

**Supporting Information for  
How water manifest the structural regimes in ionic liquids**

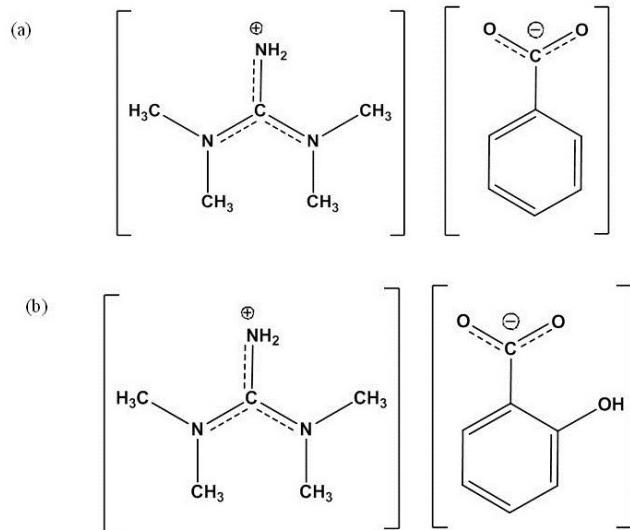
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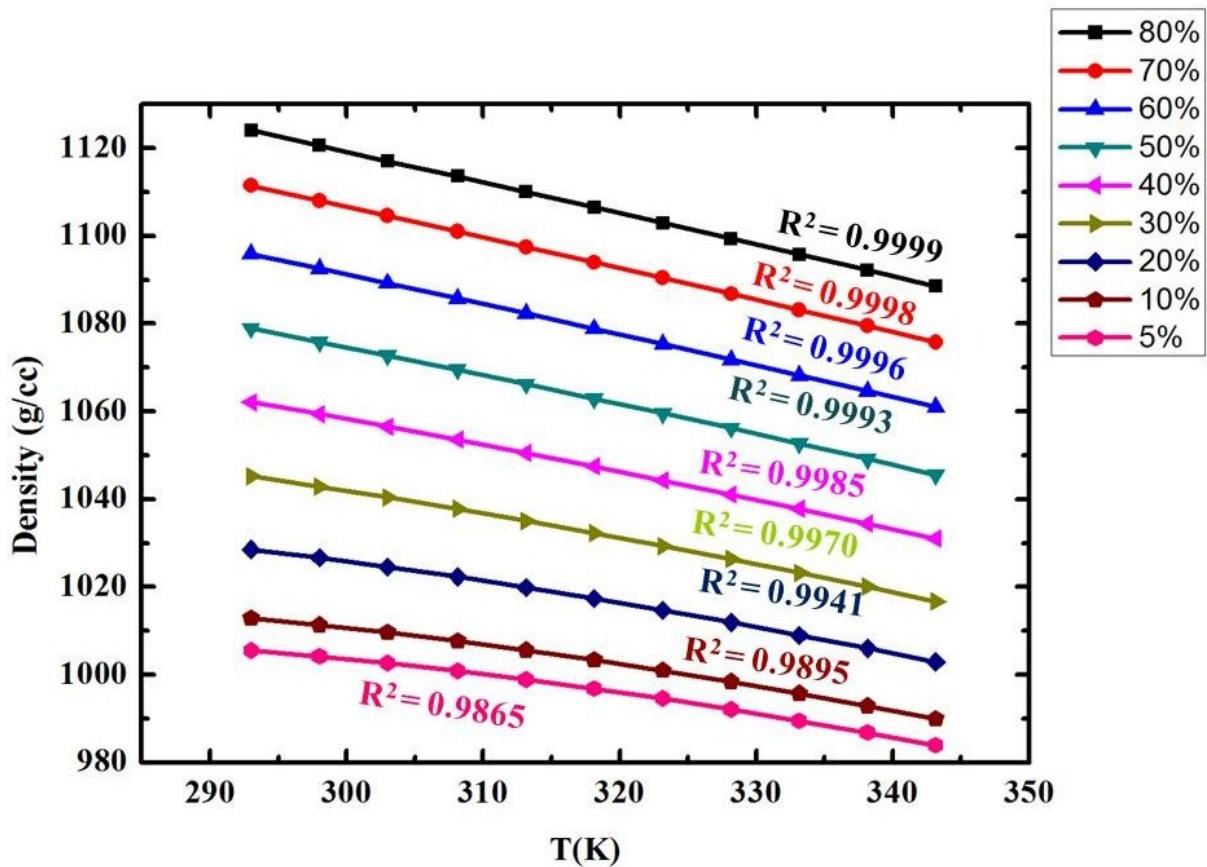
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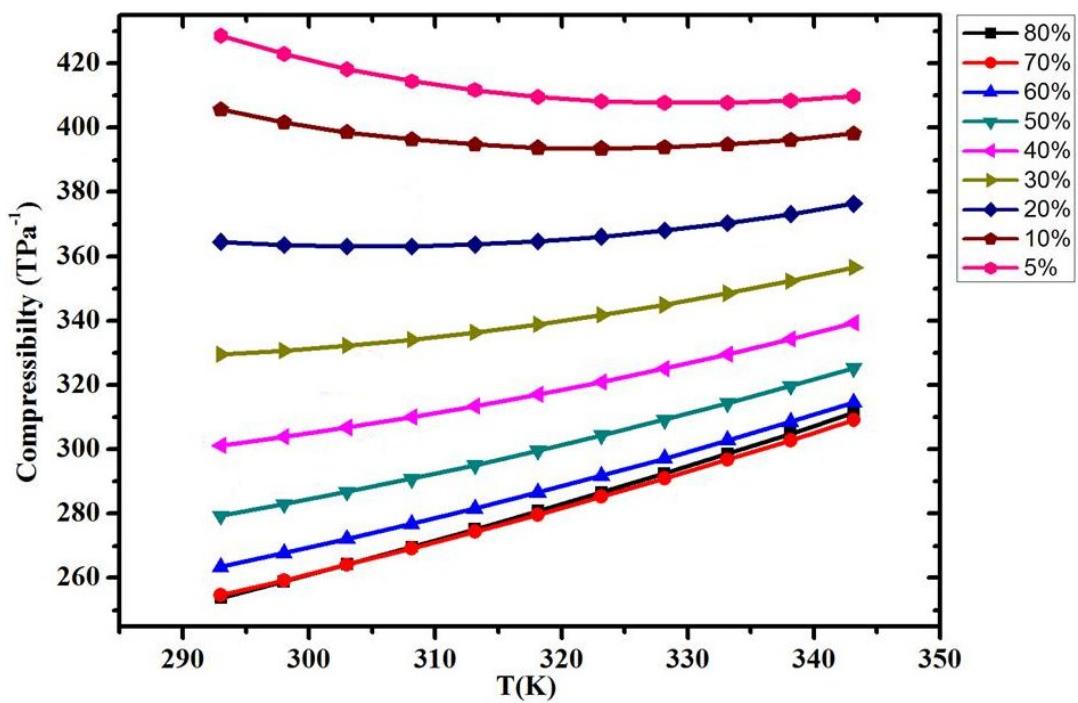
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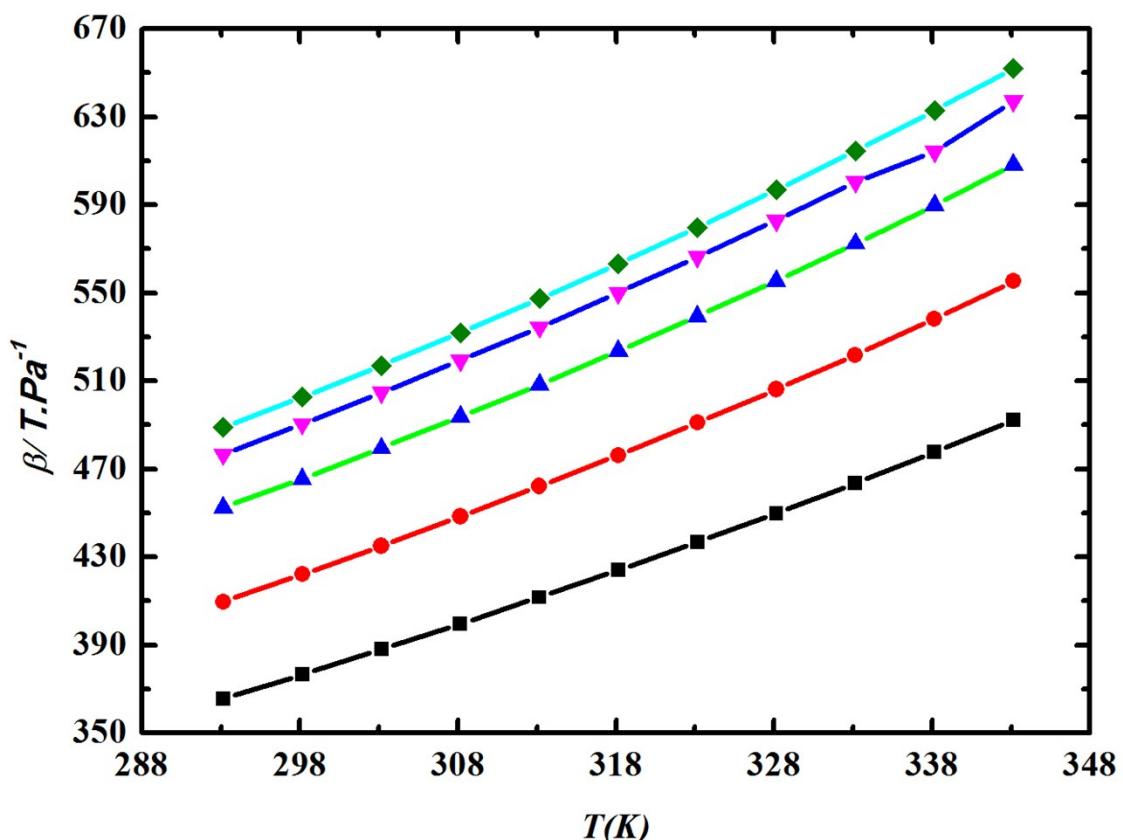
**Figure S1.** Molecular structures of (a) 1,1,3,3-tetramethylguanidinium benzoate and (b) 1,1,3,3-tetramethylguanidinium salicylate.



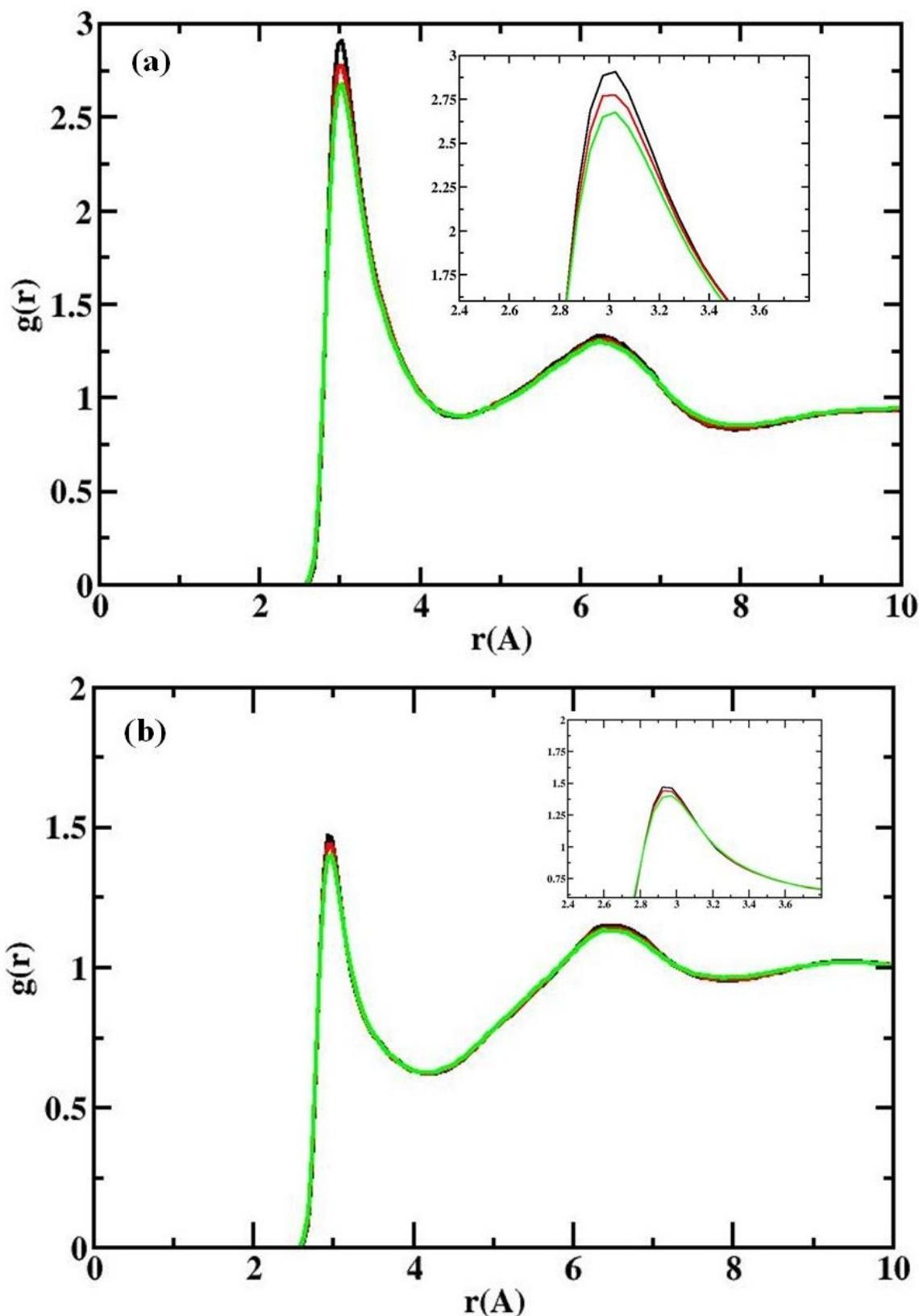
**Figure S2.** Variation in density of the binary mixtures of [TMG][BEN]/water with temperature at different concentration of IL. Experimental points are connected to aid the eye. The  $R^2$  value of linear regression is included for each solution.



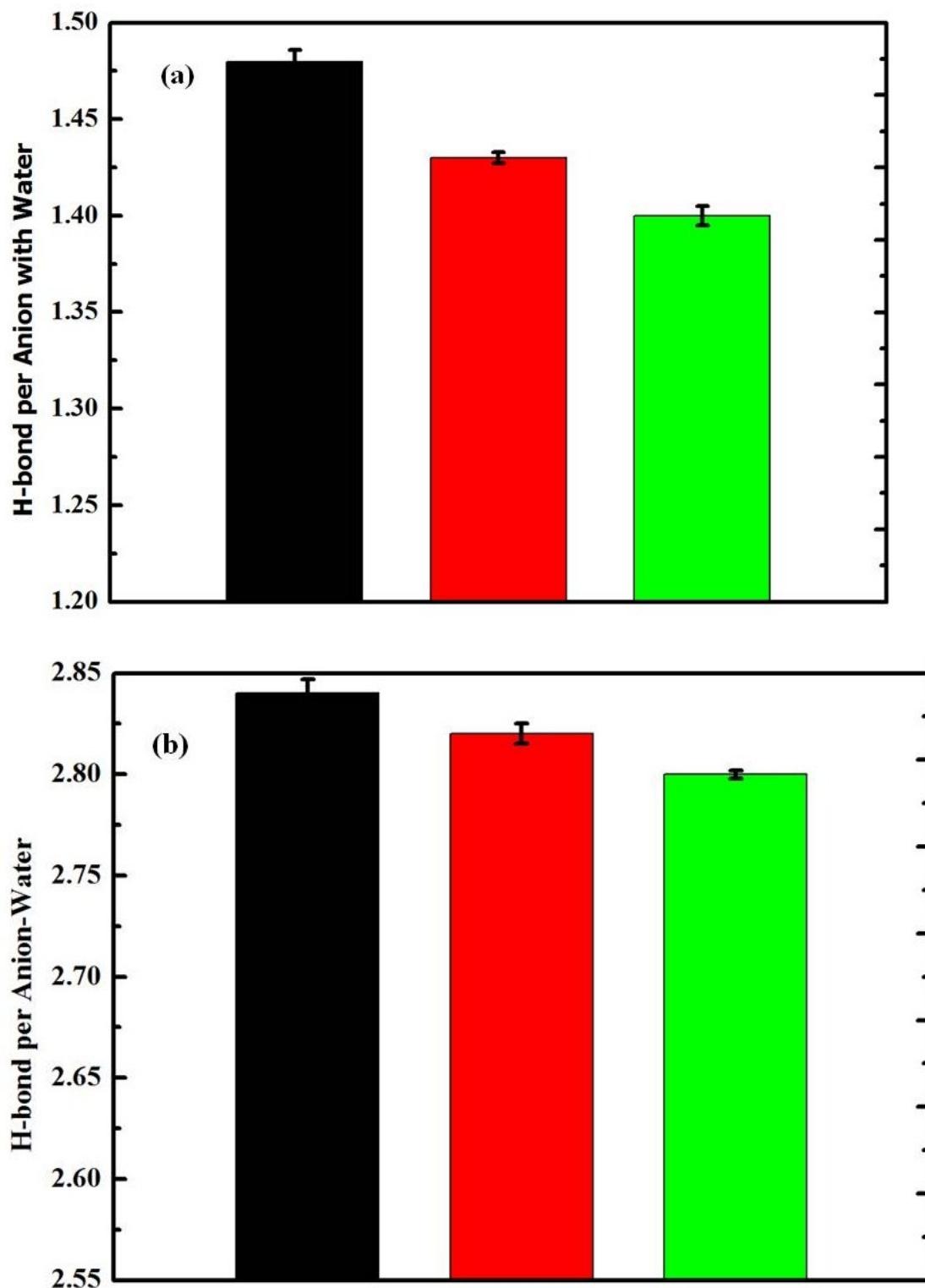
**Figure S3.** Variation in isentropic compressibility of the binary mixtures of [TMG][BEN]/water with temperature at different concentration of IL.



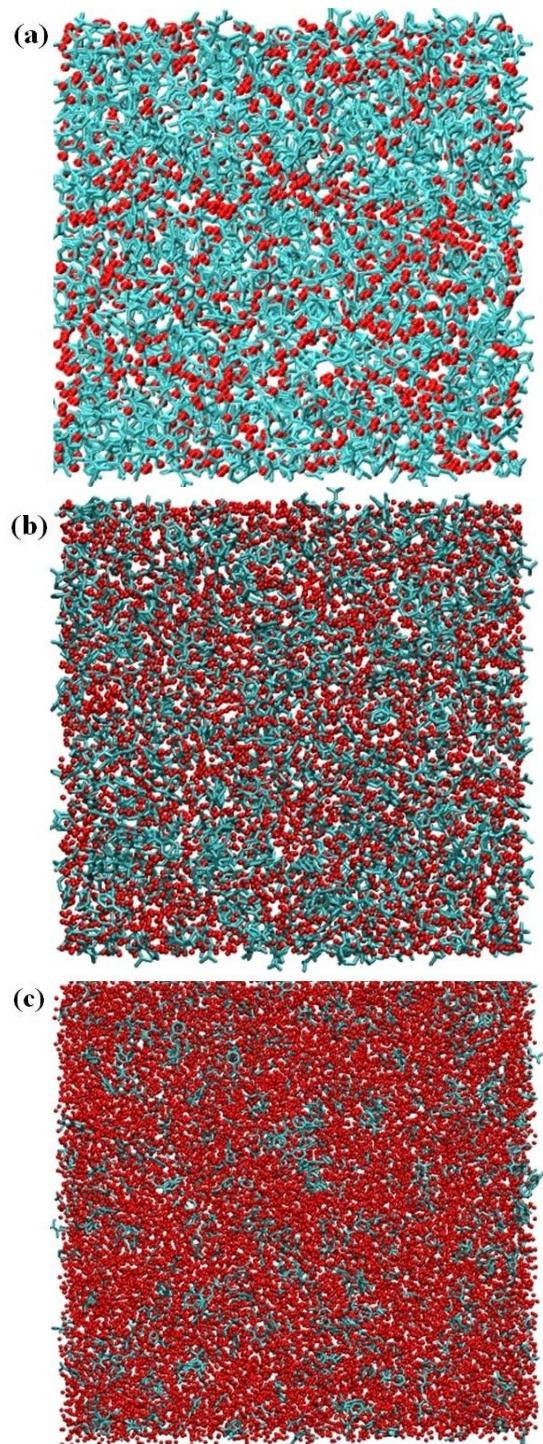
**Figure S4.** Experimental values of compressibility of the following ILs as a function of temperature. ■, [DMEA][Ace]; ●, [DMEA][Pro]; ▲, [DMEA][But]; ▼, [DMEA][Pent]; ▨, [DMEA][Hex]. Data adopted from Ref. 40.



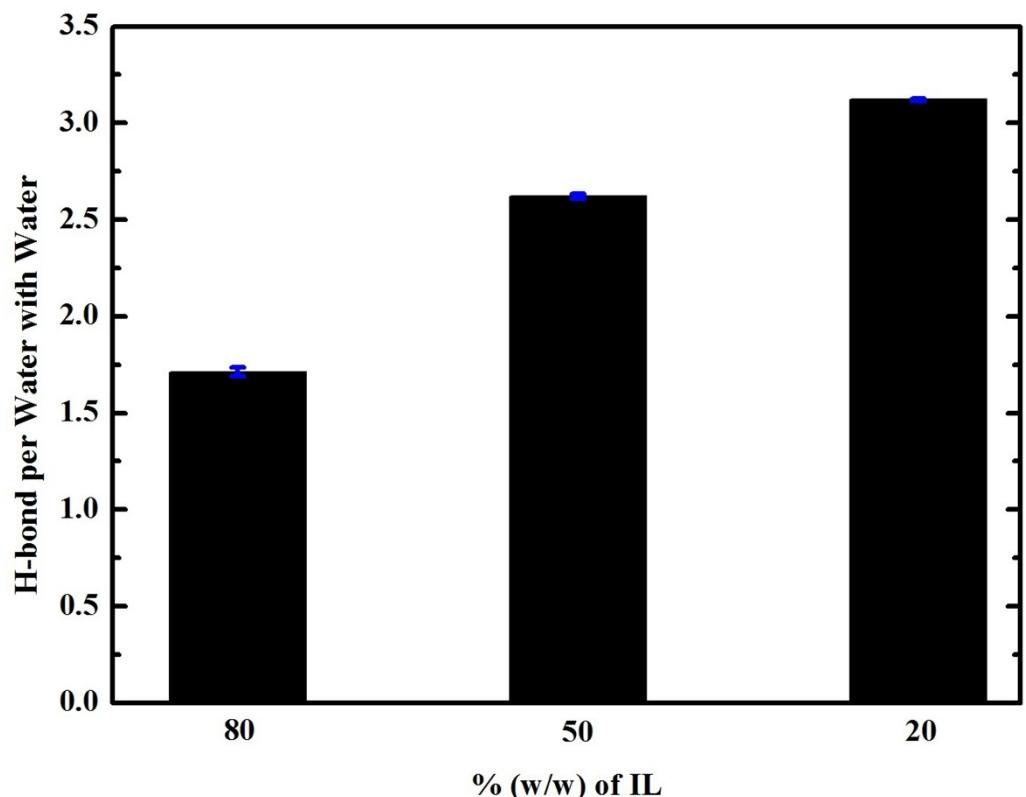
**Figure S5.** Distribution of water around the IL cations in the IL/water binary mixtures as obtained from liquid phase simulations: (a) 80 wt% IL solution, and (b) 20 wt% IL solution. Site-site RDFs are drawn for  $\text{O}_w-\text{N}_{\text{TMG}}$ . Color scheme: black for 298K, red for 313K and green for 343K.



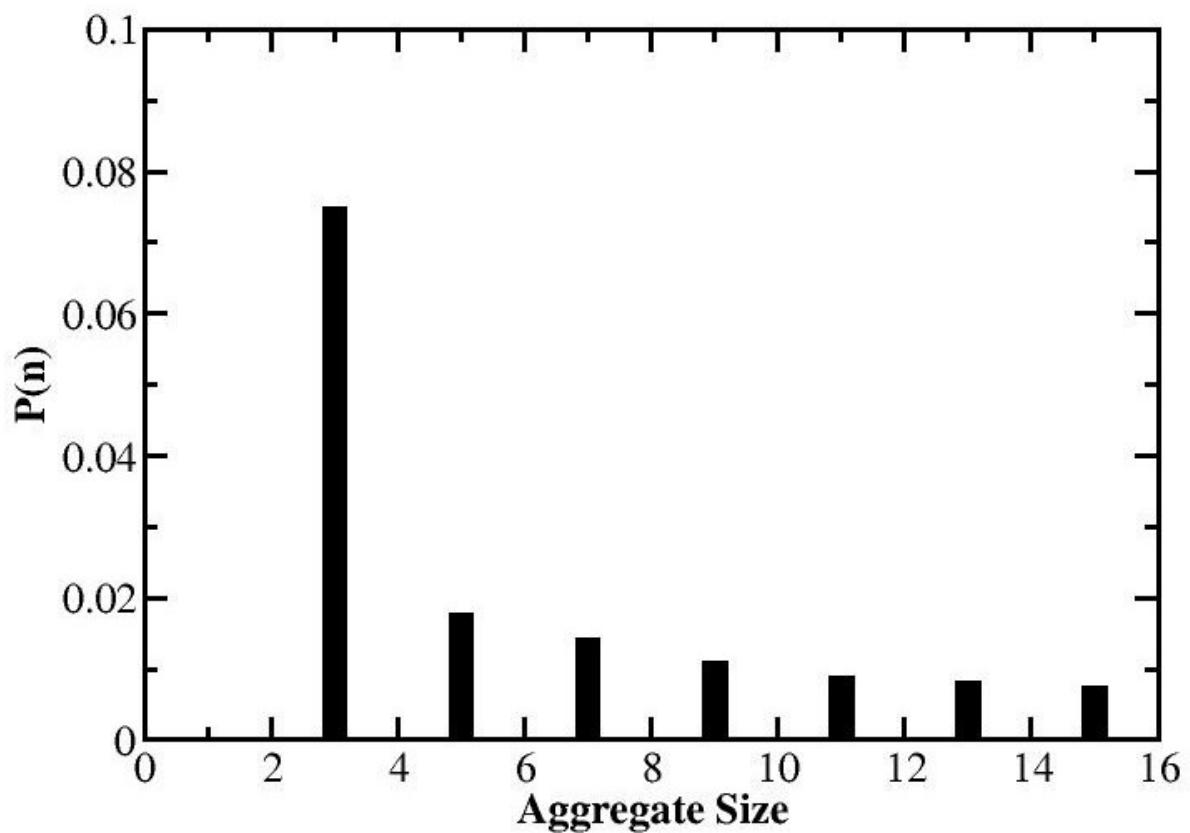
**Figure S6.** . Hydrogen bond analysis for (a) 80 wt% IL and (b) 20 wt% IL aqueous solutions depicting the average number of H-bonds between IL anion and water with temperature. Color scheme: black for 298K, red for 313K and green for 343K.



**Figure S7.** Snapshots from the simulation boxes of [TMG][BEN]/water mixtures at (a) 80 wt% IL (b) 50 wt% IL and (c) 20 wt% IL content. Color scheme: cyan for IL, red for water.



**Figure S8.** Hydrogen bond analysis depicting the average number of H-bonds between water-water in different IL/water binary solutions at 298K.



**Figure S9.** Size distribution of the water aggregates in 80 wt% IL solution of [TMG][BEN] at 298K.

**Table S1.** List of systems simulated.  $N_{IL}$  and  $N_W$  represent number of ionic liquid and water molecules in the simulation systems.

Composition (wt %)	$N_{IL}$	$N_W$	T (K)	Simulation box volume at equilibrium (nm <sup>3</sup> )
80 % [TMG][BEN] + 20 % water	512	1688	298	221.33
80 % [TMG][BEN] + 20 % water			313	225.19
80 % [TMG][BEN] + 20 % water			343	231.24
50 % [TMG][BEN] + 50 % water	512	6749	298	363.38
50 % [TMG][BEN] + 50 % water			313	369.21
50 % [TMG][BEN] + 50 % water			343	380.92
20 % [TMG][BEN] + 80 % water	512	26999	298	980.03
20 % [TMG][BEN] + 80 % water			313	994.90
20 % [TMG][BEN] + 80 % water			343	1025.10
80 % [TMG][SAL] + 20 % water	512	1801	298	229.55
80 % [TMG][SAL] + 20 % water			313	233.40
80 % [TMG][SAL] + 20 % water			343	239.59
50 % [TMG][SAL] + 50 % water	512	7205	298	383.13
50 % [TMG][SAL] + 50 % water			313	390.29
50 % [TMG][SAL] + 50 % water			343	400.80
20 % [TMG][SAL] + 80 % water	512	28820	298	1042.28
20 % [TMG][SAL] + 80 % water			313	1055.28
20 % [TMG][SAL] + 80 % water			343	1061.20

**Table S2.** Average interaction energies (kcal/mol) of various components in the IL/water mixtures.

		298 K	313 K	343 K
80 % [TMG][BEN] + 20 % water	Anion-Water	-38.72 ± 0.29	-37.70 ± 0.13	-36.52 ± 0.13
	Cation-Water	-8.90 ± 0.09	-8.62 ± 0.09	-8.40 ± 0.07
	Cation-Anion	-8.38 ± 0.07	-7.96 ± 0.12	-7.49 ± 0.05
	Water-Water	-3.21 ± 0.003	-3.08 ± 0.002	-2.83 ± 0.002
50 % [TMG][BEN] + 50 % water	Anion-Water	-104.87 ± 0.65	-102.26 ± 0.36	-98.32 ± 0.19
	Cation-Water	-25.20 ± 0.03	-24.94 ± 0.02	-24.39 ± 0.02
	Cation-Anion	-2.31 ± 0.36	-2.72 ± 0.16	-3.11 ± 0.14
	Water-Water	-5.44 ± 0.007	-5.28 ± 0.004	-5.03 ± 0.003
20 % [TMG][BEN] + 80 % water	Anion-Water	-132.03 ± 0.61	-130.21 ± 0.89	-126.38 ± 0.63
	Cation-Water	-39.38 ± 0.06	-39.28 ± 0.05	-39.06 ± 0.04
	Cation-Anion	-21.36 ± 0.21	-22.69 ± 0.20	-20.50 ± 0.22
	Water-Water	-8.14 ± 0.006	-7.96 ± 0.008	-7.59 ± 0.004

**Table S3.** Fit parameters of the anion–water hydrogen bond time correlation function for representative IL/water binary mixtures with temperature. All  $\tau$  values are in picosecond.

Composition (wt %)	T (K)	c <sub>1</sub>	τ <sub>1</sub>	c <sub>2</sub>	τ <sub>2</sub>	c <sub>3</sub>	τ <sub>3</sub>	τ <sub>avg</sub>
80 % [TMG][BEN] + 20 % water	298	0.30	49.07	0.17	1.38	0.53	339.90	316.87
80 % [TMG][BEN] + 20 % water	313	0.60	32.16	0.20	200.71	0.20	5.51	143.78
80 % [TMG][BEN] + 20 % water	343	0.15	111.82	0.51	17.45	0.34	1.50	78.32
20 % [TMG][BEN] + 80 % water	298	0.20	1.28	0.64	10.65	0.16	37.88	22.94
20 % [TMG][BEN] + 80 % water	313	0.65	8.56	0.13	32.79	0.22	1.16	18.38
20 % [TMG][BEN] + 80 % water	343	0.10	25.28	0.63	6.04	0.27	1.08	12.69

**Table S4.** Fit parameters of the water–water hydrogen bond time correlation function for representative IL/water binary mixtures with temperature. All  $\tau$  values are in picosecond.

Composition (wt %)	T (K)	c <sub>1</sub>	τ <sub>1</sub>	c <sub>2</sub>	τ <sub>2</sub>	c <sub>3</sub>	τ <sub>3</sub>	τ <sub>avg</sub>
80 % [TMG][BEN] + 20 % water	298	0.28	27.05	0.33	165.63	0.39	0.83	148.12
80 % [TMG][BEN] + 20 % water	313	0.50	0.94	0.40	16.77	0.10	110.94	72.26
80 % [TMG][BEN] + 20 % water	343	0.36	0.02	0.36	2.61	0.28	19.12	16.55
20 % [TMG][BEN] + 80 % water	298	0.81	0.98	0.19	6.23			4.09
20 % [TMG][BEN] + 80 % water	313	0.14	5.81	0.86	0.91			3.39
20 % [TMG][BEN] + 80 % water	343	0.92	0.79	0.08	5.48			2.53

Table S5. Radius of gyration, Rg (Å) of the IL clusters at different water content and temperature

Composition (wt %)	298 K	313 K	343 K
80 % [TMG][BEN] + 20 % water	7.71 ± 0.09	7.90 ± 0.18	8.25 ± 0.06
50 % [TMG][BEN] + 50 % water	7.48 ± 0.07	7.76 ± 0.07	7.99 ± 0.09
20 % [TMG][BEN] + 80 % water	5.56 ± 0.09	6.72 ± 0.11	7.68 ± 0.10