Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Divergent trend in density *versus* viscosity of ionic liquid/water mixtures: A molecular view from guanidinium ionic liquids

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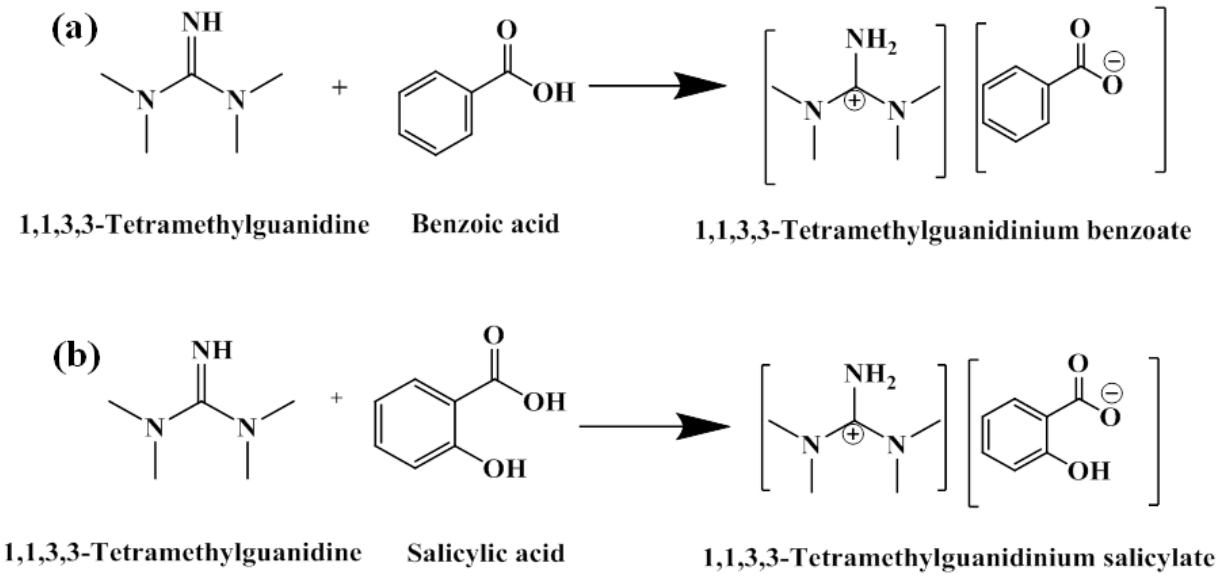


Figure S1. Scheme for synthesis of (a) 1,1,3,3-tetramethylguanidinium benzoate and (b) 1,1,3,3-tetramethylguanidinium salicylate.

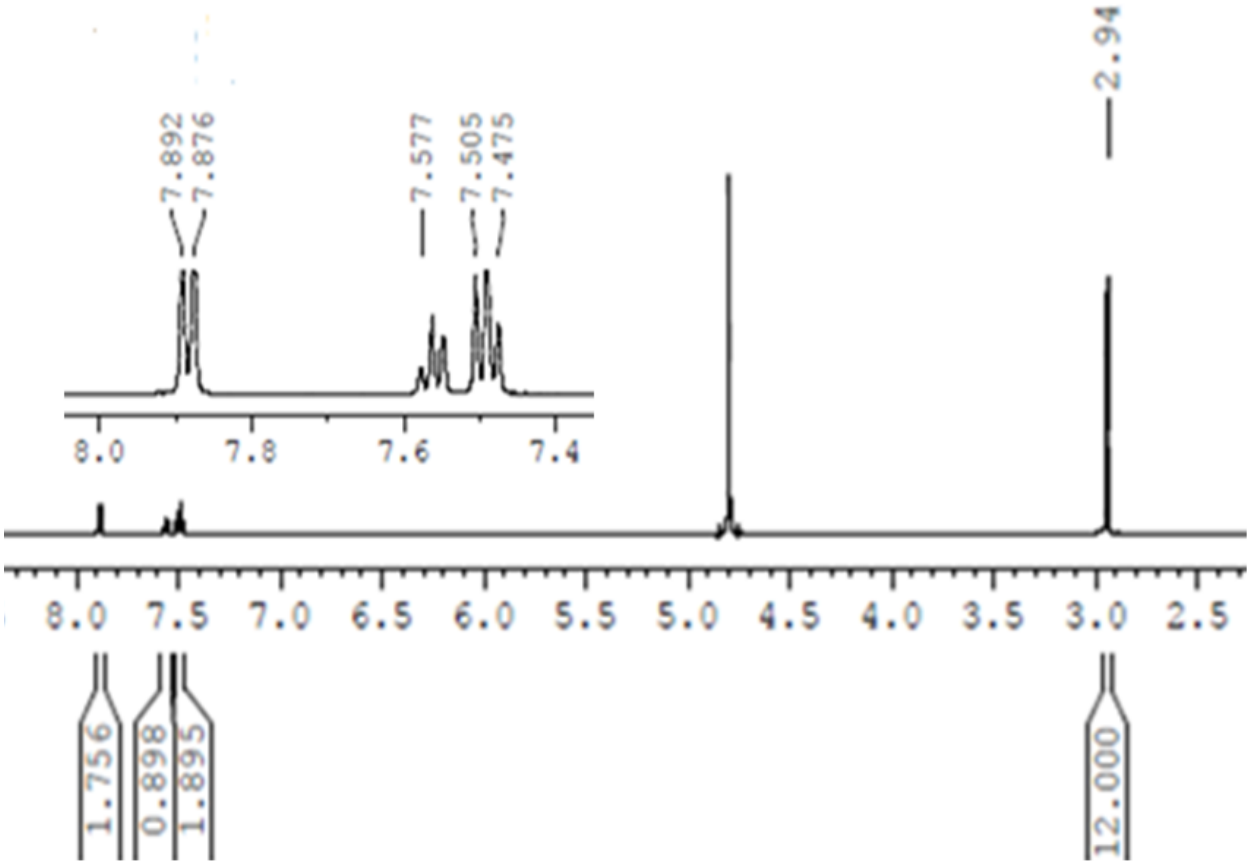


Figure S2. The ^{1}H NMR (500MHz, D2O) spectra of [TMG][BEN].

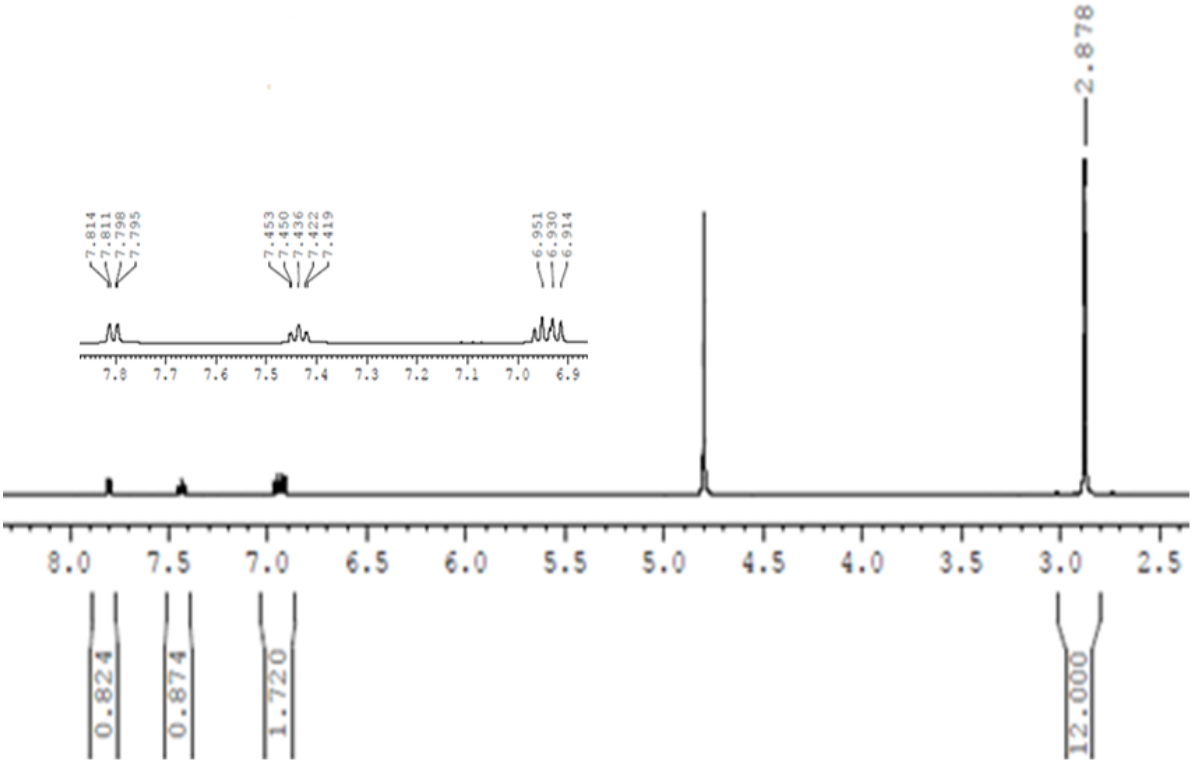
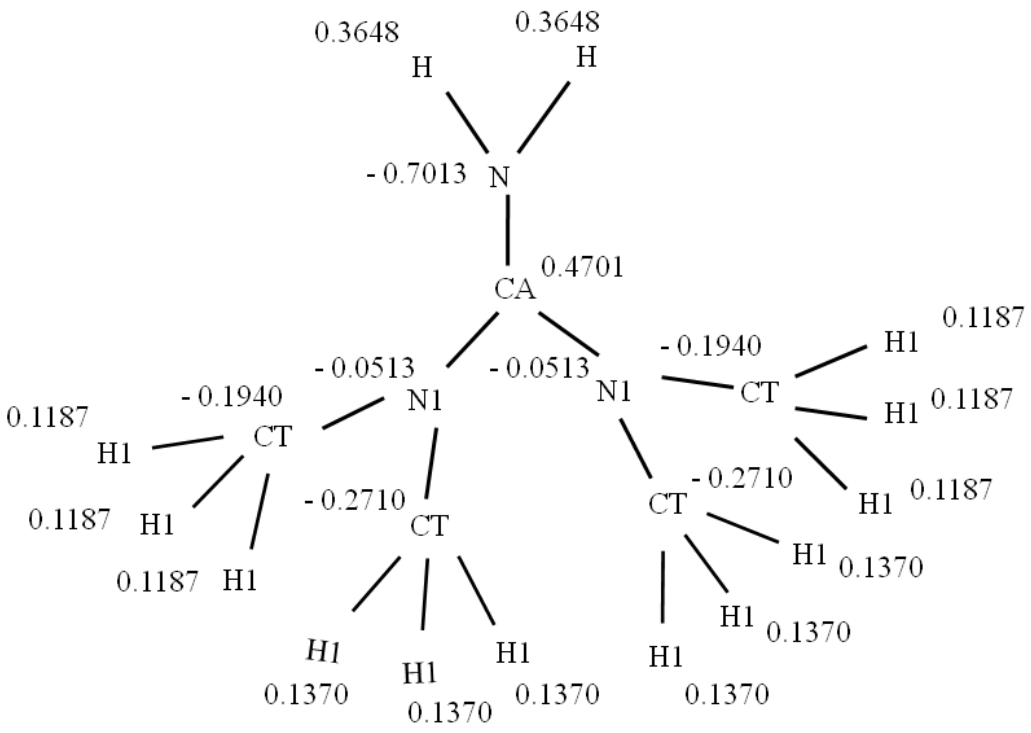
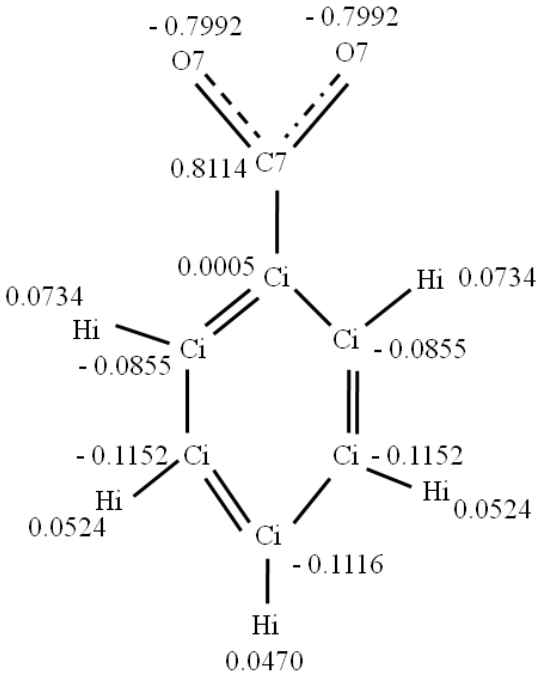


Figure S3. The ^{1}H NMR (500MHz, D2O) spectra of [TMG][SAL].

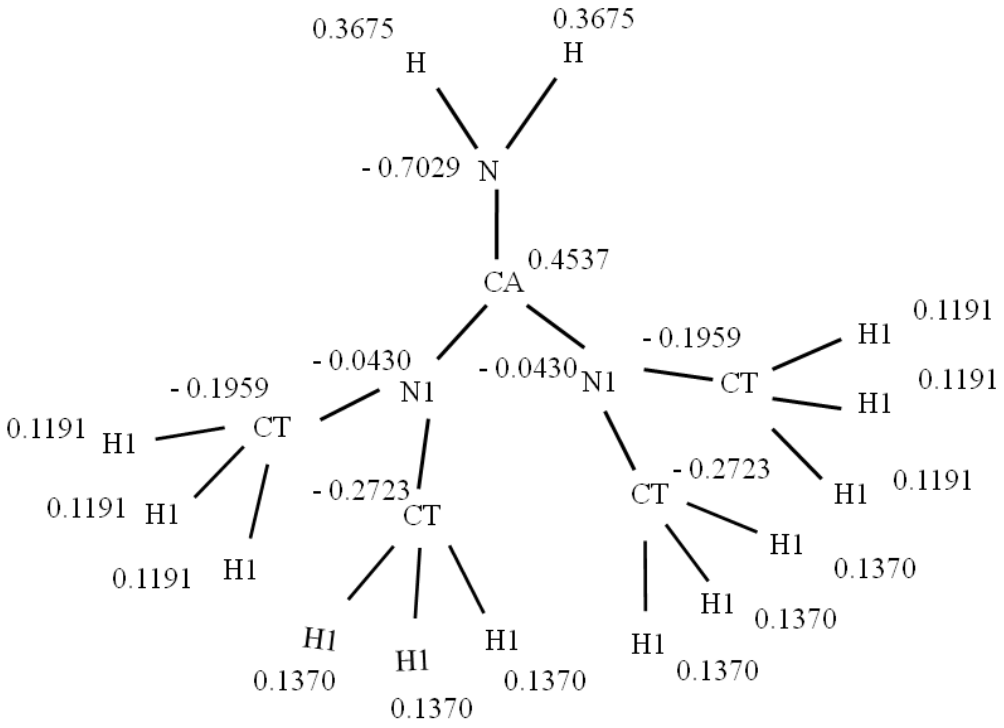


(a)

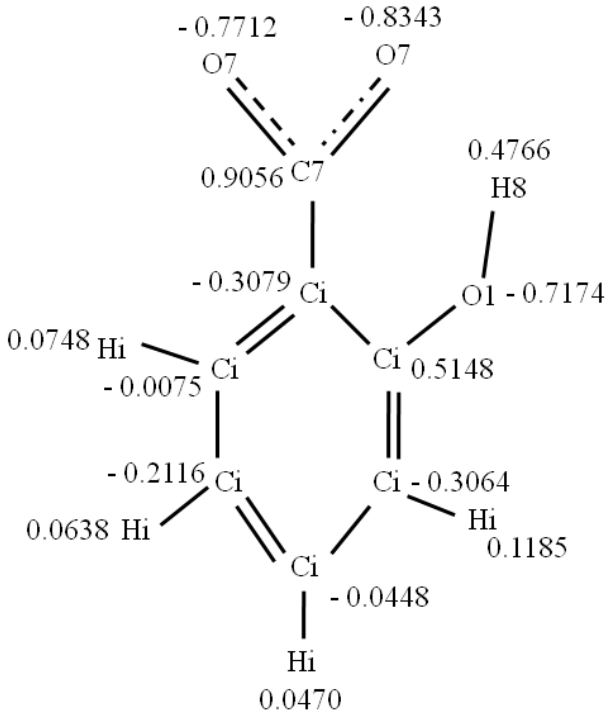


(b)

Figure S4. The point charge on (a)[TMG] cation and (b) [BEN] anion in [TMG][BEN], as obtained from *ab initio* quantum mechanical calculations

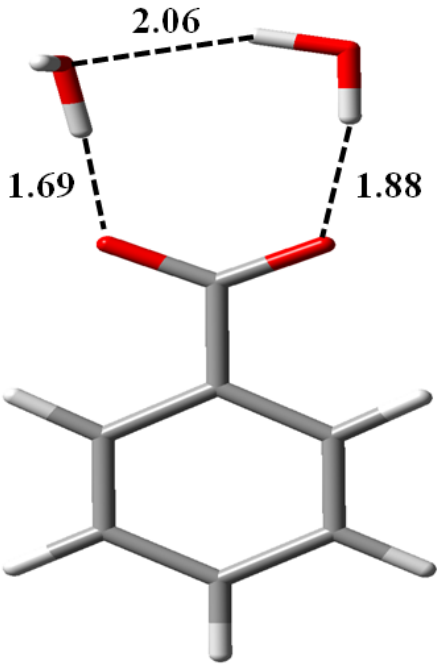


(a)



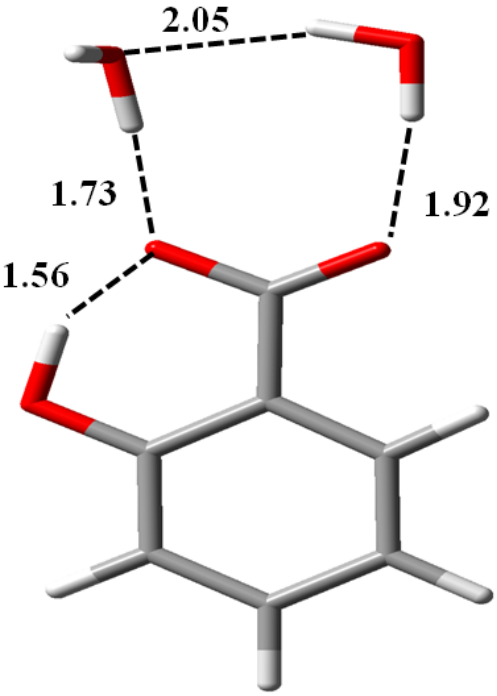
(b)

Figure S5. The point charge on (a)[TMG] cation and (b) [SAL] anion in [TMG][SAL], as obtained from *ab initio* quantum mechanical calculations



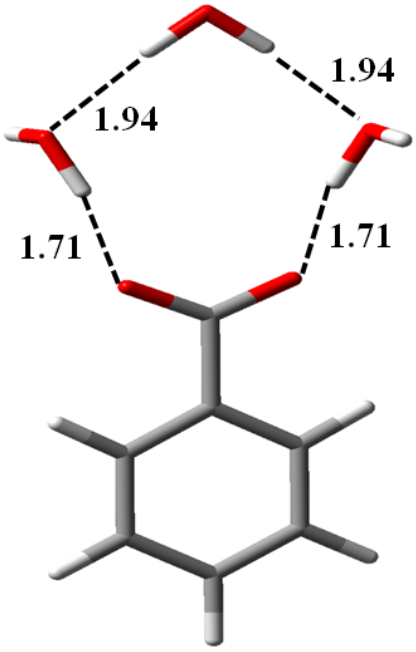
△E= − 33.075

(a)



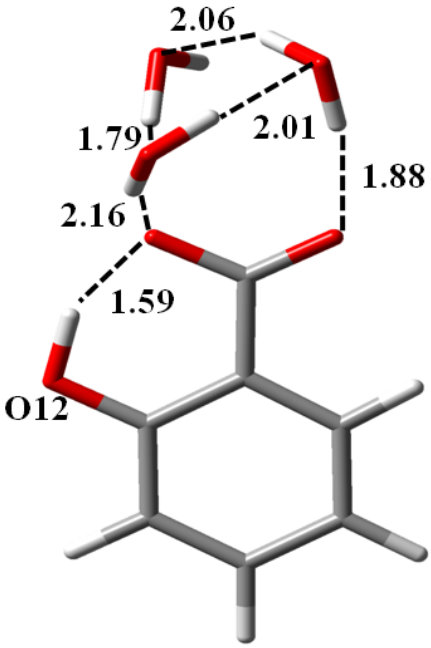
△E= − 29. 54

(b)



△E= − 45.442

(c)



△E= − 41.085

(d)

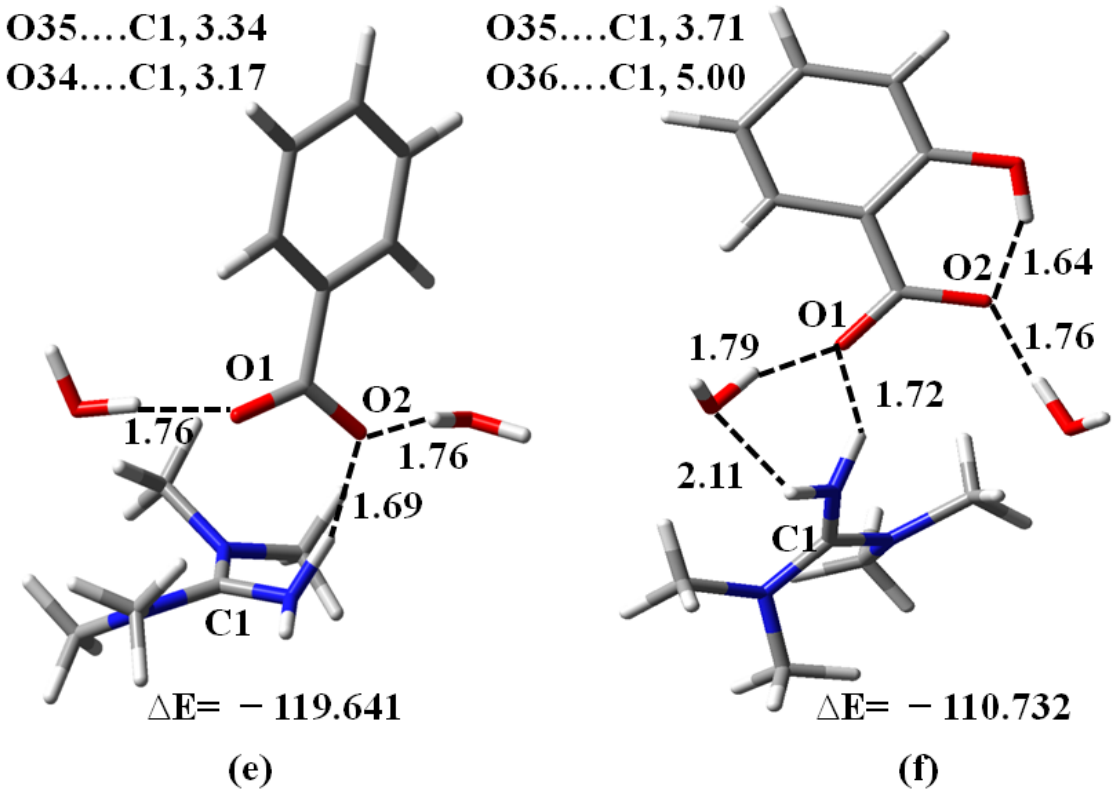


Figure S6. Minimum energy structures of (a) [BEN] anion + 2 water molecules, (b) [SAL] anion + 2 water molecules, (c) [BEN] anion + 3 water molecules, (d) [SAL] anion + 2 water molecules, (e) [TMG][BEN] + 2 water molecules, and (f) [TMG][SAL] + 2 water molecules, as obtained from *ab-initio* quantum mechanical calculations. The dotted lines represent the H-bonding interactions and the corresponding distance values are included. The distance between carboxylate oxygens (O1 and O2) and cation central carbon (C1) are shown, which signify the presence of electrostatic interactions between the ions. Interaction energies (ΔE) are obtained by subtracting the energies of the individual optimized structures of the ion(s) and water from the energy of the optimized structure of the complex. All distance are in Å and energies in kcal/mol.

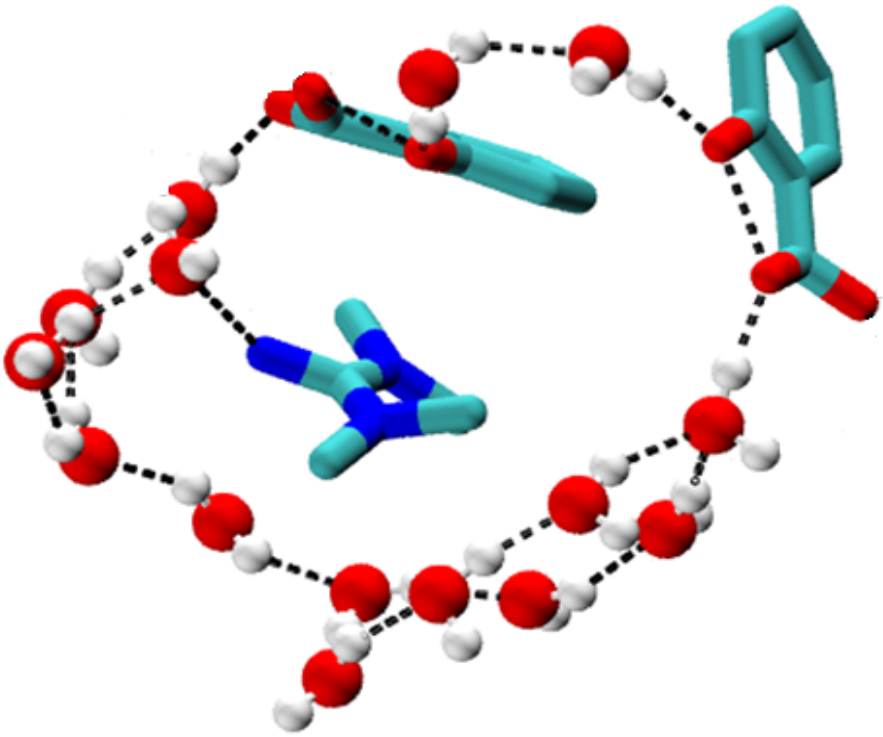


Figure S7. Spatial arrangement of water around a representative [TMG][SAL] ion pair in the 50:50 IL/water binary mixture. Formation of a water cage is evident. Color scheme: red for oxygen, blue for nitrogen, white for hydrogen. For clarity, the hydrogens of IL cation and anions are omitted. The dotted lines represent the H-bonds.

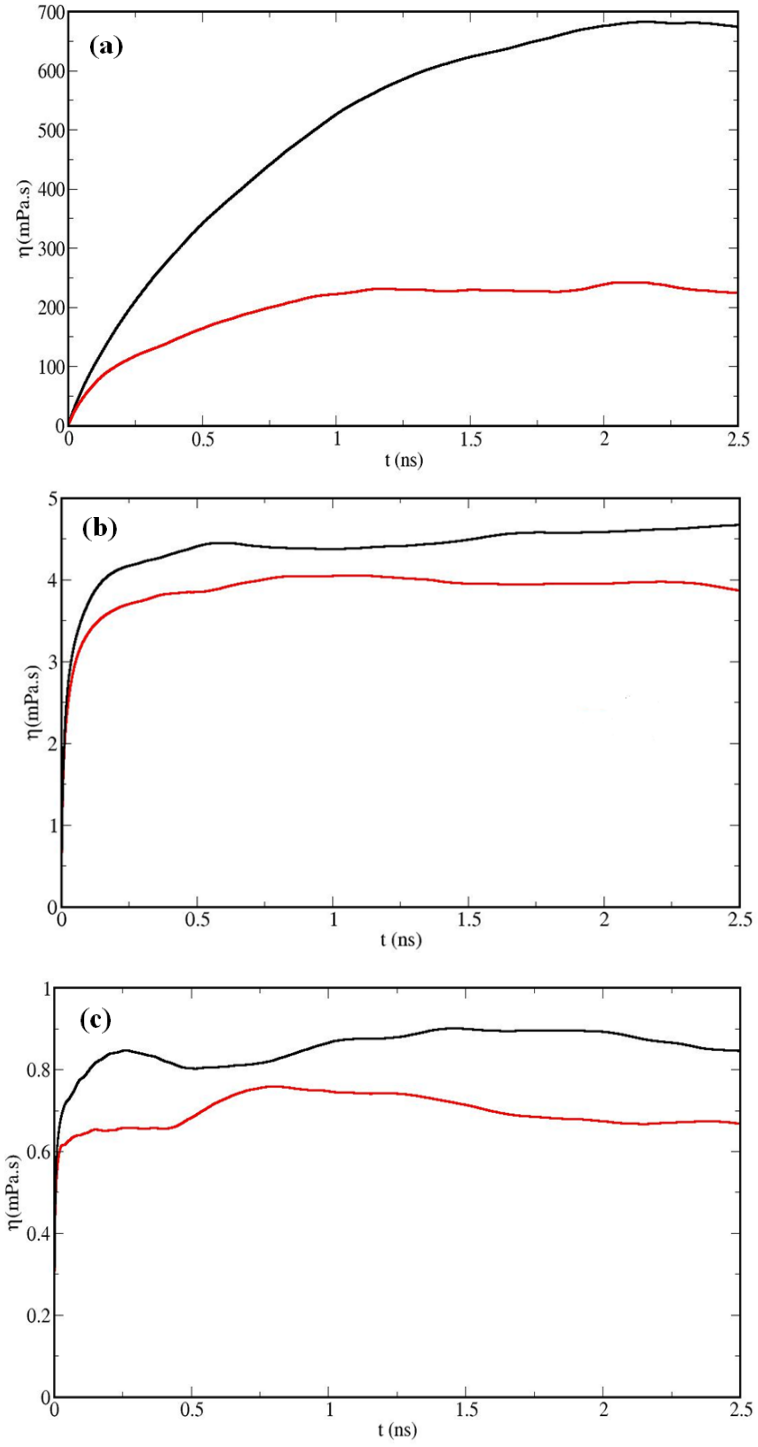


Figure S8. Running values of shear viscosity from the stress time autocorrelation functions for (a) 80% IL+20% water solution, (b) 50% IL+ 50% water solution and (c) 20% IL+80% water solution. The block averaged viscosity are plotted by dividing the 30 ns trajectories into twelve windows of 2.5 ns length. Color scheme: black for [TMG][BEN], red for [TMG][SAL].

Table S1. . Force field parameters for the benzoate anion that are used in this work (Ref. 28). For atom notations, refer to Fig. S4.

Bond Parameter

Bond	K_r (KJ $mol^{-1}Å^{-1}$)	r_0 (Å)
Ci – Hi	367.35	1.08
Ci – Ci	469.44	1.40
Ci - C7	400.38	1.49
C7 - O7	392.37	1.27

Angle Parameter

Angle	K_Θ (KJ $mol^{-1}rad^{-1}$)	Θ (^{0})
Ci - Ci - Hi	35.03	120
Ci - Ci - Ci	63.06	120
Ci - Ci - C7	85.09	120
Ci - C7 - O7	80.61	120
O7 - C7 - O7	83.08	120

Dihedral Parameter

Dihedral Angle	Kφ (KJ $mol^{-1}Å^{-1}$)	γ (^{0})	n
Ci - Ci - Ci - Hi	3.63	180	2
Ci - Ci - Ci - Ci	3.63	180	2
Ci - Ci - C7 - O7	1.05	180	2
Hi - Ci - Ci - Hi	3.63	180	2
Hi - Ci - Ci - C7	3.63	180	2
Ci - Ci - Ci - C7	3.63	180	2

Improper Parameter

Improper Angle	Kφ (KJ $mol^{-1}Å^{-1}$)	(^{0})	n
Ci - Ci - Ci - Hi	15.023	180	2
Ci - Ci - Ci - C7	15.023	180	2
C7 - Ci - O7 - O7	15.023	180	2

Nonbonded van der Waals Parameter

Atom Type	σ(Å)	ε (kJ mol^{-1})
Ci	1.86	0.07322
Hi	1.27	0.03138
C7	1.97	0.10983
O7	1.57	0.19874

Table S2. Force field parameters for the salicylate anion that are used in this work (Ref. 28). For atom notations, refer to Fig. S5.

Bond Parameter

Bond	Kr (KJ mol $^{-1}$Å^{-1})	r_0 (Å)
O7 - C7	392.00	1.28
C7 – Ci	400.00	1.49
Ci – Ci	469.00	1.40
Ci - O8	450.00	1.36
O8 - H8	552.99	0.95
Ci - Hi	367.00	1.08

Angle Parameter

Angle	K_Θ (KJ mol^{-1}rad^{-1})	Θ (^{0})
O7 - C7 - O7	83.00	120
O7 - C7 - Ci	80.54	120
C7 - Ci - Ci	85.01	120
Ci - Ci - O8	70.00	120
Ci - Ci - Ci	63.00	120
Ci - Ci - Hi	35.00	120
Ci - O8 - H8	35.00	113

Dihedral Parameter

Dihedral Angle	Kφ (KJ mol $^{-1}$Å^{-1})	γ (^{0})	n
O7 - C7 - Ci - Ci	1.05	180	2
C7 - Ci - Ci - O8	3.62	180	2
C7 - Ci - Ci - Ci	3.62	180	2
C7 - Ci - Ci - Hi	3.62	180	2
Ci - Ci - O8 - H8	0.84	180	2
Ci - Ci - Ci - Hi	3.62	180	2
Ci - Ci - Ci - Ci	3.62	180	2
O8 - Ci - Ci - Ci	3.62	180	2
O8 - Ci - Ci - Hi	3.62	180	2
Hi - Ci - Ci - Hi	3.62	180	2

Improper Parameter

Improper Angle	Kφ (KJ mol^{-1}Å^{-1})	(^{0})
C7 - Ci - O7 - O7	15.023	180
Ci - Ci - Ci - C7	15.023	180
Ci - Ci - Ci - O8	15.023	180
Ci - Ci - Ci - Hi	15.023	180
Atom Type	σ(Å)	ε (KJ mol^{-1})
Ci	1.87	0.07350
Hi	1.28	0.03150

C7	1.97	0.11098
O7	1.57	0.19950
H8	0.00	0.00000
O8	1.62	0.17850

Table S3. Force field parameters for the TMG cation that are used in this work (Ref. 29). For atom notations, refer to Fig. S4.

Bond Parameter

Bond	Kr (KJ $mol^{-1}Å^{-1}$)	r_0 (Å)
CT - H1	349.99	1.085
CT - N1	299.99	1.467
N1 - CA	349.99	1.33
CA - N	349.99	1.332
N - H	489.99	0.995

Angle Parameter

Angle	KΘ (KJ $mol^{-1}Å^{-1}$)	Θ (^{0})
CT - N1 - CT	70.00	115
CT - N1 - CA	50.00	121
H1 - CT - H1	37.00	108
H1 - CT - N1	52.00	110
N1 - CA - N	74.00	119
N1 - CA - N1	70.00	121
CA - N - H	50.00	121
H - N - H	26.00	117

Dihedral Parameter

Dihedral Angle	Kφ (KJ $mol^{-1}Å^{-1}$)	γ (^{0})	n
CT - N1 - CT - H1	0.08	0	3
CT - N1 - CA - N	1.40	180	2
CT - N1 - CA - N1	1.40	180	2
H1 - CT - N1 - CA	0.00	0	3
N1 - CA - N - H	0.93	180	2

Nonbonded vander waals Parameter

Atom Type	ε (KJ mol^{-1})	σ(Å)
CT	0.1094	1.91
H1	0.0160	1.39
N1	0.1700	1.82
CA	0.0860	1.91
N	0.1700	1.82
H	0.0160	0.60