Effects of anion size and concentration on electrolyte invasion into molecular-sized nanopores

Ling Liu¹, Xi Chen¹,²,⁵, Taewan Kim³, Aijie Han³ and Yu Qiao³,⁴,⁵

¹ Department of Earth and Environmental Engineering, Columbia University, New York, NY 10027, USA
² Department of Civil and Environmental Engineering, Hanyang University, Seoul 133-791, Korea
³ Department of Structural Engineering, University of California—San Diego, La Jolla, CA 92093-0085, USA
⁴ Program of Materials Science and Technology, University of California—San Diego, La Jolla, CA 92093-0085, USA
E-mail: xichen@columbia.edu and yqiao@ucsd.edu

New Journal of Physics 12 (2010) 033021 (10pp)
Received 1 October 2009
Published 12 March 2010
Online at http://www.njp.org/
doi:10.1088/1367-2630/12/3/033021

Abstract. When an electrolyte solution is pressurized into a molecular-sized nanopore, oppositely charged ions are strongly inclined to aggregate, which effectively reduces the ion solubility to zero. Inside the restrictive confinement, a unique quasi-periodic structure is formed where the paired ion couples are periodically separated by a number of water molecules. As the anion size or ion concentration varies, the geometrical characteristics of the confined ion structure would change considerably, leading to a significant variation in the transport pressure. Both experimental and simulation results indicate that, contradictory to the prediction of conventional theory, infiltration pressure decreases as the anions become larger.
1. Introduction

The behavior of electrolytes in confined nanoenvironments, e.g. biological cavities [1] and various nanotubes/nanopores [2, 3], has drawn considerable attention owing to their key roles in biological transport [3, 4], water purification [5], energy dissipation, conversion and storage [6, 7], and many other promising applications of nanofluidics [8]–[10].

From the bulk to the confined state, both water molecules and ions experience substantial changes in their molecular configurations and properties. For water, the local density is no longer evenly distributed [11], the hydrogen bonding is typically weakened [12], and the dipole orientation usually becomes more ordered [13]; for ions, the hydration shell could be considerably distorted [14]. As a consequence, some unique molecular configurations have been discovered, such as the $n$-gonal ring [15] and the double helical chain [16] structures. The resulting intrinsic nanofluid properties, such as infiltration and transport behavior, are strongly dependent on the characteristic length scale [17]–[19].

In a macroscopic channel, the required pressure associated with the intrusion of a nonwettable liquid column is governed by the classic Laplace–Young equation. For electrolytes of different ion sizes but similar surface tensions, their infiltration pressures should be nearly the same. That is, as the anions exist only beyond the outer Helmholtz plane (OHP) at a large solid surface, their sizes have only negligible effects on the solid–liquid interfacial tension [20].

For the infiltration of charged particles into nanometer-scale channels, the required pressure may increase as the ion size becomes larger [20, 21], since a ‘free volume’ must be maintained between the confined ion and the solid surface.

When the pore size is further reduced to the molecular scale, it is envisioned that new and counterintuitive phenomena may arise. Within the restrictive confinement (smaller than 1 nm), the hydration shell surrounding the ions [22] can no longer exist and the ions and water molecules must look for a new equilibrium configuration [2]. The infiltrated water molecules and ions may form a quasi-one-dimensional structure that is unique to the molecular-sized nanopores; depending on the type/size and concentration of the ions, the structural features

New Journal of Physics 12 (2010) 033021 (http://www.njp.org/)
Figure 1. MD simulation of electrolyte infiltration into a molecular-sized silicon dioxide nanotube: (a) the computational model, where the most notable result is the ion couples formed right after the cation and anion enter the nanopore; (b) confined molecular structures of three electrolytes showing the size-dependent separations between neighboring ion couples and two paired ions.

of the confined molecules/ions may be different, which, during a pressure-induced infiltration process, could lead to different pressure gradients and a new trend of ion-dependent infiltration behavior.

2. Computational model and method

To explore the underlying molecular mechanisms, we investigate the infiltration process of three electrolytes, which are of the same cation but different anions, into molecular-sized nanopores using molecular dynamics (MD) simulations. A long, straight and rigid silicon dioxide nanotube with a diameter of 7.4 Å is adopted as a model structure of the molecular-sized nanopore (figure 1(a)). The partial charges are incorporated, and the dielectric permeability is fixed as 1. One of the ends of the nanotube is immersed in an electrolyte reservoir bounded by two rigid planes in the axial direction, and the periodic boundary condition is imposed in the four lateral directions of the computational cell. Initially, a specific amount of the electrolyte is contained in the reservoir so that the pressure inside is close to the ambient condition (zero) after equilibrium. Subsequently, by moving the bottom rigid plane (piston) upwards (in a quasi-static manner, while holding the other rigid plane fixed), the pressure inside the reservoir is increased and the infiltration of water molecules and ions starts. Three types of salts (NaF, NaCl and NaBr) at two representative concentrations (mole fraction, \(X = 0.06\) and 0.08) are examined. Simulations are performed with the COMPASS forcefield [23] and the NVT ensemble. Long-range electrostatic interaction is estimated by the Ewald summation technique.

New Journal of Physics 12 (2010) 033021 (http://www.njp.org/)
Figure 2. The infiltration sequence of ions identified in simulation is verified through energy analyses in (a) a schematic of three successive key stages. In every stage, (b) energy variations are associated with the motion of a cation or an anion, through which the energetically favorable option is identified.

3. Results and discussion

3.1. Ion couple and quasi-periodic electrolyte structure inside the molecular-sized nanotube

Figure 1(b) shows the ‘steady-state’ molecular structures of the three electrolytes ($X = 0.08$) when they infiltrate into the molecular-sized nanopore, where the confined liquid phase is entirely different from its continuum counterpart. These snapshots are obtained from MD simulations. Interestingly, the infiltrated ions tend to form cation–anion couples in an ordered sequence; the spacing is different for different salts, and water molecules are sandwiched between ion couples. This unique structure raises several fundamental questions: Why and how do the infiltrated ions form an ordered sequence? Are these nanocrystalline-like ion couples stable? Why does the spacing between adjacent ion couples depend on ion size? What is the implication for the required work of electrolyte infiltration?

3.2. Theoretical verification of ion couple structure formation

In order to theoretically verify the infiltration sequence discovered in simulation as well as the basis for the formation of nanocrystalline-like ion couples, a separate energy analysis is carried out. Starting from an empty nanotube, we compare the energy variations associated with the entry of a cation and an anion in three successive stages (figure 2(a)). Sodium bromide is taken as an illustrative example and all findings hold for the other two electrolytes. Stage 1 refers to the infiltration of the first ion, where ‘1C’ illustrates the possibility that a cation would first infiltrate the nanopore, and ‘1A’ corresponds to the alternative case of anion infiltration. In either
The formation and stability of the ion couple structure are examined by comparing the energetics of three possible ionic configurations inside the nanopore: (a) a nanocrystalline-like structure that mimics the structure observed in MD simulation (figure 1), where \( a \) and \( b \) are averaged from MD snapshots as approximately 2.5 and 21.5 Å, respectively; (b) a scattered structure that assumes that no ion couple is formed and all ions are alternately and uniformly distributed with a uniform spacing of 12 Å; (c) an aggregated structure that assumes that ion couples further aggregate to form a continuous ion strand with a uniform spacing of 2.5 Å. (d) As a cation and an anion approach each other to form a couple, water molecules, if any in between, have to switch positions with a neighboring ion.

In this case, a counter charge is placed outside the tube so as to neutralize the system. The examined ion is then perturbed by several angstroms along the axial direction, causing a variation of the system potential energy, as plotted in figure 2(b). By comparing the energy variations of both possibilities, it is made clear that a cation should first infiltrate as it is able to decrease the system energy. In the subsequent stage 2 where a cation has already infiltrated, configuration ‘2C’ is found to be more energetically favorable than ‘2A’ and thus another cation should enter the nanopore. Following the two previously infiltrated cations, the third infiltrated ion is found to be a Br\(^-\) anion\(^6\).

Driven by an energetic preference, the Na\(^+\) cation infiltrated in stage 2 and the Br\(^-\) anion infiltrated in stage 3 should approach each other inside the nanopore. For verification, we consider two possible configurations of the confined Na\(^+\) and Br\(^-\) ions: a nanocrystalline-like structure that mimics the structure observed in simulation (figure 3(a)), and a uniformly scattered ion structure (figure 3(b)). The energy is calculated as \(-710\) and \(-216\) kcal mol\(^{-1}\), respectively, for these two configurations. That is, the formation of an ion couple could favorably reduce the system potential by \(~90\) kcal mol\(^{-1}\). Meanwhile, there is an energy barrier that needs to be overcome: for a cation and an anion to approach each other, any water molecule initially between them must escape (figure 3(d)); when a water molecule and an ion are about to switch their positions, a moderate energy barrier may arise given the limited space inside the nanopore. Such an energy barrier is computed as \(~5\) kcal mol\(^{-1}\) for bypassing Na\(^+\) and \(~94\) kcal mol\(^{-1}\) for

\(^6\) Water molecules may infiltrate the nanopore before/after the infiltrated ions.
bypassing $\text{Br}^-$. Therefore, the formation of ion couples is energetically favored via consecutive switching of positions between $\text{H}_2\text{O}$ molecules and $\text{Na}^+$. Therefore, the formation of ion couples is energetically favored via consecutive switching of positions between $\text{H}_2\text{O}$ molecules and $\text{Na}^+$.

After the infiltration of the first three ions, there is only one net positive charge inside the channel and one counter-charge outside, which leads to a situation similar to the end of stage 1 (‘1C’ in figure 2(a)). Thus, the subsequent infiltration of ions would repeat stages 2 and 3; more and more cations and anions would be driven into the nanopore and then paired inside to form ion couples (consistent with the MD simulation in figure 1(b)). If the nanocrystalline-like structure (figure 3(a)) is stable, the ion couples should not further aggregate to form a continuous ion strand (figure 3(c)). Although the energy analysis shows that the aggregated structure has a lower energy ($\sim-880 \text{ kcal mol}^{-1}$) than the nanocrystalline-like structure, it is important to note that, for the aggregated structure to form, the bounded water molecules must be able to switch their positions with $\text{Br}^-$, which requires a prominent energy barrier ($\sim 94 \text{ kcal mol}^{-1}$ per switch). Thus, from the energy point of view, aggregation of ion couples is unlikely to occur, and the ion couple structure is quite stable. Although such an ion couple structure is discovered in a $\text{SiO}_2$ nanotube, when the nanopore is neutral (e.g. a carbon nanotube, CNT), we envision that a similar periodic structure of ion couples would still form, although the overall infiltrated structure should become neutral.

3.3. Ion size/concentration-dependent parameters: $a$ and $b$

With the energetically driven formation of ion couples, eventually a quasi-periodic chain of ion couples (led by a cation) forms inside the nanopore, which holds for all electrolytes under investigation. Denote the separation between the cation and the anion in an ion couple as $a$, and the averaged spacing between ion couples as $b$ (figure 1(b)). From MD simulations (and taking average values), $a$ is measured as 2.13, 2.55 and 2.64 Å, respectively, for the NaF, NaCl and NaBr solutions (and it is insensitive to the ion concentration, $X$); the corresponding values of $b$ are 14.75, 19.16 and 21.58 Å, respectively, for $X = 0.08$, and 26.75, 36.29 and 40.00 Å, respectively, for $X = 0.06$.

The ionic bonding is the dominant factor that influences the distance between ions in a couple. The ionic bond lengths$^7$ are calculated as 2.02, 2.39 and 2.52 Å, respectively, for $\text{F}^-$, $\text{Cl}^-$ and $\text{Br}^-$, which are quite close to the values of $a$ reported above. The small difference is attributable to the environmental factors (nanopore, water molecules, other ions, etc).

The variation of $b$ implies that, when paired with a cation, anions of different size and concentration have different capabilities of entering the nanopore. Theoretically, when a particle (molecule or ion) infiltrates a nanopore, the route that consumes the least energy is along the tube axis; when the infiltration path deviates from the axis, a larger particle needs to spend more energy than a smaller one. As an illustration, in figure 4 we plot the energy maps associated with the in-plane motion of three anions ($\text{F}^-$, $\text{Cl}^-$ and $\text{Br}^-$) inside the cross-section of the nanopore. This energy map is obtained via a separate energy analysis when an anion is placed at the entrance of the pore. For $\text{F}^-$, a large plateau is found in the central part of the channel, within which the energy is only slightly varied; by contrast, the radial gradient is close but much higher for the two larger anions, $\text{Cl}^-$ and $\text{Br}^-$. This explains that $\text{Cl}^-$ and $\text{Br}^-$ have a lower chance than $\text{F}^-$ to enter the nanopore; so do the ion couples when the anions are paired with $\text{Na}^+$. When

$^7$ Ionic bond length is calculated as the separation between a cation and an anion after the geometric optimization in which no other atom is present.

New Journal of Physics 12 (2010) 033021 (http://www.njp.org/)
Figure 4. Energy contours of three individual cations moving within the cross-section of the nanopore under investigation. The energy value at the center is adopted as the ground state, and the diameter of the black circle equals 4.5 Å.

Figure 5. Energy variations as three different ion couples (with the same cation but different anions) move from the tube opening to 500 Å inside the nanotube.

the ion concentration is lower in the reservoir, the ion infiltration probability is also decreased, leading to a larger $b$.

3.4. Influence of ion couple structure on infiltration pressure

Both MD simulation snapshots (section 3.1) and energy analysis (section 3.2) have verified the infiltrated quasi-periodic ion couple structure, whose geometric parameters $a$ and $b$ are both dependent on anion size and concentration (section 3.3). It is important to note that in a pressure-induced infiltration process, additional work must be done to transport one of such ion couples from the pore entrance towards the interior (and such extra work needs to be continuously supplied in order to transport the ion couple structure in order to sustain the electrolyte infiltration). The required energy to move one unit of ion couple, $E_{in}$, arises from the electrostatic interaction between the ion couple and an anion effectively left outside the nanopore. In figure 5, $E_{in}$ is quantified as the energy variation associated with the motion of an ion couple moving from the tube opening to about 500 Å inside the nanopore (where
the interaction with the anion fades out and a ‘steady state’ is reached). For the Na\(^+\)/F\(^-\), Na\(^+\)/Cl\(^-\) and Na\(^+\)/Br\(^-\) ion couples, \(E_{in}\) is calculated to be about 0.43, 0.49 and 0.53 kcal mol\(^{-1}\), respectively. The additional energy required for continuously infiltrating/transporting the entire quasi-periodic chain (figure 3(a)) can be translated into a new equivalent surface energy term, \(\Delta \gamma' = E_{in}/\pi bD\), where \(D\) denotes the effective diameter of the nanotube. Therefore, according to the classic Young’s equation, the required total infiltration pressure is \(P_{in} = 4(\Delta \gamma + \Delta \gamma')/D\), where \(\Delta \gamma\) is the surface energy associated with the fluid transition from the bulk to the confined state (\(\Delta \gamma \approx 0\) in the present study). Finally, \(P_{in}\) is predicted to be 11.61, 10.31 and 9.62 MPa, respectively, for the three electrolytes at \(X = 0.08\). In essence, the smaller the anion, the shorter the ionic bond length and thus the smaller the \(a\) and \(E_{in}\); however, the larger infiltration probability leads to a smaller \(b\)—the term associated with ion couple density contributes more and leads to a larger \(P_{in}\), which appears to be a counterintuitive phenomenon in the present study (when the nanopore structure is different, the tendency of ion-size-dependent infiltration behavior may change, although the formation of a similar ion couple structure is robust inside a molecular-sized nanopore). Since \(b\) is a function of \(X\), \(P_{in}\) also varies with ion concentration as shown in figure 6, where it is almost doubled as the ion concentration is reduced by 25%.

4. Experimental validation

These uncovered molecular mechanisms imply that the infiltration pressure is highly dependent on the anion size. A validation experiment was performed by using a well-crystallized zeolite Y (ZY). The as-received material was provided by Zeolyst (ref. no. CBV-901) with a crystal size of 10–50 µm. The specific nanopore surface area was 700 m\(^2\) g\(^{-1}\) and its nanopore size (≈ 0.7 nm) was very close to that used in simulation (the XRD test has confirmed that the pore size was highly uniform). In order to remove the aluminum defects (so as to mimic the pure silicon dioxide tube in simulation), the ZY sample was dried in vacuum at 120°C for 10 h, treated in silicon tetrachloride vapor in a nitrogen environment at 450°C for 30 min, and...
furnace cooled and thoroughly rinsed in distilled water. After the pH value reached around 7, the material was hydrothermally treated in a saturated water steam flow at 650 °C for 48 h, with a water supply rate of 30 ml min\(^{-1}\). The ZY sample was then refluxed in a 7.5% ethylenediaminetetraacetic acid solution at 85 °C for 12 h, repeatedly filtered and rinsed in distilled water, and finally calcined in vacuum at 400 °C for 24 h.

In a stainless steel cylinder, about 0.1 g of the treated ZY sample was immersed in about 7 g of an aqueous solution of NaF, NaCl or NaBr. The salt concentration was 0.8 M. The cylinder was sealed by a stainless steel piston equipped with a reinforced o-ring. By using a 5580 type Instron machine, the piston was compressed into the cylinder at a constant rate of 5 mm min\(^{-1}\). When the pressure applied on the piston exceeded a critical value, the infiltration process began, associated with a rapid system volume decrease. From the average of multiple infiltration tests (where repeatable behavior was found), the values of the critical pressure were measured to be 250, 230 and 160 kPa for NaF, NaCl and NaBr solutions, respectively. It is clear that as the anion size increases, the infiltration pressure decreases, which qualitatively agrees with the prediction of MD simulation and energy analyses.

5. Conclusion

To summarize, through MD simulation, it is discovered that in a molecular-sized nanopore, anions have considerable influence on solid–liquid interaction, as they are directly exposed to the nanopore inner surface. Unique to such a restrictive confinement is that the zero ion solubility leads to the formation of highly stable nanocrystalline-like cation–anion couples, whose periodic structural features depend on anion size, which leads to an unconventional negative correlation between the required ion transport pressure and anion size. The relationship between anion size and infiltration pressure is qualitatively validated by a pressure-induced infiltration experiment on a dealuminated ZY.

Acknowledgments

YQ was supported by the National Science Foundation (NSF) and the Sandia National Lab under grant no. CMMI-0623973. XC was supported by NSF under grant no. CMMI-0643726, a World Class University (WCU) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology of Korea (R32-2008-000-20042-0), and by National Natural Science Foundation of China grant no. 50928601. LL acknowledges the support of the American Academy of Mechanics and the Robert M and Mary Haythornthwaite Foundation.

References

[1] Yin H, Hummer G and Rasaiah J C 2007 J. Am. Chem. Soc. 129 7369
[2] Liu L, Chen X, Lu W and Qiao Y 2009 Phys. Rev. Lett. 102 184501

8 It is verified that further reduction of the loading rate does not change the infiltration behavior, indicating quasi-static loading condition.
9 The difference between the magnitudes of infiltration pressure measured in experiment and simulation is attributed to the effect of surface treatment and electrolyte concentration used in experiment.
[3] Fornasiero F, Park H G, Holt J K, Stadermann M, Grigoropoulos C P, Noy A and Bakajin O 2008 Proc. Natl Acad. Sci. USA 105 17250
[4] Chen X, Cui Q, Yoo J, Tang Y and Yethiraj A 2008 Biophys. J. 95 563
[5] Shannon M A, Bohn P W, Elimelech M, Georgiadis J G, Marinas B J and Mayes A M 2008 Nature 452 301
[6] Chen X, Surani F B, Kong X, Punyamurtula V K and Qiao Y 2006 Appl. Phys. Lett. 89 241918
[7] Liu L, Qiao Y and Chen X 2008 Appl. Phys. Lett. 92 101927
[8] Mattia D and Gogotsi Y 2008 Microfluid. Nanofluid. 5 289
[9] Schoch R B, Han J Y and Renaud P 2008 Rev. Mod. Phys. 80 839
[10] Whitby M and Quirke N 2007 Nat. Nanotechnol. 2 87
[11] Thomas J A and Meggaughey A J H 2008 J. Chem. Phys. 128 084715
[12] Gordillo M C and Marti J 2000 Chem. Phys. Lett. 329 341
[13] Wang J, Zhu Y, Zhou J and Lu X H 2004 Phys. Chem. Chem. Phys. 6 829
[14] Shao Q, Huang L L, Zhou J, Lu L H, Zhang L Z, Lu X H, Jiang S Y, Gubbins K E and Shen W F 2008 Phys. Chem. Chem. Phys. 10 1896
[15] Koga K, Gao G T, Tanaka H and Zeng X C 2001 Nature 412 802
[16] Qiao Y, Liu L and Chen X 2009 Nano Lett. 9 984
[17] Chen X, Cao G, Han A, Punyamurtula V K, Liu L, Culligan P J, Kim T and Qiao Y 2008 Nano Lett. 8 2988
[18] Liu L, Zhao J B, Yin C, Culligan P J and Chen X 2009 Phys. Chem. Chem. Phys. 11 6520
[19] Qiao Y, Cao G and Chen X 2007 J. Am. Chem. Soc. 129 2355
[20] Han A and Qiao Y 2006 J. Am. Chem. Soc. 128 10348
[21] Wasan D T and Nikolov A D 2003 Nature 423 156
[22] Wieckowski A 1999 Interfacial Electrochemistry (New York: Marcel Dekker)
[23] Sun H 1998 J. Phys. Chem. B 102 7338