

Stability and Structure of the Aqueous LiTFSI-LiCl Interface: Supporting Information

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Table S1 Potential energy parameters for Madrid, modified AMBER and TIP4P/2005 derived potentials for aqueous LiCl and LiTFSI solutions. Lennard-Jones energy and size parameters are denoted by ϵ and σ respectively.

Model	Species	ϵ (kJ/mol)	σ (nm)	Charge (e)
Madrid	Li ⁺	0.435090	0.143970	+0.85
Madrid	Cl ⁻	0.076923	0.469906	-0.85
Modified AMBER	O	0.878640	0.295992	-0.466
Modified AMBER	S	1.04600	0.356359	+0.911
Modified AMBER	N	0.711280	0.325000	-0.598
Modified AMBER	C	0.457730	0.339967	+0.3165
Modified AMBER	F	0.255224	0.311815	-0.1405
TIP4P/2005	O	0.774900	0.315890	0
TIP4P/2005	H	0	0	+0.5564
TIP4P/2005	M	0	0	-1.1128

Table S2 Concentration, the corresponding number of species, and simulation lengths of each aqueous LiTFSI and LiCl liquid-vapour system studied. All boxes are of dimensions 5 × 5 × 16 nm.

Concentration (molal)	System	Li ⁺	Cl ⁻	TFSI ⁻	H ₂ O	NVT eq. (ns)	NVT pr. (ns)
1	LiCl	75	75	-	4169	60	60
1	LiTFSI	75	-	75	4182	500	100
10	LiCl	745	745	-	4139	60	60
10	LiTFSI	322	-	322	1789	900	100
20	LiCl	1490	1490	-	4139	120	120
20	LiTFSI	397	-	397	1103	900	100

Table S3 Number of species and simulation lengths for biphasic LiCl-LiTFSI systems at various concentrations. Simulation box dimensions are 5 × 5 × 10 nm.

Concentration (molal)	Li ⁺	Cl ⁻	TFSI ⁻	H ₂ O	NPT eq. (ns)	NVT pr. (ns)
10	1607	745	322	5928	1200	60
13	1320	968	352	5643	1200	60
16	1562	1192	370	5424	1200	60
20	1887	1490	397	5242	1200	60

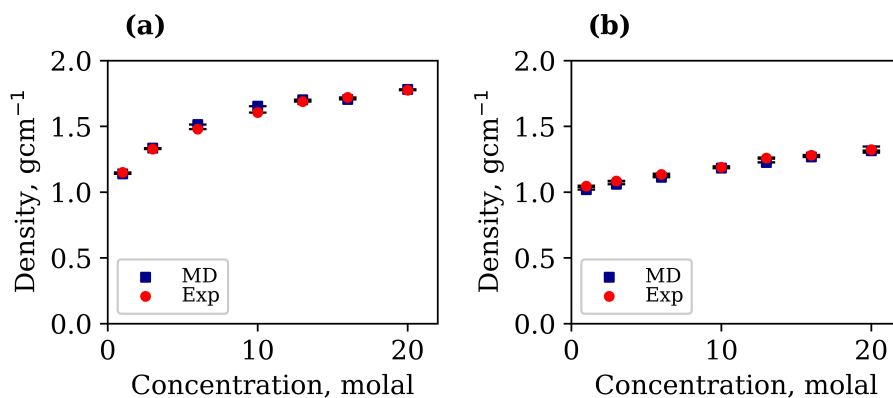


Figure S1 Calculated (blue) and experimentally measured (red) densities of aqueous LiTFSI (a) and LiCl (b) systems of different concentrations between 1 molal and 20 molal, measured at 294.15 K and 1 atm, with the corresponding error bars.

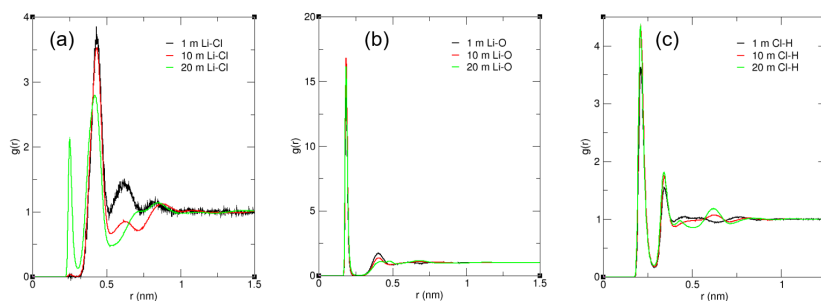


Figure S2 Radial distribution functions of (a) Li^+ with Cl^- , (b) Li^+ with O (water), and (c) Cl^- with H (water), all shown for the 1 molal LiCl aqueous system (black), the 10 molal system (red) and the 20 molal system (green).

Table S4 Coordination number of Li^+ ions with water and Cl^- ions, using a first solvation sphere radius of 0.25 nm from the centre of the Li^+ ion.

Concentration (molal)	Li-Cl CN	Li- H_2O CN
1	0	3.999
10	0.001	3.992
20	0.159	3.496

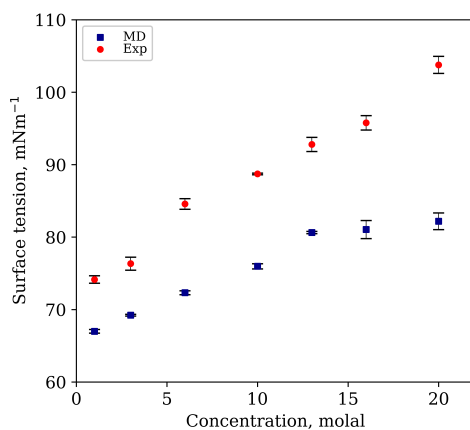


Figure S3 Calculated (blue) and experimentally measured (red) surface tensions with respective errors in mN/m of LiCl-vapour systems of 1, 3, 6, 10, 13, 16 and 20 molal

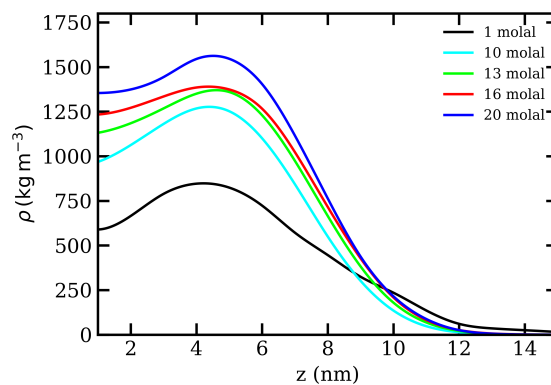


Figure S4 Density profiles of TFSI^- molecules in the 1 (black), 10 (cyan), 13 (green), 16 (red) and 20 (blue) molal $\text{LiTFSI}(\text{aq})$ -vapour systems in the interfacial region. Profiles are aligned with respect to the Gibbs dividing surface of each system by shifting in the z -direction.

Table S5 Surface excess (molecules nm^{-2}) of TFSI⁻ anions with respect to the Gibbs dividing surface of water calculated using a hyperbolic tangent fit of the TFSI⁻ density profile for each system, where liquid-vapour systems are denoted 'LV' and liquid-liquid systems are denoted 'LL'.

System	Surface excess, molecules nm^{-2}
1 molal L/V	0.446
10 molal L/V	0.319
13 molal L/V	0.237
16 molal L/V	0.338
20 molal L/V	0.239
10 molal L/L	-0.054
13 molal L/L	-0.041
16 molal L/L	-0.003
20 molal L/L	-0.014

Table S6 Experimental interfacial tension measurements for LiCl-LiTFSI biphasic systems of concentrations between 10 and 20 molal.

Conc. LiTFSI (molal)	Conc. LiCl (molal)	Interfacial tension (mN/m)	Error (mN/m)
10	10	1.1189	0.0242
13	10	1.4874	0.0269
16	10	1.6406	0.0351
20	10	2.0416	0.0153
10	13	2.4411	0.1031
13	13	3.2739	0.0425
16	13	3.6189	0.0086
20	13	4.1059	0.0343
10	16	3.2611	0.0475
13	16	4.5274	0.19
16	16	5.0131	0.0347
20	16	5.8608	0.0686
10	20	4.4394	0.2027
13	20	5.9915	0.2099
16	20	6.841	0.0455
20	20	8.3581	0.0968

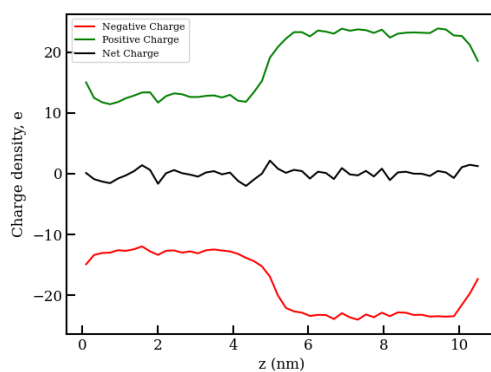


Figure S5 Charge density profile of positive (green), negative (red) and net (black) charge as a function of z position in nm, in the 10 molal LiCl-LiTFSI biphasic system.

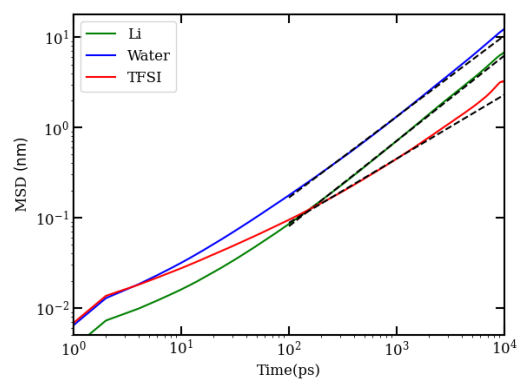


Figure S6 Mean square displacement against time of Li^+ (green), TFSI^- (red) and water (black) in the 10 molal LiCl-LiTFSI biphasic system. The dashed lines indicate free diffusion. Data beyond 10^4 ps are affected by statistical error.

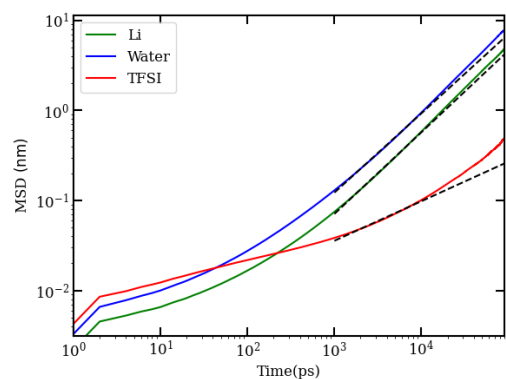


Figure S7 Mean square displacement against time of Li^+ (green), TFSI^- (red) and water (black) in the 20 molal LiCl-LiTFSI biphasic system. The dashed lines indicate free diffusion. Data beyond 10^4 ps are affected by statistical error.