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Influence of anions on liquid infiltration and defiltration in a zeolite Y

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In pure water a hydrothermally treated zeolite Y is hydrophilic, while with the addition of an electrolyte it can no longer be soaked up spontaneously. The effective degree of hydrophobicity increases with the ion concentration, which is reflected by the increase in infiltration pressure. The pressure-induced infiltration behavior is not only determined by the cations, but also highly dependent on the anion species. This phenomenon can be attributed to the confinement effect of nanopore walls.

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I. INTRODUCTION

Understanding the behaviors of liquids in nanoporous materials has immense importance to a wide variety of scientific and engineering fields, including micro- and nanotransportation [1], phase transformation in heterogeneous liquids [2], surface processing in nanoenvironment [3], synthesis of nanostructured materials [4–6], advanced energy conversion and storage systems [7–9], etc. In the past, the study in this area was focused on spontaneous surface diffusion and reactions of guest molecules in host nanotubes or nanopores [10]. For instance, as a nanoporous material is immersed in a suspension of colloidal particles, it may selectively adsorb the species that are wettable to its inner surface, and hence the mixture is separated or purified [11]. As the guest molecules infiltrate into the nanopores, the system free energy must decrease; that is, the effective guest-host interfacial tension should be smaller than the summation of their surface tensions; otherwise, the guest infiltration is energetically unfavorable. Since the surface and interface tensions can be affected by the temperature and electric potential, a few field-responsive systems have been developed so as to control the guest-host interactions under optimum conditions [12,13].

Recently, use of a mechanical method to control infiltration and defiltration has been an active area of research [14–16]. In such a system, the nanopore surface can be nonwettable to the liquid phase, so that under atmosphere pressure the nanopores remain empty. As a quasistatic pressure is applied, the liquid phase can be compressed into the nanopores when the capillary effect is overcome. According to experimental investigation, under this condition multiple guest species, either wetting or nonwetting to the nanopore surface, tend to enter the host simultaneously, while the nanopore size must be sufficiently large and the structure of the confined liquid may be highly nonuniform [17–19]. In some of the systems [20,21], once the guest molecules enter the host, they are "locked" inside and do not come out even after the external pressure is released. Due to the large specific nanopore surface areas, these systems are typically of high energy absorption efficiency, providing a promising mechanism for the development of liquid dampers and protection layers. In some other systems [22], the guest molecules can be separated from the host once the external pressure is relatively low, and these systems essentially become liquid springs. Since the infiltration condition is dependent on temperature and electric potential, they can be employed for high-energy-density and large-displacement actuation [12,13].

In addition to modifying nanopore size and surface properties, another important way to adjust system performance is to control the liquid composition. In a previous investigation, it was observed that as an electrolyte was added in the liquid phase, the infiltration pressure can increase, which is related to the variation in surface tension [23]. In conventional electrophysics theory, it is often assumed that the solid-liquid interfacial tension is dominated by cations [24,25]. When an electrolyte dissolves in water, water molecules tend to form clusters surrounding cations, so that they are solvated. The anions can be unsolvated. As a solid is exposed to an electrolyte solution, immediately next to the solid surface there is a thin liquid layer of high density of solvated ions, which induce countercharges in the solid phase. The excess cations and the countercharges lead to a ζ potential normal to the solid-liquid interface. The influence of anions is secondary. These effects are captured by the classic Good–Van Oss–Chaudhury (GVC) equation [26].

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2[\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + \sqrt{\gamma_1^{+}\gamma_2^{-}} + \sqrt{\gamma_1^{-}\gamma_2^{+}}], \qquad (1)$$

where γ_{12} is the interfacial tension; the subscripts "1" and "2" refer to materials "1" and "2" across the interface, respectively; the superscripts of "LW," "+," and "−" refer to Lifshitz–van der Waals, acidic, and basic components of surface tension, respectively. More detailed discussions of interfacial tension have been given elsewhere [27–29]. In the current study, we experimentally investigate the anion effect on the effective solid-liquid interfacial tension in the nanopores of a zeolite Y. The testing data show that in nanopores the effect of anions is comparable with that of cations, which may be attributed to the unique ion structure in a nanoenvironment.

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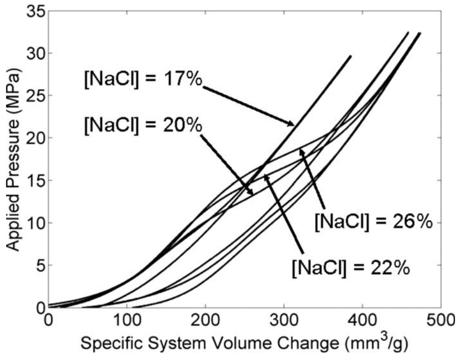

FIG. 1. Sorption isotherm curves of sodium-chloride-based systems.

II. EXPERIMENT

The testing system was produced by suspending 0.5 g of Zeolyst CBV-901 zeolite Y in 7.5 g of an aqueous solution of sodium salts. The silica/alumina ratio of the zeolite Y was 80. It was characterized in a gas absorption analysis by using a Micromeritics ASAP-2000 system. The effective nanopore size was 0.74 nm, the specific nanopore surface area was 638 m^2/g, and the specific nanopore volume was 280 mm^3/g. The defect density at the nanopore surface was modified through a 24-h hydrothermal treatment. About 2 g of zeolite was placed in a quartz tube furnace, with the temperature maintained at 650 °C. Both ends of the tube were open to air. At one end, warm water was pumped into the tube at a constant rate of 0.5 ml/s. As water approached the heating zone, it rapidly evaporated and the steam passed through the zeolite to the other end of the tube. During the treatment, the negatively charged hydroxyl groups were deactivated, so that the nanopore surfaces were nearly perfect [30].

The zeolite suspension was placed in a steel cylinder. Its compressibility was analyzed by driving a steel piston into the cylinder in a type 5583 Instron machine. The piston moved at a constant rate of 1 mm/min. The gap between the piston and the cylinder was sealed by a reinforced polyurethane o-ring. As the zeolite suspension was compressed, the inner pressure increased continuously. After the infiltration was completed, the piston was moved out at the same speed. The liquid phase was an aqueous solution of sodium chloride (NaCl) or a solution of sodium chloride and sodium bromide (NaBr) mixture. In the NaCl solution, the concentration of NaCl, [NaCl], varied in the range of 0–26%. In the NaCl and NaBr solution, [NaCl] was kept at 13% and the NaBr concentration, [NaBr], varied in the range from 10% to 64%. Sodium bromide was employed as the second electrolyte because its solubility is much higher than that of NaCl and the ion size of bromine is larger than that of sodium ions. Typical infiltration curves are shown in Figs. 1 and 2. Additional experiments were performed on systems based on saturated sodium chloride solution ([NaCl]=26%) at different temperatures, with the temperature being controlled by a water bath. The measurement results of infiltration pressure are shown in Fig. 3.

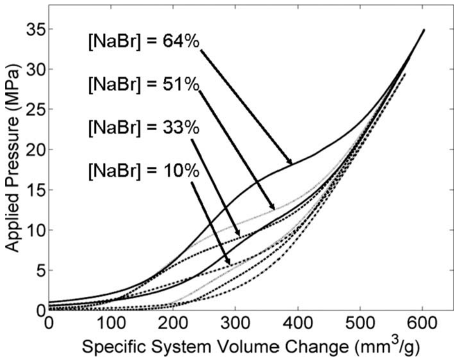

FIG. 2. Sorption isotherm curves of sodium-bromide-modified systems. All the systems contained 13% of sodium chloride.

III. RESULTS AND DISCUSSION

Since the silica/alumina ratio is high, the zeolite Y is hydrophobic in the gas-absorption test (i.e., an external pressure must be applied to force the water vapor molecules into the nanopores). However, in liquid water the material is effectively hydrophilic. Once it is immersed in water, it would be soaked up spontaneously. Under this condition, the loading-unloading curve is quite linear, since the nanopores have been occupied and no further infiltration can take place. Similar behaviors are observed in all of the systems with [NaCl] lower than 17%. The difference in effective degrees of hydrophobicity of nanopore surfaces in water vapor and in liquid water may be related to the entrapped gas molecules [31] as well as the liquid-liquid interaction [32], the details of which are still under investigation.

When [NaCl] reaches 20%, as shown in Fig. 1, a clear infiltration plateau shows up in the sorption isotherm curve in the pressure range of 7–17 MPa. If the external pressure is lower than this range, the system response is quite linear, indicating that the liquid phase does not enter the nanopores. When the pressure is above this range, the nanopores have been filled and thus the pressure-induced infiltration ceases. Within this pressure range, the liquid phase is forced into the nanoporous environment, leading to a rapid decrease in system volume. The total infiltration volume is arround

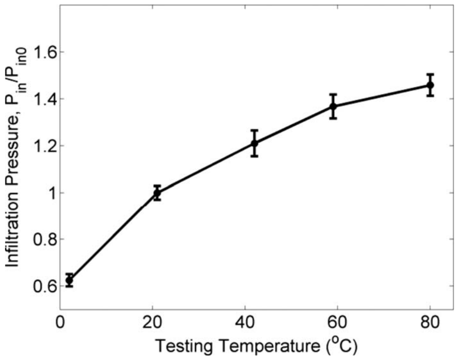

FIG. 3. Thermal effect on infiltration pressure of saturated sodium-chloride-solution based systems, where $P_{\mathrm{in}0}$ is the infiltration pressure at room temperature.

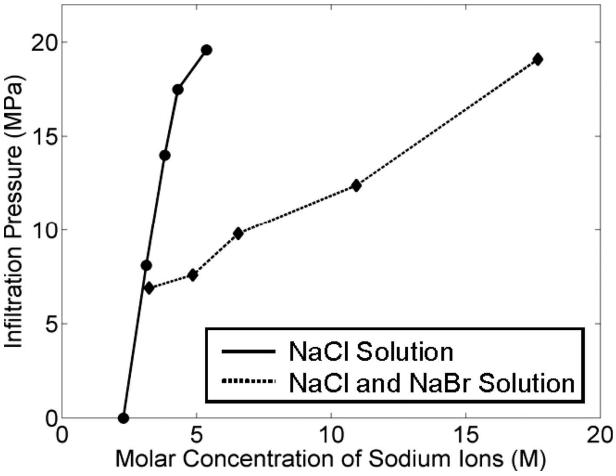

FIG. 4. The infiltration pressure as a function of the molar concentration of sodium cations.

200 mm^3/g, slightly smaller than the specific pore volume measured in the gas-absorption analysis, probably due to the van der Waals distance between the confined liquid molecules and the nanopore surface. Clearly, with the addition of NaCl, the zeolite Y becomes nonwettable to the liquid phase, which is in agreement with the classic surface theory that the surface tension of an electrolyte solution increases with the electrolyte concentration [33]. That is, as more cations are solvated in the liquid phase, at a solid-liquid interface the surface ion density increases, and thus the solid-liquid interfacial tension tends to be higher. In the zeolite system under investigation, as [NaCl] is increased form 17% to 20%, the excess interfacial tension varies from negative to positive, causing an abrupt change in the sorption isotherm profile. Note that, while the nanoporous structure of zeolite Y is highly regular, the slope of the infiltration plateau is significant, indicating that the nanopore walls offer a considerable resistance to liquid motion, which may be associated with the energy barrier among tetrahedral sites [34]. The details of the solid-liquid interaction in nanopores are still under investigation. By using the classic Laplace-Young equation [35], the effective excess interfacial tension can be assessed as $\Delta\gamma = P_{in} r/2 = 2.4\ \mathrm{mJ/m^2}$ when [NaCl]=20%, where $r \sim 0.37$ nm is the nanopore radius and $P_{in} \sim 13$ MPa is the infiltration pressure. For self-comparison purposes, the value of P_{in} is taken as the pressure at the middle point of the infiltration plateau.

As the NaCl concentration increases, P_{in} increases rapidly. When [NaCl] reaches 26%, the infiltration pressure rises to about 20 MPa by nearly 100%, as shown by the solid line in Fig. 4. Clearly, as more ions are added in the liquid phase, the repelling effect of the nanopore walls becomes more pronounced. The thermal effect on infiltration pressure shown in Fig. 3 indicates that the effective excess interfacial tension is also quite sensitive to temperature, compatible with the previous experimental results on a thermally controllable smart liquid [36].

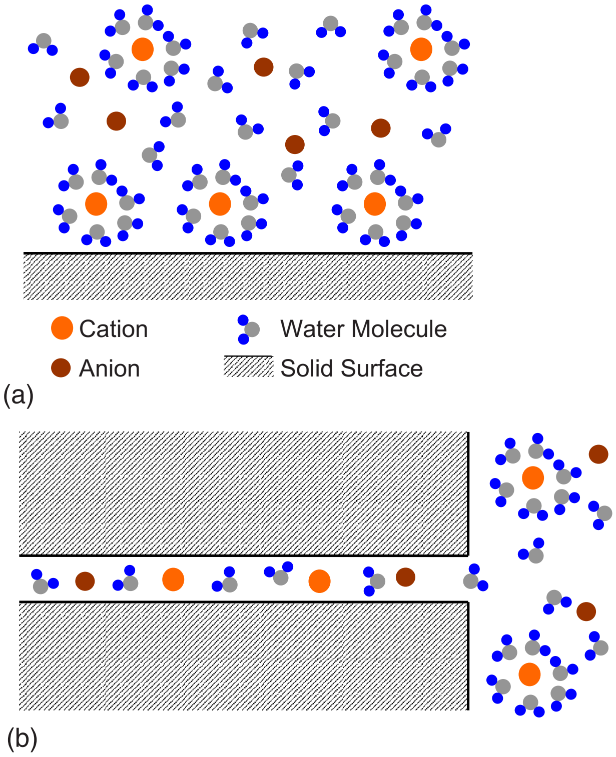

FIG. 5. (Color online) Schematics of liquid-solid interfaces (a) at a large solid surface and (b) in a nanopore.

If in a nanopore $\Delta\gamma$ were dominated by the cations and the effects of anions were secondary, when another sodium salt of a higher solubility, such as NaBr, is added, as the concentration of Na^+ becomes higher, the infiltration pressure should keep rising, until it saturates. However, the testing data of NaCl/NaBr-mixture-based systems (Fig. 2) show a contradictory trend. As [NaBr]=10%, while the concentration of Na^+ is higher than that of the NaCl solution of [NaCl]=20%, the infiltration plateau is much lower. The value of P_{in} rises as [NaBr] becomes larger, but P_{in} exceeds 7 MPa only when [NaBr]=33%, where the sodium cation concentration is nearly 50% higher than that in the neat NaCl solution of [NaCl]=20%. Eventually, when [NaBr] reaches 64%, the infiltration pressure is about 18 MPa, still lower than that of the system based on saturated neat NaCl solution (also see Fig. 4). Note that the infiltration volumes of NaCl-based and NaCl/NaBr-based systems are about the same, as it should be, since the nanoporous structure is independent of the liquid composition.

The experimental observation must be attributed to the unique ion structure at the solid-liquid interfaces inside nanopores. As depicted in Fig. 5(a), at a large solid-liquid interface the anion density in the double layer, which is often referred to as the outer Helmholtz plane (OHP), is quite low. Its concentration in the bulk phase has only a secondary effect on the interfacial potential and the interfacial tension. In a nanopore, especially when the nanopore size is comparable with the Debye length [Fig. 5(b)], the ordinary double-layer structure breaks down. Not only may the water molecular cluster surrounding a solvated ion not be fully developed, but also anions can enter the nanopore and be in direct contact with the solid surface [37]. Thus, the anion species can have a considerable influence on the effective solid-liquid interfacial tension. The van der Waals size of a bromine ion is 0.37 nm and that of a chlorine ion is 0.34 nm. In a nanopore the solid-ion distance of bromine tends to be smaller, which may lead to a smaller effective interfacial tension, the details of which need to be examined through molecular dynamics simulations.

IV. CONCLUSIONS

In summary, in a nanopore, anions have a pronounced influence on the effective solid-liquid interfacial tension, which should be attributed to the unique ion structure in a nanoenvironment. The free energy of sodium-bromide-based systems is much lower than that of sodium-chloride-based systems. At the saturation level of sodium salts, the effective interfacial tension of the latter is higher, even though the solubility of the former is much larger.

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