Quantification of the impact of water on the wetting behavior of hydrophilic ionic liquid: a molecular dynamics study

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ABSTRACT

We have used molecular dynamics (MD) simulations to investigate the effect of water on the wetting behaviour and the interfacial structure of ionic liquid (IL) 1-ethyl-3-methylimidazolium tetrafluoroborate \([\text{EMIM}]\text{[BF}_4]\) droplets on graphite surfaces which is a prerequisite for the IL-based applications where the solid-fluid interface is involved. A slight decrement in the value of the contact angle has been found while adding water up to 17 wt\% \((x_w\sim0.68)\) afterward, the contact angle increases. The non-monotonic behaviour in the contact angle of IL-water droplet with the addition of water molecules was examined through several key parameters, such as solid-fluid interaction energy, the density profile of each species, cluster formation, and the number of formed hydrogen bonds (HBs) for the different weight percentages of water molecules. The results indicate that the hydrogen bond network and the cluster formation among the water molecules play a vital role during the transition from IL rich medium to water rich medium of the droplet.

1. Introduction

The wetting behaviour of ionic liquid (IL) on a solid substrate has importance in various applications such as pixel displays fluidic devices, micro-lenses, and digital microfluidic devices \([1,2]\). For example, the efficiency of digital micro/nano-fluidics devices where a liquid droplet is placed on the solid substrate, strongly depends on the wettability of ILs on the substrate. Due to their extreme viscous nature, ILs are unable to wet the surface efficiently, and hence manipulating or controlling the droplet in these devices is very challenging. Thus, the water content in hydrophilic ionic liquids can provide an essential role in the performance of these devices. Moreover, most of ILs are hygroscopic \([3]\) and thus the wetting of ILs in presence of water is required to understand at the molecular level. Further, the addition of water also changes the various properties of ILs such as conductivity, solubility, surface tensions, diffusion coefficients, viscosities, and molecular polarity \([4–9]\) which can be important for many applications such as in nano-lubrication, in electrochemical devices, etc. Therefore, understanding the wetting and interfacial behaviour of ILs in presence of water at solid surfaces will be essential for realising their full potential. There have been multiple studies published recently on the wettability of different ILs illustrating how the selection of anion, cationic chain length, temperature, type of substrate, application of electrical field, and surface interaction potential affects the wettability of ILs \([4–23]\). Understanding the wetting and interfacial characteristic of IL droplets on a solid surface is purposeful for designing and managing IL related chemical engineering processes\([24–26]\). Moreover, various technologically motivated research studies attempted to elucidate the role of water molecules in IL/water interfaces, which is yet to understand correctly\([4,27–32]\).

To illustrate the wetting and interfacial behaviour of ILs on a solid surface, an ample number of studies have been conducted both experimentally and theoretically \([10,11,14,16–18,20,33–39]\). Qualitatively the wetting behaviour of ILs depends on the relative interaction between dispersion and electrostatic forces, as shown by several studies \([20,39]\). Pereira et al. \([19]\) elucidate the effect of hydrogen bond formation in ILs to wet polar and non-polar surfaces. The effect of the alkyl chain and surface tension on the wetting behaviour of ILs on the graphite surface was investigated by Bordes et al. \([40]\) and Bhattacharjee et al. \([12]\) wherein the wettability of ILs increases with increasing alkyl chain length. The effect of the nanodroplet size on the contact angle was examined through surface interaction energy by various authors \([16–18,33,36,38]\). Guan et al. \([16]\) reported that the wettability of ILs nanodroplet decreases with the increase of the viscosity of the IL. Malali and Foroutan \([18]\) observed a dense layer of cation for \([\text{BMIM}]\text{[PF}_6]\) on the crystallographic titanium dioxide surface due to the strong interaction between the IL molecules and the surface atoms. A significant role of charged moieties of the cation is observed for the adsorption of IL molecules on the boron nitride surface, as stated by Ghahami et al. \([36]\). Although the above mention parameters dominate the wetting and interfacial behaviour of pure ILs, the inherent characteristics in the wetting behaviour of ILs with an increase in water content are still not investigated yet to the best of our knowledge.

Recent studies on the microenvironment of water and IL, both experimentally \([41–45]\) and computationally \([9,46–54]\), illustrate the presence of water in small quantity, leading to...
form isolated water molecule in which significant interaction between anion and water dominates. However, with an increase in water content, the water molecules start to interact with each other to form clusters and lead to a strong network of water molecules at higher water content. Zhong et al. [9] reported the structural behaviour of 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] at different water concentrations and found, at the mole fraction of water $x_w < 0.2$, the water molecules are typically in isolated form in the cation-anion network of ILs; with an increase in water concentration ($x_w = 0.2–0.8$), the water molecules are found in cluster form, and at $x_w > 0.8$, the degree of association increases, and the system eventually move to water-rich mixture. Interestingly, the threshold value of water, which is ($x_w = 0.8$), was also found for 1-ethyl-3-methylimidazolium ethylsulfate [C₂MIM][EtSO₄]/water mixture in a recent molecular dynamics simulation study by Bernardes et al. [55]. However, others [9,56] reported significant water clustering at $x_w > 0.4$ for [BMIM][BF₄]/water. On the other hand, Niazi et al. [57] reported insignificant water cluster formation in chloride and acetate based ILs even at moderately higher water mole fractions, followed by an incremental rise in cluster formation at $x_w > 0.7$.

Thus, from the above mentioned studies, molecular dynamics has prevailed as a powerful tool for an in-depth understanding of the water–ILs system at the nanoscale [48,57–63]. ILs behaviour in aqueous solutions has been subject to numerous investigations [59,60,64,65]. Depending on the alkyl chain length, concentration and selection of anion/cation, self-organisation, aggregation, and phase separation behaviours, clusters, are some of the traits that have also been studied for various ILs in presence of water [32,45,66–70]. Similar changes at the solid-liquid interface may cause differences in macroscopic wetting, affecting both the contact angle and spreading kinetics.

Wetting characteristics of ionic liquid in an aqueous solution are subject to a fewer number of studies [71–73]. The small amount of water with IL has been reported to have an insignificant impact on the electrowetting of IL [BMIM][BF₄] droplets as shown by Paneru et al. [72]. However, a significant effect of water concentration on the wetting and interfacial behaviour is reported by Wang et al. [74] wherein the interaction of water molecules with 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl) – imide, [RMIM][NTF₂] ions through hydrogen bonding is responsible for disrupting the IL molecular layering. A precursor film of a thickness (10⁻⁶–10⁻¹⁰ m depending on the system) is usually found when macroscopic drop spreads on a solid surface [75–77]. The effect of water on macroscopic spreading behaviour is expected to understand for the design of IL-based fluidic technologies and assist in understanding the complex wetting behaviour of analogous complex fluids [78]. Here, MD simulations are performed to study the impact of water concentration on the wetting and interfacial behaviour of hydrophilic imidazolium-based IL [EMIM][BF₄] on the graphite surface.

## 2. Computational model and methods

MD simulation was performed on LAMMPS [79] to investigate the impact of water concentration on the wetting and the interfacial behaviour of a hydrophilic IL [EMIM][BF₄] droplet. Non-bonded interaction parameters of the ILs were taken from the work of Agilio Padua and J.N. Canongia Lopes, which was modeled through all-atom optimised potentials for liquid simulations (OPLS-AA) force field [80–83]. This force field reproduces well the structural and interfacial properties of ILs [84–90]. We do not use any scaling factor for screening the electrostatic interaction in the model. The extended simple-point-charge model (SPC/E) was used to describe the interaction of water molecules [91] as it predicts the structural and dynamical properties of an aqueous system reasonably well [92–94]. The SPC/E water model is also found well suited for the hydrated system where water molecules are found in cluster form [95]. Therefore, several authors used this water model to study the effect of water molecules on the properties of ILs [48,54,96,97]. 12–6 L potential parameters for the carbon–carbon interactions of graphite surface were taken from Werder et al. [98]. Geometric mixing rules were applied to cross-LJ interactions.

ILs pairs and water molecules were initially placed randomly inside a cubic box using Packmol software [99]. Before placing on the graphite, the box of IL and water was equilibrated in canonical ensemble (NVT) at 300 K for 5 ns, keeping the box dimension ($20.4 \text{ nm} \times 20.4 \text{ nm} \times 20 \text{ nm}$) large enough compared to the droplet radius (2-3 nm depending on the water concentration) to obtain a spherical droplet surrounded by vapour phase. We also performed annealing (350–300 K for another 5 ns) to ensure proper mixing of the droplet. Finally, the droplet was placed just above the graphite surface (within 10 Å from the surface). The X-Y dimension of the simulation box (given in table 1) was adjusted in such a way that the surface remained periodic and was very large compared to the droplet base radius (3-4 nm). Another run for 20–30 ns was carried out for further equilibration of the droplet on the surface with a time step of 1 fs and the droplet gradually wet the surface during the equilibration. The equilibration period of the droplet over the surface is determined through solid-liquid interaction energy as discussed in the result and discussion section. The various steps of the simulation are shown in Figure 1.

The dimension of the graphite surface and the number of water molecules for the studied range of water concentration (0–41 wt.%) are listed in Table 1. The system size effect on the contact angle of the IL droplet is found to be insignificant when the droplet consisted of 250 IL molecules or more. Therefore 250 IL and required water molecules based on wt. % of water is used to prepare the aqueous IL droplet. The positions of surface atoms were fixed during the simulations. The

### Table 1. The weight percentage of water added for fixed 250 ion-pair of IL [EMIM][BF₄].

| Weight % of water | Water molecules | $x_w$ (mole fraction of water) | Sheet-dimension $(L \times W)$ nm² |
|-------------------|----------------|-----------------------------|----------------------------------|
| 2                 | 55             | 0.18                        | 20.418 × 20.448                  |
| 4                 | 110            | 0.30                        | 20.418 × 20.448                  |
| 7                 | 220            | 0.46                        | 20.418 × 20.448                  |
| 17                | 550            | 0.68                        | 20.418 × 20.448                  |
| 23                | 825            | 0.77                        | 20.418 × 20.448                  |
| 33                | 1375           | 0.85                        | 20.418 × 20.448                  |
| 41                | 1925           | 0.89                        | 20.418 × 20.448                  |
cutoff distance for intermolecular interaction used is 12 Å, and the PPPM method with an accuracy of 0.0001 is applied for long-range interactions [100]. The bonds terminating in hydrogen atoms are considered rigid in the case of IL whereas, in the case of the SPC/E water model, two O-H bonds and the H-O-H angle are made rigid using SHAKE [101] algorithm. A Nosé-Hoover [102,103] thermostat with a relaxation constant of 1.0 ps was used to perform the simulation at a constant temperature. The velocity Verlet algorithm with a time step of 1 fs was used to solve the equation of motion. The z-dimension of the simulation box normal to the graphite surface was taken as 20 nm to avert the interaction among periodic images of the drop.

3. Contact angle estimation

The contact angle of a droplet is measured as the angle between the tangent across the vapour-liquid interface drawn at the three-phase contact line and the solid substrate. For this, two types of binning are employed in this work, to locate the liquid-vapour interface; a rectangular binning with a thickness of 1 Å along the z-direction normal to the surface and a cylindrical binning along the radial direction from the centre of the droplet as described by Ruijter et al. [104]. The radius of each radial bin is varied in such a way that each bin is of equal volume (95 Å³). We have considered an atomic resolution to compute the number density of the aqueous mixture in each bin. The liquid-vapour interface is then traced for each rectangular bin by fitting the radial density \( \rho(r) \) using the following equation.

\[
\rho(r) = \frac{\rho^l + \rho^v}{2} - \frac{\rho^l + \rho^v}{2} \tanh\left\{ \frac{2(r - r_c)}{d} \right\}
\]

(1)

Where, \( \rho^l \) and \( \rho^v \) represent the liquid and vapour density, \( d \) is the interfacial thickness, and \( r_c \) is the location of the interfacial point for a given z-bin. Finally, the interfacial points for each z-bins are fitted into a circle using the least square method (the interfacial points up to 12 Å from the surface are ignored due to the density fluctuation near the surface) and evaluate the tangent of the circle at the three-phase contact line. The atomic position of the 1st layer of the graphite sheet is considered the reference plane to estimate the contact angle \( \theta \) of the droplet.

4. Results and discussion

4.1 Equilibrium of droplet

The equilibration of the droplet on the graphite surface is traced through the graphite-droplet interaction energy (\( E_{\text{inter}} \)) to be more or less constant over time. The graphite-droplet interaction energy is computed as the intermolecular pair potential between graphite and aqueous droplet with time. First, we define two separate groups that include two different sets of atoms. Here, the first group represents the atoms of an aqueous droplet whereas the second group represents the set of atoms of graphite surface. During the simulation, we store the interaction energy that includes the sum of all ‘pair’ contributions between these two groups at the interval of 0.1 ps and averages the over production period. The evolution of solid-fluid interaction energy of the droplet for the two systems, i.e. 2 wt.% (\( x_w \sim 0.18 \)) and 41 wt.% (\( x_w \sim 0.89 \)) of water are shown in Figure 2. Here, we have normalised the interaction energy by the total number of molecules. To attain the equilibrium state for 2 wt.% (\( x_w \sim 0.18 \)) is taken significantly more time (\( \approx 27 \text{ns} \)) as compared to 41 wt.% (\( x_w \sim 0.89 \)) (\( \approx 11 \text{ns} \)) (see Figure 2). This is due to the fact that the 2 wt. % water-IL system has a slow dynamic in nature. At low water concentration, the dynamics of the IL-water mixture mainly depends on the viscosity of the neat IL, whereas at higher water concentration, the water cluster dominates the system and accelerate the system dynamics [105].

Primarily the cation of the droplet takes a longer time to attain equilibrium due to large size, reordering at the vicinity of the surface, and high interaction with a graphite surface.
Conversely, at the higher percentage of water, the system has been diluted, and normalised interaction energy decreased significantly, as shown in Figure 2(b). Once the system reached equilibrium, additional 10 ns of the simulation was conducted to calculate the contact angle, density contour, hydrogen bond calculation, and cluster analysis of IL/water droplet on the graphite surface.

### 4.2. Contact angle

To explore the effect of water concentration on the wettability of the IL-water droplet on the smooth graphite surface, we calculate the contact angle of the droplet at a different weight percentage of water, as shown in Figure 3. We use the atomic resolution of the droplet to evaluate the contact angle of the IL-water droplet as described in the previous section. Initially, the contact angle of the droplet slightly decreases and is almost constant for intermediate concentrations i.e. ($x_w$ $\sim$ 0.18 to $x_w$ $\sim$ 0.68), then onwards the contact angle starts to increase, as shown in Figure 3. At lower concentration ($x_w$ < 0.18) when water molecules are typically in isolated form, IL droplet spreads more on the graphite surface and leads to a decrease in contact angle. On the other hand, at higher concentrations of water ($x_w$ > 0.68), the interaction among water molecules dominates the system and drives the system toward the contact angle of the pure water droplet. The presence of water molecules significantly alters the ordering and orientation of interfacial IL molecules at the solid-fluid interface and the hydrogen bonding between water and IL molecule is found to play a vital role in disrupting the IL layering [74,106–108]. Therefore, we critically examine the density profile, hydrogen bond profile, and cluster formation at the solid-fluid interface to correlate the macroscopic wetting behaviour of IL droplets in the presence of water. The value of the contact angle for aqueous IL ([EMIM][BF$_4$]) (i.e. beyond 41 wt.% i.e. ($x_w$ $\sim$ 0.89) are taken from our previous publication [71].

### 4.3. Density profile

Further, the effect of water molecules on the wetting behaviour of IL is examined by a density contour of each species. We compute the average density of each bin for 5 ns at the interval of 0.01 ps. Density distribution of IL and water within the droplet for different wt. % of water are separately shown in Figure 4(a,b), respectively. It can be noticed from the IL density (see Figure 4(a)) profile that pure IL droplet has multiple peaks (multi-layer of IL), which are dissolved (vanished) as the concentration of water increases, except the first peak (i.e. near the surface). In particular, at low water content (< 4 wt.% i.e $x_w$ $\sim$ 0.30), the water molecules are distributed uniformly across the droplet without any noticeable association of water molecules, i.e. water molecules are preferentially in isolated form. At the 7 wt.% of water, the water molecules start to accumulate above the 1st layering of IL. Hence, the aggregation of water molecules is observed (i.e. $Z$ $\approx$ 5 Å), which is associated with the 2nd layer from the surface (see Figure 4b-iv, cyan stripe at $Z$ $\approx$ 5 Å). Interestingly, we do not observe many water molecules in the 1st layer (i.e. $Z$ $\leq$ 3.35 Å), which is due to the strong ordering of cations and anions of IL molecules near the surface to maximise the surface interaction with the IL molecules.
Additionally, an increase in the water concentrations (17 wt.% ($x_w \sim 0.68$) and 23 wt.% ($x_w \sim 0.77$)), the degree of association of water molecules increases, and start forming the water network and disrupt the IL layering as can be seen in Figure 4 (a, b). Finally, a continuous phase of IL-water solutions appears at the bulk of the droplet beyond 33 wt. % ($x_w \sim 0.85$) of water. However, at these concentrations, we still observe intense layering of IL molecules near the surface, whereas intense layering of water molecules is found in the 2nd layer (i.e. $Z \approx 5$ Å) from the surface.

For further illustration, the z-density profile of each species within the droplet is calculated using a cylindrical section of radius 20 Å, as shown in Figure 5. Here, it can be noticed that the multi-peak curve (wavy in nature) gets smooth/filtered while adding water to it (except the first layer). The first layer from the surface does not get affected due to the strong interaction between IL molecules and surface atoms. Conversely, water density is uniformly distributed (no multiple layers observe) within the bulk of the droplet, and a dense layer of water molecules is appeared next to the IL layer near the surface at higher concentrations, as shown in Figure 5. With the addition of water, the interaction energy between cation and anion has been enfeebled as the interaction energy decreases with an increase in the water concentration (shown in supporting information Figure S1). Moreover, at a higher weight percentage of water (above 23 wt.% i.e. ($x_w \sim 0.77$), water molecules dominate the system due to the strong association of water molecules, which can be examined through cluster formation within the droplet, discussed in the next section, and hence, the contact angle of the droplet increases with a further increase in water concentration.

It can also be noticed that the vapour-liquid interface of water molecules crosses the vapour-liquid interface of IL molecules at higher concentrations (in between 23 wt.% to 33 wt. %) that also indicates the transition between IL rich to the water-rich system (as shown in Figure 5). We have also investigated the solid-liquid interface through a separate simulation (shown in supporting information Figure S2) where the IL-water mixture is placed on the surface in a rectangular box. The z-density profile shows the same behaviour as in the case of the spherical droplet (shown in supporting
To identify the layers of IL, we separately plot the anion and cation density with an increase in water content for the IL-water system. The ordering of cations and anions is quite different that can easily be distinguished from the density profile (See Figure S3). In the IL-rich phase, where the number of water molecules is essentially less, the water molecules mainly are in isolated form without affecting the IL layers. However, in the water-rich phase, the water molecules disrupt the IL layers except for the first layer near the surface. Hence, the ordering of cation and anion changes with the addition of water molecules due to the strong association of water molecules. As a result, the anion and cation in the IL layers are smoothed out with an increase in water concentration that can be easily noticed from the density profile of anion and cation at higher concentrations of water (See Figure S3).

5. Water clustering within the droplet

The density contour across the droplet reveals that at low water content, the water molecules are distributed uniformly within the droplet without affecting much the IL layering. With increasing the water content, the layering of IL molecules gets smooth except for the first layer near the surface. To understand the transition between IL-rich to the water-rich system, we examine the cluster formation within the droplet with the addition of water molecules.

We evaluate the formation of water clusters to understand the network formation of water molecules within the IL-water droplet. For this calculation, we examine the centre of mass of each water molecule during the last 2 ns of the simulations to collect information about the cluster distribution. A water molecule will be considered as a part of a cluster if this water molecule is within a certain distance of another water molecule in the same cluster. The distance criteria for cluster calculation for a pair of species can be determined from the respective radial distribution function (RDF). For clustering among water molecules, the O-O distance should be less than 0.35 nm which corresponds to the first minimum of the O-O RDF of water molecules. Figure 6 shows the cluster size distribution normalised with the total number of water molecules present in the system at different concentrations of water. Here, the Y-axis of the plot represents the percentage of water molecules (for a given weight % of water in an aqueous [EMIM][BF$_4$] system) present in the corresponding cluster size. At low concentrations (up to 7 wt. %), most of the water molecules are found either in isolated form or in a small cluster (in the range of 1–12 molecules).
within the droplet with an increase in water concentration, the size of the cluster increases. For example, at 23 wt.% of water, the cluster size is uniformly distributed across the number of water molecules present in the system, shown as a pink line in Figure 6. This indicates the formation of a water network within the droplet. Further, with an increase in water concentration (see 33 wt.% in Figure 6), water molecules suddenly move to larger cluster sizes and form a strong water network within the droplet and disrupt the IL layering. Therefore, the transition between IL-rich to the water-rich system can be found in between 23–33 wt% of water, ($x_w$ $\sim$ 0.77 to $\sim$ 0.85). Hence, the contact angle of the droplet increases towards the contact angle of the pure water droplet on the graphite surface. However, near the surface, larger water cluster formation is observed at higher water concentrations ($x_w$ > 0.85) compared to the bulk of the droplet. This may be due to the strong association of water-anion compared to the water-water near the surface and can be explained through the hydrogen bond profile near the surface which is discussed in the next section.

6. Hydrogen bond analysis

The anion-water interaction is found to have a significant effect at low concentrations of water in the IL-water system [53,109–111]. Both experimental [112] and computational investigations [9,51] elucidate the impact of water on the nano-structure of the imidazolium-based IL, where the anion [BF$_4$] is strongly hydrogen-bonded to water molecules at low water concentrations. For example, Toshiyuki et al. [53] investigated [EMIM][BF$_4$] and water within a range of mole fraction 0.09 $\leq x_w $ $\leq$ 0.34 through ATR-IR spectroscopy and found that water molecules are in isolated form and form hydrogen bonds (HBs) with anions at $x_w$ $\leq$ 0.2; while the molar fraction $x_w >$ 0.3, water molecules form HBs among themselves in the solutions, which further weakens the interactions between cation [EMIM] and water as well as anion [BF4] and water. Similarly, Jing Zhou [113] investigated 1-butyl-3-methylimidazolium acetate ([BMI-M][Ac]), 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF$_4$] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide [BMIM][TF$_2$N] with entire range ($x_w$ = 0, 0.1, 0.3, 0.5, 1.0) of water and found weakening of HB interaction between cation and anion with the increase of water content. Because the water molecules form HB with anions by destroying the HB network between cations and anions. On the other hand, Porter et al. [114] perform MD simulation of hydrophilic IL [EMIM][BF$_4$] as well as hydrophobic IL [EMIM][NTF$_2$] at low water concentration ($x_w$ < 0.1) and reveals that the water molecules with varying cluster sizes are typically each hydrogen-bonded to two anions, which is in line with the experimental observation [109]. Similarly, Koishi et al. [48] have also observed strong interaction between water-anion in the case of [BMIM][BF$_4$] at low water concentrations.

![Figure 7. Hydrogen bond (HB) geometric criteria (a) for water-water (b) for anion-water.](image-url)

![Figure 8. Hydrogen bond distribution in the droplet (a-g) water-water hydrogen bond. (h-n) Anion-water hydrogen bond for different weight percentages of water.](image-url)
Correspondingly, we evaluate the HB between anion-water and water-water based on geometric criteria [48], as shown in (Figure 7).

Figures 8 and 9 shows the distribution of the HB between water-water and water-anion within the droplet. We have also reported the total average number of HBs for the whole system normalised by the total number of water molecules. We can observe that the number of HBs between water-water increases, and water-anion decreases with the increase in water concentration. Furthermore, water-water and anion-water HBs are both uniformly distributed in the droplet due to the hydrophilic nature of IL molecules. More importantly, at 23 wt.% (x_w < 0.77) water-water and anion-water both have the same HB value (i.e. HB_{w-water} = HB_{a-water} = 0.83), and beyond 23 wt. % (x_w < 0.77) water-water HB dominates over anion-water HB. Hence, the contact angle of the droplet increases beyond 23 wt. % as water-water interaction drives the system. In addition, we have also examined the hydrogen bond profile normal (i.e. along Z direction) to the surface to analyze the HBs near the surface and the bulk of the droplet, as shown in Figure 9. We can observe that near the surface HB between water-water is less compared to the bulk of the droplet (HB_{@surface} < HB_{@bulk}) See Figure 9), whereas the HB between anion-water is more near the surface compared to the bulk of the droplet. This observation suggests that the HB between anion and water molecule is more preferable compared to that between water molecules near the surface.

7. Conclusions

The presence of water as an impurity in ILs plays a different role than in the aqueous phase of IL. In summary, we conducted MD simulations to explore the impact of water molecules on the wetting behaviour and the interfacial structure of [EMIM][BF4] IL droplets on graphite surfaces over the wide range of water percentage 0 wt.%—41 wt.% (x_w < 0-0.89). We quantified various important parameters, such as the solid-fluid interaction energies, contact angle, density contours, cluster formation, and the average number of HBs for the different weight percentages of water molecules. It has been found initially contact angle of the droplet slightly decreases when adding water up to 17 wt. %, (x_w < 0.68) and then onwards, the contact angle starts to increase (water molecules dominated). The density profile normal to the surface shows that there is not much effect on the layering of IL molecules at a low concentration of water, whereas, at a high concentration of water molecules, the layering of IL molecules gets disrupted except the 1st layer near the surface. The degree of association of water molecules increases with an increase in water concentration, as observed from cluster analysis. We found that the IL rich regime of the droplet transforms into a water-rich regime above 23 wt.% of water concentrations. Hydrogen bond analysis reveals that the water-water hydrogen bonding dominates over the anion-water hydrogen bond above 23 wt.% water, which is responsible for the increase of contact angle of the droplet above this concentration. We believe that our study can provide an in-depth understanding of the wetting behaviour of IL in presence of water, which could be useful in many industrial applications.

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