# **Supporting Information**

# <sup>3</sup> "Washing-out" Ionic Liquid from Polyethylene Glycol to form Aqueous Biphasic Systems

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### 1. Experimental Methods

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<sup>15</sup> The polyethylene glycol (PEG) polymer of average molecular weight 1500 g·mol<sup>-1</sup> (PEG 1500) was supplied by Fluka and used as received. The IL used, 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim]Cl), was purchased from Iolitec. The IL was dried under moderate temperature (343 K) and high vacuum conditions (< 0.1 mbar), for a minimum of 48 h, before use. Its purity was additionally checked by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and found to be > 99 wt%. The water content in the IL was <sup>20</sup> < 0.03wt%.

The ternary phase diagrams, at 323.15 K and 333.15 K, were determined according to the protocol established by Ruiz-Angel et al.<sup>1</sup> The phase diagrams were determined gravimetrically within  $\pm 10^{-7}$  kg.

#### 2. Computational Methods

# 25 **2.1. Molecular Dynamics Simulation Calculations**

MD calculations were performed for the TEG/[C<sub>4</sub>mim]Cl binary mixture and for different concentrations of the TEG/[C<sub>4</sub>mim]Cl/water ternary system. The simulations were carried out using the isothermal-isobaric NpT (T = 298.15 K and p = 1 bar) ensemble and the GROMACS 4.07 molecular dynamics package.<sup>2</sup> The equations of motion were integrated with the Verlet-Leapfrog <sup>30</sup> algorithm<sup>3</sup> and a time step of 2 fs was considered. The Nosé-Hoover thermostat<sup>4,5</sup> was used to fix the temperature while the Parrinello-Rahman barostat<sup>6</sup> was employed to fix the pressure. Starting configurations were generated in cubic boxes with lateral dimensions of 45 Å, and periodic boundary conditions were applied in three dimensions.

The systems were prepared by randomly placing all species in the simulation box. For the calculations of the binary systems, 90 [C<sub>4</sub>mim]Cl ion pairs and 120 TEG molecules were incorporated each box, while for the ternary solutions, (90/90/90/60/60) [C<sub>4</sub>mim]Cl ion pairs, in (120/120/120/80/80) TEG molecules, and (60/120/180/200/380) water molecules were included, in s order to reproduce different concentrations ( $H_2O/TEG = 0.0, 0.5, 1.0, 1.5, 2.5, 4.75$ ), all with the same TEG/IL proportion (1.33). A 10,000 step energy minimization was performed followed by two simulations, the first one with 50,000 steps for equilibration and the final one with 10,000,000 steps (20 ns) for production. Potentials available in the literature were used for all the species considered in the simulations. The potential used for TEG is based on the OPLS all-atom potential from Jorgensen <sup>10</sup> and Tirado-Rives<sup>7</sup> for diethylene glycol using the ESP charges taken from the Automatic Topology Builder website<sup>8</sup> calculated for the B3LYP/6-31G\* optimized structure 3.6.9.12of tetraoxatetradecane-1,14-diol.

To test and validate the force field selected for TEG, preliminary MD calculations of pure TEG and of binary aqueous solutions (the rigid SPC/E model<sup>9</sup> was used for the water molecules) of the polymer were carried out, under varied simulation conditions. The values of the densities of pure TEG (1124.17 kg.m<sup>-3</sup>) and of the aqueous solutions of TEG as a function of the polymer concentration (Table S1 of the ESI) calculated from the MD results are in good agreement with the experimental literature data<sup>10-13</sup> (Figure S4 of the ESI), affording further consistency to our results.

The all-atom force field parameters for the IL cation were obtained from the work of Cadena and <sup>20</sup> Maginn<sup>14</sup> and for the anion from the OPLS all-atom potential.<sup>15</sup> The atomic charges for the cation were recalculated in this work with the CHelpG scheme using an optimized geometry for the [C<sub>4</sub>mim]-Cl dimer in the gas-phase, imposing a total charge of +1 in the cation and of -1 in the anion. The calculations considered the B3LYP/6-311+G(d) approach as included in the Gaussian 09 code,<sup>16</sup> i.e., using the same computational strategy employed by Morrow and Maginn for the [C<sub>4</sub>mim][PF<sub>6</sub>] IL.<sup>17</sup> It is worth noting that the effect of concentration was not taken into account in the calculation of the charges of the IL ions, and these might actually vary with the water composition of the system. Nevertheless, preliminary tests performed showed no significant variation (≈5%) in the results obtained for the charges calculated using the IL dimer and using the cation and anion in aqueous environments.

#### 30 **2.2. DFT Calculations**

The hybrid meta GGA density functional calculations were performed with the M06 approach<sup>18</sup> as implemented in the Gaussian 09 code<sup>16</sup>. The atomic electronic densities were described by means of the aug-cc-pVDZ basis set, <sup>19,20</sup>which incorporates diffuse and polarization functions. The absence of

imaginary vibrational frequencies was used to confirm that all the molecular systems studied were true minima on the potential energy surface. Due to the large number of conformational degrees of freedom of TGA, the calculations involving this species followed the computational strategy below: Ten different initial configurations for TGA were taken from the classical MD simulations and then fully <sup>5</sup> optimized at the DFT level using tight criteria (opt=tight and scf=tight keywords in the Gaussian code) but employing a basis set without diffuse functions. Some of the most favorable configurations were further modified and were also fully optimized. The most favorable configurations retrieved from the previous steps were reoptimized with the larger aug-cc-pVDZ basis set. In the case of the different sized water clusters, the calculations were directly performed on the geometries available at The "0 Cambridge Cluster Database<sup>21</sup>, while the calculations on the chloride-water clusters were based on the geometries reported by Xantheas<sup>22</sup>, by Gora et al.<sup>23</sup> and by Neogi and Chaudhury<sup>24</sup>. The absence of imaginary vibrational frequencies (M06/aug-cc-pVDZ level of theory) was used to confirm that all the molecular systems studied were true minima on the potential energy surface.

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**Table S1.** Interaction energies for some complexes fully optimized at the M06/aug-cc-pVDZ level of theory.<sup>a</sup>

System	$\Delta E^{\rm o} / (\rm kJ \cdot mol^{-1})$
Cl <sup>-</sup> - H <sub>2</sub> O	-89.5; -88.2 <sup>b</sup>
Cl <sup>-</sup> - TEG	-98.8; -96.2 <sup>b</sup>
H <sub>2</sub> O - TEG	-33.5; -30.4 <sup>b</sup>
$Cl^{-}-(H_2O)_2$	-112.0 <sup>c</sup> ; -100.0 <sup>d</sup>
$Cl^{-}-(H_2O)_3$	-169.7 <sup>c</sup> ; -123.8 <sup>d</sup>
$Cl^{-} - (H_2O)_4$	-219.8 <sup>c</sup> ; -136.4 <sup>d</sup>
$H_2O - H_2O^e$	-11.9; -11.1 <sup>b</sup>
$H_2O - (H_2O)_2$	-45.9 <sup>f</sup> ; -33.9 <sup>g</sup>
$H_2O - (H_2O)_3$	-83.4 <sup>f</sup> ; -37.5 <sup>g</sup>

<sup>a</sup>  $\Delta E^{\circ}$  includes the zero-point energy corrections. <sup>b</sup>Geometry of the complex optimized with counterpoise corrections. <sup>c</sup>Energy variation <sup>20</sup> corresponding to the reaction Cl<sup>-</sup> + n H<sub>2</sub>O  $\rightarrow$  [Cl(H<sub>2</sub>O)<sub>n</sub>]<sup>-</sup>. <sup>d</sup>Energy variation corresponding to the reaction Cl<sup>-</sup> + (H<sub>2</sub>O)<sub>n</sub>  $\rightarrow$  [Cl(H<sub>2</sub>O)<sub>n</sub>]<sup>-</sup>. <sup>e</sup>High-level computational results range from -12.5 to -13.2 kJ·mol<sup>-1</sup> <sup>25</sup> and benchmark experimental value is -13.22±0.12 kJ·mol<sup>-1</sup> <sup>26</sup>. <sup>c</sup>Energy variation corresponding to the reaction H<sub>2</sub>O + n H<sub>2</sub>O  $\rightarrow$  [H<sub>2</sub>O(H<sub>2</sub>O)<sub>n</sub>]. <sup>g</sup>Energy variation corresponding to the reaction H<sub>2</sub>O +  $(H_2O)_n \rightarrow$  [H<sub>2</sub>O(H<sub>2</sub>O)<sub>n</sub>].

<sup>25</sup> **Table S2.** Energies calculated for the reaction  $[Cl-TEG]^- + (H_2O)_n \rightarrow TEG + [Cl(H_2O)_n]^-$  with n = 1 - 4.

n	$\Delta E^{\rm o} / (\rm kJ \cdot mol^{-1})$
1	9.4
2	-1.2
3	-25.0

4 -37.5

s **Table S3.** Densities ( $\rho$ ) for binary mixtures of water + TEG at *T*=298.15 K calculated from the MD simulations.

x <sub>water</sub>	$\rho / (kg \cdot m^3)$
0.00	1124.17
0.09	1125.21
0.20	1124.63
0.50	1124.72
0.60	1123.98
0.70	1122.14
0.80	1115.41
0.90	1093.16
1.00	999.35

**Table S4.** Electronic energies and zero-point energy corrections for the different systems fully <sup>10</sup> optimized at the M06/aug-cc-pVDZ level of theory. All values in atomic units (Hartrees).

System	Energy		Zero-point correction
	without counterpoise	with counterpoise	
Cl	-460.2647903	—	0.000000
$H_2O$	-76.4067548	—	0.021555
TEG	-691.4265552	—	0.271731
$Cl^{-}$ - $H_2O$	-536.7076847	-536.7071581	0.023610
Cl <sup>-</sup> - TEG	-1151.7273406	-1151.7264232	0.270080
H <sub>2</sub> O - TEG	-767.8491001	-767.8478427	0.296317
$Cl^{-} - (H_2O)_2$	-613.1265463	—	0.048706
$Cl^{-} - (H_2O)_3$	-689.5609940	_	0.075965
$Cl^{-}$ (H <sub>2</sub> O) <sub>4</sub>	-765.9910484	—	0.101747
$H_2O - H_2O$	-152.8212515	-152.8209500	0.046301
$H_2O - (H_2O)_2$	-229.2463020	_	0.073222
$H_2O - (H_2O)_3$	-305.6710361	—	0.098463

Table S5. Interaction energies for some complexes fully optimized at the M06/aug-cc-pVDZ level of

theory.<sup>a</sup>

System	$\Delta E^{\mathbf{e}} / (\mathbf{k} \mathbf{J} \cdot \mathbf{mol}^{-1})$	$\Delta E^{\rm o} / ({\rm kJ} \cdot {\rm mol}^{-1})$
Cl <sup>-</sup> - H <sub>2</sub> O	-94.9; -93.5 <sup>b</sup>	-89.5; -88.2 <sup>b</sup>
Cl <sup>-</sup> - TEG	-94.5; -92.1 <sup>b</sup>	-98.8; -96.2 <sup>b</sup>
H <sub>2</sub> O - TEG	-41.6; -38.1 <sup>b</sup>	-33.5; -30.4 <sup>b</sup>
$Cl^{-} - (H_2O)_2$	-126.7 <sup>c</sup> ; -106.3 <sup>d</sup>	-112.0 <sup>c</sup> ; -100.0 <sup>d</sup>
$Cl^{-} - (H_2O)_3$	-199.4 <sup>c</sup> ; -131.0 <sup>d</sup>	-169.7 <sup>c</sup> ; -123.8 <sup>d</sup>
$Cl^{-} - (H_2O)_4$	-260.6 <sup>c</sup> ; -144.9 <sup>d</sup>	-219.8 <sup>c</sup> ; -136.4 <sup>d</sup>
$H_2O - H_2O^e$	-20.3; -19.5 <sup>b</sup>	-11.9; -11.1 <sup>b</sup>
$H_2O - (H_2O)_2$	$-68.4^{\mathrm{f}}; -48.0^{\mathrm{g}}$	-45.9 <sup>f</sup> ; -33.9 <sup>g</sup>
$H_2O - (H_2O)_3$	-115.6 <sup>f</sup> ; -47.2 <sup>g</sup>	-83.4 <sup>f</sup> ; -37.5 <sup>g</sup>

<sup>a</sup>  $\Delta E^{\circ}$  and  $\Delta E^{\circ}$  are used to denote electronic energies without and with the zero-point energy corrections, respectively. <sup>b</sup>Geometry of the <sup>5</sup> complex optimized with counterpoise corrections. <sup>c</sup>Energy variation corresponding to the reaction Cl<sup>-</sup> + n H<sub>2</sub>O  $\rightarrow$  [Cl(H<sub>2</sub>O)<sub>*n*</sub>]<sup>-</sup>.<sup>d</sup>Energy variation corresponding to the reaction Cl<sup>-</sup> +  $(H_2O)_n \rightarrow [Cl(H_2O)_n]^{-}$ .<sup>e</sup>High-level computational results range from -12.5 to -13.2 kJ·mol<sup>-1</sup> <sup>25</sup> and benchmark experimental value is -13.22±0.12 kJ·mol<sup>-1</sup> <sup>26</sup>. <sup>f</sup>Energy variation corresponding to the reaction H<sub>2</sub>O + n H<sub>2</sub>O  $\rightarrow$  [H<sub>2</sub>O(H<sub>2</sub>O)<sub>*n*</sub>]. <sup>g</sup>Energy variation corresponding to the reaction H<sub>2</sub>O + n H<sub>2</sub>O  $\rightarrow$  [H<sub>2</sub>O(H<sub>2</sub>O)<sub>*n*</sub>].

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**Table S6.** Energies calculated for the reaction  $[C|TEG]^{-} + (H_2O)_n \rightarrow TEG + [Cl(H_2O)_n]^{-}$  with n = 1 - 4.<sup>a</sup>

п	$\Delta E^{\rm e} / (\rm kJ \cdot mol^{-1})$	$\Delta E^{\rm o} / ({\rm kJ} \cdot {\rm mol}^{-1})$
1	-0.38	9.4
2	-11.84	-1.2
3	-36.51	-25.0
4	-50.48	-37.5

<sup>a</sup>  $\Delta E^{e}$  and  $\Delta E^{o}$  are used to denote electronic energies without and with the zero-point energy corrections, respectively.

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<sup>5</sup> **Figure S1.** Experimental phase diagrams for the ABS composed of PEG 1500 and [C4mim]Cl at 323.15 K (red squares) and 333.15 K (black dots). The mixture points a, b and c, correspond respectively to the following compositions of [C4mim]Cl /PEG-1500 (wt%), 54/35, 60/30 and 70/20. Upon heating up to 401 K these mixtures remained biphasic and no significant change in their phase ratio was observed.



Figure S2. Experimental phase diagrams for the ABS composed of PEG 1500 and [C<sub>4</sub>mim]Cl at
<sup>5</sup> 323.15 K (red squares) and 333.15 K (black dots). The blue triangles represent the compositions of the biphasic regions at which the additional MD simulations were performed.

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Figure S3. Radial distribution functions for the interactions of the Cl<sup>-</sup> anion with the hydrogen atom of the terminal hydroxyl group of TEG for the ([C<sub>4</sub>mim]Cl/water) binary system and for ([C<sub>4</sub>mim]Cl/TEG/water) ternary mixtures at different concentrations of the biphasic region of the phase diagrams.



**Figure S4.** Experimental<sup>11</sup> and calculated (this work) densities ( $\rho$ ) for binary mixtures of water (1) + TEG (2) at *T*=298.15 K.

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**Figure S5.** Views of the most stable configurations optimized at the M06/aug-cc-pVDZ level of theory for (a) Cl<sup>-</sup>-H<sub>2</sub>O, (b) Cl<sup>-</sup>(H<sub>2</sub>O)<sub>2</sub>, (c) Cl<sup>-</sup>-(H<sub>2</sub>O)<sub>3</sub>, (d) Cl<sup>-</sup>-(H<sub>2</sub>O)<sub>4</sub>, (e) (H<sub>2</sub>O)<sub>2</sub>, (f) (H<sub>2</sub>O)<sub>3</sub>, (g) (H<sub>2</sub>O)<sub>4</sub>, (h) TEG, (i) Cl<sup>-</sup>-TEG and (j) H<sub>2</sub>O-TEG. Numbers refer to distances in Å and parenthesis are used for optimal distances obtained with counterpoise corrections. Color code for spheres is: Green, Cl; red, O; grey, C; white, H.

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