Water Flow inside Polamide Reverse Osmosis Membranes: A Non-Equilibrium Molecular Dynamics Study

Yang Song, Fang Xu, Mingjie Wei,* and Yong Wang* 

State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, and College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, Jiangsu, P. R. China

ABSTRACT: Water flow inside polyamide (PA) reverse osmosis (RO) membranes is studied by steady state nonequilibrium molecular dynamics (NEMD) simulations in this work. The PA RO membrane is constructed with the all-atom model, and the density and average pore size obtained thereby are consistent with the latest experimental results. To obtain the time-independent water flux, a steady state NEMD method is used under various pressure drops. The water flux in our simulations, which is calculated under higher pressure drops, is in a linear relation with the pressure drops. Hence, the water flux in lower pressure drops can be reliably estimated, which could be compared with the experimental results. The molecular details of water flowing inside the membrane are considered. The radial distribution function and residence time of water around various groups of polyamide are introduced to analyze the water velocities around these groups, and we find that water molecules flow faster around benzene rings than around carboxyl or amino groups in the membrane, which implies that the main resistance of mass transport of water molecules comes from the carboxyl or amino groups inside the membranes. This finding is in good consistency with experimental results and suggests that less free carboxyl or amino groups should be generated inside RO membranes to enhance water permeance.

1. INTRODUCTION

The freshwater scarcity has become a worldwide problem due to the rapidly growing population, energy demand, and industrialization.¹ In many regions of the world, desalination is an increasingly common solution to supply potable water. Among all desalination technologies, reverse osmosis (RO) technology is the most internationally widespread technology, due to its less stuff cost, lower energy consumption, and smaller equipment size.² In this technology, the performance of membranes predominantly determines the efficiency of this process. For most commercial RO membranes, which are mostly interfacially polymerized polyamide (PA) from m-phenylenediamine (MPD) and trimesoyl chloride (TMC),³ a salt rejection as high as >99% is typically reached, which meets the demand for the seawater or wastewater desalination. However, the water flux remains insufficient so that the net cost of RO water is not as low as expected.³ High permeability for water and excellent exclusion of solutes are important for selective permeable membranes, which both evaluate the performance of RO membranes. Owning higher performance of membranes could not only reduce equipment sizes but also improve the efficiency of the membrane separation process. Therefore, developing RO membranes with high water permeability without sacrificing salt rejection is greatly demanded.⁴ In the process of developing advanced RO membranes, the state-of-the-art PA RO membranes have achieved overwhelming success since the 1970s.⁴ From that time, a significant development has been witnessed in terms of materials synthesis as well as fabrication processes.⁶ To further enhance the water flux of PA RO membranes, it is important to understand the molecular mechanism of water transport through the membrane. However, the conventional experimental methods could hardly detect behaviors of fluid molecules at a microscopic scale, especially in the nanoscale confinement. As a consequence of this, the theory of mass transport in RO membranes is far from elucidated.⁷

Nowadays, with the improvement of the computational capabilities, computer simulations are widely used to observe these behaviors of nanoscale fluids so as to study the membranes’ performance.⁸ As a classical method of computer simulations, the molecular dynamics (MD) simulation offers a useful way to investigate the behaviors of water molecules inside nanconfined channels.⁹ Kotelyanskii et al. investigated the statistical and dynamic properties of water molecules in an atomic PA membrane.¹⁰ They found that the rate of water diffusion depended significantly on water—water hydrogen bonding interactions. Ding et al. were also focused on the molecular details of water molecules inside the PA RO membranes and found that the hydrogen bond number per molecule and mean square displacements of water molecules significantly decreased inside the membrane with respect to the bulk phase due to the extreme confinement.¹¹ These molecular understandings from
MD simulations help to reveal the behavior of water molecules inside the PA membranes. However, in the RO process, the movement of water molecules is forced by pressure drops, so this is a typical nonequilibrium condition. Correspondingly, the statistical mechanical linear response theory used in an equilibrium condition may not faithfully reflect water flowing through membrane pores in the real RO process. Compared to the equilibrium MD simulations, the NEMD simulations can directly obtain the macroscopic water flux from the molecular trajectories of the simulations. Thus, the NEMD could truly simulate the RO process. Ding et al. and Shen et al. used this method to study the water flux in RO membranes. Shen et al. applied forces on rigid sheets outside the water reservoir to produce a pressure drop. However, this process cannot be maintained in a steady state due to the gradually decreasing water molecules in the water reservoir during the process of the solution passing through PA membranes. For this reason, the water flux calculated in small time scale cannot be expanded to the experimental time scale (several hours). Hence, their nonsteady state simulations are hard to reliably predict the flux of fluids in the experimental time scale.

In most simulation works on mass transport of RO membranes, the system was usually built up by considering both the hydrated membrane and outside water or solution reservoirs. Such a built system is advantageous when investigating the gating effect and simulating the whole membrane separation process. However, this system is not reliable to analyze the transport resistance. Generally, the mass transport resistance comes from two parts of the RO process, namely, the water entrance into and exit from the membrane (interfacial resistance) and the water transport inside the membrane (intragranular resistance). In all-atom MD simulations, it is practically impossible to build up the membrane system with the thickness at the experimental scale (>100 nm). Usually, the water flux is estimated by scaling the simulated flux with the membrane thickness. In this scaling estimation, the interfacial resistance is also multiplied for the systems with water reservoirs, which is apparently not reliable, as interfacial resistance is independent of the membrane thickness. In addition, the system considering also outside water reservoirs does not allow the effect of pressure drops on the two specific transport resistances to be distinguished.

In this work, we are focused on understanding the main resistance for the water transport inside RO membranes. We apply a steady state nonequilibrium dynamics simulation (SS-NEMD) to study the behavior of water molecules flowing inside the RO membranes, by directly applying external force on the water molecules, since there are no water reservoirs outside the membranes. One of the advantages of this SS-NEMD lies in the fact that once the simulations reach the steady state the statistic and macroscopic properties of water remain unchanged regardless of the simulation time. During the simulations, once the steady states are reached, we examine how the pressure drop affects the macroscopic water flux. Furthermore, the effect of functional groups on water transport inside PA RO membranes is also revealed, which has not been reported yet.

2. METHODS

2.1. Force Field. We performed MD simulations with the LAMMPS program. The atomic interaction was modeled with the all-atom optimized potentials for liquid simulations (OPLS-AA) force field. The OPLS-AA potential is composed of nonbonded interactions and intramolecular interactions. Intramolecular interactions are described by bond vibration, bond angle, and torsion angle potentials.

\[
U_{\text{OPLS}} = U_{\text{ab}} + U_{\text{bond}} + U_{\text{ang}} + U_{\text{tor}}
\]

Nonbonded interactions \(U_{\text{ab}}\) consist of a sum of standard 12-6 Lennard-Jones (LJ) and electrostatic potentials:

\[
U_{\text{ab}}(r_{ij}) = U_{\text{LJ}} + U_{\text{coul}} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + k_{\text{coul}}\frac{q_i q_j}{r_{ij}}
\]

where \(\epsilon_{ij}\) is the LJ energy, \(\sigma_{ij}\) is the LJ diameter for atoms \(i\) and \(j\), \(q_i\) and \(q_j\) are their partial charges, and \(k_{\text{coul}}\) represents the electrostatic constant. Mixing rules are used: \(\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}\) and \(\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}\), when atoms are different species. Nonbonded interactions are calculated between all atom pairs of different molecules in addition to all pairs on the same molecule separated by three or more bonds, though the interaction is reduced by a factor of \(1/r^6\) for atoms separated by three bonds. The cutoff distance of all LJ interactions is 10 Å. All electrostatic interactions are calculated in real space, if atom pairs are closer than 10 Å. However, outside this range, the interactions are calculated in reciprocal space by using the Ewald algorithm with a precision of 10⁻⁴. The potential for bond stretching is presented by eq 3:

\[
U_{\text{bond}}(r_{ij}) = k_i(r_{ij} - r_0)^2
\]

where \(r_{ij}\) represents the distance between atoms \(i\) and \(j\) and \(r_0\) is the equilibrium separation. The harmonic form of the angle stretching potential is the following:

\[
U_{\text{ang}}(\theta_{ijk}) = k_\theta(r_{ij} - r_0)^2
\]

The \(i, j, k\) and \(l\) represent three atoms. \(\theta_{ijk}\) is the angle of the vectors \(r_{ij}\) and \(r_{jk}\), and \(\theta_0\) is the equilibrium value. At last, the torsional potential in OPLS is given by:

\[
U_{\text{tor}}(\phi) = \frac{k_\phi}{2}\sum_{n=1}^{4}[1 - (-1)^n \cos(n\phi)]
\]

in this equation, \(\phi\) is the dihedral angle, and \(k_\phi\) is the energy.

2.2. Construction of the RO Membrane. In this work, we constructed an all-atom model. The main advantage of the atomistic model is that it describes the complex macro-molecular system in a detailed all-atom representation and provides a direct quantitative prediction of the polymer structural and dynamical properties. The chemical structures of monomers of PA considered in our simulations, TMC and MD, as well as the repeat unit of PA are shown in Figure 1a. Each PA chain is set to have 50 repeat units, as shown in Figure 1a, and the units are linked with each other by forming amide bonds through the reaction between COOH and NH₂ groups. The constructed PA chains are therefore terminated with a COOH group on one end and NH₂ group on the other. Nine such PA chains are packed in the simulation box, and at the very beginning, the PA chains are almost linear. To obtain the random structure of PA and to minimize the energy of the PA membrane, a simulation was performed with a thermostat at a temperature of 1000 K for 1 ns and then set to 300 K in a box.
with a three-dimensional periodic boundary, in which \( L_x = 8 \) nm, \( L_y = 9 \) nm, and \( L_z = 15 \) nm.

After that, we constructed the hydrated PA membranes. Ding et al. constructed the hydrated PA membranes by an NEMD simulation,\(^\text{19}\) by which the process simulated the experimental method. Unlike their work, we constructed the hydrated PA membranes by adding water molecules directly into the simulation box, since we needed to construct only a hydrated membrane without water reservoirs. As the water content in the hydrated membranes is experimentally measured to 23 wt %,\(^\text{27}\) we randomly inserted 1200 water molecules into the simulation box. After the initial minimization, the simulations were performed 2 ns in a canonical ensemble (NVT), in which the temperature was set to 300 K. In addition, the system pressure was increased from 1 to 100 bar using an isothermal−isobaric ensemble (NPT). The purpose of this step is to compress the system sufficiently to render it ready for the method of shrinking boxes (\( T = 300 \) K and \( P = 100 \) bar). The final dimensions of the orthorhombic cell of the final hydrated membranes were \( L_x = 4 \) nm, \( L_y = 4.5 \) nm, and \( L_z = 7.5 \) nm, as shown in Figure 1b.

### 2.3. Details of SS-NEMD Simulations

To investigate water molecules flowing inside the membrane, the periodic boundary conditions were employed in all three directions. The pressure drops in the simulations were 2 orders of magnitude higher than experimental values, since a small force led to a low signal-to-noise ratio, such that extremely long sampling would be needed to measure the streaming motion with a small uncertainty, which resulted in the large computational cost. As fluid atoms could not distinguish between a situation where the flow is driven by a pressure or by an external field,\(^\text{28}\) the force or gravity field could represent the pressure drop in the NEMD simulations. The pressure drops inside the membrane can be related to the constant applied force by \( \Delta P = P_1 - P_2 = nF_z/A \) on each water molecule in the \( z \)-direction.\(^\text{27}\) After simulations, the water flux in the membrane was directly obtained by counting numbers of water molecules though a particular plane across the flowing direction.

To simulate the driven flow, Frentrup et al.,\(^\text{30}\) Huang et al.,\(^\text{31}\) and Muscatello et al.\(^\text{32}\) achieved a pressure gradient by applying a force to particles in a thin slab some distance away from the membrane. In this manner, the particles with dynamics perturbed by the external force are not close to the system of interest, i.e., the region close to the membrane. However, as we are focused on water flow inside the membrane in this work, we have to construct the hydrated PA membranes without the outside water reservoirs; thus, there is only the membrane and its hydrations. Therefore, following a frequently used method,\(^\text{29,33}\) we applied the external force directly to the water molecules. A set of external forces (in the \( z \) direction of the simulation boxes) was added on water molecules so as to simulate the pressure drops (180, 270, 360, 450, 540, and 630 MPa) across the membranes, which could drive the water flowing through the RO membranes. In the SS-NEMD simulations, a microcanonical ensemble (NVE) was performed on water molecules with the NVT on polyamides, so that water molecules could move freely from being interrupted by thermostats, which comes with the NVT ensemble, and that the extra heat generated by the external force can be removed completely by the polymer. The temperature of water molecules remains around 300 K no matter what with the pressure drops ranging from 0 to 630 MPa (shown in Figure S2). In addition, to avoid the polyamide chains flowing with water molecules in the \( z \) direction, we pinned 5% of the membrane to fixed points during the simulations. During the first 3 ns (or sooner) of each simulation, the system was going to reach the steady state and the data collected in this period were not used for further analysis. The whole data acquisition

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**Figure 1.** (a) The chemical equation of polymerization of MPD and TMC to produce polyamide. (b) Snapshot of the final configuration of hydrated PA. The atoms of PA are marked with the blue, and water molecules are represented by red (O) and white (H), respectively.

**Figure 2.** (a) Change of PWF with time through the RO membrane at \( \Delta P = 270 \) MPa. (b) PWF through the RO membrane as a function of pressure drops.
stage lasted 10 ns, and atomic trajectories were recorded every 10000 steps with a time step of 1 fs to examine the structural and dynamic properties of water in the RO membrane.

3. RESULTS AND DISCUSSION

3.1. Pure Water Flux. In this work, the pure water flux (PWF) is calculated as water molecule flow rate per membrane area. Six pressure drops are applied on water molecules to investigate the effect of pressure drops on the transport properties. The water flux at \(\Delta P = 270\) MPa is shown in Figure 2a. In this case, the points of water flux recorded by the trajectories are oscillated around the line \(y = 37.22\), which indicates a water flux of 37.22 molecules/ns/nm\(^2\). Since there is no obvious tendency of continuous increase or decrease in the PWF, we believe the simulation is in a steady state.

The PWFs of the other five pressure drops are calculated the same as in the case of \(\Delta P = 270\) MPa. Figure 2b shows the water flux as a function of pressure drops. It is obvious that the water flux increases almost linearly with pressure drops despite small fluctuations due to the random thermal motion. The pressure drops in our simulations are much higher than those in experimental RO processes. This is because it is practically impossible to investigate the water flux at a relatively low pressure drop within a few nanoseconds. However, it is worth noting that the fitted line is xeroidal which indicates that a doubled pressure drop will approximately lead to a doubled PWF. Hence, the water flux at low pressure drops can be reliably predicted. If \(\Delta P = 5\) MPa, the PWF will be calculated as 0.687 molecules/ns/nm\(^2\), which is a number of magnitudes higher than those obtained in experiments (0.001–0.004 molecules/ns/nm\(^2\)).

There is another issue which will take effect on the PWF for the RO process. Shen et al.\(^{13}\) pointed out that experimentally measured macroscopic water flux is inversely proportional with the thickness of the PA selective layer. Usually, the thickness of the PA selective layer is around 200 nm.\(^{34}\) Accordingly, the equivalent experimental water flux at 5 MPa with a membrane thickness of 7.5 nm (L\(_z\)) should be in the range 0.026–0.107 molecules/ns/nm\(^2\). From Figure 2b, the estimated water flux at 5 MPa is about 0.687 molecules/ns/nm\(^2\). The value is obviously higher than the experimental result because we only consider water flow inside the membrane. The transport resistance is actually composed of several processes, including the concentration gradient in the fluid bulk phase, the water entering membranes, the one inside membrane pores, etc. In this work, we are focused on the transport behaviors of water inside RO membranes and try to find out the main factor of transport resistance for water molecules through the PA RO membranes. The process of water molecules entering into RO membranes and the concentration gradient are not considered here. Since the process of water molecules flowing into the membrane will undoubtedly consume a significant amount of energy due to the molecules colliding with the membrane, this process would directly decline the velocity of water molecules.

3.2. Physical Properties of the Membrane. Differing from the carbon nanotubes which have well-defined hollow channels with permanent shapes, pores in RO membranes are dynamic and ever changing while water molecules flowing inside the membrane, and few researchers use SS-NEMD to analyze the behavior of water flowing through RO membranes.\(^{13}\) It is important to understand the physical properties of the RO membrane, as they determine the dynamic properties of water molecules in it.

Figure 3 shows the average density profiles across the hydrated membrane. It is obvious that the density of hydrated membrane fluctuates around 1.3 g/cm\(^3\), which is in good agreement with the experimental results.\(^{36}\) The density of the hydrated membrane is almost constant in different positions in the z direction of simulation boxes, and the oscillation within a reasonable range is the influence of the presence of voids inside the membrane. Figure 3 also depicts the average density profiles of water molecules inside the membrane. The total density of the water is around 0.38 g/cm\(^3\). By comparing the density of water and hydrated membrane (about 0.38 g/cm\(^3\) of water per 1.3 g/cm\(^3\) hydrated polyamide),\(^{18}\) the pore volume fraction (Φ) can be calculated to be 0.3. In addition, the density of bulk water \(\sim 1\) g/cm\(^3\) or unexpected high density cannot be observed in Figure 3. This predicts no macroscopic phase separation between polymer and water molecules.

To further investigate the existence of macroscopic phase separation and the free volume size of the membranes, the average radius of pores is calculated by the water–water radial distribution function \(g(r)\) inside the membrane. Figure 4a describes the radial distribution function \(g(r)\) among water molecules, the tendency of which is consistent with the work of Ding et al.\(^{18}\) We continued our analysis of the membranes by investigating the pore size. The effective pore size can be estimated by eq 6 according to Debye\(^{37}\) with an ideal random porous structure

\[
\ln[g(r) - 1] \propto \text{const} - \frac{r}{\xi}
\]

where \(\xi\) is the correlation length that determines the characteristic size of the minority phase, i.e., water-filled spaces in the membranes.\(^{18}\) Figure 4b represents the correlation function derived from Figure 4a as defined by eq 6.

Then, the oscillated slope can be roughly fitted into a linear slope after the first peak, from which \(\xi = 1.5\) was calculated. To connect the correlation length \(\xi\) and the pore volume fraction \(\Phi\) to the average pore area per unit volume \((S/V)\), the Debye theory follows.\(^{37}\)

\[
\frac{S}{V} = \frac{4\Phi(1 - \Phi)}{\xi}
\]

From the previous calculations, \(S/V = 5.6\) nm\(^{-1}\) is estimated. If the pores are close to cylinders, spheres, and slit-like shapes, the average pore radii are 0.36 nm (2V/S), 0.54 nm (3V/S), and 0.18 nm (V/S), respectively. Therefore, the pore diameter is in the range 0.36–1.08 nm, which is in good consistency with the
experimental values. In all cases of water transport, the flux is almost linear with the square of the pore radius. That is why the pore size is an essential parameter we have to take into account. In this work, the diameter of the pores is in the range of a couple of water molecules (about 0.32 nm for a single one), so that most water molecules will collide with the pore wall composed of various functional groups of PA membranes. Hence, the interaction between water molecules and the PA membranes can be expected to dominate the water molecules flowing through the pores due to the slippery theory of mass transport.

3.3. Interactions between Water Molecules and the Functional Groups in PA Membranes. To reveal the interactions between water molecules and functional groups, the radial distribution function, \( g(r) \), was explored. The radial distribution function between water molecules and functional groups of polyamide is shown in Figure 5a. Oxygen atoms of carboxyl groups, nitrogen atoms of amino groups, and carbon atoms of benzene rings were considered as characteristic atoms which were presented as functional groups of polyamide. The radial distribution function here could be defined as the local density of water molecules around the functional groups divided by the bulk density of water inside the membrane. In Figure 5a, \( r \) presents the distance between water molecules and functional groups and \( g(r) \) represents the degree of aggregation. For the pair of oxygen atoms in water molecules and oxygen atoms of carboxyl groups (\( O_w-O_{PA} \)), the curve begins to rise when \( r = 0.23 \) nm, which means that the minimum distance between water and carboxyl groups in the membrane is 0.23 nm. At \( r = 0.26 \) nm, there is a sharp peak. The intensity of the peak is 2.7, implying that the water density here is roughly 1.7 times higher than the average density in the membrane. From \( r = 0.4 \) nm, \( g(r) \) begins to oscillate around 1, which presents that this functional group hardly has any affinity to water in that range. For the pair of oxygen atoms in water molecules and nitrogen atoms in amino groups (\( O_w-N_{PA} \)), the minimum distance between the water and amino groups is 0.25 nm. The intensity of a small peak is 1.3 at \( r = 0.28 \) nm, and the amino groups have little affinity to water when \( r \) is beyond 0.5 nm. In contrast, the curve of the \( O_w-C_{PA} \) (the pair of oxygen atoms in water and carbon atoms of benzenes) is not like the two curves discussed above, and one can hardly observe any small peak, which indicates that water molecules are randomly located around benzene rings in a short distance.

The shape of the hydration shell is obviously different from one functional group to the other. As shown in Figure 5a, water molecules have the highest affinity to carboxyl, followed by amino groups, and then benzene rings. It is mostly possible that water molecules are more likely to attach to the carboxyl or amino groups rather than benzene rings when water molecules are moving inside the membrane. Consequently, water molecules around the carboxyl or amino groups might have lower velocities than those around benzene rings.

To further confirm this speculation, the residence time is calculated from time correlation functions to investigate velocities of water around functional groups. The dynamical properties of a fluid are conveniently described through consideration of a time correlation function \( R(t) \), which can be cast in the form

![Figure 4](a) Radial distribution function calculated for water oxygen atoms within polyamide. (b) Correlation function derived from part a as defined by eq 6.

![Figure 5](a) Radial distribution function of oxygen atoms of water (\( O_w \)) with oxygen atoms of carboxyl groups (\( O_{PA} \)), nitrogen atoms of amino groups (\( N_{PA} \)), and carbon atoms of benzene rings (\( C_{PA} \)). (b) Residence correlation functions for water molecules in the first hydration shell of carboxyl groups, amino groups, and benzene rings (\( \Delta P = 270 \) MPa).
\[ R(t) = \frac{1}{\Omega} \left[ \frac{1}{N} \sum_{t=1}^{N} \frac{1}{N_{\text{occu}}} \sum_{i=1}^{N} \theta(t_{0})\theta(t_{0} + t) \right] \]

where \( t_{0} \) is the initial time, \( t_{0}^{\text{ff}} \) and \( t_{0}^{\text{first}} \) are the first and last immediate times, respectively, and the moments are both selected in 1 ns after the system being in steady state. \( N_{i} \) is the total number of time origins, and \( N_{\text{occu}} \) is the number of water molecules in the confined space, which is averaged over all of the time origins. \( \Omega \) in the above equation is the normalization constant given by

\[ \Omega = \frac{1}{N} \sum_{t=1}^{N} \sum_{i=1}^{N} \theta(t_{0})\theta(t_{0}) \]

From the radial distribution function, we know that the first coordination shells of carboxyl groups, amino groups, and benzene rings are 2.7, 2.8, and 3.7 Å, respectively. If water molecules selected lie within the first coordination shell at both time steps, the \( \theta(t) \) takes 1. Otherwise, it takes 0.

Figure 5b shows the residence time distribution for water molecules around carboxyl groups, amino groups, and benzene rings (\( O_{W}-O_{PA}, O_{W}-N_{PA}, O_{W}-C_{PA} \), respectively). \( R(t) \) represents the percentage of initial selected water molecules remaining inside the shell. As seen in Figure 5b, all three curves decay very rapidly at the beginning and then follow by a slower decay. Compared to the curves of \( O_{W}-O_{PA} \) and \( O_{W}-N_{PA} \), \( O_{W}-C_{PA} \) drops faster. All sets of residence times of water around the three distinct groups of PA are listed in Table 1.

### Table 1. Residence Time of Water near the Different Groups of PA under Various Pressure Drops

<table>
<thead>
<tr>
<th>functional groups</th>
<th>( \Delta P = 180 )</th>
<th>270</th>
<th>360</th>
<th>450</th>
<th>540</th>
<th>630 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>carboxyl groups</td>
<td>66.1</td>
<td>51.9</td>
<td>39.2</td>
<td>36.0</td>
<td>33.2</td>
<td>31.1</td>
</tr>
<tr>
<td>amino groups</td>
<td>68.9</td>
<td>48.5</td>
<td>41.4</td>
<td>34.4</td>
<td>33.6</td>
<td>32.8</td>
</tr>
<tr>
<td>benzene rings</td>
<td>56.5</td>
<td>41.0</td>
<td>33.3</td>
<td>28.5</td>
<td>27.5</td>
<td>26.3</td>
</tr>
</tbody>
</table>

The water around benzene rings has a shorter residence time than the other two, which means that benzene rings have the weakest affinity to water and water molecules around benzene rings flow with the fastest velocity in the three cases. These simulation findings are nicely supported by experimental works. Wang et al. used 3,5-diamino-N-(4-aminophenyl) benzamide (DABA) to partially replace MPD to react with TMC in the interfacial polymerization of PA RO membranes. With the ratio of DABA to MPD increased from 0 to 12.5%, the water permeance of the produced RO membranes was enhanced evidently from 37.5 to 55.4 L/m²/h without any sacrifice of salt rejection. Each DABA molecule carries three primary amino groups and two benzene rings, whereas each MPD molecule carries two amino groups and one benzene ring. That is, DABA has a higher ratio of benzene to amino groups than MPD, and RO membranes prepared from larger dosages of DABA have a higher concentration of benzene rings compared to amino and carboxyl groups. Therefore, as predicted by our simulation, PA RO membranes containing more benzene rings would reduce the mass transport resistance of water inside the membranes. Similarly, they also obtained enhanced permeance by partially replacing TMC with isophthaloyl dichloride (IPC) which has a higher ratio of benzene to acyl chloride as a result of the increased concentration of benzene in the membranes. Therefore, as supported by the experimental results, our simulation suggests that more benzene rings help to enhance the water transport inside the membrane.

To obtain the residence time with different pressure drops, we compute the integral for the corresponding residence correlation functions. Interestingly, with increasing pressure drops, the residence time of water molecules near all three types of groups drops obviously. However, unlike the rule of PWF with pressure drops, the tendency of the residence time is not linear any more. This suggests that the effect of the hydrophilicity of groups on PWF is not proportional. After all, it is still evident that the residence time of water near carboxyl or amino groups is always longer than those near benzene rings independent of the pressure drops. Therefore, the results of residence time confirm that the benzene rings of RO membranes have lower transport resistance to water molecules. This is in good consistency with previous works reporting that carbon materials, such as carbon nanotubes and graphene, which have hydrophobic surfaces, exhibit faster water transport than hydrophilic surfaces.

### 4. CONCLUSIONS

In this work, the SS-NEMD method is conducted to investigate water molecules flowing inside the RO membrane. By this method, a set of the steady state pure water flux is measured. As expected, the pure water flux increases linearly with the pressure drop. From our simulations of higher pressure drop (around 100 MPa), the values of fluid flux in the condition of lower pressure drop (less than 5 MPa) could be reliably determined, so as to compare the simulation results with experimental data. In addition, the molecular details of hydrated membranes are revealed. The physical density of the hydrated membranes is measured to be 1.3 g/cm³, and the averaged pore size is estimated to be 0.6–1.22 nm. Both are consistent with experimental data. We find that the residence time of water molecules around benzene rings is obviously shorter than those around carboxyl or amino groups in the membrane. The short residence time indicates the faster flow of water molecules, so water molecules move faster around benzene rings of the membranes, which is also confirmed by the experimental work on hydrophobic carbons. These findings are expected to increase our understanding on the water transport behavior in RO membranes and also the rational design of advanced RO membranes with upgraded permeance.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcb.6b11536](https://doi.org/10.1021/acs.jpcb.6b11536).

PWF of water molecules as a function of simulation time, which could confirm the achievement of steady state; the temperature of the water molecules was also provided to make sure the extra heat, which came from the external forces, was completely removed by the PA atoms (PDF)

### AUTHOR INFORMATION

**Corresponding Authors**

*E-mail: mjwei@njtech.edu.cn.*

*E-mail: yongwang@njtech.edu.cn.*

**ORCID**

Mingjie Wei: 0000-0001-7601-4749
Yong Wang: 0000-0002-8653-514X

Notes
The authors declare no competing financial interest.

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