Supplementary Data

Understanding of the temperature effect on the transport dynamics and structures in polyamide reverse osmosis system via molecular dynamics simulation

Ke Li,[a] Lifen Liu,[b] HaoWu,[b] Shanlong Li,[a] Chunyang Yu, *[a] Yongfeng Zhou[a] and Deyue Yan[a]

[a]School of Chemistry & Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Key Laboratory of Electrical Insulation and Thermal Aging,Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, China 200240

[b]Center for Membrane and Water Science & Technology, Ocean College, Zhejiang University of Technology, Hangzhou, China 310014

E-mail addresse: chunyangyu@sjtu.edu.cn (C. Yu)

Contents

8. Hydrogen bonds within polymer chains varied with temperature

1. Interactions between water molecules and polymer chains characterized by RDFs

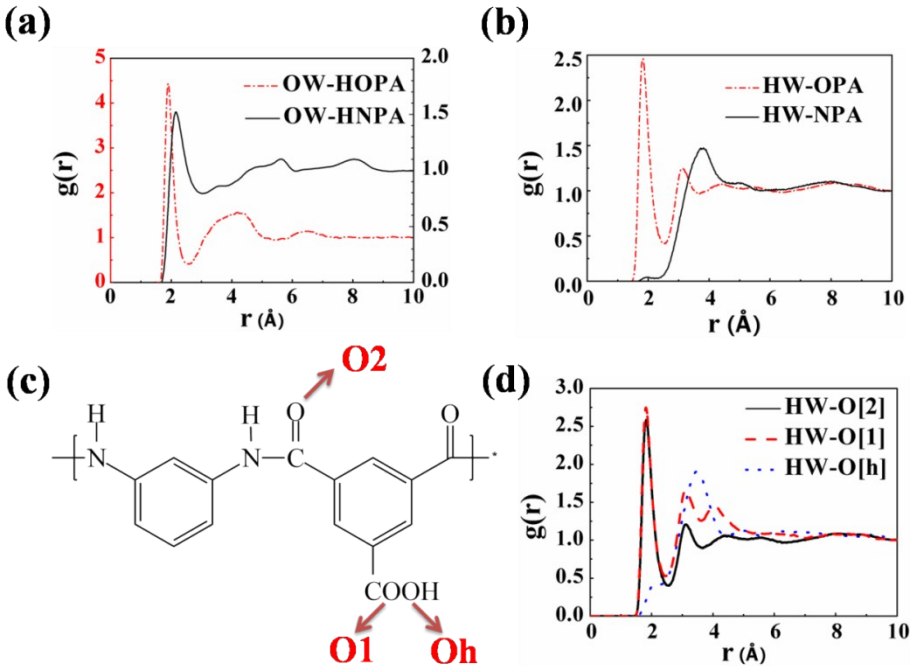

Fig. S1 RDFs between (a) oxygen atoms of water (OW) and hydrogen atoms of PA membrane, which either bonded to oxygen atoms (left axis) or bonded to nitrogen atoms (right axis); (b) hydrogen atoms of water (HW) and oxygen atoms of PA membrane, hydrogen atoms of water (HW) and nitrogen atoms of the PA membrane; (c) scheme shows different kinds of oxygen atoms on the polymer chains; (d) hydrogen atoms of water and different kinds of oxygen atoms on the polymer chain.

2. Coordination number Ncof water molecules analyzed by RDFs

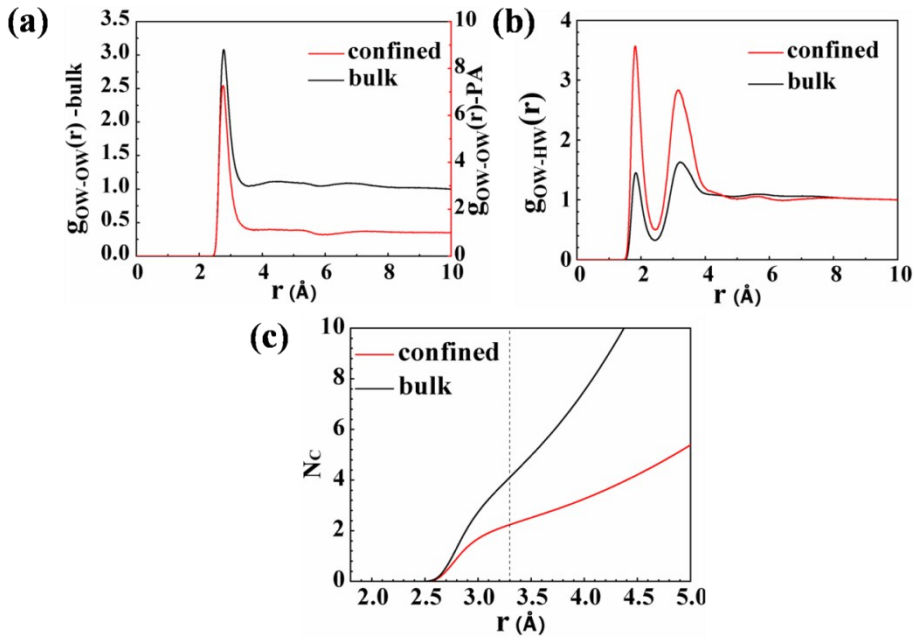

Fig. S2 RDFs between (a) oxygen atoms of water in bulk (left axis) and in confined membrane (right axis); (b) hydrogen and oxygen atoms of water; (c) Coordination number of water molecules (Nc), which was calculated from the integration of the RDFs shown in (a).

3. Tetrahedral order parameter of water molecules (q)

Tetrahedral order parameter is defined as $\frac{3}{32}\sum_{j=1}^{3}\sum_{k=j+1}^{4}(\cos\psi_{jk}+\frac{1}{3})$, of which ψ_{jk} is the angle subtended at the central atom between the jth and kth bonds, and 3/32 normalizes q to range (0,1), hence the q is zero if and only if the bonds are arranged perfectly tetrahedrally, and more distorted the structure, the closer the q value is to 1. In order to calculate ψ_{jk}in the confined membrane, we considered the hydrogen bonds between water molecules and between water molecules and PA membrane.

4. The partial structure factor S(Q)

The partial structure factor S(Q) is defined as

$$S(Q)=\frac{<\sum_{j=1}^{N}\sum_{k=1}^{N} exp(-iQr_j)exp(iQr_k)>}{N}$$

In the formula, Q is the momentum transfer vector, r_j and r_k are the position vectors of the oxygen atoms of the water molecules j and k, respectively.The brackets stand for an ensemble average. In order to facilitate comparison, the number of water molecules (N) is used to normalize S(Q).

5. RDFs of salt ions within RO membrane under EMD and NEMD simulations.

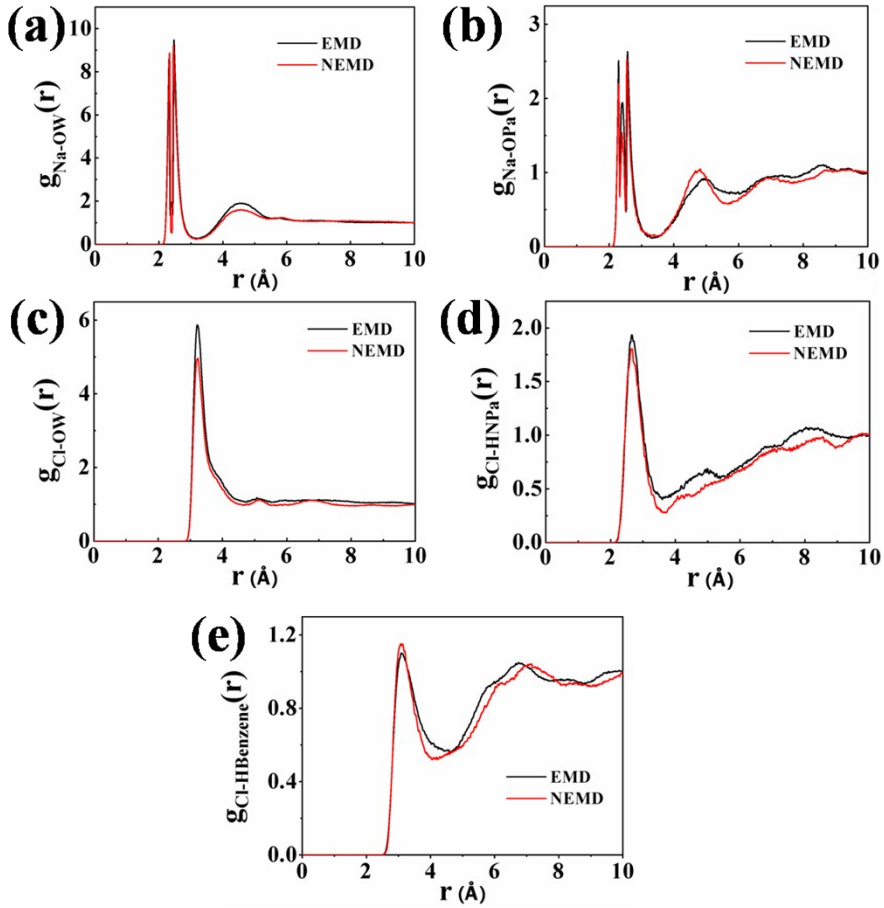

Fig. S3 RDFs between Na^+ and the oxygen atoms of water (OW) (a), between $Na^+$and oxygen atoms of the polymer(b), between Cl^- and the oxygen atoms of water (OW) (c), between Cl^-andamide hydrogen atoms (d), between $Cl^-$and hydrogen atoms of aromatic rings (e) obtained from EMD and NEMD simulations.

6. The self-diffusion coefficient of water molecules

Figure S4 shows the time evolution of mean square displacement (MSD) for water molecules in bulk and in confined polyamide membrane, the self-diffusion coefficient Ds can be computed from the MSD when extracted from a linear part of the curve.

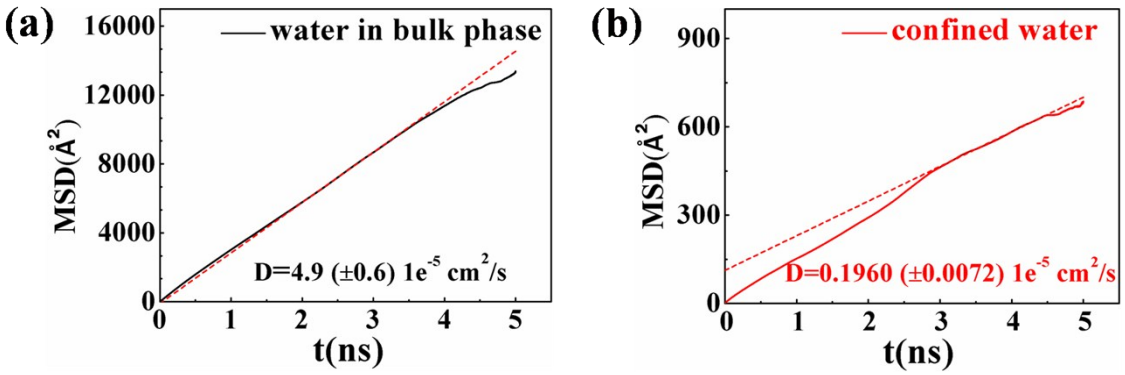

Fig. S4 Mean square displacement of the water molecules (a) in bulk and (b) in confined polyamide membrane.

7. Water flux under NEMD

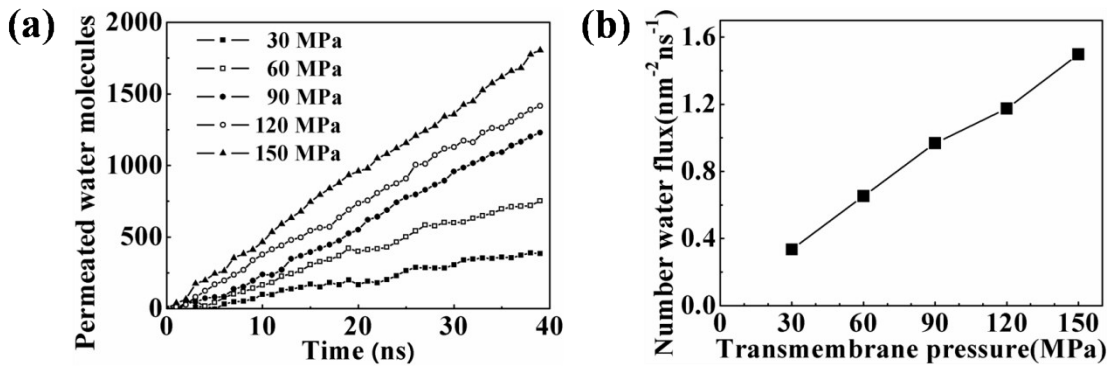

Fig. S5 (a) The number of water molecules transported through the membrane as a function of simulation time for pure water under different pressures; (b) Number of water molecules as a function of pressure.

By linear fitting the curve in Fig. S5a, the water flux can be calculated as shown in Fig. S5b. For example, when operated at 150 MPa, 1742 water molecules passed through the membrane with a cross-sectional area of 30 nm^2 (5nm×6nm) during 40 ns, so the water flux was 1.5 $nm^{-2}ns^{-1}$ at this condition. The experimentally-measured macroscale water flux for a typical commercial RO membrane is in the range of 2.4×10^5 to 9.8×10^5 m s^{-1} at 4.1 MPa, and the water flux can be written as $J_W = -\frac{K(\Delta P - \Delta\pi)}{L}$, ΔP, Δπ are the pressure difference across the membrane and osmotic pressure respectively.. For the commercial RO membrane, $\Delta P - \Delta\pi$=4.0 MPa, L=200 nm, for our membrane model, $\Delta P - \Delta\pi$=150 MPa, L=9 nm. Therefore, in our simulation, the J_w should be between 0.02 and 0.082 m s^{-1} according to the proportional relationship. The number of water molecules were $(10^6/18)\times6.02\times10^{23}$ m^{-3}. By unifying the units, we can know the reasonable value of water flux should be between 0.7 $nm^{-2}ns^{-1}$ and 2.7 $nm^{-2}ns^{-1}$ under current conditions,. The value of number

water flux in our simulation at 150 MPa falls within this range.

8. Hydrogen bonds within polymer chains varied with temperature

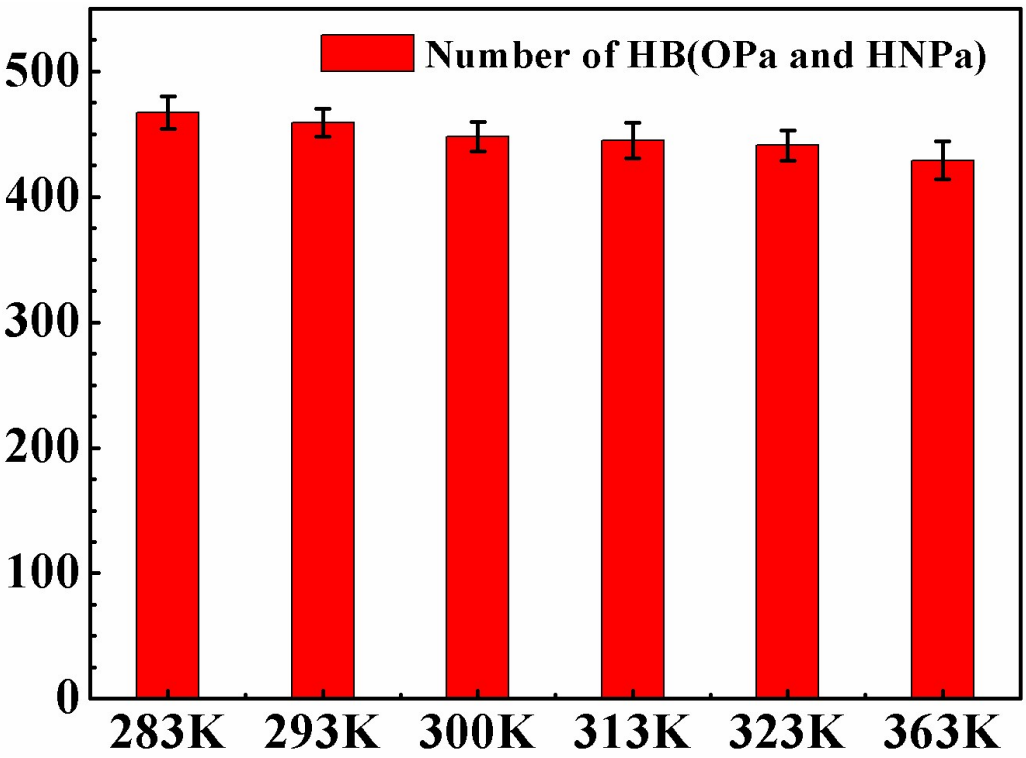

Fig. S6 Numbers of hydrogen bonds between oxygen atoms (OPa) and hydrogen atoms (HNPa) in amide bonds at different temperatures in the NEMD simulation without salt ions

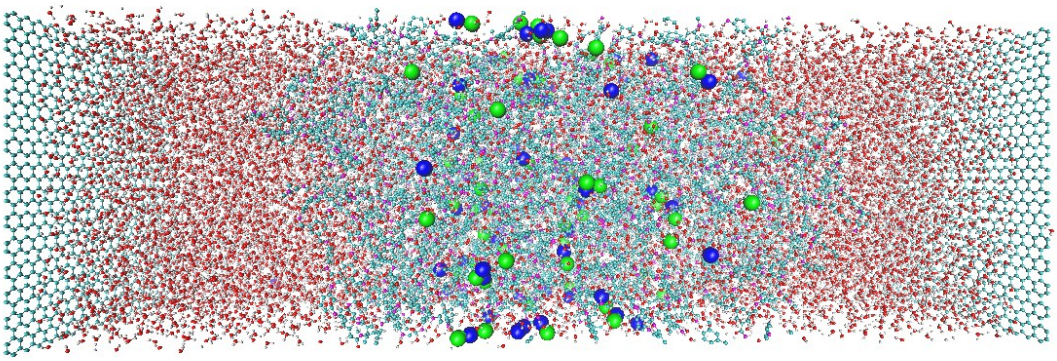

Fig. S7 Simulation setup of the membrane with salt ions. Water molecules are colored with red and white; graphene carbon atoms which used only as a model for exerting pressure are colored with green; membrane atoms are colored with cyan. Na^+ is represented by blue particles and Cl^- is represented by green particles, both are magnified to see clearly.

The insertion method of salt ions into the membrane:

We used a function of the gromacs software package (gmx genion) to insert salt ions into the membrane. The essence of this function is to randomly select a reasonable position that occupied by a water molecule and replaced it with salt ion. After the insertion, we immediately balanced it for a long enough time to ensure that the salt ions had formed a stable hydration layer before analysis.