Effects of addition of ethanol on the infiltration pressure of a mesoporous silica

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The energy absorption behaviors of mesoporous silica particles immersed in aqueous solutions of ethanol were investigated. Addition of ethanol could significantly lower the infiltration pressure, which has great potential in developing selective protection systems. The ethanol concentration of the confined liquid inside the nanopores was higher than outside.

I. INTRODUCTION

Developing nanoporous technologies has been an active research area for many years.[1] A number of techniques have been established to synthesize microporous, mesoporous, and macroporous materials with various pore sizes, specific areas, surface properties, and pore structures. They have been widely applied in catalysis, selective absorption, and purification processes.[2,3]

Recently, a novel application of nanoporous materials in advanced protection devices has drawn increased attention.[4–7] When hydrophobic nanoporous materials, e.g., silicalites or nanoporous silicas, are immersed in water, at the atmosphere pressure p_{at}, the liquid phase cannot enter the nanopores due to the capillary effect. As the pressure increases to a critical value p_{in}, the pressure-induced infiltration can occur. As the pressure is reduced back to p_{at}, for reasons that are still under investigation, the confined liquid remains in the nominally energetically unfavorable nanopores and, therefore, the excess solid–liquid interface energy cannot be released. Since the specific areas of the nanoporous materials are usually in the range of 100–1000 m^2/g, the effectiveness of energy absorption of such systems can be much higher than that of conventional energy-absorbing materials such as reinforced polymers and shape memory alloys.[8,9] This technique has immediate applicability in the development of "liquid armors," programmable catalysis, and other areas.[10,11]

One of the vital factors dominating the system performance is the infiltration pressure p_{in}. In an impact test, only the energy carried by the portion of incident pulse with the pressure higher than p_{in} can be dissipated by the nanoporous system; that is, the energy absorption is selective. This characteristic is beneficial to minimizing the weights and sizes of the protection systems that can filter out the "peaks" of stress waves. However, currently, the researches in this area are limited to systems based on pure water, in which p_{in} is primarily determined by the surface-treatment techniques and the pore sizes. To adjust the infiltration pressure in a broader range, in the current study, we investigated the effects of addition of chemical admixtures.

II. EXPERIMENTAL

A. Choice of materials

The admixture should have the following characteristics: (i) the molecules are much smaller than the pore size such that the "repelling" effect is negligible;[12] (ii) the molecules are capable to form strong bonds with water; and (iii) it is energetically favorable for the admixture molecules to enter the nanopores. Based on these criteria, ethanol is an attractive candidate.

Ethanol is a material commonly used in industry. The chemical formula is C_2H_5OH, with an atomic weight of 46.07 amu.[13] At p_{at}, it is in liquid form in the temperature range of –114.3 to 78.4 °C, and at room temperature the weight density is 789 kg/m^3.[13] The molecular size of ethanol is comparable to that of water. It is easily soluble in water, and it wets silica even after surface treatments.[14]

There are two possible results when the mesoporous particles are immersed in an aqueous solution of ethanol. The first is selective absorption; that is, only ethanol molecules can enter the nanopores. Under this condition, ethanol would fail to promote water infiltration. The second possibility is the desired mixed infiltration; i.e., the ethonal and water molecules enter the nanopores simultaneously. Due to the confinement effect of pore walls, it is not clear whether the composition of the confined liquid inside the nanopores is the same as that outside.

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The nanoporous material used in the current study is end-capped Fluka 100 C_8 reversed phase mesoporous particles, with the particle size in the range of 15–35 μm, the surface coverage of hydrophobic functional groups around 10–12%, and an average pore size of 7.8 nm. The standard deviation of pore-size distribution was 2.4 nm. According to the results of the Berrett-Joyner-Halenda (BJH) testing performed at The Quantachrome Instruments (Boynton Beach, FL), the specific area and the pore volume were 287 m^2/g and 0.55 cm^3/g, respectively.

B. Experimental procedure

The mesoporous silica particles were immersed in a mixture of Pharmco (Brookfield, CT) 95% ethanol and distilled water and sealed in a 304 stainless steel container, as depicted in Fig. 1. The volume fraction of ethanol in the liquid phase c, was in the range of 0% to about 50%. The experiments were carried out using a type 5569 Instron machine (Canton, MA) in displacement control mode. The crosshead speed was set to 1 mm/min. As the load P increased, the piston was pressed into the container, and at the critical pressure p_{in}, the pressure induced infiltration occurred. As the load was reduced back to zero, the "non-outflow" of the confined liquid caused pronounced hysteresis of the absorption isotherm, as shown in Fig. 2. The pressure was calculated as $p = P/A_0$, where $A_0 = 286$ mm^2 is the cross-sectional area of the container; and the specific volume change was defined as the ratio of the volume variation to the weight of silica particles.

A substantial set of systems with different ethanol contents were tested. It was found that when c was higher than about 50%, infiltration could occur spontaneously at atmosphere pressure. When c was relatively low, the infiltration pressure was positive. The results of p_{in} are shown in Fig. 3 as a function of c.

After the loading–unloading infiltration test, the liquid was filtered by an AMTS 40-60 filter (En Harod Ihud, Israel) so as to remove the silica particles. Then, its composition was analyzed by a Shimadzu (Columbia, MD) GC-17A gas chromatography analyzer equipped with an Rtx-5 flame ionization detector, and the results are given in Fig. 4. The injection volume was 0.1 μl; the

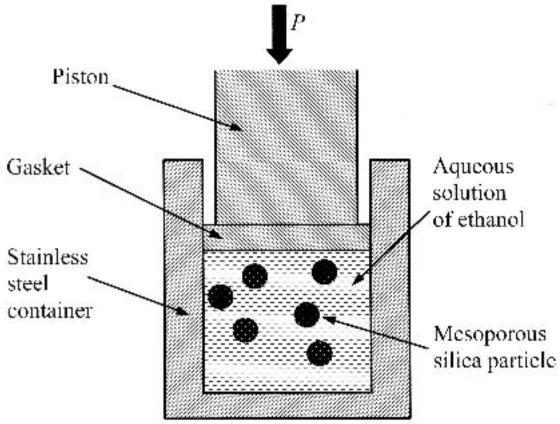

FIG. 1. Schematic diagram of the nanoporous energy absorption system.

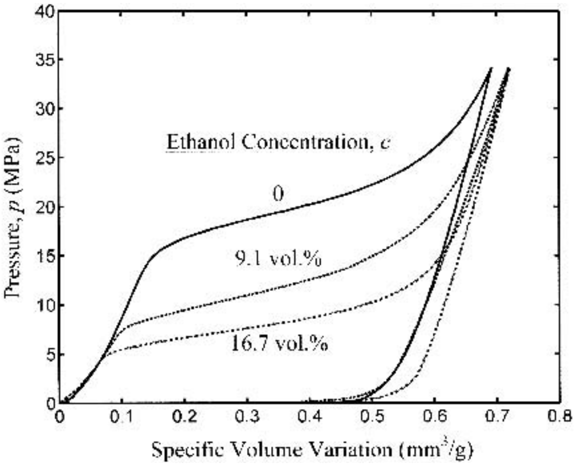

FIG. 2. Sorption isotherm curves.

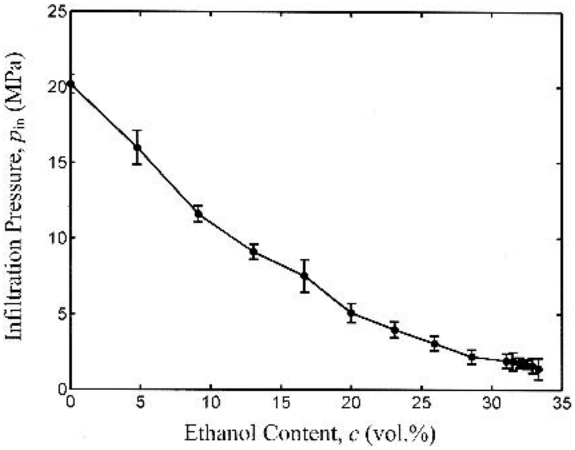

FIG. 3. Infiltration pressure as a function of the ethanol concentration.

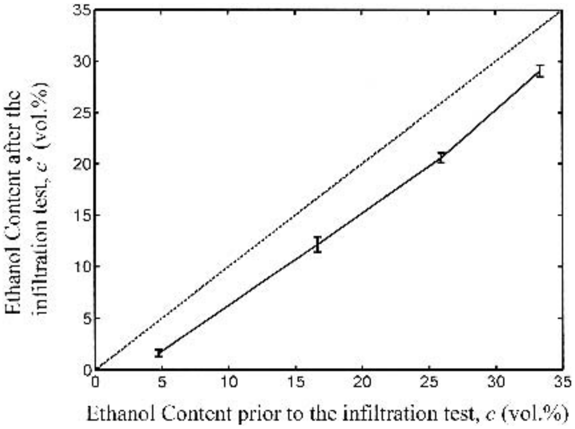

FIG. 4. Variation in ethanol content outside the nanoporous particles after the infiltration tests.

temperatures of the column, the injection part, and the detector were 110, 220, and 300 °C, respectively. The carrier gas was nitrogen and the flow rate was 1.4 ml/min.

III. RESULTS AND DISCUSSION

The plateaus in the isotherm curves in Fig. 2 are associated with the pressure induced infiltration.[5–7,15] For the system based on pure water ($c = 0$), when the pressure is low, the system response is quite linear, which is dominated by the effective bulk modulus of the porous particle–liquid system K_0. As the pressure rises to about 17 MPa, the water starts to enter the relatively large pores, and as a result, the compressibility of the system increases significantly. With the increase in pressure, the smaller pores are involved in the infiltration process. When p reaches about 30 MPa, most of the porous space is filled and the effective bulk modulus converges to K_0. For the sake of simplicity, in the following discussion, p_{in} is taken as the pressure at the middle point of the plateau, which is defined as the region between the two points where the slopes of the isotherm curve are reduced by 50% from K_0.

As the ethanol content increases, it can be seen that there is a consistent decrease in infiltration pressure (see Fig. 3). The width of the plateau region, however, is quite insensitive to the variation in c. The specific volume change associated with the infiltration is around 0.52 cm^3/g, close to the BJH testing result of the specific pore volume, indicating that the addition of ethanol does not affect the accessibility of pore surfaces.

According to Fig. 3, the relationship between the infiltration pressure and the ethanol content is quite nonlinear, which is different from the results of conventional interface theories. Since ethanol molecules are neutral, at an infinitely large interface, the acid and base components of the Lewis acid–base interaction are nearly constant,[15] and therefore, the degree of nonlinearity of concentration dependence of the interface energy is low. The nonlinear phenomenon observed in the nanoporous system demonstrates that the heterogeneous structure of the confined liquid in nanopores must be taken into consideration, as will be discussed shortly.

Figure 4 shows that, after the infiltration test, the ethanol content outside the nanoporous particles is decreased. Accordingly, the ethanol concentration of the confined liquid must be higher; that is, the infiltration of the aqueous solution of ethanol can be considered a combination of selective absorption and mixed absorption. The difference between the ethanol contents before and after the infiltration tests, c and c^*, is around 4.3%. This value is quite insensitive to c. In a liquid filled mesopore, according to the nuclear magnetic resonance (NMR) experiments, there is an interface layer at the solid–liquid interface. In the interface layer, the surface diffusion is dominant, while in the interior the single-file diffusion model can describe the molecular behaviors quite well.[16] The thickness of the interface layer d is in the range of 0.5–2 nm. The structure of the liquid in the interior is similar to that of bulk phase, while the properties of the interface layer are strongly dependent of the solid–liquid interaction.

The systems tested in the current study consisted of 0.5 g nanoporous silica particles, and the total pore volume V_p was 0.27 cm^3. The liquid volume V_l was 2.90 cm^3. Thus, according to mass conservation, the 4.3% difference between c and c^* should be balanced by the increase in ethanol concentration of confined liquid by 42%, which, since the ethanol content variation was insensitive to c, must be related to the heterogeneous interface layer structure. Assuming that the liquid composition in the interior of a nanopore is the same as c^*, the ethanol concentration in the interface layer, c_i, can be assessed as

$$\left(1 + \frac{8.8r^2}{2rd - d^2}\right) \cdot x \quad ,$$

where r is the pore radius and $x = 4.3\%$ is the difference between c and c^*. If r is taken as 7.8 nm, when $d \approx 1.5$ nm, c_i tends toward 100%. Under this condition, the confined liquid consists of a saturated ethanol layer at the solid–liquid interface and a bulk phase in the interior. Note that the actual structure is likely in between the fully heterogeneous case and the fully homogeneous case.

It is clear that the above discussion does not constitute a quantitative model. The variation of the effective contact angle as the "flow" direction changes, the phase transformation in the nanoenvironment, and the stability of the confined liquid are still inadequately understood. Nevertheless, this study provides the basic experimental data for further investigation, which would be immensely important to the design of selective protection devices.

IV. CONCLUSIONS

The effect of addition of ethanol on pressure induced infiltration of a hydrophobic mesoporous silica has been investigated experimentally. The phenomenon of "non-outflow" leads to the pronounced hysteresis of absorption isotherms. The following conclusions are drawn:

(1) With ethanol, the infiltration pressure can be adjusted in a broad range from 0 to about 20 MPa.

(2) The ethanol content of the liquid in the nanopores is higher than it is outside, which can be related to the heterogeneous structure of the confined liquid.

(3) The addition of ethanol does not affect the accessible pore volume fraction.

(4) The relationship between the infiltration pressure and the ethanol content is nonlinear.

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