Probing Nano-Wettability of Hydrophilic/Hydrophobic Ionic Liquids Using Molecular Dynamics Simulation

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Introduction

Nano-wettability is a very important branch of science and has recently attracted a tremendous amount of attention due to its application in lubricant,[1] digital microfluidic devices,[2] bio-nano-electro mechanical systems (NEMSs)[3] and membrane channels.[4]
In the present work a series of hydrophilic and hydrophobic 1-ethyl-3-methylimidazolium room temperature ionic liquids (RTILs) have been employed to probe the wettability in nano-scale using molecular dynamics (MD) simulation. The simulation results confirm droplet size, intrinsic viscosity and simulated temperature play the dominant role in the wettability of ionic liquids (ILs) in nano-scale.

Simulations

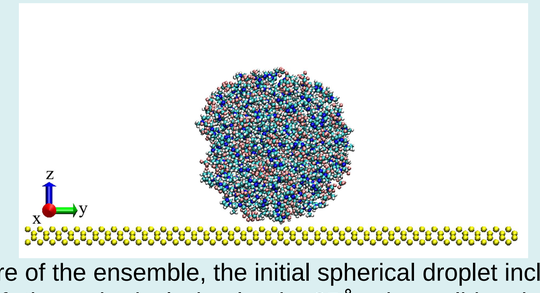

Figure 1 Initial structure of the ensemble, the initial spherical droplet included 253 [Emim][BF_4] ion pairs which radius of the spherical droplet is 25Å, the solid substrate with dimension of $76.8 \times 153.6 \times 5.76 Å^3$ consists of 3200 silicon atoms.

The nano-wettability of hydrophilic and hydrophobic imidazolium based RTILs was probed by performing the MD simulations of the morphological transition of an isolated ILs droplet in the vacuum on a solid silicon substrate from the initial structure to its equilibrium state which is generally a quasi-hemispherical liquid droplet resting on top of the silicon substrate.

All MD simulations were carried out using the general purpose parallel MD simulation open-source package DL_POLY 4.06. After the simulation, the physical properties were characterized using the DL_POLY analysis tools, and the structures were visualized with a molecular graphics software named visual molecular dynamics (VMD).

Results and Discussion

Effect of the size of droplet on nano-wettability

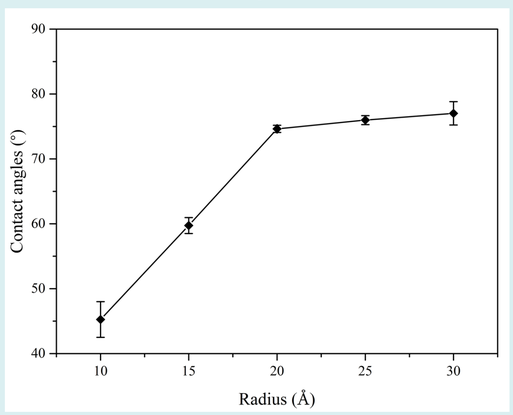

Figure 1 The contact angles of [Emim][BF_4] droplet with different radius on the silicon surface at the equilibrium state. Lines are drawn only for guiding purposes.

➢ **The contact angles increase with increasing droplet size then tend to be saturation**

Effect of the hydrophobicity and hydrophilicity on nano-wettability

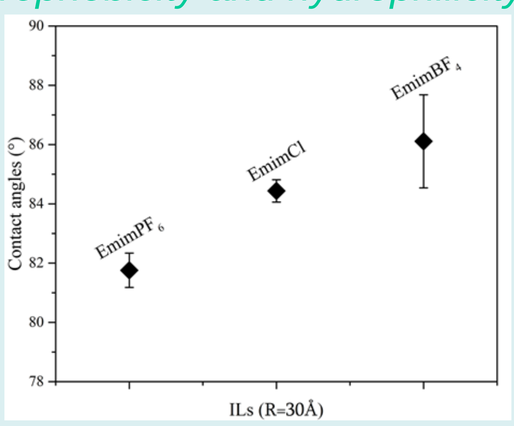

Figure 2 The contact angles for hydrophilic ILs ([Emim][Cl] and [Emim][BF_4]) and hydrophobic IL ([Emim][PF_6]), the radius for ILs droplet is 30Å.

➢ **Nano-wettability has little dependence on the hydrophobicity and hydrophilicity**

Effect of the intrinsic viscosity on nano-wettability

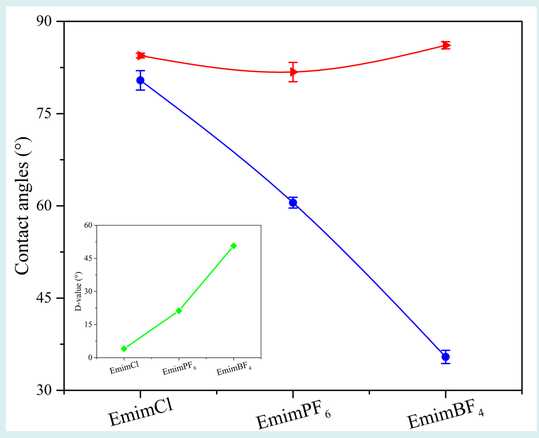

Figure 3 The contact angles for three kinds of ILs droplet with radius of 30Å on silicon surface: ▸represents different temperature (T=300K, 350K, 375K for [Emim][BF_4], [Emim][PF_6], [Emim][Cl]), ●represents same temperature (T=400K), where the bottom-left corner inset shows the D-value of the contact angle during different temperature. Lines are drawn only for guiding purposes.

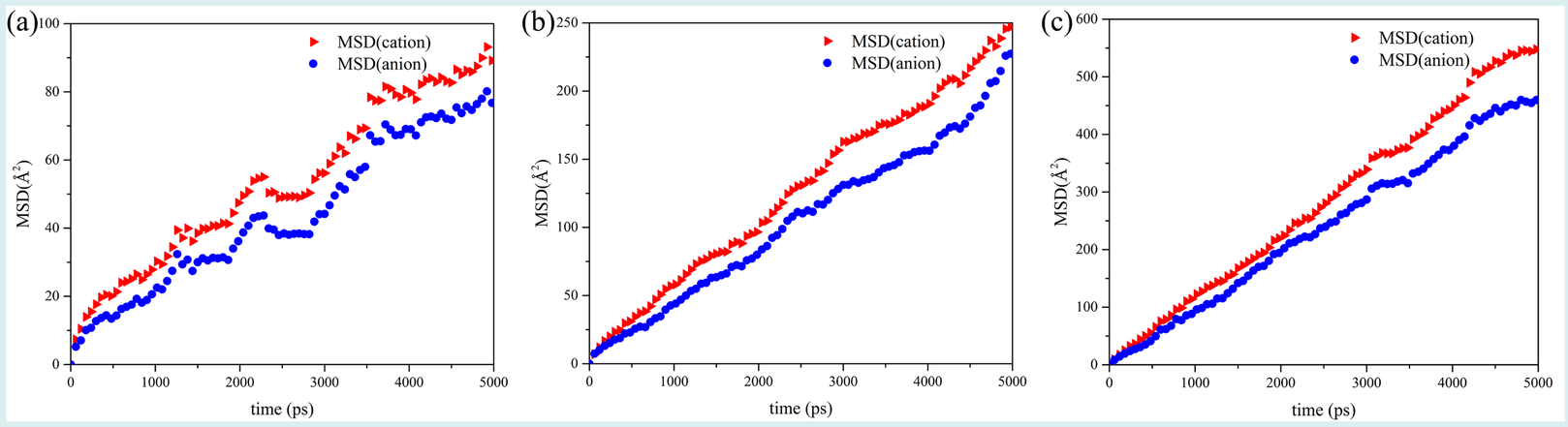

Figure 4 The MSDs of imidazolium cations and anions for three ILs at t=400K, (a) represents [Emim][Cl], where (b) and (c) represent [Emim][PF_6] and [Emim][BF_4] respectively, the radius for all ILs droplets is 30Å.

➢ **The wettability of ILs nano-droplet decreases with the increasing of viscosity**

Effect of the simulated temperature on nano-wettability

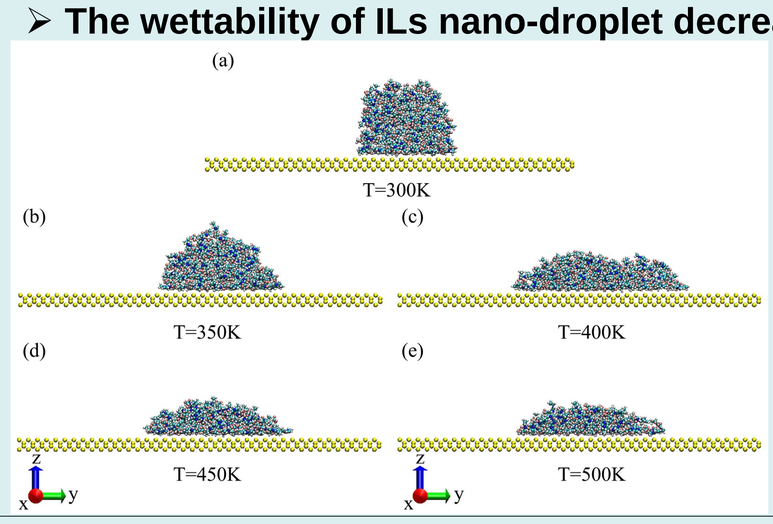

Figure 5 The equilibrium shapes of [Emim][BF_4] ILs droplet with radius of 20Å on silicon surface during different temperature.

➢ **The wettability of ILs nano-droplet increases with the increasing of temperature then reaches saturation**

Conclusions

- The contact angles increase remarkably with increasing size of ILs droplet during the smaller radius then tend to be saturation in the larger radius.
- The wettability of ILs nano-droplet decreases with the increasing of viscosity.
- Hydrophobicity and hydrophilicity of ILs have a trivial impact on wetting properties on the solid surface at the nanometer scale.
- The wettability of ILs continuously enhances and eventually reaches the level of saturation with the increasing of temperature.

References

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[3] D. J. Harrison et al., Science 261 (1993).
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