

Effects of cation size on infiltration and defiltration pressures of a MCM-41

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With the nanopore structure, ionic charge, solvent, and testing condition being kept the same, the cation size effects on liquid motion in a MCM-41 are investigated by using chloride salts. As the cation becomes larger, both infiltration and defiltration pressures decrease. The variation in infiltration pressure is more pronounced. © 2008 American Institute of Physics.

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Molecular and ionic transport in nanotubes and nanopores has been an increasingly active research area,^{1–3} which is essential to the studies on biochemical phenomena,⁴ advanced energy systems,^{5,6} sensors and actuators,^{7,8} etc. When an electrolyte is added in a solvent, ions are solvated.⁹ In a molecular cluster, ions and solvent molecules are attracted by relatively strong Coulomb forces. At a finite temperature, such a structure can reach the steady state. When the solution is in contact with a solid surface, because the forces from the solid atoms and from the liquid molecules are different, the distribution of ions becomes heterogeneous.¹⁰ Close to the solid-liquid interface, the ion density is relatively high. The thickness of the interface zone is characterized by the Debye distance, often in the range of 0.5–10 nm. The major characteristics of this structure can be captured by the classic outer Helmholtz plane model. The surface ion density, the ion mobility, and the Debye distance determine the surface capacity, the interfacial tension, and their sensitivities to environmental variations.¹¹

At the inner surface of a nanotube or a nanopore where the tube/pore size is comparable with the Debye distance, the classic interface theory is no longer valid. As the volume to surface area ratio becomes small, the bulk liquid phase does not exist.¹² Since the cation-solid and anion-solid interactions are different, the confined liquid can be of a net electric charge, especially when the system is subjected to an external mechanical,¹³ electric,¹⁴ or thermal loading.^{13–17} The nanotube/nanopore wall also strongly constrains the solvated structure and the ion diffusion. If the space is insufficient, the ions may not be fully solvated.¹⁸ The anions may contact the solid surface, resulting in a “squeezing” effect.¹⁹ Under controlled conditions, the unique liquid structures in nanotubes or nanopores tend to cause higher molecular/ionic transport rates.^{20–22} If the environment varies, it may take a long time for the confined liquid to reach the new equilibrium condition, since the bulk “reservoir” phase is absent and the molecules and ions must diffuse along the axial direction.²³ At the nanometer scale, the repelling effect of solid surfaces can be pronounced.²⁴ Even if the nanopore surface is wettable and a large driving force is applied, the nanopore size must be much larger than the solvent and solute molecules.^{25,26}

Although, as discussed above, investigations have been intensively carried out in this area, the research is still at its early stage, partly because of the difficulties in direct obser-

vation of ionic behaviors in nanotubes/nanopores and the lack of systematic testing data. In the current research, to investigate the effect of ion size in nanoenvironment, a MCM-41 was synthesized. In a polypropylene bottle, 4 parts of SiO₂, which was provided as a water glass that contained 14% sodium hydroxide and 27% silica, 1 part of cetyltrimethyl ammonium bormide, 1.1 parts of sodium oxide, 0.3 parts of ammonium hydroxide, and 200 parts of de-ionized water were vigorously stirred for 1 h at room temperature.²⁷ By dropping acetic acid into the mixture, the pH value was kept at 10. After addition of 15% sodium chloride (NaCl) solution, the liquid became single phased and clear. It was sealed in an autoclave at 95 °C for 72 h.²⁸ The particles were collected by vacuum filtering, washed by warm water, and dried at elevated temperature. The nanopores were created by combusting the material at 550 °C for 6 h, so that the template was removed. In order to reduce the effective nanopore size and to modify the nanopore surfaces, the MCM-41 particles was vacuum dried at 100 °C for 24 h, and then fully exposed to dry toluene that contained 2.5% chlorotrimethylsilane at 95 °C for 36 h.^{29–31} The byproduct of chlorine acid was removed by repeated rinsing with dry toluene and warm water and vacuum drying at 50 °C.

The nanoporous structure of the surface-treated MCM-41 was characterized by a Micrometrics TriStar-3000 porosimetry analyzer through the Barret-Joyner-Halenda method. The average nanopore diameter was 2.1 nm, with the standard deviation of 0.2 nm. The specific surface area was 620 m²/g. In a stainless steel cylinder, the MCM-41 particles were sealed with de-ionized water or 5M aqueous solution of lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), or cesium chloride (CsCl). A steel piston was intruded into the cylinder at 0.5 mm/min by a type 5582 Instron machine. The cross-sectional area of the piston, A_p , was 286 mm². When the piston load F reached about 25 kN, it was reduced back to zero with the same quasistatic loading rate.³² Figure 1 shows typical sorption curves, where the applied pressure is calculated as F/A_p and the system volume change is taken as $A_p d_p$, with d_p being the displacement of the piston.

With the hydrophobic silyl groups on the inner surfaces of nanopores, the MCM-41 particles cannot be soaked by the liquid phase without the aid of pressure. With the increasing of the applied pressure P , initially the system volume relatively slowly decreases, as shown in Fig. 1. For an electrolyte solution based system, when P reaches about 30 MPa, the ratio between the system volume change and the pressure

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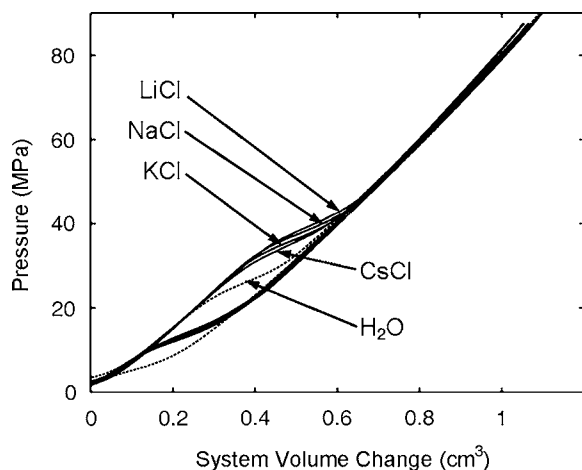


FIG. 1. Typical sorption curves of various electrolyte solutions. The dashed line indicates the behavior of the pure water based system.

largely increases, indicating that liquid begins to enter the nanoporous space. Because the pore size distributes in a certain range, the slope of the infiltration plateau is always positive and the profile reflects the nanopore volume distribution.³³ When P increases to more than 40 MPa, the infiltration plateau ends. When unloading is performed, the sorption curve is quite elastic when P is higher than about 22 MPa. In the pressure range of 9–22 MPa, there is a defiltration plateau in the sorption curve, where the liquid molecules come out of the nanopores. Eventually, when the nanopores are empty, the unloading curve becomes identical to the lower-pressure section of the loading curve. For self-comparison purpose, in this article the infiltration pressure P_{in} and the defiltration pressure P_d are defined as the pressures at the middle points of the infiltration and defiltration plateaus, respectively. The middle point is set as the intersection of the sorption curve and the middle line between the low-pressure and high-pressure linear sections. When the liquid phase is de-ionized water, the sorption curve is similar with that of electrolyte solutions, while P_{in} and P_d are much lower, in agreement with the variation in effective surface tension.^{34–36}

It is clear that the infiltration pressure decreases as the cation size increases (Fig. 2). The ionic radii of cesium, potassium, sodium, and lithium are 1.67, 1.38, 1.02, and 0.76 Å, respectively.³⁷ Compared with P_{in} , the variation in defiltration pressure is less pronounced. For the LiCl solution

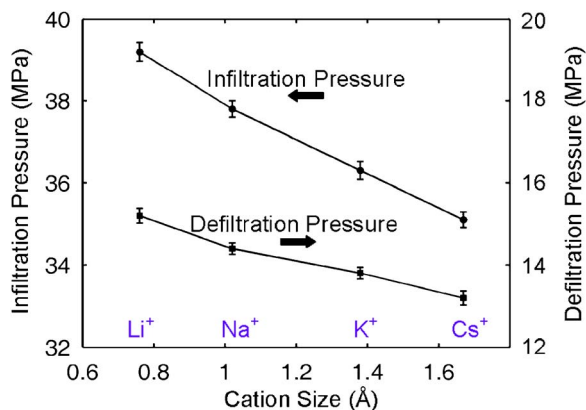


FIG. 2. (Color online) The influence of the cation size on the infiltration and defiltration pressures.

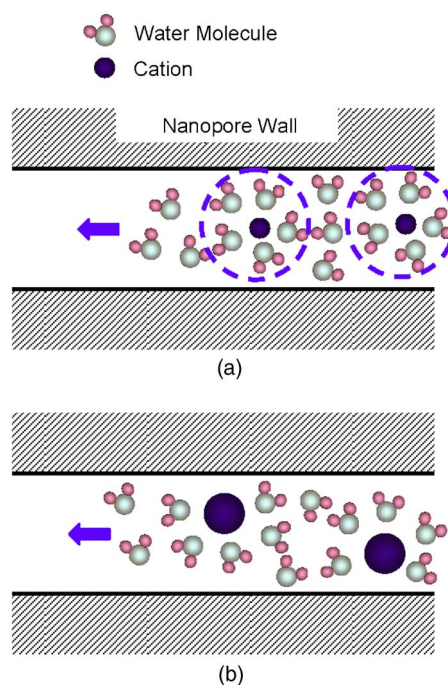


FIG. 3. (Color online) Schematic of the infiltration process of (a) relatively small and (b) relatively large ions in a nanopore. The anions are not shown.

based system, P_d is 15.2 MPa. As the cation size increases, P_d slightly decreases to 13.2 MPa for CsCl. This cation size effect should be associated with the small nanopore diameter. The average nanopore size of the MCM-41 under investigation is 2.1 nm. Without any confinement effect of solid surfaces, in bulk liquid phase a solvated cation is surrounded by a number of water molecules, forming a cluster through strong hydrogen bonds. The motion and the exchange of mass/energy with environment dominate the liquid transport behaviors. If the cation is Li^+ , its size is 0.076 nm. The molecular size of water is about 0.35 nm, and the van der Waals distance is around 0.3 nm.³⁸ Thus, by accounting for the two water molecules on both sides of a cation, the characteristic length scale of the molecular cluster is smaller than the nanopore size. Under this condition, the configuration of the molecular cluster may not be disturbed much by the nanopore walls, as depicted by the dashed circles in Fig. 3(a). If the cation is Cs^+ , since the ion size is quite large (~ 0.17 nm), the characteristic length scale of the molecular cluster is close to 1.5 nm, comparable with the nanopore size. If the van der Waals distance between the water molecules and the nanopore walls are taken into consideration, the nanopore size becomes insufficient for a fully developed solvated ion, as depicted in Fig. 3(b). The testing data indicate that the repelling effect of the nanopore surface to partly solvated large cations is lower than to fully solvated small cations, probably because that the system free energy is reduced when the cations are exposed to the solid surface.

At the equilibrium condition, the driving force and the resistance of infiltration are balanced with each other. The resistance is offered by the nanopore wall, which can be taken as $\gamma(2\pi r)$, where r is the nanopore radius and γ is the effective excess interfacial tension. The driving force of infiltration is caused by the pressure difference outside and inside the nanopores, which can be assessed as $P_{in}(\pi r^2)$. Thus, $\gamma = P_{in}r/2$. This mean-field analysis is consistent with the classic Laplace–Young equation.³⁹ For the solutions of

CsCl, KCl, NaCl, and LiCl, the values of γ are 17.3, 18.0, 18.9, and 19.6 mJ/m², respectively. The difference in system free energies of CsCl and LiCl solutions is at the level of 2 mJ/m².

The confined liquid molecules do not immediately diffuse out of the nanopores when $P(\pi r^2)$ is smaller than $\gamma(2\pi r)$. The pressure must be overdecreased to nearly 20 MPa below P_{in} before defiltration begins, which may be caused by the additional resistance to molecular motion among tetrahedral sites of silyl groups. The liquid molecules and ions must overcome the energy barrier through thermal motion and therefore when temperature increases defiltration becomes easier.^{40,41} During defiltration, since the most dominant factor is the relatively irregular nanopore surface features where a fully developed molecular cluster can be disrupted, the effect of cation size is suppressed. As a result, when the cation changes from Li⁺ to Cs⁺, the effective interfacial tension decreases from 7.6 to 6.6 mJ/m² by only 1 mJ/m², about one half of that in infiltration.

In summary, through a pressure-induced infiltration experiment on a surface-treated MCM-41, it is measured that the infiltration pressure decreases as the cation size increases. When the cation changes from lithium to cesium, the infiltration pressure and the effective interfacial tension are reduced by nearly 10%. The cation size effect is less pronounced during defiltration. These phenomena can be attributed to the confinement effect of nanopore surfaces that if the cation size is relatively large the solvated structure cannot be fully developed.

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