Hydrogen Bonding

Very Important Paper

Ion Selectivity of Water Molecules in Subnanoporous Liquid-Crystalline Water-Treatment Membranes: A Structural Study of Hydrogen Bonding

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Abstract: We demonstrate hydrogen-bonded structures of water in self-organized subnanoporous water treatment membranes obtained using synchrotron-based high-resolution soft X-ray emission spectroscopy. The ion selectivity of these water treatment membranes is usually understood by the size compatibility of nanochannels in the membrane with the Stokes radius of hydrated ions, or by electrostatic interaction between charges inside the nanochannels and such ions. However, based on a comparison between the hydrogen-bonded structures of water molecules in the nanochannels of the water treatment membrane and those surrounding the ions, we propose a definite contribution of structural consistency among the associated hydrogen-bonded water molecules to the ion selectivity. Our observation delivers a novel concept to the design of water treatment membranes where water molecules in the nanochannel can be regarded as a part of the material that controls the ion selectivity.

Membrane technologies for producing fresh water from seawater or brackish water have attracted attention because separation can be done with relatively low energy and a simple process.[1] The separation technologies of reverse osmosis (RO) and nano-filtered membranes have been developed.[2–4] Recently, self-organized nano- or subnanoporous liquid-crystalline (LC) membrane materials,[5–8] with uniform pore diameter size have been reported to show unique properties for water treatment,[5,7,8] while for normal RO and nano-filtered membranes the pore sizes are distributed. In the self-organized LC membranes, a consistent size of water channels having a subnanometer to nanometer scale is formed by self-assembly of columnar (Col) or bicontinuous cubic (Cub_b) LC monomers, which are preserved by in situ polymerization.[5–8] The nanochannels have a diameter ranging from 0.6 to 2.2 nm depending on the design of the self-assembled and monomer chemical structures.[7,8] To achieve more efficient separation properties and have deeper insight into the behavior of water molecules in such materials, it is important to study the hydrogen-bonded structures of the molecules in the nanochannels.

For the Col and Cub_b LC membranes obtained by polymerization of an ionic monomer, it is very interesting that a divalent sulfate ion (SO_4^{2-}) with larger ionic radius permeates the membranes more effectively than a monovalent ion (Cl^-). For example, the permeability of MgSO_4 is 73 ± 5%, which is more than double the 30 ± 6% value for NaCl. The mechanism of selective ion permeation is generally explained by the relationship between the sizes of ions and pores, which is typically the case for ion removal in a composite RO membrane. However, this behavior cannot be explained by the sieving effect and implies the presence of another driving force for ion selectivity. He and co-workers discussed that apart from the size of ion hydration nuclei relative to the pore size, the energy required for dehydration plays an essential role in the ion selectivity of bioinspired graphene nanopores.[9] Kawakami and co-workers reported that the electrostatic interaction of water molecules with water treatment membranes affected the permeability of water.[10] These discussions are consistent with MD simulations applied for different sizes of nanochannels,[11–14] where the determinant factors for the ion selectivity are the pore size, end groups in the nanopores, membrane surface charge, and properties of ion hydration.

In the present study, we investigated hydrogen-bonded structures of water in the nanostructured water treatment LC membranes formed by in situ polymerization of compound 1 (Figure 1a) with synchrotron-based high-resolution X-ray emission spectroscopy (XES) (Figure 1b). We demonstrate the hydrogen-bonded configuration of hydrating water of the ionic solute to understand the microscopic mechanism of the selective ion permeation of monovalent chloride and divalent sulfate ions in LC membranes with subnanopores.

XES is a unique tool for probing the element-specific valence electronic structure of materials.[15] Figure 2a displays
how the valence electronic structure of water is obtained after oxygen 1s core excitation. Decay of the O 1s core hole by selective transition from the p-symmetric 1b2, 3a1, and 1b1 valence states accompanies the X-ray emission. Because the XES process obeys the strict symmetry selection rule, O 1s XES is very sensitive to changes in the local hydrogen-bonded configuration of water.[16] This is demonstrated in Figure 2b by comparison of XES spectra for an isolated water molecule with a hydrogen-bonded water molecule. The most striking change upon condensation from the gas phase to the liquid phase is the splitting of the single 1b1 peak in an H2O molecule to double 1b1′ and 1b1′′ peaks in liquid H2O. The 1b1′ peak position is smoothly connected to the corresponding peak in H2O ice[17,18] and can be associated with tetrahedrally coordinated H2O molecules (effectively four hydrogen bonds per molecule). The 1b1′′ peak between the 1b1 and the gas-phase 1b1 peaks can be associated with highly distorted hydrogen-bonded H2O molecules.[18–20] For aqueous salt solutions, the XES profile of water is further modulated due to a change in the hydrogen-bonded structures of water molecules hydrating the solutes.[21,22] This is demonstrated at the bottom of Figure 2b and is discussed below in detail.

An LC polymer film was prepared from compound 1 by spin-coating and photopolymerization (see Experimental details in the Supporting Information). Figure 1a is a schematic drawing of an LC monomer benzyl triethylammonium tetrafluoroborate (1; top). The LC monomers were self-assembled to form a bicontinuous cubic liquid-crystal (Cubh) structure (middle left). Ions are selectively transported (middle center) through subnanopores composed of a stack of the four LC monomers, where water forms specific hydrogen-bonded structures (middle right). Tetraethylammonium tetrafluoroborate [N(C2H5)4BF4] (2) as a reference has the same moiety as compound 1 (bottom).
triethylammonium moiety (also shown in Figure 1a) as a model compound to obtain insights into the ionic interactions between the cationic moiety and the inorganic anions (SO$_4^{2-}$, Cl$^-$) because this cationic moiety plays a key role in the nanochannel of 1.

XES spectra of pure liquid H$_2$O absorbed in the LC membrane and hydrating water of permeating solutes, MgSO$_4$ and NaCl were collected at the SPring-8 BL07LSU HORNET station using a high-resolution XES spectrometer.$^{[23]}$ A custom-made ambient pressure cell was used to expose the LC membrane to humidity-controlled moisture and nitrogen as a carrier gas. By carefully increasing the humidity, it was possible to control the accumulation of H$_2$O molecules in the LC membrane (Figure 1b).

XES measurements of the hydrating water in the MgSO$_4$ and NaCl solutions were performed by simply circulating concentration-controlled (1 molL$^{-1}$ and 3 molL$^{-1}$ for NaCl and 1 molL$^{-1}$ and 2.5 molL$^{-1}$ for MgSO$_4$) solutions through the tube. One XES spectrum was obtained in a few hours by scanning approximately 100 $\times$ 100 $\mu$m$^2$ area, giving time- and space-averaged information for hydrogen-bonded structure of water. Details of the experimental setup and operating condition are described elsewhere.$^{[24]}$ All measurements were done at room temperature.

The O 1s XES spectra of the LC membrane (Figure 3, spectra A, B) are compared with bulk liquid H$_2$O (Figure 3, spectrum C). First, we examined the contribution of ether O atoms in the LC membrane to the O 1s XES spectra by flowing dried N$_2$ gas through the tube. With a relative humidity of 10%, we obtained spectrum A in Figure 3. The relative area intensity of the XES spectra of the bulk liquid H$_2$O to spectrum A is 6.1, as evaluated from Figure 3. This value is close to the expected relative XES intensity of 7.3 estimated from the experimental geometry (detailed estimates are discussed in the Supporting Information). Therefore, we conclude that spectrum A roughly represents the electronic structure of ether O atoms in the LC membrane. Next, to extract the electronic structure of water absorbed by the LC membrane, spectrum A was subtracted from the XES spectrum of the fully humidified (95% relative humidity) LC membrane (spectrum B in Figure S2), and the result is shown as spectrum B in Figure 3. The relative area intensity of spectrum B to spectrum A is 1.5, which is much larger than the expected intensity of 0.36 for water fully incorporated into the subnanopores (detailed estimates are discussed in the Supporting Information). The large signal intensity of spectrum B should be due to accumulation of bulk liquid H$_2$O on the LC membrane after the subnanopores are filled with H$_2$O molecules. With an equal integrated area intensity between 515 and 530 eV, spectrum C for the bulk liquid H$_2$O was subtracted from spectrum B (Figure 4a). The obtained profile directly reflects the modulation of the hydrogen-bonded structures of hydrating water molecules from the bulk liquid H$_2$O. The two significant valleys in the plot at the 1b$_1$’ (525.7 eV) and 1b$_1$” (526.5 eV) positions indicate the loss of water molecules.
of the structures of all the water molecules are modulated in the concentration (3 mol L\(^{-1}\)/C\(_0\)). The structures of \(\text{H}_2\text{O}\) in the LC membrane were compared with XES spectra for the two solutes from bulk liquid \(\text{H}_2\text{O}\) dominatedly control the ion selectivity. The normalized permeation if the hydrogen-bonded structures of water molecules (Figure 2b)\([15,16]\) in the LC membrane. Deconvolution of the 1b\(_1\) profile into Gaussian peaks (Figure 4a) requires the presence of a broad positive peak 1b\(_{1\text{LC}}\) centered around the middle of the 1b\(_1\) and 1b\(_{1\text{v}}\) valleys. The 1b\(_{1\text{LC}}\) peak must represent the hydrogen-bonded structures of water in the subnanopore of the LC membrane because the 1b\(_{1\text{LC}}\) peak compensates for the loss of the bulk liquid \(\text{H}_2\text{O}\) components (1b\(_1\) and 1b\(_{1\text{v}}\)). The broad profile of the 1b\(_{1\text{LC}}\) peak implies the presence of several hydrogen-bonded configurations of water in the subnanopores of the LC membrane.

To explore the origin of the selective ion permeation (73 ± 5% for \(\text{MgSO}_4\) and 30 ± 6% for \(\text{NaCl}\)), hydrogen-bonded structures of \(\text{H}_2\text{O}\) in the LC membrane were compared with those in the \(\text{MgSO}_4\) and \(\text{NaCl}\) hydrations (Figure 4b). We measured XES for two different concentrations of each solute, 1 mol L\(^{-1}\) and 2.5 mol L\(^{-1}\) for \(\text{MgSO}_4\) and 1 mol L\(^{-1}\) and 3 mol L\(^{-1}\) for \(\text{NaCl}\), to see if the concentration affects the hydrogen-bonded structures of hydrating water. This is crucial for evaluating the stability of the selective ion permeation if the hydrogen-bonded structures of water dominantly control the ion selectivity. The normalized difference XES spectra for the two solutes from bulk liquid \(\text{H}_2\text{O}\) reflect the modulation of the hydrogen-bonded structures of hydrating water (Figure 4b).

In the \(\text{MgSO}_4\) solution, hydrating water has hydrogen-bonded structures similar to those of water in the subnanopores of the LC membrane, which is significantly different from water in the \(\text{NaCl}\) solution. At least in the measured concentration range, it is found that the XES profile primarily depends on the ionic species and is not affected by the concentration of each salt. Below the critical concentration range around 3 mol L\(^{-1}\) for \(\text{MgSO}_4\) and 5 mol L\(^{-1}\) for \(\text{NaCl}\), where the hydration spheres of cations and anions overlap and form contact ion pairs,\([25,26]\) hydrogen-bonded structures do not change with concentration for each salt, which would also be responsible for the effective transportation of \(\text{MgSO}_4\) into the subnanopores of the LC membrane. Not only the XES profile that reflects the modulation of the hydrogen-bonded structures, but we also evaluate the ratio of modulation compared with the net XES intensity for water molecules in the subnanopores of the LC membrane and hydrating water of the permeating solutes. By integrating the absolute value of the difference XES spectra in the displayed energy range from 515 eV to 530 eV (Figure 4b), we found the ratio is 0.074 for water molecules in the subnanopore while 0.079 for water hydrating \(\text{MgSO}_4\) at 2.5 mol L\(^{-1}\). Intriguingly the extent of XES modulation is comparable between water molecules in the subnanopores of the LC membrane and hydrating water of \(\text{MgSO}_4\) near the critical concentration (3 mol L\(^{-1}\)). This implies the hydrogen-bonded structures of all the water molecules are modulated in the subnanopore with 0.6 nm diameter and at the critical concentration of \(\text{MgSO}_4\) solution.

From the above results, we conclude that the consistency of the hydrogen-bonded structures of water in the subnano-
of hydrating water that controls many functions of biological systems.

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Conflict of interest

The authors declare no conflict of interest.

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