Molecular dynamics simulation of nitrobenzene in heterocyclic ionic liquids

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ARTICLE INFO

ABSTRACT

The diffusions of nitrobenzene ($PhNO_2$) in 11 pure ionic liquids (ILs) and 9 binary composite ionic liquids with the volume ratio 1:1 were examined by molecular dynamics (MD) simulation. These ionic liquids contain 1-Butyl-3-methylimidazolium ([BMim]) cations or tetrafluoroborate ([BF_4]) anions, i.e., they are heterocyclic compounds. Diffusion coefficients were calculated based on the Einstein equation. The influences of the different ionic liquids on the interaction energy and the diffusion coefficient were discussed. The MD results showed that at the same simulation concentration, the interaction energy gap between $PhNO_2$ and pure ionic liquids is larger than that between $PhNO_2$ and composite ionic liquids. The gap of [Bmim] is larger than [BF_4]. The two different functional ionic liquids are composited each other in a simple and economic way, which decrease the interaction energy and have compensated for the disadvantage of mono-component ionic liquids. Most of the diffusion coefficients of $PhNO_2$ in pure or composite ion liquids belong to the same order of magnitude. These simulation results are in good agreement with electrochemistry experimental reported by Chen et al. Analyzing radial distribution functions (RDFs) showed that the bonding and non-bonding interactions are formed in $PhNO_2$–ionic liquid systems. This is basically consistent with the conclusion of the interaction energy and diffusion coefficient.

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1. Introduction

The mass transfer process is one of the very important links of the electrochemical reductions of nitrocompounds. It involves a complex physical and chemical reaction process, including diffusion processes at the electrode/solution interface and in solution [1]. So far, however, scholars have not formed a consistent view on the mass transfer mechanism. The existing research results show that the molecular structures of ionic liquid and nitrocompounds have a great influence on the diffusion of nitrocompounds [2,3], but the interaction researches and their effects between ionic liquids and nitrocompounds are few, and the effects of the interaction on the mass transfer have been little studied [4,5]. Theory and application researches of ionic liquids are producing new breakthroughs. However, as a kind of green solvent [6–11], the development of ionic liquids is a bottleneck due to the lack of the basic physical and chemical data [12]. The data need to be determined by a lot of experiments. Conventional methods such as cyclic voltammetry and ultraviolet spectrophotometry are necessary, but they do not reveal the interaction essence. With the rapid

development of computer technology, more computer simulations such as molecular dynamics (MD) simulations have been widely used to investigate the microstructure and macroscopic properties of various systems, including the diffusion of solutes in solvents [13–15].

Our research group has preliminary studied the interaction between $PhNO_2$ and 3-methylimidazolium hexafluorophosphate ionic liquids [12]. In this paper, the diffusion of nitrobenzene in pure or composite ionic liquid systems was continued to simulate with MD method. Based on the results from MD simulations, mean squared displacement of the study subject in model system can be analyzed, and diffusion coefficient can be calculated by Einstein equation. The effect of the interactions between nitrobenzene and ionic liquids on diffusion in electroreduction reaction of nitrobenzene was explored, and the origin of the interaction was revealed. Our aim is not to calculate accurate quantitative values, but we wish only to determine the trend of the diffusion of nitrobenzene in pure or composite ionic liquid systems, to compare the modeling results of the systems with each other and see whether they correlated with experimental or industrial application data. The diffusion nature of mass transfer in $PhNO_2$-IL system will be reflected with MD method. Model construction conformed to two rules as follows: (1) model should be as comprehensive as possible; and (2) each system should be

capable of being treated in reasonable time without excessive expenditure on calculations. The results obtained here may provide theoretical supports for developing new solvents in electroreduction of nitrocompounds.

2. Model construction and simulation method

The MD simulations on the diffusion of nitrobenzene in ionic liquid systems were performed using the software, Materials Studio [16]. Taking the diffusion of $PhNO_2$ in iso-volumetric ratio of [BMim][BF$_4$] and [BMim][PF$_6$] as an example, first, three-dimensional molecular structures of $PhNO_2$, [BMim][BF$_4$] and [BMim][PF$_6$] were built and optimized to the most stable configurations (Fig. 1). The Amber Force Field [17–19] and Forcite module were used for the whole calculations including energy, minimization and dynamic. The molecules of the diffusion models were calculated based on the densities of ionic liquids and the working concentration of $PhNO_2$ [20]. In order to compare the diffusion of $PhNO_2$ in different pure or composite ion liquids, the amorphous cells were then constructed with 5 $PhNO_2$ and various numbers of ionic liquid to simulate the same concentration in different ionic liquids in amorphous cell module. Physical constants and molecular numbers of 11 pure or 9 composite ion liquids are listed in Tables 1 and 2. The initial configurations of MD simulation were obtained by optimizing these amorphous cells. Van de Waals (vdW) interactions were calculated based on atomic group. The electrostatic interactions were calculated through the Ewald method [21–23], which improves a lot of the description of electrostatics for a periodic system with respect to a cutoff-based scheme while retains the reliability of simulated results.

After checking the simulation parameters by estimating the density of $PhNO_2$–ionic liquid system, the temperature 298 K was selected according to the experiments of the electrochemical reduction of nitrocompounds in ionic liquids, and MD simulation was carried out in the NVT ensemble [24–26]. The coupling to the heating bath to control temperature was carried out using the Berendsen method [27] with a relaxation time of 0.1 ps. From the literatures [28–30], the time step is usually between 0.5 and 2 fs and MD simulation of the diffusion runs for 200–1000 ps. To ensure the accuracy of computing result in the shortest possible time, in this work, the time step was set to 1 fs and MD simulation ran for 2000 ps. The trajectory was recorded every 500 fs. Taking 5PhNO$_2$/27[BMim][BF$_4$]/24[BMim][PF$_6$] as an example, configurations of MD simulation at different times are shown in Fig. 2. Whether the model system has reached equilibrium or not was ascertained by the equilibrium criteria of energy [31] i.e., the energy fluctuation should be confined to 5–10%. Taking the model system of 5PhNO$_2$/40[OMim][BF$_4$] as an example, according to the simulation results at 298 K (Fig. 3), the total energy fluctuates in a range of 14,960 ± 60 kJ/mol, which indicates that the system has reached an equilibrium state.

3. Results and discussion

3.1. Interaction energy

From Fig. 2, as time goes on, the molecular conformation and the relative position of nitrobenzene in ionic liquids are changed, which

Table 1
Physical constants and molecular numbers of pure ionic liquids.

No.	Ionic liquids	Density (g/mL)	Molecular weight	Molecular numbers
1	[BMim][BF$_4$]	1.208	226.02	53
2	[BMim][OAc]	1.200	198.26	59
3	[BMim][Otf]	1.292	288.29	45
4	[BMim][F$_3$Ac]	1.236	253.01	48
5	[BMim][NO$_3$]	1.203	201.22	60
6	[BMip][BF$_4$]	1.204	237.05	50
7	[OMim][BF$_4$]	1.120	282.13	40
8	[HMim][BF$_4$]	1.149	254.08	45
9	[BMim][PF$_6$]	1.380	284.18	48
10	[BMim][TF$_2$N]	1.445	419.36	35
11	[EMim][BF$_4$]	1.294	197.97	65

indicates that the interaction between nitrobenzene and ionic liquid happens. This leads to the diffusion of nitrobenzene. The $PhNO_2$–ionic liquid interaction energy (ΔE) is calculated using the following equation [32]:

$$\Delta E = E_{\text{Total}} - \left(E_{\text{PhNO}_2} + E_{\text{IL}} \right)$$

where E_{Total} is the total energy of the whole $PhNO_2$–ionic liquid system from MD simulations, E_{PhNO_2} and E_{IL} are the single point energies of the free 5PhNO$_2$ and all the ionic liquids in the model system, respectively. Obviously, a larger ΔE in magnitude indicates a stronger interaction between $PhNO_2$ and ionic liquid. A larger absolute value of ΔE ($|\Delta E|$) implies $PhNO_2$ diffuses in the ionic liquid more easily and tightly [33], i.e., the low (high) diffusion coefficient is related to the roughness (smoothness) of the energy landscape explored by the diffusing molecule. At 298 K, interaction energies of $PhNO_2$–[BMim] ionic liquid and $PhNO_2$–[BF$_4$] ionic liquid systems are shown in Tables 3 and 4.

All interaction energies ΔE in Tables 3 and 4 are negative, showing that the combination processes of $PhNO_2$ compounds with [BMim] or [BF$_4$] ionic liquids are largely exothermic, and the intermolecular interactions are attractive. From Table 3, in 7 pure [BMim] ionic liquids, the ΔE of [BMim][F$_3$Ac] is the highest, and that of [BMim][OAc] is lowest. This shows that the diffusion interaction between $PhNO_2$–[BMim][F$_3$Ac] is the strongest, while $PhNO_2$–[BMim][OAc] is the weakest. The order of the interaction between $PhNO_2$ and 7 different anion ionic liquids is [BMim][F$_3$Ac] > [BMim][Otf] > [BMim][NO$_3$] > [BMim][TF$_2$N] > [BMim][PF$_6$] > [BMim][BF$_4$] > [BMim][OAc]. But the difference between $PhNO_2$ and 6 composite [BMim] ionic liquids is significantly less than that between $PhNO_2$ and 7 pure [BMim] ionic liquids, which shows that the compound of different [BMim] ionic liquids makes the function of the ionic liquids complementary.

Seen from Table 4, in 5 pure [BF$_4$] ionic liquids, the ΔE of [BMip][BF$_4$] is the highest, and that of [HMim][BF$_4$] is lowest. The order of the interaction between $PhNO_2$ and 5 different cation ionic liquids is [BMip][BF$_4$] > [OMim][BF$_4$] > [BMim][BF$_4$] > [EMim][BF$_4$] > [HMim][BF$_4$]. Additionally, the difference between $PhNO_2$ and 3 composite [BF$_4$] ionic liquids is significantly less than that between $PhNO_2$ and 5 pure [BF$_4$] ionic liquids, and is less than that between $PhNO_2$ and 6 composite [BMim] ionic liquids, which shows that the compound of different [BF$_4$]
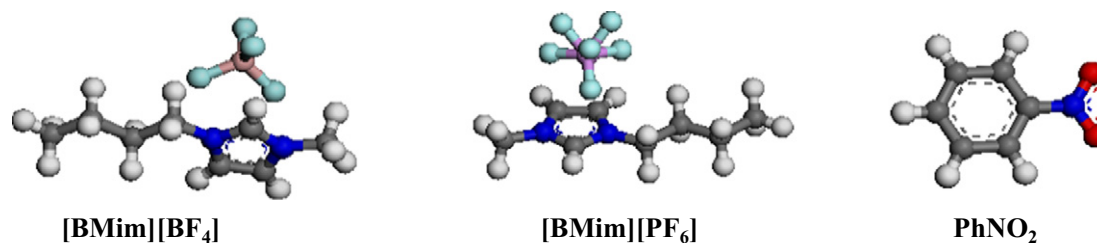

[BMim][BF$_4$]   [BMim][PF$_6$]   PhNO$_2$

Fig. 1. The optimized configurations of PhNO$_2$, [BMim][BF$_4$] and [BMim][PF$_6$].