Effect of hydrophilicity on water transport through sub-nanometer pores

Fang Xu, Mingjie Wei **, Xin Zhang, Yong Wang *

State Key Laboratory of Materials-Oriented Chemical Engineering, and College of Chemical Engineering, Nanjing Tech University, Nanjing, 211816, Jiangsu, PR China

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ABSTRACT

Pore hydrophilicity is crucial parameter for water transport through nanopores. However, the effect of pore hydrophilicity on water permeance at the sub-nanometer scale remains unclear because it cannot be described by the conventional fluid mechanics. Herein, to determine the separate relationship between water permeance and pore hydrophilicity at the sub-nanometer scale, an equation derived from interfacial friction is obtained to exclude the effects of other variables. Using non-equilibrium molecular dynamics, we investigate water transport through a series of nanopores which is constructed from 12 types of functionalized covalent organic frameworks (COFs) with various degrees of hydrophilicity but similar skeletons and sub-nanometer pore sizes. The variable-excluded permeance has a linear relationship with contact angle. However, this linear relationship is not applicable to the hydrophobic and extremely hydrophilic nanopores under experimental pressure drops. For experimental predictions, the final relationship is corrected by considering the combined effect within all-range degrees of hydrophilicity. Therefore, a range of moderate pore hydrophilicity is suggested for the application of sub-nanometer pores in water transport. This study reveals the quantitative effect of pore hydrophilicity on water permeance at the sub-nanometer scale, which can be useful for the screening of nanomaterials for various applications.

1. Introduction

Water transport through nanopores is a fundamental process related to many important fields such as geophysical processes [1,2], biological systems [3], energy storage and conversion [4–6], as well as membrane processes [7,8]. Water transport through a confined space exhibits unique characteristics that differ from those of bulk water, which are caused by many factors. Among these, pore hydrophilicity plays a significant role with decreasing confined size as it can dramatically change the water structures and dynamics inside the nanopores, particularly at the sub-nanometer scale [9–17].

However, the exact effect of pore hydrophilicity on water transport, which is crucial for designing the nanomaterials for various applications, remains unclear in non-continuum mechanics. Although there have been some investigation on water transport through various nanopores [14,15,18–20], they are not competent for describing the situation in sub-nanometer pores. This is owing to certain limitations, of which one is viscosity.

Water transport through the nanopores can be described by combining the expressions for the modified Sampson and modified Hagen–Poiseuille (HP) equations when the characteristic flow dimension is larger than 1.6 nm [14,15,18–20]. However, the modified HP equation is not applicable to water transport through sub-nanometer pores. Only one or two water layers exist inside the sub-nanometer pores, which implies that almost all water molecules directly interact with the pore wall and two adjacent water layers with differences in velocity do not exist. In this case, the water viscosity in the equation is meaningless as the interaction of the pore wall instead of water on water dominates the transport at the sub-nanometer scale.

Second limitation includes the parameter describing the pore hydrophilicity. A parameter termed as slip length is commonly used to characterize pore hydrophilicity in nanopores of pore sizes larger than 1.6 nm [14,20,21]. Slip length is calculated from the interfacial velocity and velocity gradient. However, the velocity gradient does not exist in sub-nanometer pores because hardly any water lamination is observed with different velocities. Therefore, slip length is not only obscure but also difficult to measure. Hence, it is necessary to apply a more intuitive property such as contact angle to characterize the pore hydrophilicity in transport equations.

Finally, another limitation is the relationship of pore hydrophilicity...
with water permeance at the sub-nanometer scale. In our previous study [16], it was revealed that a threshold pressure drop ($\Delta P_s$) existed particularly for the highly hydrophobic nanopores, exceeding which, a stable and constant water permeance was observed. Additionally, the interfacial velocity should be equal to zero under the experimental pressure drops ($\Delta P_s$) according to the boundary condition (completely hydrophilic) in the traditional HP equation. Accordingly, the flux of the sub-nanometer pores should be zero if the degree of pore hydrophilicity exceeds that in the HP equation. Therefore, high $\Delta P_s$ values are required to obtain a measurable flux for extremely hydrophilic sub-nanometer nanopores. Based on the above discussion, the relationship between permeance and hydrophilicity varies with $\Delta P$, implying that water transport cannot be predicted merely by one expression.

To quantitatively determine the effect of pore hydrophilicity on water permeance at the sub-nanometer scale, nanopores that can exhibit a series of hydrophilicities are needed. Fortunately, covalent organic frameworks (COFs), a class of crystalline porous polymers, satisfy the requirement of nanopores with various hydrophilicities. COFs are typically synthesized via the self-condensation of organic monomers including a knot and linker [22,23]. Owing to the intrinsic porosity, COFs present a molecular platform for fabricating nanopores with desired structures and properties [22]. The pore shape and size can be determined through the topology-directed growth of COFs. In particular, their pore walls can be modified by tailor-made functionalization via predesigning [22,24,25] and post-synthetic modification [26,27]. Furthermore, COFs allow the integration of various functional units into the pore walls with the desired composition and density, affording a full spectrum of tailor-made interfaces [22]. Therefore, COFs provide unlimited potential for the development of nanopores with desired hydrophilicities even at the sub-nanometer scale, which is well suitable for our research.

In this study, a series of 12 types of COFs are used as models to investigate the quantitative relationship between pore hydrophilicity and water permeance via non-equilibrium molecular dynamics (NEMD) simulations. These COFs are constructed from a water-stable parent COF, and modified using various functional groups in the pore walls. Therefore, these COFs possess different pore hydrophilicities but similar structures and sub-nanometer pore sizes. An equation derived from the interfacial friction coefficient is proposed to address the first limitation. The properties of 12 COFs related to water transport, including pore hydrophilicity characterized by contact angle, are analyzed to resolve the second limitation. To establish the relationship with pore hydrophilicity, water permeance is then calculated by excluding other parameters affecting it through the proposed equation. Furthermore, the applicability range of pore hydrophilicity for this relationship is discussed under practical experimental $\Delta P_s$ values. Finally, the corrected quantitative relationship between water permeance and hydrophilicity is established within all-range degree of hydrophilicity to address the third limitation by combining the effect of hydrophobicity and completely hydrophilicity.

2. Models and methods

2.1. Model

The COF series was computationally designed based on an experimentally synthesized super-microporous phosphazene-based COF (MPCOF) [28]. The atomic structure of MPCOF was obtained from the CoRE COF database [29], which constructed and compiled the solvent-free and disorder-free COF structures from the experimental characterizations. According to the experimental methodology [28], MPCOF was synthesized from hexachlorocyclotriphosphazene (HECTP, knot) and p-phenylenediamine (Pa, linker). The latter was easily grafted by various functional groups affording the COFs with various degrees of hydrophilicity. Twelve functionalized MPCOF-Rs (including the original MPCOF) were constructed from the corresponding monomers, Pa-R (Fig. 1). The unit cell of each MPCOF-R was first optimized using the Perdew–Burke–Ernzerhof (PBE) GGA exchange correlation functional by Cambridge Sequential Total Energy Package (CASTEP). Thereafter, a fragment of each MPCOF-R was selected as the model, which could be extended to an infinitely large structure via periodical boundary conditions. To investigate the effect of pore hydrophilicity on permeance, it was necessary to consider three processes: entry, internal transport, and leaving. Therefore, all MPCOF-R multilayers were constructed with 14 monolayers along the transport direction resulting in thicknesses of $\sim$5 nm.

Water transport through each MPCOF-R was simulated in a system shown in Fig. 2. It consisted of two water reservoirs serving as the feed and permeate side, as well as two additional pistons to exert the pressure differences. The multilayer surface was placed parallel to the xy plane, where the periodical boundary condition was applied. Pressure differences were applied in the z direction, along which the water molecules passed through the MPCOF-R multilayers.

2.2. Methods

The interactions of all atoms were represented by the Lennard-Jones (LJ) and Columbic potentials. The TIP4P-Ew [30] model was used for the water molecules. To decrease the high frequency vibrations and reduce the simulation time, the SHAKE algorithm was used to constrain the bonds and angles of the water molecules. LJ parameters for the atoms of MPCOF-R series were obtained from the Dreiding force field [31], which was successfully applied in other COF-based simulations [29,32,33]. The Lorentz-Berthelot mixing rule was adopted for all pair-wise LJ terms. The atomic partial charges were described by electrostatic potential (ESP) charges, which were calculated using the grid-based ChelpG algorithm based on the density functional theory (DFT) [33]. The atom types as well as the calculated atomic partial charges of MPCOF-R series are shown in Fig. S1 and Table S1. Each system was initially subjected to energy minimization with a tolerance of 10$^{-5}$ eV to compute the long-range electrostatic interactions.

All simulations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [34]. Each system was initially subjected to energy minimization with a tolerance of 10$^{-5}$ eV. The temperature was set at 300 K for all simulations. The skeletal atoms of the multilayers were fixed (gray atoms in Fig. 1), whereas the functional groups (colored atoms in Fig. 1) could move freely during all simulation processes.

For the NEMD simulations, the external force $f$ along the z/z direction was applied to each atom of the two pistons to obtain the desired pressures on the pistons. The relationship is described as:

$$P = \frac{fn}{A}$$  \hspace{1cm} (1)

where $P$ is the desired pressure on the piston, $A$ is the area of the piston, and $n$ represents the atom number of the piston. During simulations, two pistons can self-adjust their positions under $P_{\text{feed}}$ and $P_{\text{permeate}}$ to produce $\Delta P$, which can be calculated using the following equation:

$$\Delta P = P_{\text{feed}} - P_{\text{permeate}}$$  \hspace{1cm} (2)

where $P_{\text{feed}}$ (50–200 MPa) and $P_{\text{permeate}}$ (1 atm) are the pressures on feed and permeate pistons, respectively. The applied $\Delta P$ varied from 50 to 200 MPa, which was much higher than the practical experimental usage. Such high $\Delta P$ is commonly used in NEMD to reduce the thermal noise and enhance signal/noise ratio within the simulation time scale of nanoseconds [35–39]. Each simulation was performed for 20–50 ns with a time step of 2 fs. The trajectory was saved every 1 ps and analyzed using the self-compiled codes after the simulation reached a steady state.

To calculate the diffusion coefficients of in-pore water molecules, the
outside reservoirs were removed while the in-pore water molecules remained inside the nanopores. The size of the simulation box was then set equal to each MPCOF-R cell and the periodic boundary condition was applied in all dimensions to simulate the in-pore behavior of the water molecules. Simulations in this part were first equilibrated for 3 ns and then performed in the NVT ensemble for 20 ns with a time step of 1 fs to collect the trajectories.

3. Results and discussion

3.1. Theory

For water transport through a cylindrical nanopore, the total resistance comprises the interfacial resistance and interior resistance [20, 21, 40]. The interfacial resistance can be expressed by the Sampson equation [18–20], which considers it as the flow resistance of an infinitely thin orifice and is close to the exact solution within 1% error [41]. Therefore, the pressure drop at the pore entrance/exit can be described as:

\[
\Delta P_1 = \frac{QC\mu_\infty}{R^3}
\]

where \(Q\) is the volumetric water flux per unit time, \(C\) is the loss coefficient of both the water entry and exit process, \(\mu_\infty\) is the viscosity of water in the reservoir, i.e., bulk water viscosity, and \(R\) is the effective radius of the nanopore. Equation (3) describes the condition for a single pore. Considering the overall surface area of the multilayer, the equation can be written as:

\[
\Delta P_1 = \frac{\pi C\mu_\infty}{\Phi R} F
\]

where \(F\) is the water flux based on the surface area and \(\Phi\) is the surface porosity.

The interior resistance can be calculated using the modified HP expression when the pore size is larger than 1.6 nm [14, 15, 18–20], but it cannot describe the water flow through the sub-nanometer pore. This is because the water viscosity and slip length of the pore wall in this equation are meaningless at the sub-nanometer scale, as discussed in the
Introduction section. On the one hand, the derivation of the HP equation starts from the analysis of the forces between any two adjacent circular water layers with different velocities inside the nanopore. However, only one or two water layers exist inside the sub-nanometer pores, which implies that almost all water molecules directly interact with the pore wall and two adjacent water layers with different velocities do not exist. The interfacial layer is defined as \( r > R - d_{\text{water}} \) (\( R \) is the pore radius and \( d_{\text{water}} \) is the diameter of the water molecules) in this study. As shown in Fig. S2, the interfacial water of almost all MPCOF-Rs accounts for more than 95% of all inside water and the lowest proportion is nearly 90% for MPCOF-(OH). Therefore, it can be confirmed that almost all water molecules are inside the interfacial layer of each MPCOF-R. In this case, the analysis of force, from which the transport equation is derived, should start not from the water viscosity but from the interaction between water and the pore wall. On the other hand, no laminar with different velocities also renders another parameter (slip length) unusable due to its dependence on the velocity gradient of water. Therefore, the modified HP equation is not applicable for the sub-nanometer pores owing to these two problems.

Instead, the transport equation can be derived from the analysis of the forces between water and the pore wall, in which case the interfacial friction coefficient is introduced as [42]:

\[
\tau_{\text{friction}} = \lambda \cdot \text{an} \cdot v
\]

(5)

where \( \tau_{\text{friction}} \) is the driving force, \( \tau_{\text{friction}} \) is the frictional force along the axial direction on the contact area \( A_{\text{con}} \), \( \lambda \) is the friction coefficient, and \( v \) is the water velocity. Then, the equation can be further transformed into a detailed expression shown below:

\[
\Delta P_1 \cdot R^2 = \lambda \cdot 2 \pi R \cdot F
\]

(6a)

\[
\Delta P_2 = \frac{2\pi L}{\phi R} F
\]

(6b)

where \( L \) is the pore length. The pore lengths in this study are all approximately 5 nm, ensuring that all entrance and end effects can be decoupled [20].

The total pressure drop comprising the interfacial and interior parts can be expressed as:

\[
\Delta P = \Delta P_1 + \Delta P_2 = \frac{\pi C \mu}{\phi R} F + \frac{2\pi L}{\phi R} F
\]

(7)

In this equation, the friction coefficient \( \lambda \) is physically relevant to the interfacial interaction that characterizes the hydrophilicity of the pore wall. However, this parameter is hardly obtained in experiments, thereby limiting it to the experimental prediction. It is important to correlate this equation with a commonly used parameter characterizing hydrophilicity (e.g. contact angle of water droplets) in the experiments. For this purpose, the permeance \( F/\Delta P \) is calculated by excluding other factors to explore its relationship with the contact angle:

\[
\left( \frac{\Delta P}{F} - \frac{\pi C \mu}{\phi R} \right) \frac{\phi R}{2L} = \lambda = f(\theta)
\]

(8)

where \( \theta \) is the contact angle characterizing the pore hydrophilicity.

### 3.2. Pore hydrophilicity

Notably, the experimentally accessible \( \Delta P \) is generally less than 10 MPa, such as capillary pressure, osmotic pressure, and operation pressures for the membrane processes. According to our previous study [16], the presence of large threshold pressures \( (\Delta P_2) \) makes the simulation results at high \( \Delta P \)s unreliable for the prediction of the experimental results at low \( \Delta P \)s for the nanopores with hydrophobic pore walls. Only when the objective nanopores can be wetted under experimentally low \( \Delta P \)s, their simulation results at high \( \Delta P \)s can be used to precisely predict their experimental performance. As the MPCOFs are modified by several groups to tune the pore hydrophilicity, various MPCOF-R nanopores exhibit distinct wetting behaviors. Therefore, first, it is required to determine which MPCOF-R nanopores can be wetted under the experimentally accessible \( \Delta P \)s before the large-scale NEMD simulations are performed at high \( \Delta P \)s. Twelve MPCOF-Rs are then tested under 10 MPa to determine if these can be wetted. As shown in Table 1, MPCOF-(F)\(_4\), MPCOF-(Cl)\(_2\), and MPCOF-(OH)\(_2\) cannot be wetted under 10 MPa, indicating that their \( \Delta P \) values are greater than those that can be attained experimentally. This suggests their strong hydrophobicity and unsuitability in the applications of water treatment. Therefore, these are not further investigated in this work, whereas the remaining nine MPCOF-Rs are subjected to further examination.

To determine the quantitative effect of pore hydrophilicity on permeance, the calculation of the parameters on the left (\( \Phi, R \) and \( \lambda \)) and right side (\( \theta \)) of Equation (8) is required. The pore radius \( R \) listed in Table 1 is calculated using the software Zeo++ [43]. Porosity \( \Phi \) and length \( L \) are calculated based on the water content inside each multi-layer and the size of each COF unit cell, respectively.

It has been commonly reported that the dynamic random motions of the interfacial water molecules are strongly correlated to the surface hydrophilicity [44-46]. From Fig. S2, it is clear that all the in-pore water molecules can be recognized as interfacial water. Therefore, the dynamic random motion of water molecules is significantly affected by the interaction between the pore wall and water molecules [15]. In this study, the self-diffusion coefficient along the \( z \) direction \( (D_z) \) is used to characterize the dynamics of in-pore water molecules, such that the pore hydrophilicity can be measured by \( D_z \) of the in-pore water molecules. To calculate \( D_z \), the mean squared displacements in the \( z \) direction (MSD\(_z\)) of all in-pore water molecules should be first measured, and then \( D_z \) can be calculated using the following expression:

\[
D_z = \lim_{t \to \infty} \frac{\text{MSD}(t)}{2t}
\]

(9)

The variation in MSD\(_z\) for the nine MPCOF-Rs is shown in Fig. 3a. The MSD\(_z\) curves are linear, and the slopes of these lines represent their respective \( D_z \) values. The \( D_z \) values of the nine MPCOF-Rs shown in Fig. 3b are different from each other, indicating that the modification of the functional groups effectively changes the pore hydrophilicity.

It has been reported that the self-diffusion coefficients of the interfacial water molecules have a linear relationship with the contact angle of water on a surface [44-46]. Therefore, \( D_z \) can be translated into \( \theta \) by fitting it from the linear equation. In the case of water molecules on a completely hydrophilic surface (e.g. the boundary condition in HP equation where the fluid velocity is zero), the self-diffusion coefficients should be zero because these are all trapped by the surface and difficult to move, i.e., \( D_z = 0 \) when \( \theta = 0^\circ \). Alternately, in the case of water molecules on a completely hydrophobic surface, their self-diffusion coefficients are defined as being equal to the value of the bulk because the

<table>
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<th>Series</th>
<th>Wetting at 10 MPa</th>
<th>Diameter (Å)</th>
<th>Porosity (%)</th>
<th>Length (Å)</th>
<th>Hydrophilicity (°)</th>
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<td>18.73</td>
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</tbody>
</table>

Table 1: Properties of MPCOF-R multilayers.
super-hydrophobic surface is expected to have no interaction with the interfacial water molecules, i.e., the absence of the surface. In this case, the $D_z$ value of $2.4 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ for the bulk TIP4P-Ew water model at 300 K \cite{30} is applied to define the value of $\theta = 180^\circ$. Based on this data, the relation between $D_z$ and $\theta$ can be described as:

$$\theta = 75 \times 10^9 D_z$$  \hspace{1cm} (10)

The $\theta$ value of each MPCOF-R is computed using Equation (10) and listed in Table 1. Notably, the $\theta$ ranges from $\sim 18^\circ$ to $\sim 77^\circ$, which is essentially below 90\(^\circ\), implying they all belong to the hydrophilic category. This is consistent with the wetting behaviors of the latter nine MPCOF-Rs in Table 1. Therefore, this range of pore hydrophilicity is suitable for further investigating the water transport through the nanopores.

### 3.3. Pristine flux and permeance

Following the work of Grossman et al. \cite{47}, the numbers of water molecules in the feed, internal, and permeate side over the simulation time were tracked. The flux of each MPCOF-R was calculated by the slopes of number of permeated water molecules varying with simulation times in Fig. S3. The number of permeated water molecules increases linearly with the simulation time, indicating that the simulation systems have reached a steady state. As shown in Fig. 4a, all fluxes except that of the MPCOF-(COOH)\(_2\) are proportional to $\Delta P$, despite the varying hydrophilicities. For the most hydrophilic MPCOF-(COOH)\(_2\), the linear fitting does not start from zero because there is no flux until the $\Delta P$ reaches 50 MPa as shown in Fig. 4a, which will be discussed in the next section.

The permeance is then calculated using $F/\Delta P$ according to Fig. 4a and the results are shown in Fig. 4b. All permeances range from 200 to 1100 Lm\(^{-2}\)h\(^{-1}\)bar\(^{-1}\) (including the permeance of MPCOF-(COOH)\(_2\)). If the factor of multilayer thickness is considered (20-nm thick in typical experiments, but 5-nm thick in this work), the calculated permeances are as high as 100–270 Lm\(^{-2}\)h\(^{-1}\)bar\(^{-1}\), which are significantly greater than those of the polymeric nanofiltration membranes (10–50 Lm\(^{-2}\)h\(^{-1}\)bar\(^{-1}\)) with similar pore sizes in the experimental measurements. The exceptional permeance values of the COFs can be attributed to their high porosities and orderly straight-through nanopores. More importantly, the simulated permeances well match the results (considering the ratios of membrane thickness) of experimental fabricated IISERP-COOH-COF1 \cite{27}, TpHz \cite{48} and CTF \cite{49} membranes, whose pore sizes are all below 1 nm. Therefore, this range of pore hydrophilicity is suitable for further investigating the water transport through the nanopores.

### 3.4. Variable-excluded permeance

As derived in the Theory section, the parameters in Equation (8) such as porosity, pore size, and viscosity are excluded from the pristine permeance, such that permeance is only the function of pore hydrophilicity.

After substituting all the detailed variables in Equation (8), the variable-excluded permeance, which is the reciprocal of the left side of Equation (8), is plotted in Fig. 5a as a function of $\theta$. The fitted curve shows a good proportional relationship, from which the following expression for water transport through MPCOF-R can be obtained:

$$\left( \frac{\Delta P}{F} \right) - \frac{\pi \rho \nu_{\infty}}{2L} \frac{1}{\varnothing R} \frac{1}{0.252 \times 10^{-9} \theta}$$  \hspace{1cm} (11a)
nanopores, considering MPCOF-(COOH) thereby producing no flux and permeance. For completely hydrophilic as systematically shown in our previous work [16]. As shown in Table 1, a high hydrophilic nanopores) should be considered. For hydrophobic nanopores, a high \( \Delta P \) is observed and it rises rapidly with increased hydrophobicity as systematically shown in our previous work [16]. As shown in Table 1, three types of functionalized MoS$_2$ membranes with varying hydrophilicity, whose contact angles were different but all below 90°. Importantly, their water permeances increased with their rising hydrophobicities, which is in excellent consistence with the trend observed in our work (Fig. 5a).

However, this relationship is applicable to all range of hydrophilicities and hydrophobicities only at \( \Delta P > 100 \) MPa owing to the fitting permeance of MPCOF-(COOH)$_2$. For application under experimentally accessible \( \Delta P \), two particular cases (hydrophobic and completely hydrophilic nanopores) should be considered. For hydrophobic nanopores, \( \Delta P \) is observed and it rises rapidly with increased hydrophobicity as systematically shown in our previous work [16]. As shown in Table 1, three types of functionalized MoS$_2$ membranes with varying hydrophilicity, whose contact angles were different but all below 90°. Importantly, their water permeances increased with their rising hydrophobicities, which is in excellent consistence with the trend observed in our work (Fig. 5a).

Due to the few reports on COF membranes with sub-nanometer pore sizes, it is hard to compare this relationship with their experimental data. However, we found that this trend is close to experimental results of functionalized molybdenum disulfide (MoS$_2$) membranes, which possess similar sub-nanometer pore sizes. Ries et al. [50] fabricated three types of functionalized MoS$_2$ membranes with varying hydrophilicity, whose contact angles were different but all below 90°. Importantly, their water permeances increased with their rising hydrophobicities, which is in excellent consistence with the trend observed in our work (Fig. 5a).

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4. Conclusion

In summary, 12 types of covalent organic frameworks (COFs) are used as models to investigate the relation between water permeance and pore hydrophilicity at the sub-nanometer scale. These 12 COFs are constructed from a water-stable parent COF, MPCOF, and modified by 12 different functional groups \((-\text{F})_2, -\text{Cl}_2, -\text{SH}_2, -\text{NO}_2, -\text{H}, -\text{OH}, -\text{NH}_2, -\text{OH}_2, -\text{NH}_2\text{H}_2, -\text{SO}_3\text{H}, -\text{COOH}, -\text{COOH}_2\) to afford different hydrophilicities but similar structures and sub-nanometer pore sizes. Through the NEMD simulations, water transport through 12 MPCOF-R multi-layers is investigated. Majority of the in-pore water molecules are included in the interfacial layer, and hence the interaction between the pore wall and water molecules (pore hydrophilicity) instead of that between the water molecules (viscosity) dominates the water transport. This result suggests that the hydrophilicity of MPCOF-(COOH)$_2$ surpasses the default hydrophilicity in the HP equation. The lowest \( \Delta P \) that is needed to obtain a stable permeance for the extremely hydrophilic nanopores is called start-up pressure drop \( \Delta P_{\text{st}} \). The \( \Delta P_{\text{st}} \) of MPCOF-(COOH)$_2$ is greater than the experimentally accessible \( \Delta P \), and therefore it is difficult to generate permeance under low \( \Delta P \). Hence, the peremeances of both the hydrophobic and completely hydrophilic nanopores should be equal to zero under experimental low \( \Delta P \).

Based on the above discussion, under low \( \Delta P \) the relationship established in Fig. 5a and Equation (11b) is applicable to a range of pore hydrophilicities that are neither hydrophobic nor completely hydrophilic. The correctional relationship between variable-excluded permeance and \( \theta \) at 10 MPa is plotted in Fig. 6, suggesting that the relationship established in Equation (11b) is applicable to moderate hydrophilicities. Therefore, a suitable pore hydrophilicity that is neither hydrophobic nor extremely hydrophilic should be selected to confirm an observable permeance under experimental \( \Delta P \) because of the \( \Delta P_{\text{st}} \) and \( \Delta P_{\text{st}} \) values of extremely hydrophilic and hydrophobic nanopores, respectively.

The correctional between water permeance and pore hydrophilicity described in Equation (11b) and Fig. 6 is practically significant to predict the water permeance of COF materials with sub-nanometer pores. Upon measurement of the water contact angle of the COF pore wall, the water permeance can be theoretically obtained, which can be useful for screening the COF materials for a variety of applications.
experimentally accessible $\Delta P$s. Both the hydrophobic (MPCOF-(F)$_n$, MPCOF-(Cl)$_2$, and MPCOF-(SH)$_2$) and completely hydrophilic (MPCOF-(COOH)$_n$) COFs are not found to be suitable for water transport in practical experimental applications owing to the existence of high threshold pressure drop ($\Delta P_T$) and high start-up pressure drop ($\Delta P_a$). Based on the final corrected relationship, water transport can be quantitatively described under the experimental $\Delta P$s. Therefore, an appropriate hydrophilicity of the sub-nanometer pores is required for its application in water transport. This study systematically analyzes the quantitative effect of pore hydrophilicity on water transport through sub-nanometer nanopores, which is expected to guide the experimental prediction of permeance for nanoporous materials and can thus be employed for screening the nanomaterials for various applications.

Author statement

Fang Xu: Conceptualization, Methodology, Software, Validation, Investigation Formal analysis, Writing - original draft, Visualization. Mingjie Wei: Formal analysis, Writing - review & editing, Funding acquisition. Xin Zhang: Software, Formal analysis. Yong Wang: Formal analysis, Writing - review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

$\Delta P_T$ threshold pressure drop 
$\Delta P$ desired pressure on a piston 
$f$ external force on piston atoms 
$n$ atom number of a piston 
$A$ area of a piston 
$p_{\text{feed}}$ pressure on the feed piston 
$p_{\text{permeate}}$ pressure on the permeate piston 
$\Delta P_1$ pressure drop at the pore entrance/exit 
$Q$ volumetric water flux per unit time 
$\mu$ viscosity of bulk water 
$R$ effective radius of the nanopore 
$F$ water flux based on surface area 
$\Phi$ surface porosity 
$f_{\text{driving}}$ driving force 
$f_{\text{friction}}$ frictional force 
$A_{\text{in}}$ contact area inside nanopores 
$\lambda$ friction coefficient 
$v$ water velocity 
$\Delta P_2$ pressure drop inside nanopore 
$L$ pore length 
$\theta$ contact angle 
$\pi$ Pi

$D_z$ self-diffusion coefficient in the z direction 
$MSD_z$ mean squared displacements in the z direction 
$\Delta P_a$ start-up pressure drop

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2020.118297.

References


