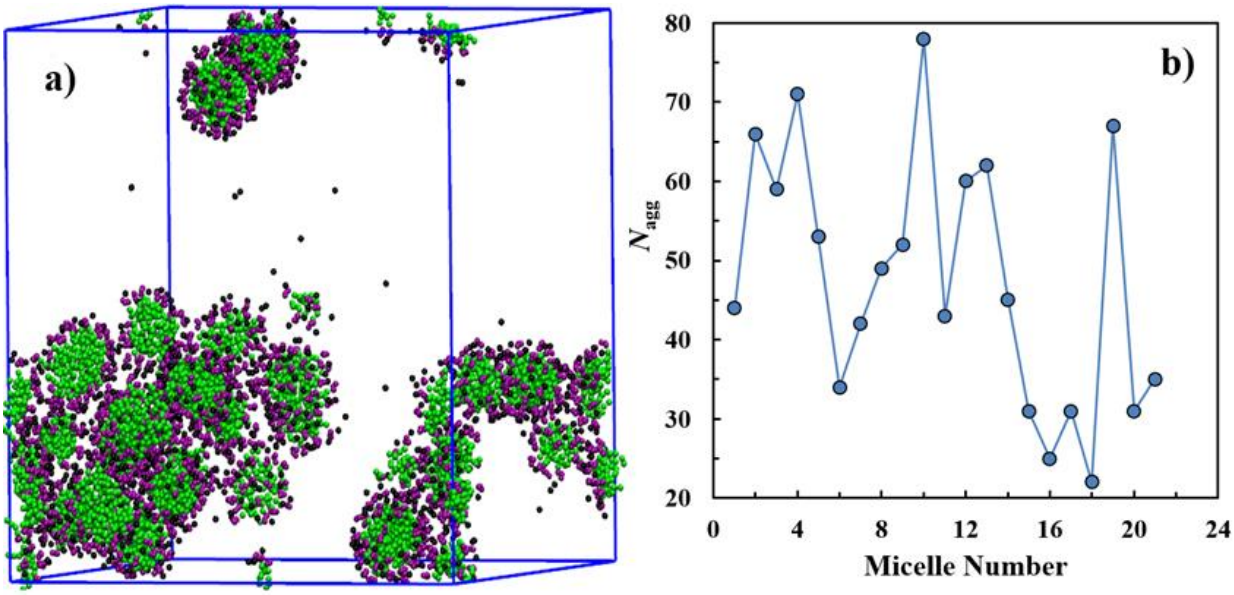

Figure S3. a) Final snapshot of the CG-MD simulation of [C_{14}mim][Cl]/H2O system at 298 K and 0.089 M. Color code is as in **Figure S1**. b) Micelle size distribution.

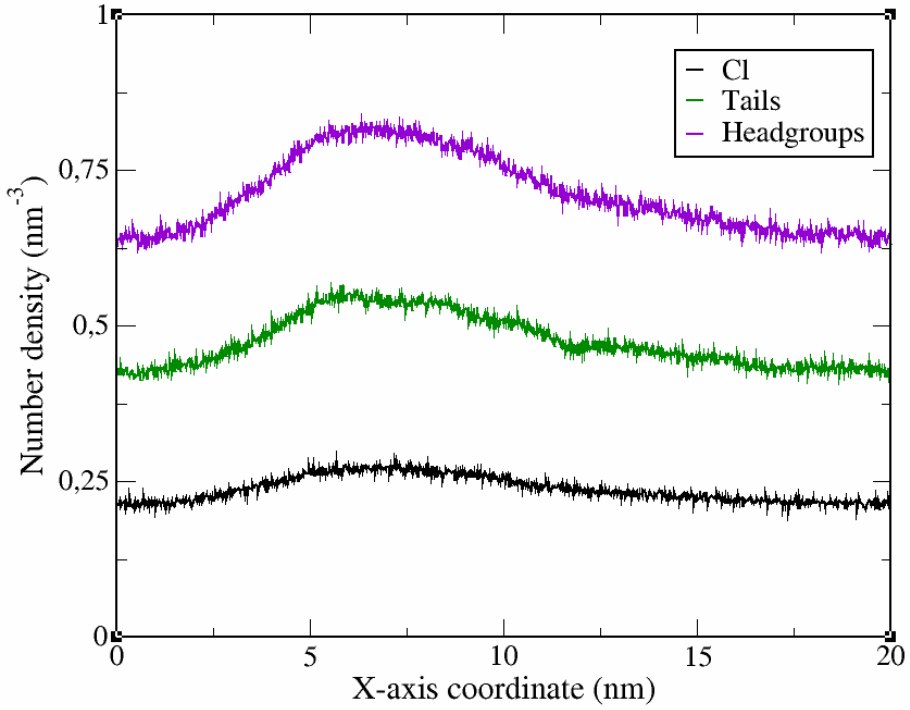

Figure S4. Number density profile of the different bead types along the *x*-axis of the simulation box for the CG-MD simulation of an aqueous solution of [C_8mim][Cl] at 298 K and 10 wt% of IL.

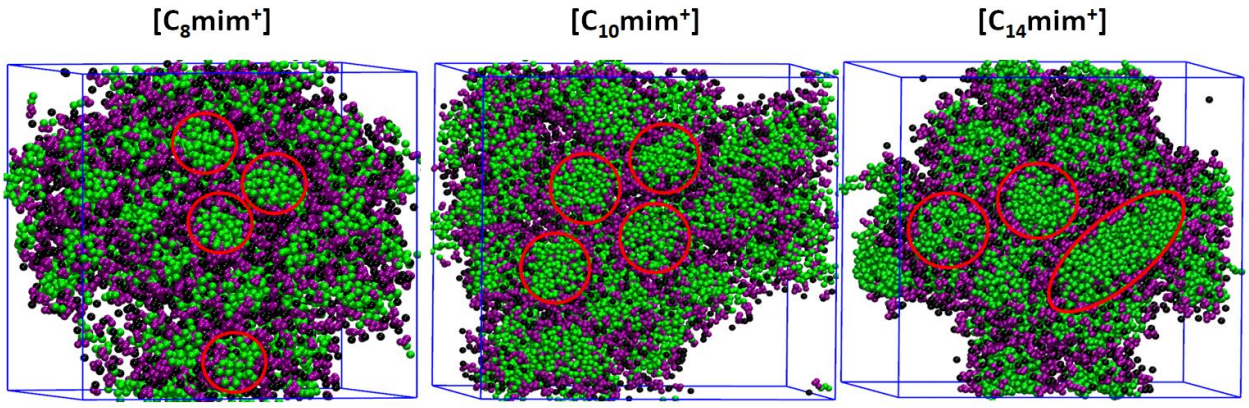

Figure S5. Final snapshots of the CG-MD simulations at 298 K and an IL concentration of 25 wt%. Color code is as in **Figure S1**.

5. Lyotropic Liquid Crystals (LLC)

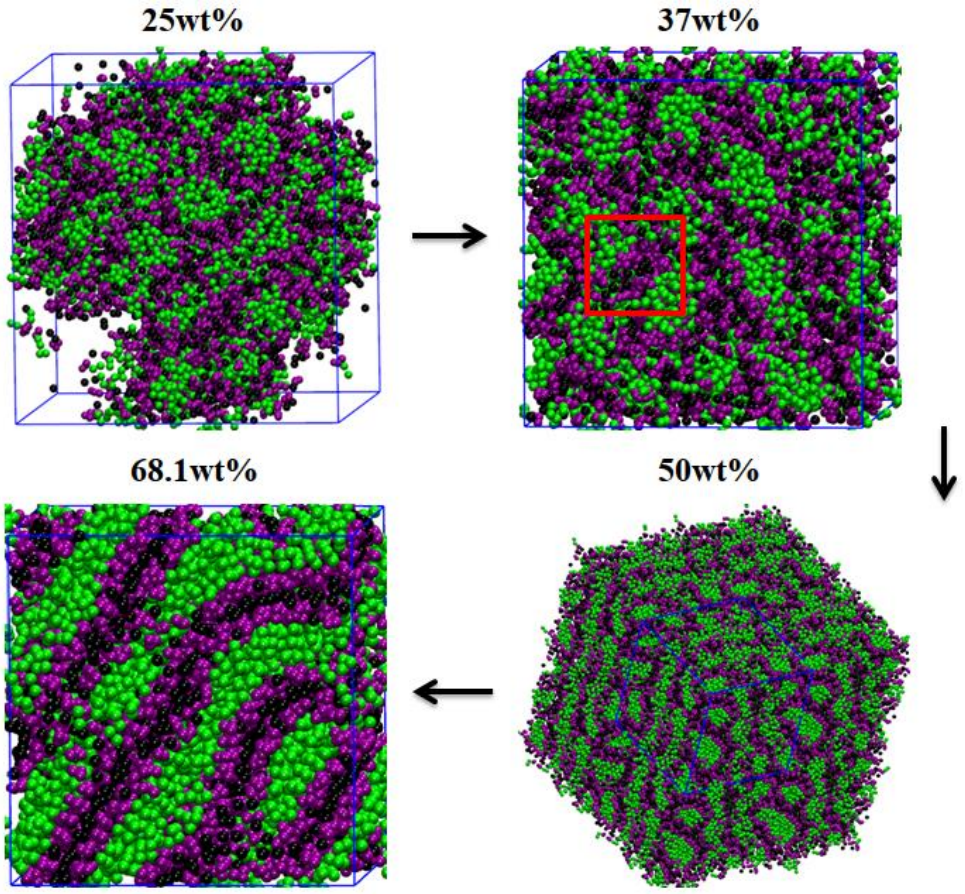

Figure S6. Final simulation snapshots for the aqueous solution of [C_8mim][Cl] at 298 K for different IL concentrations. Color code is as in **Figure S1**.

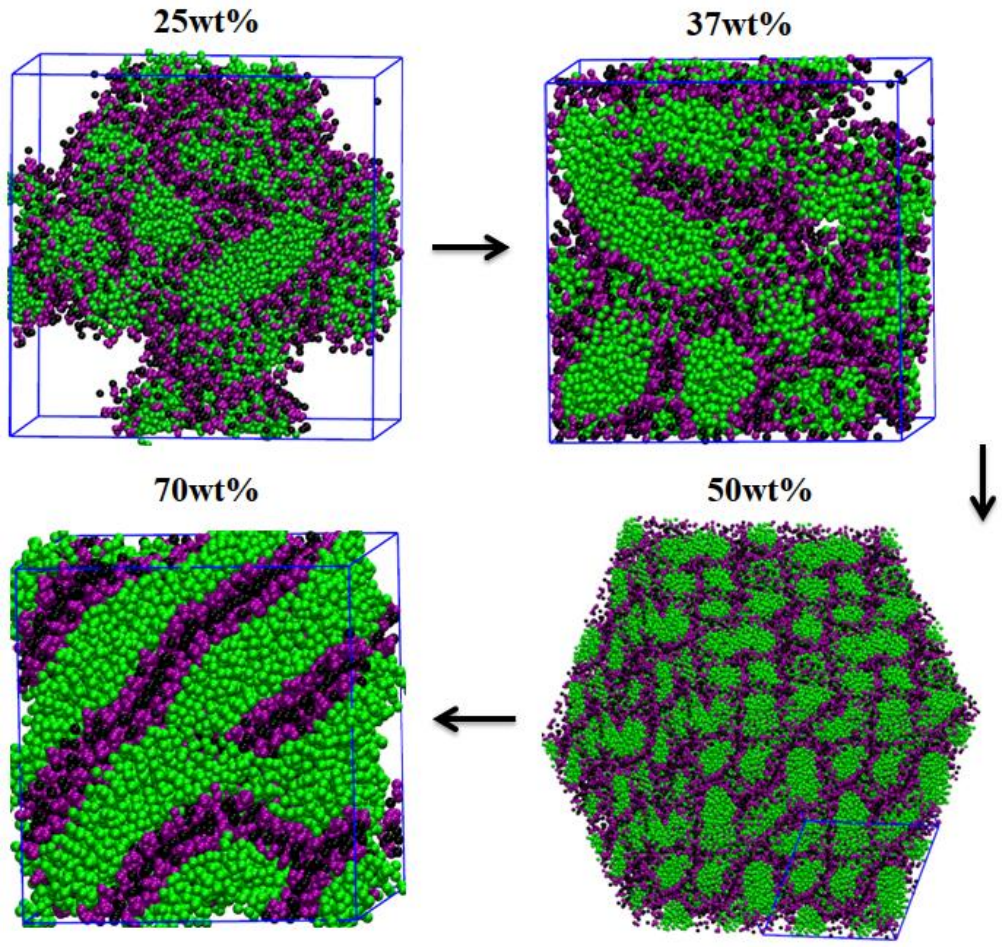

Figure S7. Final simulation snapshots for the aqueous solution of [C_{14}mim][Cl] at 298 K and different IL concentrations. Color code is as in **Figure S1**.

6. [C_4mim][Cl]/H_2O system

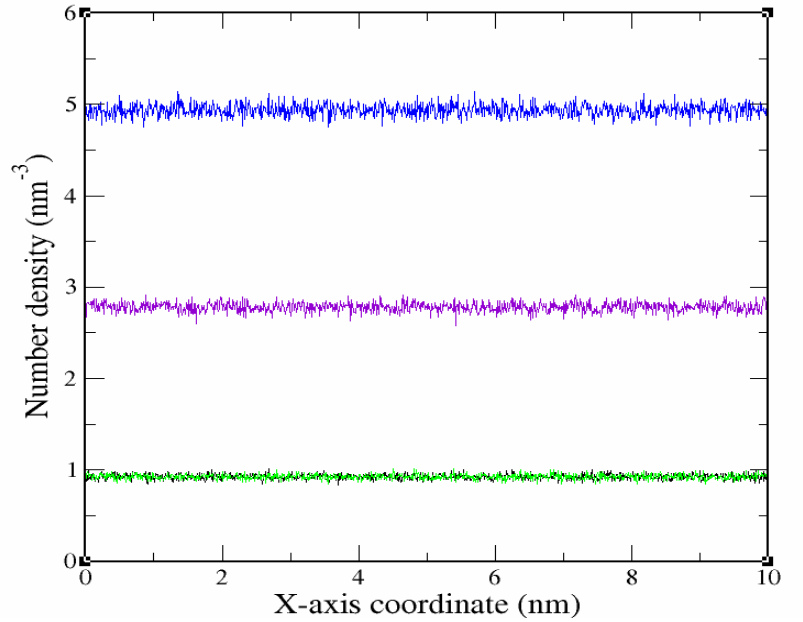

Figure S8. Number density profile of water molecules (blue), imidazolium head groups (purple), alkyl tails (green) and chloride anions (black) along the x-axis of the simulation box for the CG-MD simulation of an aqueous solution of [C_4mim][Cl] 1.5 M.

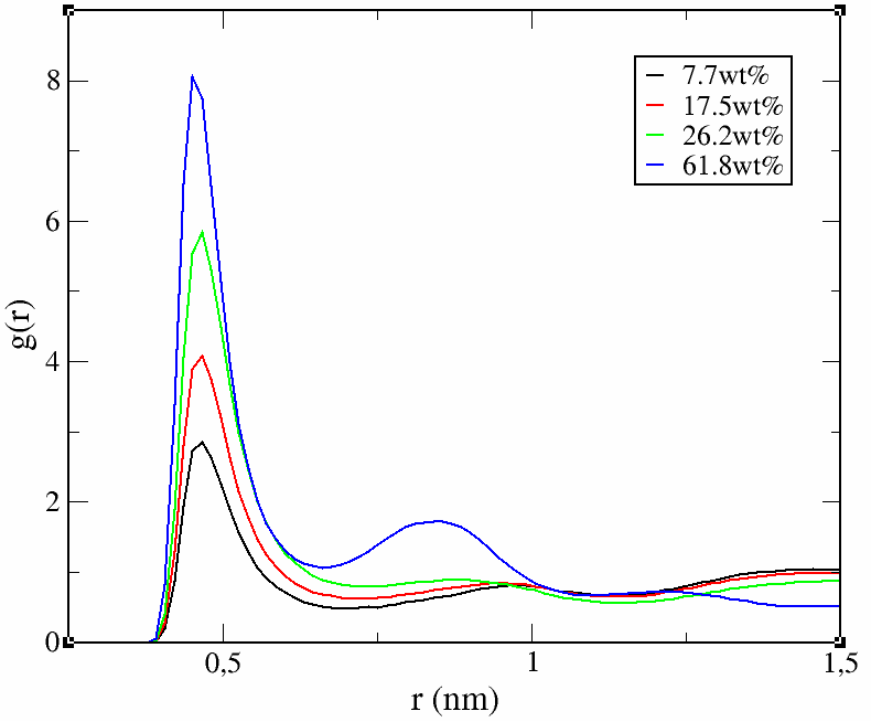

Figure S9. RDF between alkyl tails as obtained from the trajectories of the CG-MD simulations of aqueous solutions of [C_4mim][Cl] at 298 K, as a function of the IL concentration.

7. References

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