CHARACTERISTIC INVESTIGATION OF STATIC LIQUID DESICCANT DEHUMIDIFICATION PROCESS BY MOLECULAR DYNAMICS

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ABSTRACT

Liquid desiccant dehumidification has been prevalent in recent years for air conditioning with the superiority of energy saving. The microscopic details of dehumidification processes should be obtained to deepen the understanding of the mechanism and then to promote the development of this technology. In this paper, the dehumidification processes under different gas densities and temperatures were simulated by molecular dynamics. The energy characteristic and trajectory of the water molecule absorbed by liquid desiccants were reported. The interactions of different components on the water molecule were further analyzed. Results show that the barrier caused by nitrogen and oxygen is weak. When the water vapor molecule moves just close to the liquid-gas interface from the air, the attraction of Bromide ions ranks first, followed by that of water molecules in solution and that of Lithium ions. It is also found that with an increase in the gas density, the interactions produced by denser nitrogen molecules on every water vapor molecule are not necessarily larger, which may give guidance to investigate mechanisms of dehumidification under higher pressures. In addition, higher pressures may significantly enhance the dehumidification under high temperature conditions in terms of the net absorbing rate.

KEY WORDS: Liquid desiccant, Molecular dynamics, Mass transfer, Molecule behavior, Interaction

1. INTRODUCTION

Liquid desiccant dehumidification has been demonstrated as an efficient method to remove moisture in the air especially when solar energy and waste heat can be recycled. Inorganic salt solutions like lithium bromide (LiBr) and lithium chloride (LiCl) aqueous solution are usually taken as preferred liquid desiccants in those systems[1,2]. As a vital process of dehumidification, heat and mass transfer between the liquid desiccant and air has been attached great significance. The characteristics of heat and mass transfer have been explored by extensive experiments which only reflect the macroscopic results after energy transport. But it is impossible to solve the problem how water molecules in the air behave and go into the liquid desiccant based on the macro measures.

With the development of computer in hardware and software, molecular dynamics (MD) has been demonstrated to be a promising and reliable method to predict physical properties and investigate the mechanism of chemical engineering processes. In recent years, based on molecular dynamics, investigators have conducted researches on mechanisms of evaporation and condensation, energy transport phenomena driven by heat and solution absorption processes. Guo et al. [3] proposed a novel method to obtain the condensation coefficients of gas molecules and their results showed that the condensation coefficients decreased with an increase in the temperature. After adopting classical polarization force fields, Nagata et al. [4] simulated the evaporation of pure water. By observing the trajectory of water molecules, they found that the high kinetic energy of the evaporated water molecule was obtained by the making and breaking of hydrogen bonds involving at least three water molecules at the interface. Daiguji and Hihara [5] firstly applied

molecular dynamics into LiBr absorption refrigeration to reproduce the dynamic absorption process of water molecule. Following the same idea, Zhu [6] verified the enhancement of absorption process when adding alcohol additives. Effects of the electric field intensity and the salt concentration on the water evaporation rate were also analyzed by Wang et al. for the aqueous droplet dissolved with salts [7]. They attributed higher enhancement of evaporation for the pure water than the saline solution to the strong hydration of ions.

According to the survey above, few literatures discuss the dehumidification processes by molecular dynamics in terms of the interaction components. The dominant interactions contributing to dehumidification haven't been known. In order to provide microscopic details, the processes of liquid desiccant dehumidification are simulated by molecular dynamics. Conditions with different air densities and solution temperatures were simulated and analyzed. The velocity and trajectory information were also presented in this paper.

2. METHOD

The simulated dehumidification system was composed by the air box and the solution-air box as shown in Fig. 1. Air was represented by the mixture of nitrogen molecules, oxygen molecules and water vapor molecules. The Lithium bromide solution was adopted as the liquid desiccant, consisting of 4000 water molecules and 1658 ions. To ensure the air state still existed when the number of water molecules was large, the air simulation system was firstly run in NVT ensemble with the high temperature of 370K for 5000 ps. The solution-air system was also run in NVT ensemble with the target temperature for 5000 ps to reach the equilibrium state before simulating dehumidification which run in NVE ensemble. Important thermodynamics parameters were output every 100 fs during the dehumidification run of 300 ps.
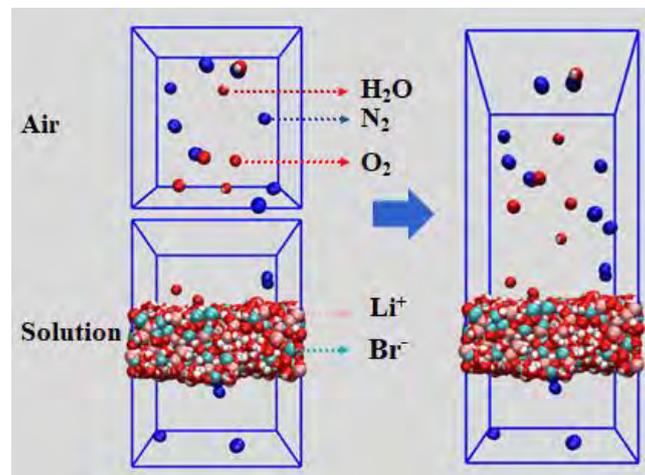
Fig. 1 The simulation system and processes

As shown in Fig. 2, microscopic processes of liquid desiccant dehumidification were investigated under three different gas densities in order to explore effects of air pressures. The air densities were increased proportionally for every air component. All systems had the same width and length of 7.5nm. In addition, all air boxes were 8 nm high to keep the equal centroid distance between the pure solution and air. For conditions of Density 1, the air box contained 4 water molecules, 8 nitrogen molecules and 2 oxygen molecules. For conditions of Density 2, the air box contained 6 water molecules, 12 nitrogen molecules and 3 oxygen molecules. For conditions of Density 3, the air box contained 8 water molecules, 16 nitrogen molecules and 4 oxygen molecules. Since all water vapor densities are smaller than that of saturation conditions, those conditions aforementioned are available. The solution-air boxes had the same nitrogen and oxygen molecules with their corresponding air boxes while the numbers of water vapor molecules were determined by MD simulation under 300K. Dehumidification processes were also simulated when the initial solution temperature changed from 300K to 360K.
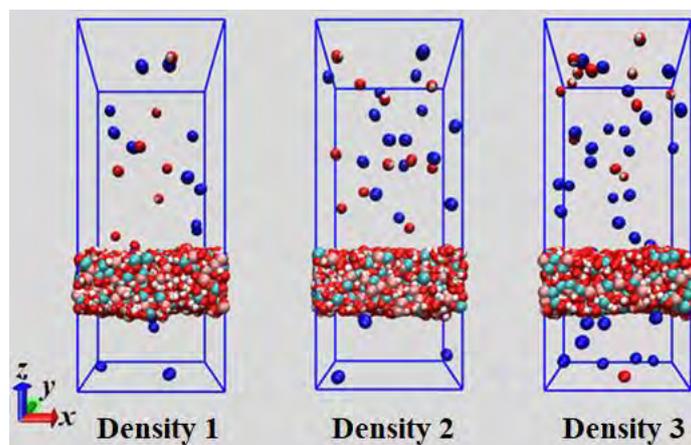
Fig. 2 Simulation system under different gas densities

All simulations were conducted using GROMACS 5.0 with periodic boundary conditions. Nonpolarizable force fields were used to describe interactions between particles. All atoms or ions were considered as Lenard-Jones (LJ) particles with charges. The intermolecular potentials were correlated by the summation of LJ potentials and electrostatic potentials. Force field parameters used in this paper are listed in Table 1. LJ interactions between different kinds of atoms were produced by LB combining rules. Bonds and angles of water molecules were constrained by SETTLE algorithm. The cutoff distance was set as 10 Å for Lenard-Jones potential and short-range electrostatic interactions. PME solver was used to deal with long-range electrostatic interactions. Newtonian equations of motion were solved by leap-frog algorithm with a time step of 1 fs. Nosé–Hoover thermostat was used to keep the system at the target temperature.

**Table 1** Parameters of atom/ion models used in this paper.

Atoms/Ions	ε, kcal/mol	σ, Å	q, e	r, Å	θ_{HOH}, °	Combining rules
Cl^-	0.1	4.401	-1			
Br^-	0.1	4.539	-1	-		
$N(N_2)$	0.1629	3.738	0	N-N: 1.098	-	LB
$O(O_2)$	0.2014	3.480	0	O-O: 1.017		
$O(H_2O)$	0.1553	3.166	-0.8476	O-H: 1	109.47	

3. RESULTS AND DISCUSSION

### 3.1 Dehumidification simulation under different gas densities

The initial temperature of solution was 300K before running in NVE ensemble. Fig. 3 illustrates the trajectory and velocity of a certain water vapor molecule at different time for conditions of Density 1. The water vapor molecule was absorbed by the solution at about 38.5 ps upon reaching the interface which could be obtained by calculating the density profile of solution. It can be seen that the velocity of the water molecule moving towards the liquid-gas interface is relatively stable unless collisions with other atoms occur. Collisions may cause the sharp change in both magnitude and direction of the velocity, accelerating the process moving towards the interface. And it must be pointed out that after entering into the liquid desiccant, the velocity fluctuates dramatically due to the huge density of molecules. The potential energy of the water vapor molecule is also shown in Fig. 3(b). During dehumidification, the potential energy of the water vapor molecule dropped sharply. In order to investigate the barrier and promotion of water molecule's movement to the liquid desiccant, the interactions between the water vapor molecule and other components in the system

are analyzed. Effects of nitrogen molecules, oxygen molecules, solution water molecules, Bromide ions and Lithium ions on a water vapor molecule are shown in Fig. 4. It is obvious that the interactions caused by gas molecules are quite limited especially oxygen, which hardly acts force on the water vapor. When the water vapor molecule just moves close to the liquid-gas interface from the air phase, the attraction of Bromide ions ranks first, followed by that of water molecules in solution and that of Lithium ions. But with the process going on, effects of Bromide ions become smaller, exceeded by the interactions of water molecules in the liquid desiccant.
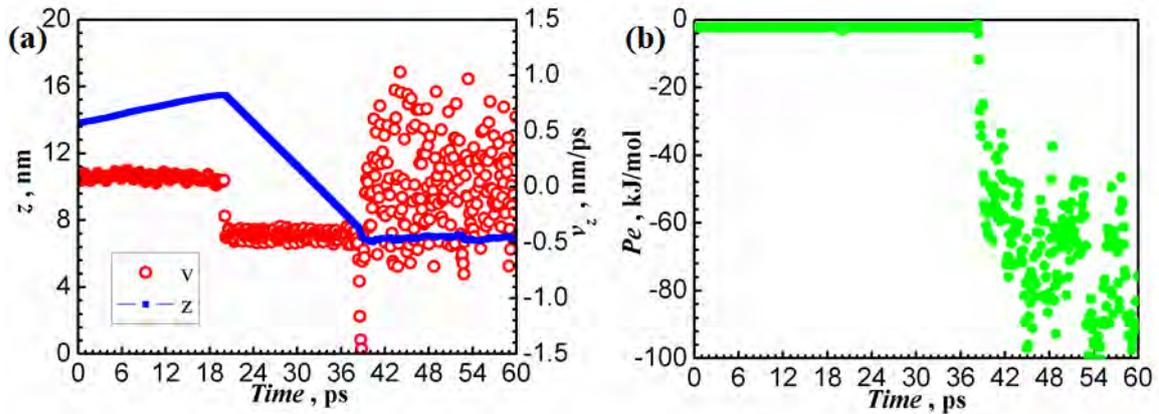

Fig. 3 Trajectory, velocity and potential energy of a water vapor molecule
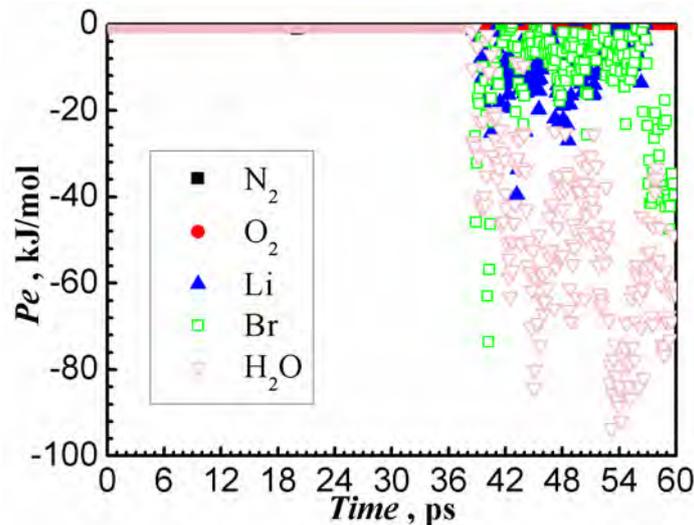
Fig. 4 Interaction contribution of different components for a water vapor molecule

In order to obtain accurate results under different gas densities, three cases with different initial configurations were simulated for every density condition. Fig. 5 gives the time in ascending order when the water vapor molecules were removed within 60 ps. Considering three cases, totally 12, 18 and 24 water vapor molecules exist for conditions of Density 1, Density 2 and Density 3 respectively. According to statistics, in the first 30ps, 66.7% of water molecules in the air moved into the liquid desiccant for all cases of Density 1. Totally 12 water vapor molecules were absorbed by the liquid desiccant for all cases of Density 2, also occupying 66.7% of initial water vapor molecules. And about 54% water molecules in the air were absorbed by the liquid desiccant for all cases of Density 3. This indicates that the absorbing rate is firstly quick and then becomes slow. Moreover, within 60 ps, all water molecules (12 in terms of number) in the air went into liquid desiccants for conditions of Density 1 where the density of nitrogen was 0.83 kg/m^3 in the air. 14 water molecules were absorbed for conditions of Density 2 with the nitrogen density of 1.245 kg/m^3. And 17 water molecules were absorbed for conditions of Density 3 with the nitrogen density of 1.62 kg/m^3.

This means with an increase in the gas density, the absorption rate increases but the mass transfer coefficient decreases due to the faster change of concentration difference.
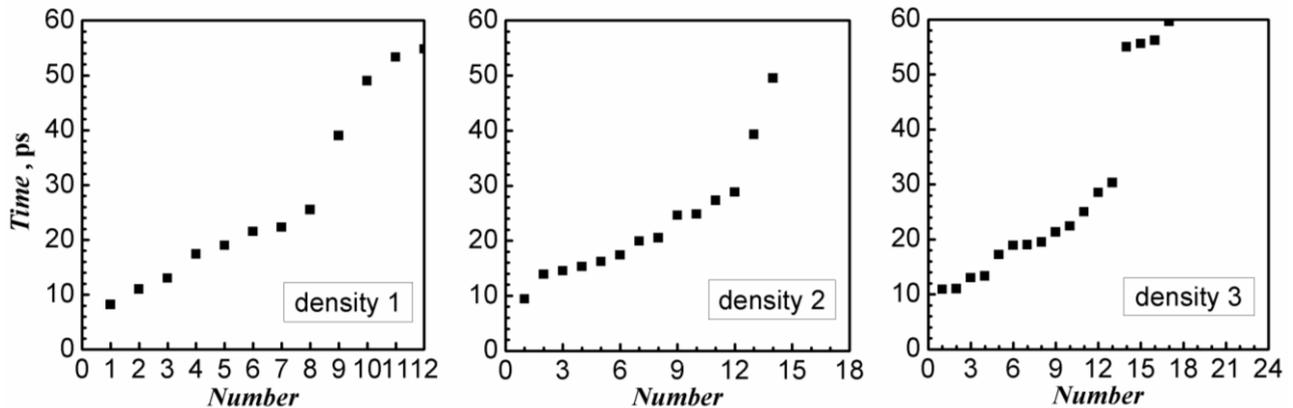
Fig. 5 Absorption time of water vapor molecules

According to the research above, the interaction caused by oxygen molecules is much less than that by nitrogen molecules. So, only nitrogen molecules are discussed based on different gas densities. Fig. 6 shows the interactions on all water vapor molecules posed by nitrogen. In this figure, all values are the average results of three cases. It is found that the interaction points increase with an increase in the gas density because the nitrogen molecules are denser in the air. After calculation, for conditions of Density 1, all nitrogen produced the average interaction of -1.33 kJ/mol for every water vapor molecule within 60 ps. For conditions of Density 2 and Density 3, the value is -1.09 and -1.89 kJ/mol. This means although the number of nitrogen molecules goes up with an increase in the air density, the inhibition level may not increase for every water vapor molecule from the aspect of interactions.
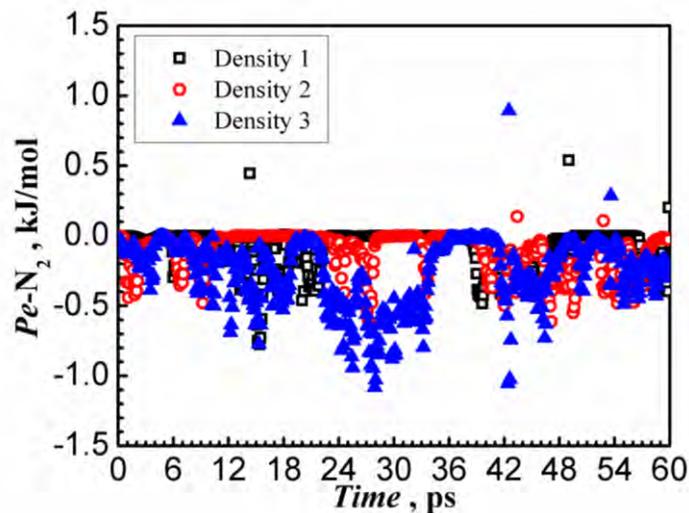

Fig. 6 Interactions between nitrogen and water vapor molecules under different gas densities

3.2 Dehumidification simulation with different temperatures

The initial temperature of solution was also set as 360K separately in order to investigate the effects of the temperature. Fig. 7 presents the absorbing time for conditions of Density 1 (Fig. 7(a) and Fig. 7(b)) and Density 3 (Fig. 7(c) and Fig. 7(d)) within 60 ps. It is clear that as the solution temperature increases, the consumed absorption time rises and fewer water vapor molecules move into the liquid desiccant within the same time period. Moreover, as mentioned in 3.1, totally 17 water vapor molecules were removed by the liquid desiccant for conditions of Density 3 and 300K within 60 ps. When the temperature increased to 360K,

only 14 water vapor molecules entered into the liquid desiccant and simultaneously 5 water molecules entered into the air space, resulting in a net absorption rate of 9 water molecules. By contrast, it is more terrible for conditions of Density 1. When the solution temperature was 300K, all 12 water vapor molecules became the liquid state and no water molecules went into air space within 60 ps. However, when the solution temperature is 360 K, the net absorption number is 1, of which 12 is the absorption number and 11 is the desorption number. It can be seen that the higher temperature shows weaker effects on the high gas density conditions. As the temperature rises, the high-density conditions under the same temperature may provide higher net absorption. Thus, higher pressure could significantly enhance the dehumidification with the condition of high temperature of solution.
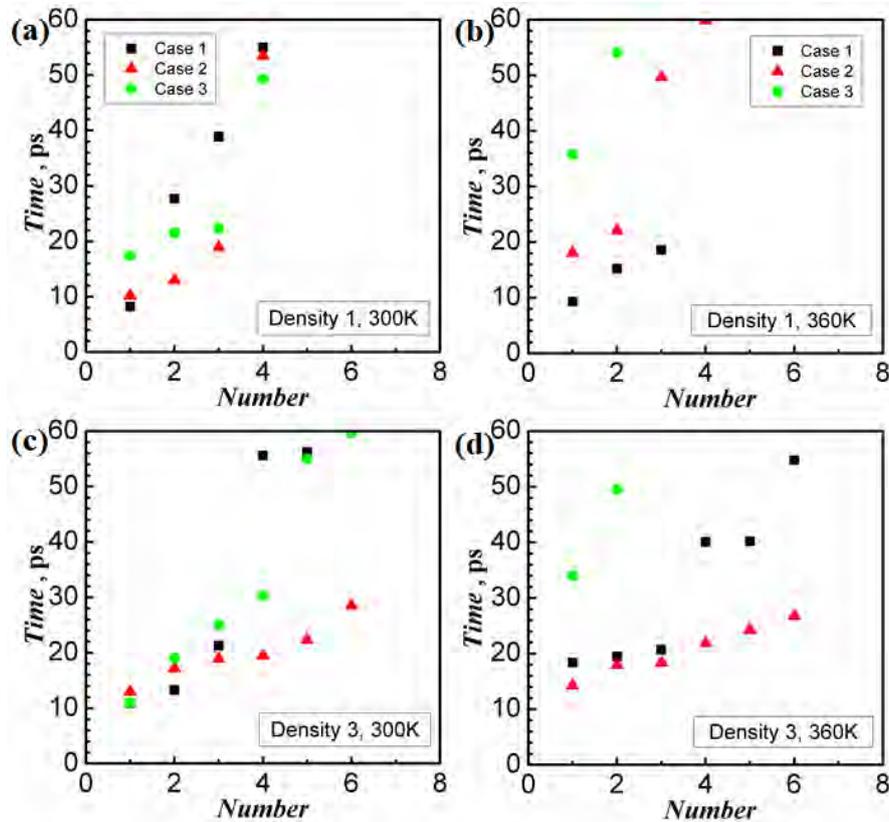
Fig. 7 Absorption time of all cases under different temperatures within 60 ps

4. CONCLUSIONS

This study shows the microscopic details of liquid desiccant dehumidification like the interactions produced by other components in the system and the trajectory of the water molecule absorbed by liquid desiccants. This helps to deepen the understanding of dehumidification processes. The effects of gas density (similar to pressure) and temperature were analyzed. Main conclusions are obtained as follows:

(1) When the water vapor molecule moves just close to the liquid-gas interface from the air, the attraction of Bromide ions ranks first, followed by that of water molecules in solution and that of lithium ions. But the tendency changes with the process going on.

(2) With an increase in the air density, the density of nitrogen rises dramatically. However, the interactions between nitrogen molecules and every water molecule are not necessarily larger. Thus, the barrier to moving towards the liquid desiccant caused by thicker gas may not dominates, which could give guidance to investigate mechanisms of dehumidification under higher pressures.

(3) As the solution temperature increases, more water molecules will escape from the liquid phase and the time used for absorbing all water molecules increases. Higher pressure could significantly enhance the dehumidification in terms of the net absorbing rate when the solution temperature is high. This may explain the better performance of high-pressure liquid desiccant dehumidification.

In this paper, water vapor molecules with similar positions show distinct behaviors. So, relationships of dehumidification with the water vapor molecule initial position, potential energy and kinetic energy deserve further study.

ACKNOWLEDGMENT

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