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Pressure-Induced Infiltration of Aqueous Solutions of Multiple Promoters in a Nanoporous Silica

Aijie Han[†] and Yu Qiao*[,†]
Department of Civil Engineering, University of Akron, Akron, Ohio 44325-3905

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Nanoporous technologies have received wide applications in a variety of areas, including catalysis, hydrogen storage, purification, selective absorption and adsorption, among others. For example, under high pressure, by forcing water into hydrophobic nanoporous particles, the system free energy can be largely increased. The excess solid−liquid interfacial energy can be regarded as being dissipated if the "outflow" is difficult, which has been observed in a few nanoporous silicas and silicalites.[1−4] The "nonoutflow" may be caused by the change in contact angle,[5] the formation of new liquid surfaces,[6] or the energy barrier of gas-phase nucleation and growth.[7] Due to the large specific surface area, the energy absorption efficiency of the nanoporous system can be higher than that of many conventional energy absorption materials by orders of magnitude.

To develop smart absorption and adsorption systems, as well as programmable catalysis techniques, intelligent purification or storage cells, and so on, the profile of the sorption isotherm must be optimized according to the functional requirement. In particular, both the range of activation pressure and the amount of energy associated with each pressure range should be controlled. One promising method is to use surfactants as promoters.[4] The promoters should be wetting to the pore wall and compatible with water, such that at the onset of the infiltration they can "carry" water molecules into the nanopores and, thus, lower the infiltration pressure. Then the promoter molecules would form an interface layer covering the pore wall, resulting in the heterogeneous structure of the confined liquid.[4] To activate the infiltration promotion mechanism, the nanopores must be much larger than the promoter molecules; otherwise, the repelling effect of pore walls would be dominant.[8] Thus, if the system is of a relatively broad pore size distribution and the molecular size of promoter is intermediate, the pressure-induced infiltration can occur only in the relatively large nanopores.[9] Note that, to control the infiltration pressure and the infiltration volume independently, the system must be of at least two degrees of freedom. Therefore, in the current study, we investigate a nanoporous system of multiple promoters.

To validate the above concepts, we tested a hydrophobic Fluka 100 C_8 reversed-phase nanoporous silica gel. The average pore size was 7.8 nm, with a standard deviation of 2.4 nm. The specific pore volume was 0.55 cm^3/g, and the specific pore surface area was 287 m^2/g. The surface coverage was 10−12%. The material was in powder form, with the particle size ranging from 10 to 35 μm. The nanoporous energy absorption system (EAS) was formed by sealing 0.5 g of the nanoporous silica gel and 7 g of aqueous solution of Sigma 61747 *N*-lauroylsarcosine sodium salt (sarcosyl) or Sigma C1254 sodium cholate hydrate (SCH) in a stainless steel cylinder. The molecular formula of sarcosyl is $CH_3(CH2)_{10}CON(CH_3)CH_2COONa$ and that of SCH is $C_{24}H_{39}NaO_5{\cdot}xH_2O$. The sarcosyl and SCH concentrations were in the range of 0−12 wt %. The molecular weights of sarcosyl and SCH are 239.39 and 430.55, respectively.

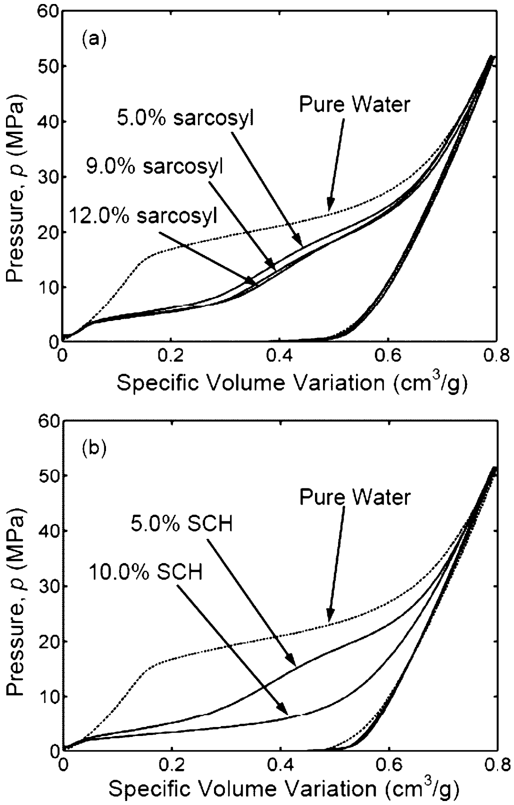

Figure 1. Sorption isotherm curves of the nanoporous systems based on aqueous solutions of (a) sarcosyl and (b) sodium cholate hydrate.

Using a type-5569 Instron machine, a steel piston was compressed into the cylinder at a constant rate of 1.0 mm/sec. As the pressure became increasingly high, the liquid infiltrated into the nanoporous particles, starting with the largest nanopores and ending with the smallest nanopores. The piston was moved back at the same rate of 1.0 mm/sec once the pressure reached 50 MPa. The sorption isotherms are shown in Figures 1 and 2. Note that the unloading curves were quite linear, indicating that the confined liquids remained in the nanopores as the pressure was reduced.

Figure 1 shows clearly that both sarcosyl and SCH can lower the infiltration pressure, p_{in}. As expected, the promotion effect is highly nonuniform. In larger nanopores, where the infiltration occurs at relatively low pressures, the decrease in p_{in} is much more pronounced than that in smaller nanopores, forming two-staged infiltration plateaus.[9] The width of the low-pressure stage indicates the volume of pores that can be easily infiltrated by the promoter molecules, which in turn determines the critical pore size, r_{cr}. For instance, in Figure 1a, the transitions from the low-pressure stages to the high-pressure stages occur at the pore sizes around 7−9 nm.

[†] Current address: Department of Structural Engineering, University of California at San Diego, La Jolla, California 92093−0085.

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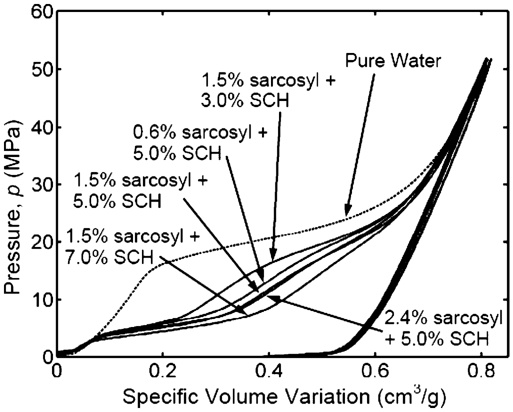

Figure 2. Sorption isotherm curves of the nanoporous systems containing multiple promoters.

The pore size calculation is discussed in detail in the Supporting Information. The critical pore size is much larger than the molecular size of sarcosyl, suggesting that, even when the pore surface is wettable, there must be a "free volume" several times larger than the promoter molecule. Similar phenomenon was also observed in the SCH-modified system.

As sarcosyl concentration increases, the width of the low-pressure stage rises; that is, the size of the free volume decreases, demonstrating that the interaction among promoter molecules must be taken into consideration. However, as the sarcosyl concentration exceeds about 9%, the sorption isotherm saturates; that is, there exists a lower bound of the free volume size, which, according to Figure 1a, is around 8 nm. Further addition of sarcosyl would cause only negligible changes in sorption isotherm profile. On the other hand, in the systems modified by SCH, the free volume can decrease continuously. As more SCH are used, the low-pressure infiltration volume keeps increasing until it approaches the total pore volume.

It can be seen that, by using either sarcosyl or SCH, the variations in infiltration pressure, p_{in}, and staged infiltration volume, V_{s}, are coupled. To adjust them separately, there must be at least one additional degree of freedom. Figure 2 shows the experimental results of systems containing both sarcosyl and SCH. The values of p_{in} and V_{s} are strongly dependent on the concentrations of both of the promoters. Because the additions of different admixtures can be controlled independently by modifying the liquid composition, the profile of infiltration plateau can be adjusted conveniently.

The sorption isotherms of these systems do not follow the principle of superposition. For instance, while the system consisting of 5.0% sarcosyl and the system consisting of 5.0% SCH are of quite different low-pressure infiltration volumes, the system based on the combination of them does not exhibit a three-staged infiltration plateau. Rather, there exists a single point of transition between the low-pressure and the high-pressure stages; that is, the sarcosyl and SCH molecules enter the nanopores simultaneously. The size of the free volume associated with the combined infiltration is between that of sarcosyl and that of SCH. On the other hand, while the coupling between the two promoters is pronounced, the tendency of the concentration effect remains. With 5.0% SCH, the influence of increasing sarcosyl concentration is negligible when it exceeds 2.4%, somewhat similar with the phenomenon of the system based on only sarcosyl, while the saturation concentration is lowered. Similarly, the addition of sarcosyl does not change the fact that the free volume keeps decreasing as the SCH concentration increases, which indicates that the SCH molecules are dominant in the infiltration process.

To summarize, by using promoters, the sorption isotherm curve of a nanoporous EAS can be controlled quite precisely. The pore size must be larger than the free volume demanded by the promoter molecules, while more detailed measurements must be performed to better understand the solid−liquid interactions in nanopores. The free volume size is dependent on the liquid composition. As the promoter concentration increases, the free volume may or may not decrease continuously. When multiple promoters are used, there is a strong coupling effect. However, the tendency of the concentration effect remains similar.

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Supporting Information Available: Definitions and determination of critical nanopore size. This material is available free of charge via the Internet at http://pubs.acs.org.

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