Supplementary Information for Intercalation-Deintercalation of Water-in-salt Electrolyte in Nanoscale Hydrophobic Confinement

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Table S1 Details of the systems at different concentrations (in molal) of the salt in WIS used in the present study.

c (m)	Number of [Li][TFSI]	Number of water
5.05 (∼5)	560	6160
10.10 (∼10)	826	4543
19.84 (∼20)	1065	2982

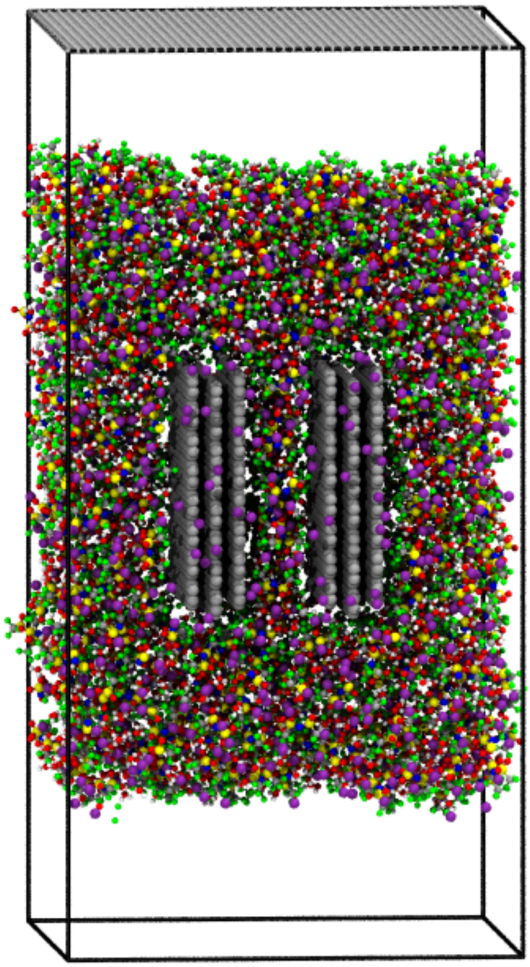


Fig. S1 Simulation snapshot depicting the simulation model. Square triple carbon sheets represent the hydrophobic confining surfaces. The vacuum region and the carbon sheet on top of the simulation box acts as natural barostat.

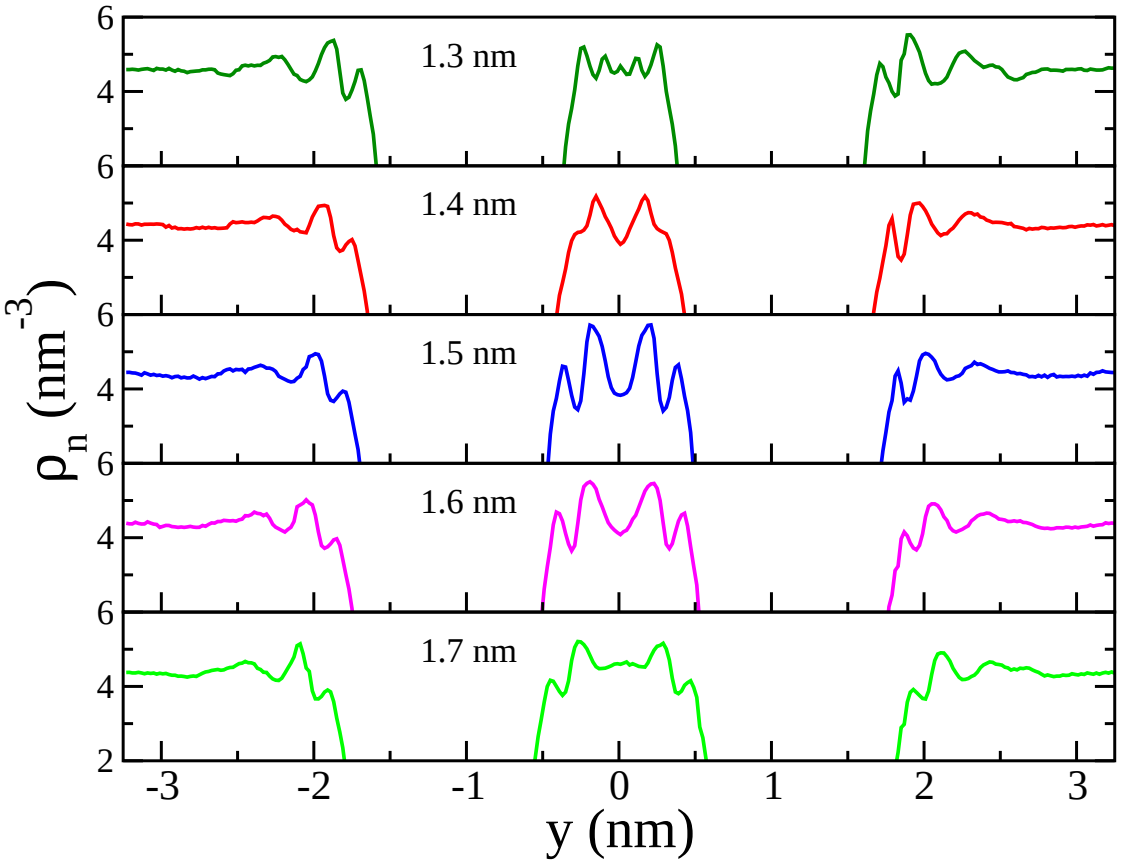


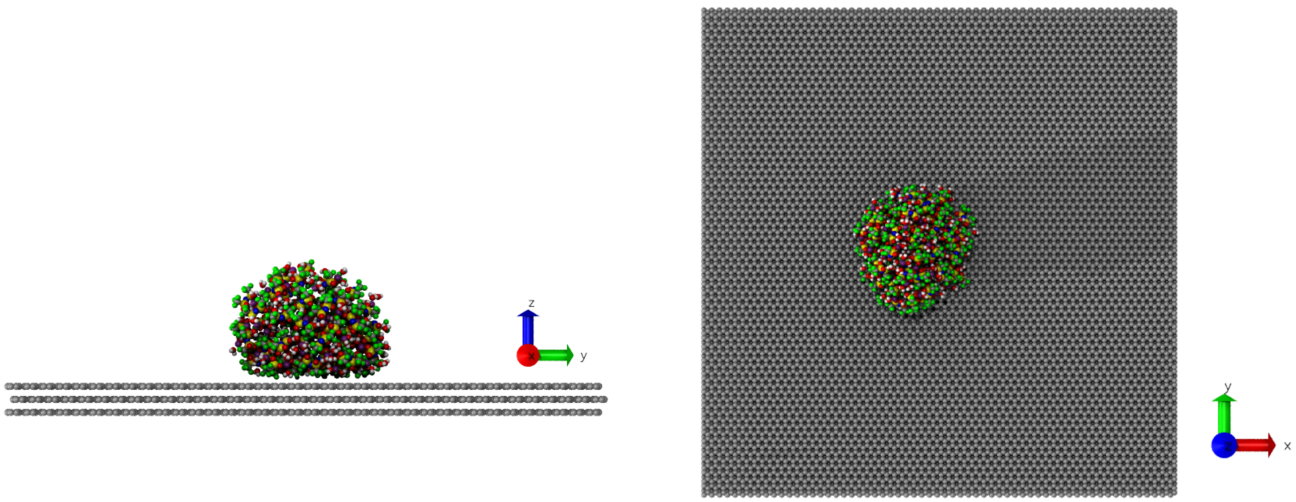
Fig. S2 The total number density profiles across the confinement for system concentration 20 m. Here, the center of the confined region is at y=0 nm, the central part corresponds to the number density inside the confinement and the left and right regions are due to WIS density outside the confinement.

Contact angle calculations

To compute contact angle formed by the WIS droplets at carbon surface, $2.9 \times 2.9 \times 2.9$ nm^3 cubic droplets of different concentrations were placed on a carbon surface in the xy plane. The simulation box is 15 nm along the z dimension. The simulation snapshots of the WIS droplet on the carbon surface are shown in Figure S3. The average number density profiles were computed on cylindrical grids with the central axis at the center of mass of the WIS. The thickness (Δr) and height (Δz) of the cylindrical grids were 0.1 nm each. Isochoric density profiles at the density corresponding to half of the bulk density were taken as liquid-vapour interface. The isochoric density profiles of the WIS droplets were fit to the circular function,

$$r(z) = \tilde{a} + \sqrt{\tilde{b}^2 - (z - \tilde{c})^2}, \tag{S1}$$

where r is the radial distance from center of the droplet in x-y plane, z is the distance in the direction perpendicular to the sheet, and $\tilde{a}$, $\tilde{b}$ and $\tilde{c}$ are the fit parameters. The fitted isodensity profiles for different concentration of WIS are shown in Figure S4.



(a) (b)

Fig. S3 Simulation snapshots showing the (a) side and (b) top view of WIS nanodroplet placed on top of the carbon surface. The WIS concentration in the droplet is 20 m.

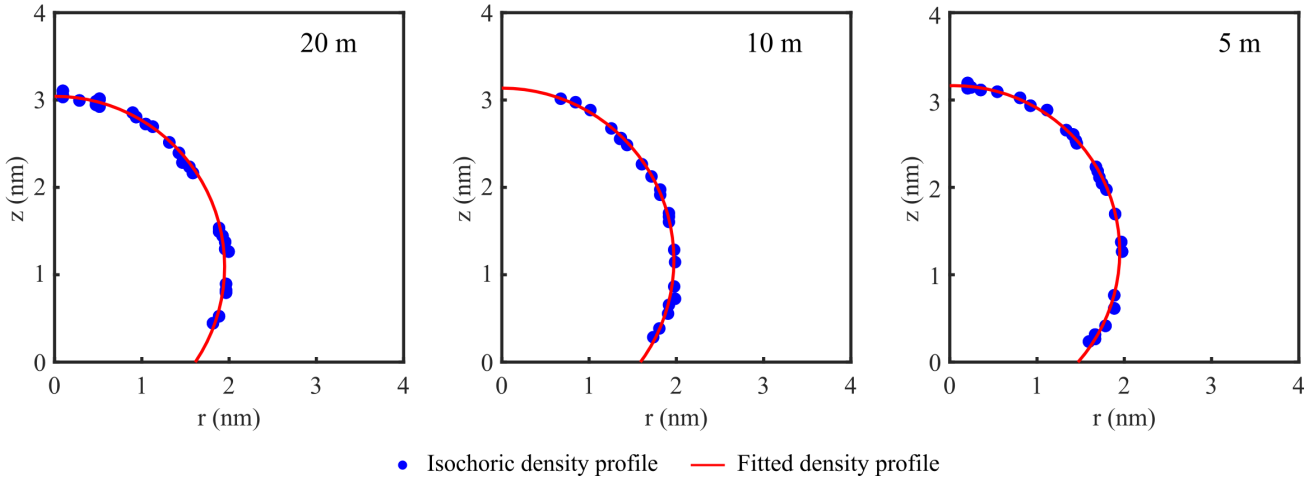


Fig. S4 The isochoric density profiles (blue dots) and circular fitted profiles (red line) obtained for (a) 20 m, (b) 10 m, and (c) 5 m concentration of WIS on carbon surface.

Surface tension calculations

We calculated the vapour-liquid surface tension of WIS solutions at different concentrations. We took a slab of WIS solution (∼2.9 nm thick) and increased the z dimension of the simulation box to 8.7 nm, which created two liquid-vapour interfaces. The systems were simulated for 20 ns and the last 15 ns were used for the calculation of surface tensions. Surface tensions were calculated by using

$$\gamma_{vl} = \frac{L_z}{2}\left[< P_{zz} > -\frac{1}{2}(< P_{xx} > + < P_{yy} >)\right], \tag{S2}$$

where γ_{vl} is the vapour-liquid surface tension, L_z is length of simulation box in the z dimension, $< P_{zz} >$ is the normal component of the pressure tensor, and $< P_{xx} >$ and $< P_{yy} >$ are the average tangential components of the pressure tensor.

Table S2 Simulated contact angles and surface tensions for different WIS concentrations.

Concentration (molal)	Contact angle (°)	Surface tension (mN m^{-1})
5	123	35.1
10	126	33.4
20	130	32.3

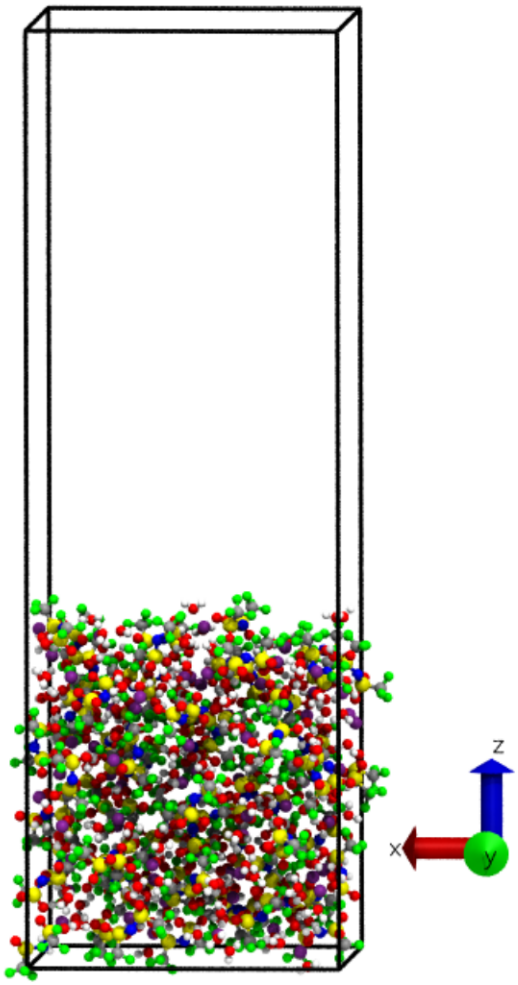


Fig. S5 Simulation snapshot depicting the setup for the surface tension calculation. A liquid slab is created in the z direction, creating two liquid-vapour interfaces.

Table S3 The free energy underlying the vapour bubble formation and gap-spanning vapour tube growth between the confining surfaces at different interplate separations and concentrations of WIS was fit using macroscopic theory. The fit parameters are:

c (m)	d (nm)	$\gamma_{vl}^{(1)}$ (k_BT nm^{-2})	$\lambda^{(1)}$ (k_BT nm^{-1})	$\gamma_{vl}^{(2)}$ (k_BT nm^{-2})	$\lambda^{(2)}$ (k_BT nm^{-1})	a	b
20	1.4	7.818	-1.021	-	-	-0.197	22.304
	1.6	6.722	0.098	2.349	0.688	-0.496	69.490
	1.7	7.677	-0.109	3.985	0.376	-0.592	88.125
5	1.7	7.685	-2.100	-	-	-0.131	27.122

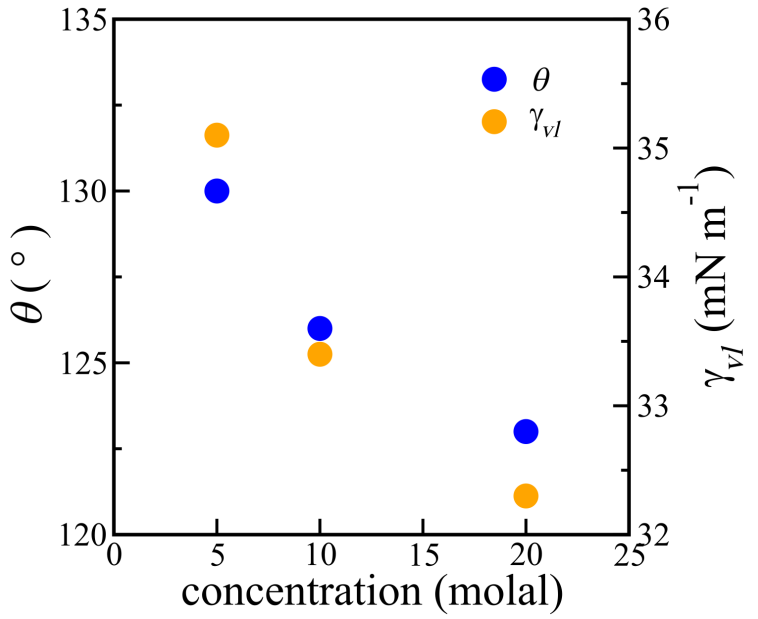


Fig. S6 Variations of the contact angle and surface tension plotted as a function of WIS concentration.

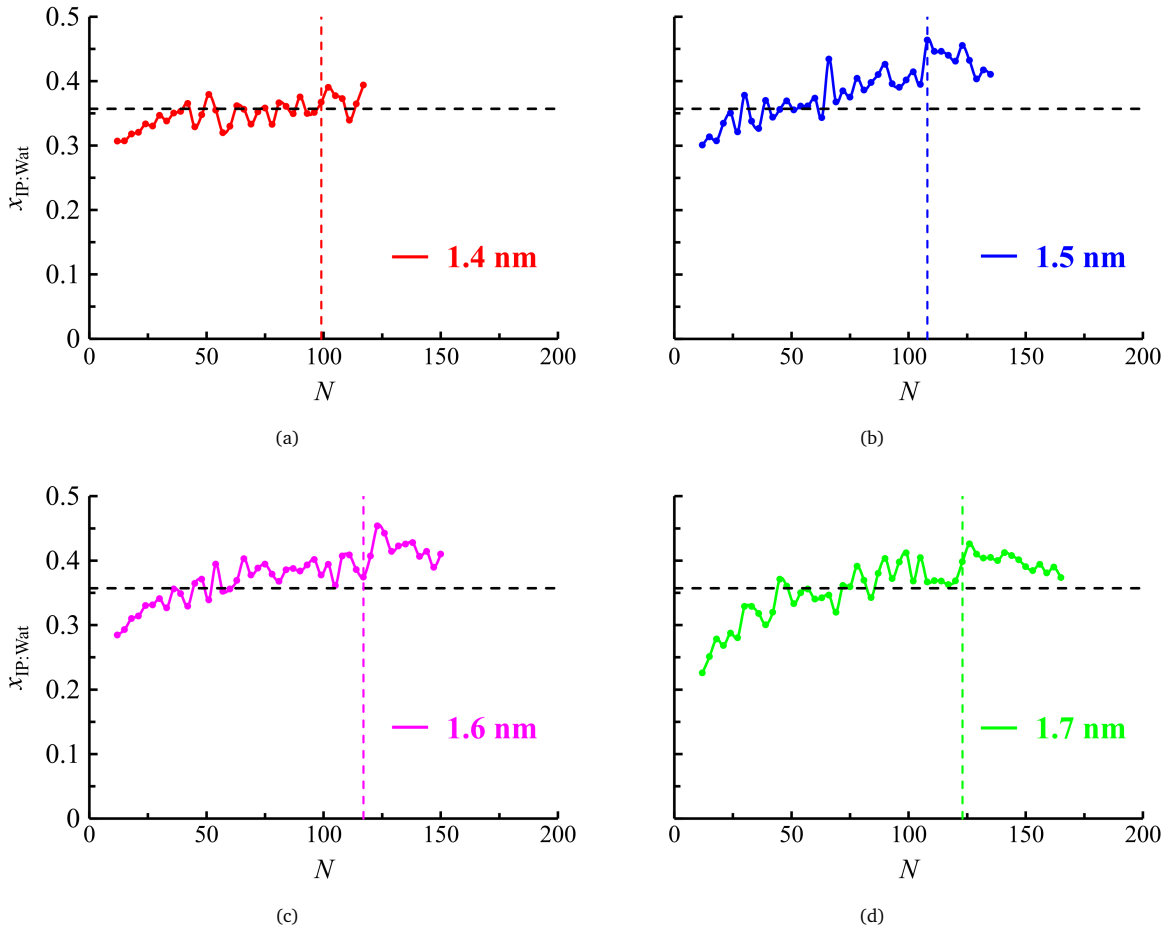


Fig. S7 The fraction of [Li][TFSI] ion pairs, $x_{IP:Wat}$, plotted against total number of species inside the confinement, N, for different interplate separations for 20 m WIS concentration. The horizontal black lines represent the $x_{IP:Wat}$ in bulk electrolyte at the given concentration. The vertical dotted lines represent the N corresponding to subcritical vapor tube formation inside the confinement.

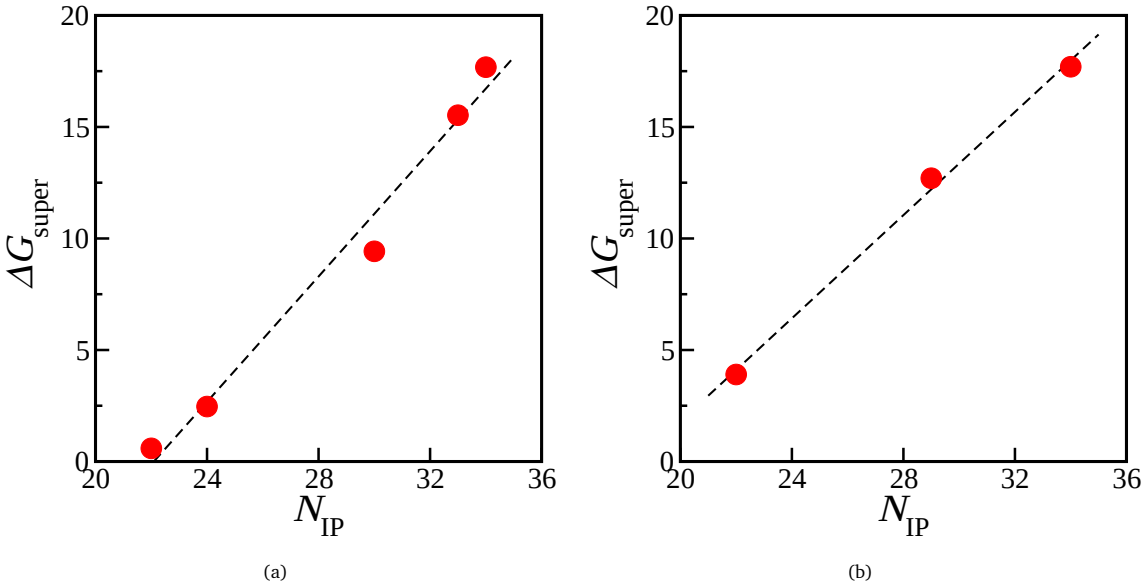


Fig. S8 ΔG_{super} plotted against N_{IP} corresponding to the condensed phase of WIS solution (a) different inter-plate separation and (b) different concentrations of WIS solution.