

Infiltration and defiltration of an electrolyte solution in nanopores

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The motion of confined liquid in a nanoporous silica is controlled by external loadings and modified using calcium chloride. The addition of calcium chloride results in a moderate increase in infiltration pressure and an order-of-magnitude increase in system recoverability, which, especially for the smallest nanopores, is contradictory to the predictions of classic interface/surface theories. This should be attributed to the confinement effect of nanopore walls. © 2006 American Institute of Physics. [DOI: 10.1063/1.2222042]

I. INTRODUCTION

Controlling motions of confined liquids in nanoenvironments has been an active research area for more than one decade, which has led to significant progresses in selective absorption and adsorption, intelligent catalysis, etc.¹⁻³ Recently, the technique of pressure induced infiltration, i.e., triggering infiltration or defiltration by directly using an external pressure, drew increasing attention.⁴⁻⁸ In a system containing nanoporous particles immersed in a nonwetting liquid, for example, the liquid can be forced into the nanopores when the pressure is sufficiently high, while the defiltration can be difficult as the pressure is lowered, causing the hysteresis of sorption isotherm. Because of the ultrahigh surface areas of nanoporous materials, the efficiency of the energy dissipation associated with the infiltration-defiltration process is much higher than that of many conventional energy absorption materials such as reinforced polymers and metal/composite foams and, therefore, such systems have great potential in developing advanced protection or damping structures.

However, although the exploratory research has shown encouraging results, currently the mechanisms and processes that govern the system performance are still inadequately understood. For instance, in large-scale systems it is well known that using chemical admixtures would lead to considerable variations in system properties, while the basic testing data of solid-liquid interactions in nanopores are lacking. In this article, we report on the experimental observations of behaviors of calcium chloride solutions in a nanoporous silica. The addition of calcium chloride can increase the infiltration pressure and largely promote the defiltration. For the nanopores where the pore sizes are comparable with the interface double layer thickness, the testing results cannot be explained by conventional interface/surface theories.

II. EXPERIMENT

The nanoporous material investigated in the current study was a hydrophobic Fluka 100 C₈ reversed phase silica gel of the average pore size of 7.8 nm and the standard deviation of 2.4 nm.⁹ The particle size was in the range of 15–35 μm. The specific pore volume was 0.55 cm³/g. To produce the testing sample, 0.5 g of the silica gel and 7 g of aqueous solution of Sigma calcium chloride hexahydrate were mixed and sealed in a steel cylinder using a steel piston with gasket. The calcium chloride hexahydrate content was in the range of 0 to 40 wt. %. Since the liquid was nonwetting to the silica gel, it could not enter the nanopores at atmosphere pressure, as depicted in Fig. 1.

Using a type 5569 Instron machine, the piston was compressed into the cylinder and when the pressure was high enough to overcome the capillary effect, the aqueous solution was compressed into the nanoporous silica and filled the porous space. Figure 2 shows typical sorption isotherm curves. The error bars were calculated based on the data scatter and the measurement tolerances of the machines. As the pressure reached about 50 MPa, the piston was moved back. Throughout the entire process, the piston speed was maintained at 0.5 mm/min, so that the applied loading was quasi-static. The loading-unloading process was repeated for 4 to 5 times for each sample. However, while the sorption

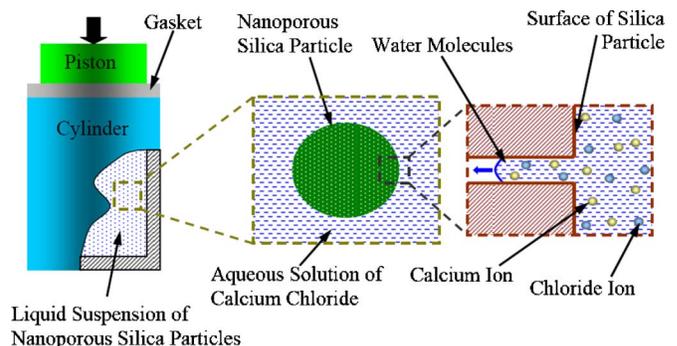


FIG. 1. (Color online) A schematic diagram of the calcium chloride modified nanoporous energy absorption system.

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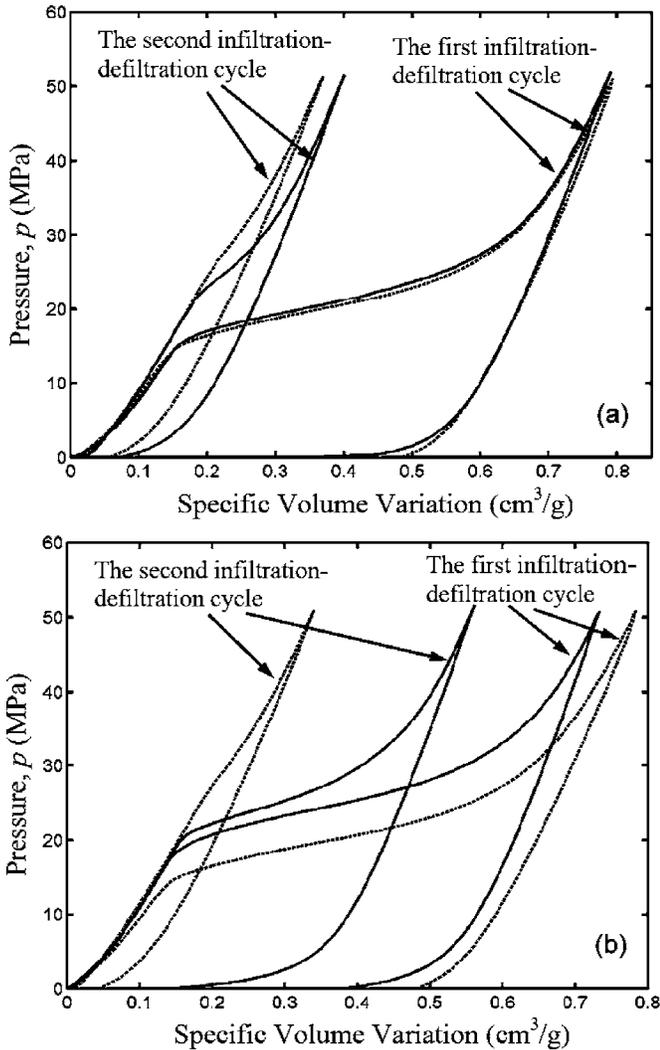


FIG. 2. Typical sorption isotherm curves of the system based on (a) 10 wt. % and (b) 30 wt. % aqueous solutions of calcium chloride. The dashed lines indicate the behavior of the pure water based system (the reference system).

isotherms were quite different in the first two cycles, from the third cycle the system behavior converged. Therefore, in the following discussion we will focus on the first two infiltration-defiltration loops.

III. RESULTS AND DISCUSSION

The dashed lines in Fig. 2 are the sorption isotherm curves of the reference system where the calcium chloride concentration is zero. Initially, since the pores are empty, the pressure induced infiltration begins as the pressure is raised to about 17 MPa. Correspondingly, the slope of the sorption isotherm curve decreases significantly, forming the infiltration plateau. If the pore size were uniform, the plateau would be flat. In the current system, however, the slope is positive due to the pore size distribution. The low-pressure section of the infiltration plateau corresponds to the relatively large nanopores, and the high-pressure section reflects the infiltration in relatively small nanopores. As the pressure increases to 27 MPa, most of the porous space is filled and the system compressibility decreases rapidly. Upon removal of the ex-

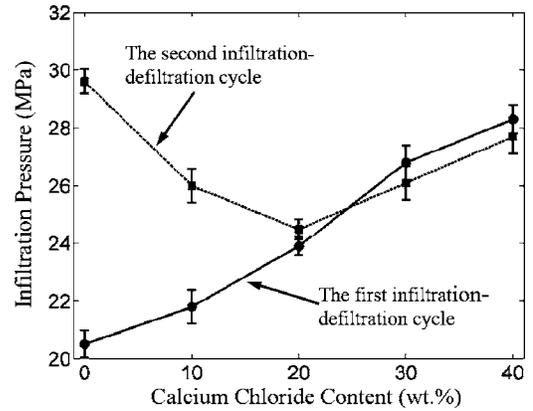


FIG. 3. The infiltration pressure as a function of the calcium chloride concentration.

ternal pressure, most of the confined liquid does not defiltrate, and consequently the sorption isotherm is highly hysteretic, resulting in the superior energy absorption characteristic. The energy absorption efficiency, E^* , can be measured by the area enclosed by the loading-unloading cycle, which is 14 J/g for the reference system. Because of the “nonoutflow,” most of the nanopores are no longer available for further energy absorption, and the accessible pore volume is greatly reduced from the second cycle. Such a system is good only for one-time use.

Through Fig. 2(a), it can be seen that the system recoverability can be improved by about 100% by adding 10 wt. % calcium chloride; that is, the calcium and/or chloride ions can promote defiltration such that more confined liquid can come out of the nanopores as the pressure is lowered. The influence of the calcium chloride on the infiltration behavior, on the other hand, is somewhat negligible: The specific volume variation and the infiltration pressure of the first cycle are about the same as that of the reference system.

As the calcium chloride concentration, c , increases, the infiltration pressure, which is defined as the pressure at the middle point of the infiltration plateau, rises considerably; and the accessible pore volume, which is defined as the width of the infiltration plateau, decreases slightly [see Figs. 2(b) and 3]. Apparently, the addition of calcium chloride makes the infiltration more difficult, and in the smallest pores the infiltration becomes impossible even under a high pressure of around 50 MPa. This is compatible with the literature data that the interface tension between silica and calcium chloride solution increases with c .¹⁰⁻¹²

The infiltration in the second loading cycle, on the other hand, is significantly promoted. The accessible pore volume of the second cycle is larger than that of the reference system by nearly an order of magnitude, indicating clearly that the “nonoutflow” associated with the unloading has been suppressed. There are two possible reasons: (a) with the addition of calcium chloride, the increase in infiltration pressure indicates that the liquid becomes more nonwetting and, therefore, the nanoenvironment is more energetically unfavorable, leading to a higher driving force of defiltration; and (b) since the gas solubility decreases as the calcium chloride concentration increases,^{13,14} the nucleation and growth of gas

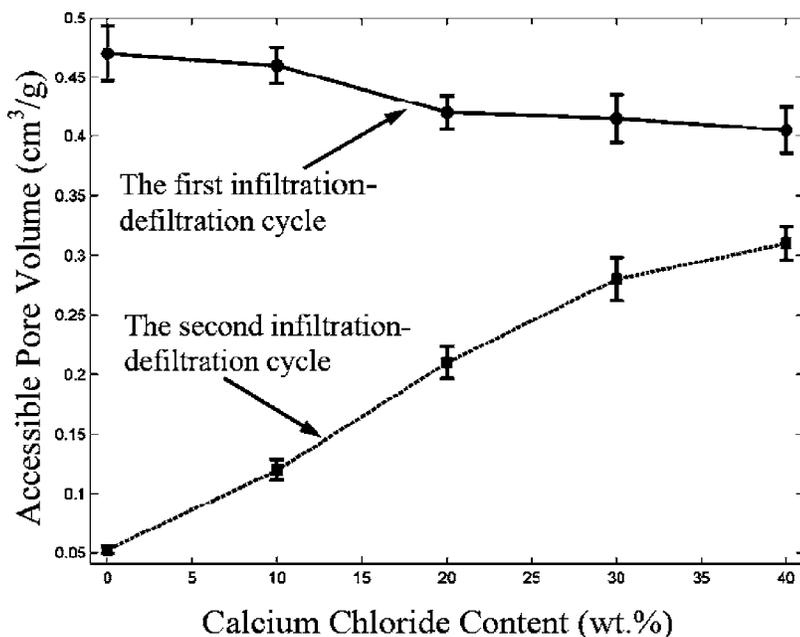


FIG. 4. The accessible pore volume as a function of the calcium chloride concentration.

nanophases in the nanopores are easier, which causes the increase in the ability of liquid desorption.^{15,16} The detailed mechanisms and processes are still under investigation.

When the calcium chloride concentration is relatively low, the infiltration pressure of the second loading cycle is much higher than that of the first one. In fact, the sorption isotherm curve of the second cycle resembles the high-pressure portion of the first cycle, suggesting that the confined liquid in the smallest nanopores defiltrates, while that in larger nanopores remains in the nanoenvironment, probably because that in smaller nanopores the energy barrier for the formation of gas nanophases is lower.¹⁷ This, together with the fact that the width of infiltration plateau increases with c , explains why the infiltration pressure of the second cycle decreases as the calcium chloride concentration rises.

It is remarkable that, as the calcium chloride concentration further increases, the characteristic discussed above is lost. Figure 3 shows that as c is higher than about 20%, the infiltration pressures of the first and the second loading cycles are about the same; that is, the average size of the nanopores where the infiltration and defiltration can occur repeatedly is about 7.8 nm, the same as the mean value of the nanoporous particles. This must be a result of the “non-outflow” in both of the largest and the smallest nanopores. The “irregular” defiltration behavior may be related to the confinement effect of pore walls. As the pore size is comparable with or even smaller than the thickness of the interface double layer, which is about 0.5–2 nm,^{18,19} the ions cannot be solvated and the thermal disarrays do not exist. Hence, the molecular/ionic configurations are fundamentally different from that at macroscopic solid-liquid interfaces, and the conventional interface/surface theories are no longer valid.

Figure 4 shows the accessible pore volumes, i.e., the widths of the infiltration plateaus, as functions of the calcium chloride concentration. As discussed above, the accessible pore volume of the first loading cycle decreases slightly as c is increased from 0 to 40 wt. %, which is consistent with the fact that the infiltration pressure rises. This effect is some-

what secondary compared with the increase in the accessible pore volume of the second loading cycle, V_2 . When c is relatively low, V_2 increases nearly linearly from about 0.05 cm³/g to about 0.25 cm³/g by almost 500% as c changes from 0 to 30 wt. %. With a higher c , the V_2 - c relation tends to converge. Note that, at a macroscopic interface, the interfacial energy is highly nonlinear to the admixture concentration when c is above 5 wt. %.^{10,11} Again, the inconsistency of the testing results of the nanoporous silica and the literature data should be attributed to the breakdown of classic electrochemical interface structures.

Figure 5 shows the defiltration pressure, which is defined as the pressure at the point in the unloading section of the first infiltration-defiltration cycle at which the slope of sorption isotherm curve is reduced by 50% from that of the linear part. As c increases from 0 to 10 wt. %, the defiltration pressure rises only slightly. However, as shown in Fig. 4, the pore volume associated with the defiltration is doubled. This is because that V_2 is quite small when c is relatively low and, therefore, even a small change in defiltration pressure can cause a large variation in defiltration volume. As V_2 increases

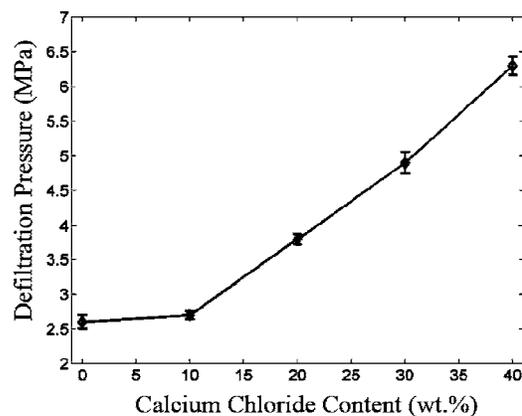


FIG. 5. The defiltration pressure as a function of the calcium chloride concentration.

with c , while the defiltration pressure increases almost linearly at a much higher rate, the sensitivity of V_2 on c is about constant, and eventually it decreases as c approaches the saturation level.

IV. CONCLUDING REMARKS

The pressure induced infiltration behaviors of aqueous solutions of calcium chloride in hydrophobic nanoporous silica particles are investigated experimentally. The addition of calcium chloride can lead to a nearly 30% change in infiltration pressure, and, more importantly, a more than 600% increase in system recoverability. Thus, compared with the pure water based system, the calcium chloride modified nanoporous system has a higher energy absorption efficiency and can work continuously under cyclic loadings, having great potential in developing high-performance protective/damping systems. The “irregular” defiltration behaviors indicate that the conventional interface/surface theories cannot be directly applied for confining nanoenvironments.

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