Infiltration of Electrolytes in Molecular-Sized Nanopores

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In both experiment and molecular simulation, it is found that a higher pressure is required to sustain the infiltration of smaller ions in a molecular-sized nanochannel. Simulations indicate that the effective ion solubility of the infiltrated liquid is reduced to nearly zero. Because of the strong interactions between the ion couples and the solid or liquid phases, an external force is required to continuously advance the confined liquid segment. The competition between the probability of ion entry and ion-couple formation causes the observed ion-size-dependent characteristics.

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Understanding ion behavior in a nanochannel has drawn increasing attention [1,2], due to its fundamental role in a number of emerging areas including selective ion conduction, absorption and adsorption, sensing, energy conversion and storage, etc. [3–5] In bulk water, a molecular cluster can be formed around a solvated ion [6]. As the ions transport inside a nanotube of a diameter comparable with the characteristic size of the molecular cluster, the solvated configuration can be distorted [7]. Insights into the molecular configurations can be sought from first principle and molecular dynamics (MD) studies [8–12].

In a small nanotube or nanochannel, liquid molecules and ions can form a quasi-one-dimensional chain [12–17]. If the nanotube or nanochannel surface is effectively nonwettable, an external driving force must be applied to force the ions and liquid molecules to enter the nanoenvironment [18–20]. That is, work must be done to increase the system free energy. It is envisioned that, for solvated ions of the same ion charge but different ion sizes, the required external force would be specific [21], depending on the variation in system free energy. It was generally predicted that for the same nanopore, if the solvent molecular or ionic size increases, less pore volume is available and the infiltration pressure should be higher. Even when the nanochannel wall is nominally wettable in the liquid phase, the channel size must be much larger than the solute molecules or ions; otherwise the repelling effect of the solid wall would prevent their infiltration. The required "free volume" can be a few times larger than the solvent molecules or ions [22,23]. This prediction, however, may break down for a very small nanochannel where the effective channel diameter is only slightly larger than the ion size. In this case, ions can directly interact with the channel wall, which not only affects the solid-liquid interaction but also dominates the configuration of the confined clusters of electrolyte particles.

To explore the unique transport behaviors of an electrolyte in molecular-sized nanochannels, we investigated a zeolite Y, ZY. Compared with many other nanoporous materials, zeolites are of highly ordered porous structures. The ZY sample has an effective pore diameter of 0.7 nm [24]; it was placed in a steel cylinder with an aqueous solution of chloride salt, with the ZY-to-liquid mass ratio of $1/10$. The salt was either LiCl, NaCl, KCl, or CsCl, and the molarity of all the solutions was $4M$. (More experimental details are given in the supplementary material [25].)

The ZY material was effectively hydrophilic. Therefore, if the liquid phase was pure water, the nanopores could be soaked up spontaneously; if an external pressure was applied, the compression behavior was quite linear, determined by the machine compliance and the liquid bulk modulus. As the electrolyte was added, the nanopore inner surface might become effectively nonwettable [26], and under ambient pressure the nanopores remained empty. As an sufficiently high external pressure was applied, pressure-induced liquid infiltration began, leading to the formation of an infiltration plateau in the sorption isotherm curve (Fig. 1). The liquid infiltration ended when the porous space was filled up. The width of the infiltration plateau reflected the accessible nanopore volume, close to the measured porosity, as it should be. The measurement results of the infiltration pressure, p_{in}, are also shown in Fig. 1. For self-comparison purpose, p_{in} was taken as the pressure at the starting point where the measured slope of the sorption isotherm curve is a constant afterwards.

It is remarkable that p_{in} decreased with the cation size. For the LiCl solution, p_{in} was nearly 15 MPa; when the electrolyte was changed to NaCl, p_{in} became 13.5 MPa; for KCl, p_{in} was largely decreased to 4 MPa. In the pure water and the CsCl based systems, the pressure-induced infiltration could not be detected, indicating that the nominal p_{in} was zero; i.e., the nanopores could be filled by the liquid phase spontaneously at ambient pressure.

In order to understand the unique ion behaviors, atomistic simulations and energy analyses are carried out and

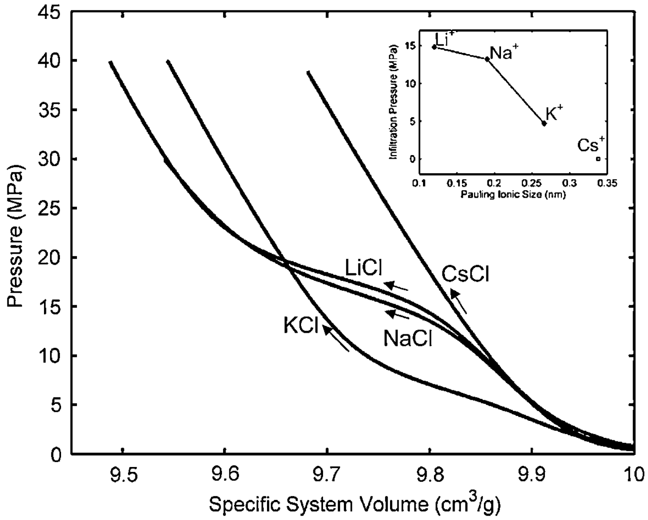

FIG. 1. Typical quasistatic sorption isotherm curves. The insert at the upper-right corner shows the infiltration pressure as a function of the Pauling cation size. The specific system volume is defined as the system volume normalized by the mass of the nanoporous material. The arrows indicate the loading direction.

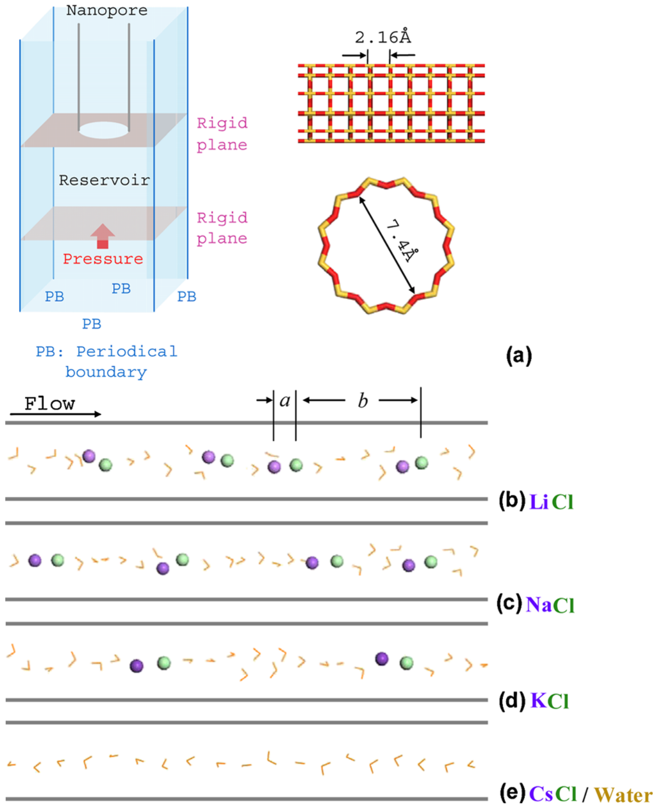

FIG. 2 (color online). The MD simulation: (a) schematic of the infiltration process and a model SiO_2 nanochannel that mimics a single nanopore of zeolite Y. Snapshots of the pressure-driven infiltrated ion or water structures of (b) LiCl, (c) NaCl, and (d) KCl electrolytes, inside the nanochannel and upon steady-state. Each Cl^- [light gray (green) ball] is followed by a cation [dark gray (purple) ball], forming a number of anion-cation couples with water molecules in between. The ion couple sizes and the distances between adjacent ion couples of different infiltrated electrolytes are significantly different. (e) In the CsCl solution, only H_2O molecules can infiltrate into the nanopore.

elaborated on below. We performed a MD simulation where a long, straight, and rigid silicon dioxide nanotube [Fig. 2(a)] with the diameter of $D_0 = 7.4$ Å (the distance between diagonal O atoms) was employed as a close analog to a ZY nanopore. The model setup was similar to that in experiment (more details are given in the materials and methods section in the supplementary material [25]). To be consistent with the experiment, ions and water molecules were mixed uniformly in the reservoir with the molarity of $4M$. Upon increase of the reservoir pressure, p, the water molecules and ions inside the reservoir-nanochannel system were redistributed, and at a critical pressure (p_{in}), they may continuously enter the nanochannel, reflecting the adiabatic pressure-driven electrolyte transport in a nanopore.

The simulation results show that for three of the electrolyte solutions under investigation, LiCl, NaCl, and KCl, only at an elevated pressure level can ions and water molecules infiltrate into the nanochannel. The value of p_{in} is the highest for LiCl and the lowest for KCl. For the CsCl solution that is of the largest cation size, water molecules enter the channel at ambient pressure whereas no ion infiltration can be observed even at $p > 100$ MPa; i.e., the nominal p_{in} of CsCl solution is zero. These observations are in agreement with the experimental results.

Owing to the strong confinement effect of the nanochannel, the infiltrated water molecules and ions maintain a quasi-one-dimensional chain, as shown in the snapshots from MD simulations, Figs. 2(b)–2(e). It is remarkable that the distribution of ions is highly regular at the steady-state: each Cl^- ion couples with a cation (Li^+, Na^+, or K^+), forming a number of anion-cation couples with ordered sequence, and the ion couples are separated by a few water molecules. It is also noteworthy that in the nanotube under investigation, the ion infiltration process in Figs. 2(b)–2(d) is always led by a cation in the flow direction and followed by the quasiperiodical anion-cation couples, and thus the electrolyte segment inside the nanopore is typically nonneutral. Such commonality of ion infiltration sequences (shared by the three electrolytes that can infiltrate into the nanochannel) can be explained via an energy analysis (section 1 of the supplementary material [25]). Compared with the uniformly scattered ion distribution in bulk liquid phase, the current atomistic simulation suggests that in a highly confined space, there is an energetic preference for a cation and anion to form a nanocrystallinelike structure (section 3 of the supplementary material [25]). That is, as the space is insufficient for any solvated structure, the effective solubility of ions is greatly reduced.

The ion-couple size, i.e., the averaged spacing between the two ions in a couple (a), and the averaged distance between adjacent ion couples (b), are different for different electrolytes [Figs. 2(b)–2(d)]: MD simulations show that the larger the cation, the larger a and b—such unique characteristics of the confined ion structure are responsible for the observed ion-size effect on the infiltration pressure, p_{in}. In particular, the value of a is dominated by the equilibrium of Coulomb attraction and van der Waals repulsion in an anion-cation couple. For Li^+-Cl^-, Na^+-Cl^-, and K^+-Cl^- ion couples, an independent energy calculation shows that the equilibrium distance is 2.05 Å, 2.39 Å, and 2.74 Å, respectively, which is close to the average values of a identified from the MD simulation snapshots: 2.20 Å, 2.55 Å, and 2.8 Å, respectively. The small difference between them can be attributed to the environmental factors, e.g., the presence of the nanochannel wall and the water molecules. Compared with a, the ion-size dependence of b is of more interest, which implies a better chance for a smaller cation to enter the nanochannel that can be validated by an independent energy barrier analysis (section 2 of the supplementary material [25]). The results show that small cations have the advantage during the competition for infiltration with water molecules, leading to a higher frequency of ion infiltration and thereby a smaller separation distance between the ion couples (i.e., a smaller b).

Immediately after the infiltration of a cation (Li^+, Na^+, or K^+), either an anion (Cl^-) or a water molecule may enter the nanotube. It is possible that near the nanochannel opening, an infiltrated cation and an anion may be separated by a few water molecules. However, since both the cation and anion cannot be fully solvated in the small nanochannel, aided by the long-range electrostatic attraction, the two ions can "aggregate" inside the tube, forming an ion couple. According to the energy analysis elaborated on in section 3 of the supplementary material[25], the aggregation of two oppositely charged ions favorably reduces the system potential, and the resulting nanocrystallinelike structure is highly stable [27].

These structural features and size-dependent variables of the infiltrated ion or molecule structure dominate the infiltration pressure, p_{in} [28,29]. When the size of nanochannel is fixed, p_{in} is governed by the effective solid-liquid interfacial tension, $\Delta\gamma$. A possible contribution to $\Delta\gamma$ arises from the difference between the free energies of the same liquid volume in bulk and confined states, denoted as $\Delta\gamma_0$. Energy analyses show that $\Delta\gamma_0$ of water, LiCl, NaCl, and KCl solutions are all small negative values, indicating that, without considering other factors, all of them should be able to spontaneously enter the tube at ambient pressure.

In the MD simulation and the experiment, however, such spontaneous infiltration is observed only with pure water and the CsCl solution. Because of the polarity of ion couples and the non-neutrality of infiltrated liquids, $\Delta\gamma$ is also dependent on the requirement of sustaining the ion transport after infiltration. As remarked earlier, when the ions and water molecules enter the nanochannel as a quasiperiodical chain, with the cation leading the infiltrated segment, the remaining electrolyte in the reservoir is non-neutral, and a negative charge is needed to effectively balance the confined charges. Since the cation in any infiltrated ion couple is closer than the anion to the effective negative charge outside the nanopore [Figs. 2(b)–2(d)], a strong net Coulomb attraction is yielded, causing an additional energy barrier, $\Delta\gamma'$. That is, $\Delta\gamma = \Delta\gamma_0 + \Delta\gamma'$. The value of $\Delta\gamma'$ can be assessed as the energy consumption by each ion couple, ΔE, multiplied by the number of ion couples per unit area of the infiltrated segment, n. Both of the variables are ion-size dependent, where ΔE is affected by a and n is influenced by b.

An energy analysis is carried out to estimate ΔE. Figure 3 plots the energy variations. Note that the second derivatives of these curves are negative, suggesting that the work required for transporting ions becomes less as the ion couple is moved farther away from the tube opening, due to the decrease in Coulomb interaction. As the ion couples have traveled for about 500 Å, the energy variations become quite slow. From Fig. 3, the K^+-Cl^- couple has the largest energy barrier, approximately 0.55 kCal/mol, followed by the Na^+-Cl^- couple with 0.53 kCal/mol, and the ΔE of Li^+-Cl^- is about 0.45 kCal/mol. Such variation is primarily due to the difference in a. With a smaller a value, the anion in the Li^+-Cl^- couple can offset more attraction between the Li^+ and the effective charge outside the nanopore, leading to a smaller net force.

The associated free energy change of the steady-state system is $\Delta\gamma' = \frac{\Delta E}{\pi b D}$, where D is the effective diameter of the liquid segment [29]. The difference of quasistatic pressure (before and after infiltration) should be balanced by

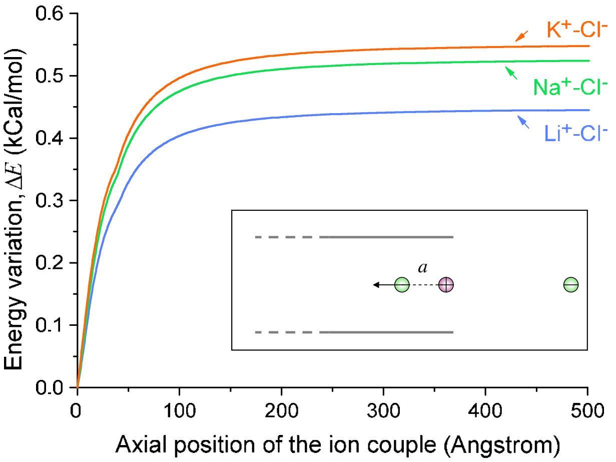

FIG. 3 (color online). Energy analysis when an anion-cation couple (with an equilibrium separation, a) is moved toward the interior of the nanopore; the net interaction energy with the system is plotted as a function of the ion couple's axial travel distance (from the pore opening).

the system free energy increase, i.e., $p_{\rm in} = 4\Delta\gamma/D$. Since $\Delta\gamma_0$ is negligible for the investigated cases, $p_{\rm in}$ is nearly proportional to ΔE and $1/b$. Although the KCl solution has the largest ΔE, its $p_{\rm in}$ is still calculated to be the lowest, 8.85 MPa, due to the large separation distance between ion couples, b. The NaCl and LiCl solutions have the $p_{\rm in}$ values of 14.64 MPa and 15.69 MPa, respectively. Using this model, the predicted ranking and values of $p_{\rm in}$ agree quite well with the data of the experiment and the MD simulation [30].

To summarize, we report an interesting phenomenon that, when other conditions remain the same, it requires a higher pressure to sustain the infiltration of an electrolyte solution of a smaller cation size into a molecular-sized nanochannel. The MD simulation indicates that the confined ions tend to form crystallinelike ion couples; i.e., a quasi-one-dimensional water molecular chain cannot dissolve any ions (nor any gas molecules [31]). There is a strong sequence preference of the ions entering the nanopore, forming a non-neutral, quasiperiodical structure. Ions of smaller sizes have a higher probability to infiltrate into the nanochannel, and thus the spacing between ion couples is smaller. In order to sustain continuous transport, an external work must be applied on the system, such that the infiltrated liquid segment could overcome the energy barrier imposed by the nonbonded interaction with the rest of the system. For smaller ions, although it requires less work to advance a unit ion couple, the spacing between ion couples is more dominant to the required work, which leads to a higher infiltration pressure.

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[28] The infiltration pressure refers to the pressure at the critical moment, after the transport of the liquid segment inside a nanopore reaches steady-state. Before such a critical point, the system free energy variation associated with infiltration is not a constant, leading to nonlinear variations in the required pressure. During steady-state transport, the pressure varies linearly with the infiltration volume.
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