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Infiltration of pressurized promoter solutions in a mesoporous silica

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Abstract

The infiltration of pressurized aqueous solutions of sodium cholate hydrate (CSH) and ammonium 8-anilino-1-naphthalenesulfonate (1,8-ANS-NH4) in a hydrophobic silica gel is investigated experimentally. The CSH and 1,8-ANS-NH4 molecules act as promoters that lower the infiltration pressure in relatively large nanopores, resulting in the staged sorption isotherm curves. When the CSH concentration and the 1,8-ANS-NH4 concentration are relatively low, the infiltration plateau can be three staged. This finding has important relevance to developing programmable nanoporous protective and damping systems. © 2007 Elsevier Inc. All rights reserved.

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1. Introduction

For the past a few years, a novel application of mesoporous materials in energy absorbing mechanical systems has become an active area of research [1-5]. When a hydrophobic mesoporous material, e.g., a surface treated mesoporous silica, is immersed in water, with the application of an external pressure, water can be forced into the mesopores, resulting in the conversion of a large amount of mechanical work to solid–liquid interfacial energy. Due to the large pore surface area, the energy density of such a nanoporous system is much higher than that of conventional protective or damping materials, e.g., reinforced polymers.

In a previous experimental study on the pressure induced infiltration [6], it was confirmed that the infiltration pressure is dependent on the liquid composition. When the liquid phase consists of a nonwetting component, e.g.,

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pure water, and a wetting component (the promoter), e.g., ethanol, the infiltration pressure can be adjusted in a wide range by changing the promoter concentration. The promoter molecules and the water molecules enter the mesopores simultaneously, while the liquid structure inside the mesopores is heterogeneous. Near the solid–liquid interface there exists a promoter rich interface layer, and in the interior the liquid composition is similar with the bulk phase. This effect provides an important method to adjust the system performance.

In another experiment [7], by using promoters of molecular sizes comparable with nanopore size, the non-uniform modification of infiltration pressure was achieved. The promoter molecules could enter only relatively large nanopores, lowering the infiltration pressure in the low-pressure range of infiltration plateau, but could not enter relatively small nanopores. Thus, not only the infiltration pressure but also the infiltration volume could be controlled. An interesting phenomenon was, although the nanopore walls were wettable, there must be a "free volume" surrounding the promoter molecule; otherwise the pressure induced infiltration could not take place. The free volume size was 2–4 times larger than the promoter molecule, and was a function of the promoter concentration. These experimental data qualitatively fit with a few molecular

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dynamics simulations [8-10], and the following discussion will be based on the assumption of "free volume".

In the ethanol modified system, the infiltration pressure can only be adjusted uniformly across the infiltration plateau. In the large-molecular-size promoter modified system, while the variation in infiltration pressure is non-uniform, the pressure and the infiltration volume are correlated, and the infiltration plateau can be divided into only two stages. In order to create more pressure windows and, more importantly, in order to adjust the pressure and the volume change separately, which is essential to the development of intelligent protection and damping systems that are of different energy absorption capacities in different pressure ranges, more degrees of freedom must be provided. One promising method to solve this problem is to use multiple promoters of different molecular sizes and solid-liquid interfacial tensions, as will be discussed in this article. According to the surface and interface theories well documented by Dullien [11], the Kelvin equation, the Washburn-type analysis, and the Darcy's law can be employed to analyze the equilibrium capillary effect, the capillary pressure driven infiltration and condensation, and the liquid penetration across porous phases, respectively. However, in a nanopore the continuum basis of the above theories may no longer be valid. For example, if across the pore cross section there are only a few admixture molecules, the ordinary surface layer cannot exist.

2. Experimental

The experimental setup is depicted in Fig. 1. In a steel container, 0.5 g of Fluka 100 C₈ reversed phase end-capped mesoporous silica gel was immersed in 7 g of aqueous solution of Sigma C6445 sodium cholate hydrate (SCH) and Sigma C3125 ammonium 8-anilino-1-naphthalenesulfonate (1,8-ANS-NH4), and compressed by a steel piston in a type 5569 Instron machine. The average pore size of the silica gel is 7.8 nm, with the standard deviation of 2.4 nm [12]. The specific surface area is $287 \text{ m}^2/\text{g}$, and the specific pore



Fig. 1. The experimental setup.

volume is $0.55 \text{ cm}^3/\text{g}$. The surface coverage is 10-12%, resulting in a high degree of hydrophobicity. The molecular formula of SCH is $C_{24}H_{39}NaO_5 \cdot xH_2O$. Its molecular weight is 430.55, and its molecular size is around 2.6 nm. The molecular formula of 1,8-ANS-NH4 is $C_{16}H_{13}NO_3$. S \cdot NH₃. Its molecular weight is 316.37, and its molecular size is about 1.7 nm. Both of the promoters are surfactants commonly used as non-denaturing detergents or fluorescent probes. They can be easily mixed with water, and are wetting to the silica gel.

The piston was compressed into the container at a constant rate of 1.0 mm/min. Under such a low loading rate, the infiltration could be regarded as quasi-static; that is, the experimental result reflected the near-equilibrium system behavior. A higher loading rate may result in a larger energy absorption efficiency due to the increase in internal friction [5], and for the sake of simplicity this effect will not be analyzed in the current study.

The force acting on the piston, F, was measured by an Instron 50 kN load cell, and the pressure in the liquid phase was calculated as $p = F/A_p$, with $A_p = 286 \text{ mm}^2$ being the cross-sectional area of the piston. The displacement of the piston, δ , was measured by a linear variable displacement transducer (LVDT), and the system volume change was calculated as $\Delta V = \delta \cdot A_p$. As the pressure reached 50 MPa, the piston was moved back at the same speed of 1.0 mm/min. Altogether nine different systems were tested, with the 1,8-ANS-NH4 and SCH concentrations in the range of 0–3 wt.%. The measured sorption isotherm curves are shown in Figs. 2–4.

3. Results and discussion

Fig. 3 shows the sorption isotherm curves of systems containing no SCH. The zero 1,8-ANS-NH4 concentration curve indicates the behavior of the system based on pure water. In section "OA", when pressure, p, is relatively



Fig. 2. Sorption isotherm curves of systems with no CSH. Sections "a" and "b" indicate stage-I and stage-II infiltration plateaus, respectively.



Fig. 3. Sorption isotherm curves of systems of 1.5 wt.% CSH. The dashed line indicates the behavior of the pure water based system. Sections "a", "b", and "c" indicate stage-I, stage-II, and stage-III infiltration plateaus, respectively.



Fig. 4. Sorption isotherm curves of systems of 3.0 wt.% CSH. The dashed line indicates the behavior of the pure water based system.

low, since the silica gel is hydrophobic, the liquid phase does not enter the nanopores, until p reaches the critical value of 17 MPa. The intrusion of the liquid phase in the nanoporous silica gel leads to the formation of the infiltration plateau, "AB". The infiltration starts with relatively large nanopores and ends with relatively small nanopores, and the slope of "AB" reflects the effect of pore size distribution. As most of the nanopores are filled, the system becomes nearly impressible again (section "BC"). The unloading path, "CD", on the other hand, is quite linear, indicating that the confined liquid cannot be released from the nanopores as the pressure is reduced, probably due to the difficulty in gas phase formation and growth in the confining nanoenvironment [13], resulting in the pronounced hysteresis and the high energy absorption efficiency.

With the addition of 1,8-ANS-NH4, since the promoter can "carry" water molecules into the nanopores, the required infiltration pressure to overcome the capillary effect is lowered considerably. Due to the relatively large molecular size, it is more difficult for the 1,8-ANS-NH4 molecules to enter into smaller nanopores than into larger nanopores. Thus, the extent of decrease in infiltration pressure is higher in the larger nanopore region. This phenomenon becomes more significant as the 1,8-ANS-NH4 concentration is increasingly high. When the 1,8-ANS-NH4 concentration increases to 3.0 wt.%, the infiltration plateau is obviously two staged. The low-pressure section, which will be referred to as stage I ("a") in the following discussion, is associated with the relatively large nanopores in which the 1,8-ANS-NH4 infiltration is easy. The highpressure section, which will be referred to as stage II ("b") in the following discussion, is related to the small nanopores. The width of the stage-I infiltration plateau indicates the specific volume of large nanopores, which is around $0.15 \text{ cm}^3/\text{g}$, about 30% of the total pore volume. The similar two-staged infiltration behavior can be obtained by adding 1.5 wt.% CSH, as shown by the zero 1,8-ANS-NH₄ concentration curve in Fig. 3. However, the width of stage-I infiltration plateau is only about $0.08 \text{ cm}^3/\text{g}$, much smaller than that of 1.5 wt.% 1,8-ANS-NH₄, suggesting that it is more difficult for the CSH molecules to infiltrate into the mesoporous silica gel. This is in consistent with the fact that the molecular size of CSH is larger than that of 1,8-ANS-NH₄. Since the area of the silica surface exposed to the liquid phase is very large and it is difficult to form micelles in the nanopores, the critical micelle concentration (CMC) is quite high, which is in agreement with the experimental observation that the infiltration pressure changes somewhat continuously as the promoter concentration increases.

With the addition of 1.5 wt.% 1,8-ANS-NH₄, it can be seen that the infiltration plateau becomes three staged. The three stages will be referred to as stage I ("a"), stage II ("b"), and stage III ("c"), respectively. The width of stage I is similar to that of the curve of zero 1,8-ANS-NH4 concentration, while the infiltration pressure is lower. The total width of stages I and II is close to that of stage I of the 1.5 wt.% 1,8-ANS-NH4 concentration curve in Fig. 2. Clearly, the transition from stage I to stage II is caused by SCH, and the transition from stage II to stage III is caused by 1,8-ANS-NH4. The three-staged sorption isotherm curve can be somewhat regarded as the superposition of the sorption isotherm curve of the system containing only SCH and the sorption isotherm curve of the system containing only 1,8-ANS-NH4.

As the SCH or 1,8-ANS-NH4 concentration increases to 3.0 wt.% (see Fig. 4), however, the simple superposition principle breaks down. Under this condition, the sorption isotherm curve is two staged again; that is, the SCH molecules and the 1,8-ANS-NH4 molecules are no longer independent of each other. Rather, they enter the nanopores as a unified system. The width of stage I is larger than either



Fig. 5. The stage-I infiltration pressure as a function of the CSH and 1,8-ANS-NH4 concentrations.

that of SCH or that of 1,8-ANS-NH4, i.e., as the promoter concentration is relatively high, they promote the infiltration of each other.

Fig. 5 shows the stage-I infiltration pressure of systems of various promoter concentrations. The data point of the pure water based system is somewhat arbitrarily chosen as the pressure at the onset of infiltration. As the promoter concentration increases, the stage-I infiltration pressure decreases, as it should, since the promoters are the wetting components in the liquid phase. The pressure-concentration relationship is quite nonlinear, even for the single-promoter systems. Depending on the type of promoter, the stage-I infiltration pressure can decrease with an either increasing or decreasing rate.

The promoter concentration effect on the width of stage-I infiltration plateau is shown in Fig. 6, which, compared with Fig. 5, is irregular. Particularly, as both of the SCH concentration and the 1,8-ANS-NH4 concentration are relatively low, the sorption isotherm is three staged, and



Fig. 6. The stage-I infiltration volume as a function of the CSH and 1,8-ANS-NH4 concentrations.

therefore the width of stage-I plateau tends to be smaller than that of two-staged cases. Nevertheless, the overall effect that addition promoters promotes stage-I infiltration is still clear. Based on Figs. 5 and 6, if the required stage-I infiltration pressure and infiltration volume are given, the concentrations of the two promoters can be determined quite conveniently. Hence, the system volume variations in low-pressure and high-pressure ranges can be controlled independently, which is the basis of the design of intelligent protection and damping systems.

Note that the loading rate employed in the current study is quite low. In actual engineering applications of energy absorption systems, it is likely that the devices would work under much higher strain rates. According to previous experimental data [5], the energy absorption efficiency of a nanoporous system would increase significantly with the loading rate, due to internal friction across the solid– liquid interface. Therefore, the quasi-static testing result is conservative, providing the lower limit of the protection capacity. In the current study, the loading rate of 1 mm/ min. was chosen for the quasi-static experiment, since if it was further lowered, e.g., to 0.5 mm/min., no detectable changes in sorption isotherm curves were observed.

4. Concluding remarks

Clearly, more details need to be examined before the solid–liquid interaction and the rate effect in nanoevironment can be fully understood. Nevertheless, according to the pressure induced infiltration experiment, it is validated that addition of promoters can significantly lower the infiltration pressure. More importantly, by using multiple promoters of molecular sizes comparable with nanopore size, the profile of sorption isotherm curve can be adjusted conveniently, leading to the development of intelligent protection and damping structures. The following conclusions are drawn:

- (1) Addition of either SCH or 1,8-ANS-NH4 can considerably lower the infiltration pressure in relatively large nanopores, while has relatively little influence in relatively small nanopores, causing the formation of two-staged infiltration plateau.
- (2) As the promoter concentrations are relatively low, the sorption isotherm curve of a system containing both SCH and 1,8-ANS-NH4 follows the simple superposition rule, leading to the formation of three-staged infiltration plateau.
- (3) As the promoter concentrations are relatively high, the interactions between SCH and 1,8-ANS-NH4 is pronounced. They promote the infiltration of each other, leading to the formation of two-staged infiltration plateau with a wider stage-I section.
- (4) By adjusting the SCH concentration and the 1,8-ANS-NH4 concentration, the stage-I infiltration pressure and the stage-I infiltration volume can be controlled separately.

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