

## Two-staged sorption isotherm of a nanoporous energy absorption system

Falgun B. Surani, Xinguo Kong, and Yu Qiao<sup>a)</sup>

Department of Civil Engineering, University of Akron, Akron, Ohio 44325-3905

(Received 18 September 2005; accepted 8 November 2005; published online 12 December 2005)

To selectively absorb impact energy, the profiles of sorption isotherms of protection systems must be adjusted in a broad spectrum. In this article, a N-Lauroylsarcosine sodium salt (sarcosyl) of intermediate molecular size is used to control the pressure induced infiltration of a nanoporous silica. The experimental result shows that the infiltration plateau of this system is two-staged; that is, not only the activation pressure but also the infiltration volume can be modified. It is noticed that the sarcosyl molecule demands a “free volume” to enter a nanopore. The free volume size decreases nearly linearly as the sarcosyl concentration increases. © 2005 American Institute of Physics. [DOI: 10.1063/1.2144280]

It has long been noticed that, by forcing a nonwetting liquid into a porous medium, the free energy of the system can be increased. However, not until recently with the development of nanoporous technologies has the application of this phenomenon in energy absorption systems become feasible. A few preliminary studies have provided proof-of-concept results that, in a system consisting of hydrophobic nanoporous particles immersed in water or an aqueous solution, as the pressure increases, the liquid can infiltrate into the nanopores.<sup>1-4</sup> As a first order estimation, the associated free energy increase can be assessed as  $E = \Delta\gamma \cdot A$ , where  $\Delta\gamma = |\gamma_{sl} - \gamma_s|$  and  $A$  is the specific surface area, with  $\gamma_{sl}$  and  $\gamma_s$  being the effective solid-liquid interface energy and the surface energy of the solid, respectively. For a number of nanoporous materials, when the pressure is reduced, the liquid cannot come out of the nanopores. Thus, during the pressure induced infiltration,  $E$  is effectively dissipated. Since the specific surface area,  $A$ , is usually in the range of 100–1000 m<sup>2</sup>/g, which is billions of times larger than in bulk materials, the energy absorption efficiency of the nanoporous system can be much higher than that of conventional protection materials such as composite materials or smart alloys.<sup>5,6</sup>

In order to develop the next-generation intelligent protection devices so as to minimize the system weight and size, the functional energy absorption component must be of a selective characteristic. That is, instead of absorbing all the energy carried by the external loading, it is desirable to filter out only the harmful part. For instance, it has been demonstrated that low-pressure stress waves cause only negligible organ damages,<sup>7</sup> and therefore dissipating energy in this pressure range should be regarded as a “waste” of the energy absorption capacity for a body armor. The controllability of the profile of sorption isotherm is also critical to damping applications, such that, with a given actuation loading, the output motion can be adjusted at specified pressure levels.

The solid line in Fig. 1 shows the sorption isotherm of an ideal pure-water-based system where the nanoporous material has a uniform pore size distribution. Initially, when the pressure is relatively low, water cannot enter the hydrophobic pores. When the pressure reaches a critical value,  $p_{in}$ , the

capillary effect is overcome and the pressure induced infiltration occurs, forming a plateau region. Eventually, when the porous space is filled, the plateau region ends and the system compressibility would decrease significantly. As the pressure is reduced, according to the experimental data,<sup>1-4</sup> the confined liquid does not “flow” out, resulting in the hysteresis behavior. The area enclosed by the loading-unloading loop indicates the absorbed energy. Note that, in reality, the system would inevitably exhibit a finite pore size distribution and consequently the slope of the plateau region is always positive.

In a recent experimental study,<sup>8</sup> it was noticed that by adding promoters such as ethanol in a nanoporous silica based system, the infiltration pressure could be adjusted in a broad range from 0 to about 20 MPa. The promoter molecules are much smaller than the pore size and can form an interface layer at the pore wall. However, in this experiment, the variation of  $p_{in}$  took place quite uniformly across the entire infiltration plateau region. To obtain a selective and/or controllable sorption isotherm, the infiltration plateau must be multiple-staged, as depicted by the dashed line in Fig. 1, so that not only the activation pressure but also the amount of energy to be dissipated in each pressure range can be adjusted.

It is envisioned that, if the molecular size of the promoter is in the intermediate range such that the molecules can enter only the pores larger than a critical value,  $r_{cr}$ , they would have little influence on the infiltration process in small

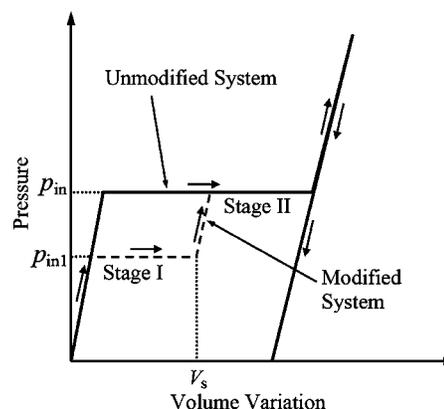


FIG. 1. A schematic diagram of sorption isotherms of ideal nanoporous systems.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: yqiao@uakron.edu

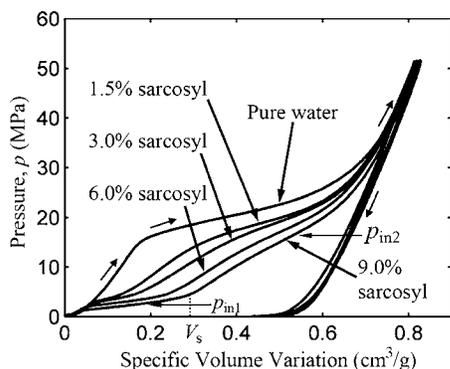


FIG. 2. The sorption isotherms of nanoporous energy absorption systems of various sarcosyl concentrations. For the curve of 9.0% sarcosyl concentration,  $p_{in1}$ ,  $p_{in2}$ , and  $V_s$  are shown.

pores. To validate this hypothesis, a pressure induced infiltration experiment was carried out on a system based on an aqueous solution of Sigma 61747 N-Lauroylsarcosine sodium salt (sarcosyl). The nanoporous material used in the current study is a Fluka 100 end-capped  $C_8$  reversed phase silica, with the average pore size of 7.8 nm and the standard deviation of 2.4 nm. The specific pore volume is  $V_0 = 0.5 \text{ cm}^3/\text{g}$  and the particle size is in the range of 10–35  $\mu\text{m}$ . The pore surface is covered by a layer of 10%–12% hydrophobic silane groups.

The chemical formula of sarcosyl is  $\text{CH}_3(\text{CH}_2)_{10}\text{CON}(\text{CH}_3)\text{CH}_2\text{COONa}$ .<sup>9</sup> Its molecular weight is 293.39 and its molecule size is about 1.8 nm, smaller than but comparable with the nanopore size. Sarcosyl is a commonly used surfactant. On the one hand, it is energetically favorable for the sarcosyl molecules to attach the pore surface; on the other hand, sarcosyl can form strong bonding with water molecules. There are two possible mechanisms of the modified infiltration: (a) homogeneous infiltration, in which the sarcosyl molecules enter the nanopores simultaneously with the water molecules, i.e., the sarcosyl molecules act as “carriers” bringing the water into the nanoenvironment; and (b) heterogeneous infiltration, where the sarcosyl molecules enter the nanopores first and form a solid-liquid interface layer, so that the pore walls become effectively wettable for water.

The infiltration experiment was performed using a type-5569 Instron machine. Each sample consisted of 0.5 g of nanoporous silica particles immersed in 7 g of aqueous solution of sarcosyl, with the initial sarcosyl concentration,  $c$ , ranging from 0 to 9.0 wt. %. The system was sealed in a stainless steel container. At a constant rate of 1 mm/min, a piston was compressed into the container. As the pressure exceeded a critical value, the pressure induced infiltration occurred and the effective bulk modulus of the system decreased considerably, resulting in the formation of the infiltration plateau, as shown in Fig. 2. The infiltration started in relatively large pores and the smaller pores were involved as the pressure became higher. Eventually all the porous space would be filled. When the pressure reached about 50 MPa, the piston was moved out at the same rate of 1 mm/min. During unloading, due to the difficulty in gas phase nucleation,<sup>10</sup> the “outflow” of the confined liquid was difficult. The load applied on the piston,  $P$ , was measured by an Instron 50KN loadcell and the pressure was calculated as  $p = P/A_0$ , where  $A_0 = 286 \text{ mm}^2$  is the cross-sectional area of the

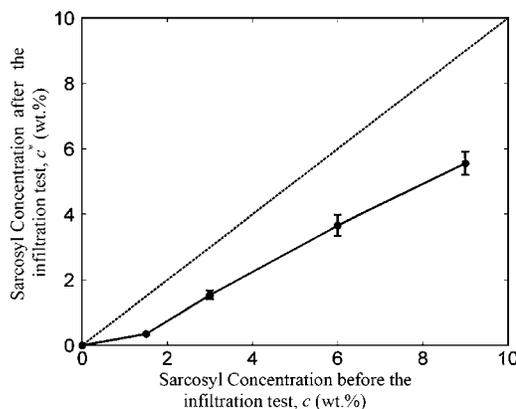


FIG. 3. The sarcosyl concentrations before and after the infiltration tests.

piston. After the infiltration experiment, the filled silica particles were removed by an AMTS 40-60 filter. The liquid phase was then analyzed by the ultraviolet (UV) light absorption method to determine the sarcosyl concentration,  $c^*$ . The results are shown in Fig. 3. Details of the UV analysis procedure are introduced elsewhere.<sup>11</sup>

Through Fig. 2, it can be seen clearly that the addition of sarcosyl has considerable influences on the sorption isotherm. The infiltration plateau is two staged, as previously predicted. The pressure in stage I is lower, indicating that it is difficult for the sarcosyl molecules to enter the small pores. As the sarcosyl concentration increases, both the stage-I infiltration pressure,  $p_{in1}$ , and the stage-II infiltration pressure,  $p_{in2}$ , are lowered, as shown in Fig. 4, where the infiltration pressure is defined as the pressure at the middle point of each stage. The  $p_{in1}$  of the system based on pure water is somewhat arbitrarily chosen as the pressure at the onset of infiltration. The stage border is taken as the point where the slope of sorption isotherm equals the average value of that of the two stages across it. The  $c$  dependence of  $p_{in1}$  suggests that, at the beginning of the infiltration, the homogeneous mode is dominant, since once the heterogeneous sarcosyl-rich interface zone is formed, further variation in sarcosyl concentration should not affect the infiltration pressure. Figure 3 indicates that the sarcosyl concentration in the liquid phase decreased after the infiltration tests, i.e., the sarcosyl content inside the nanopores must be higher than outside. This phenomenon is quite similar with the behavior of the ethanol modified nanoporous system,<sup>4</sup> which can be attributed to the formation of the interface layer at spore walls of promoter molecules, i.e., after

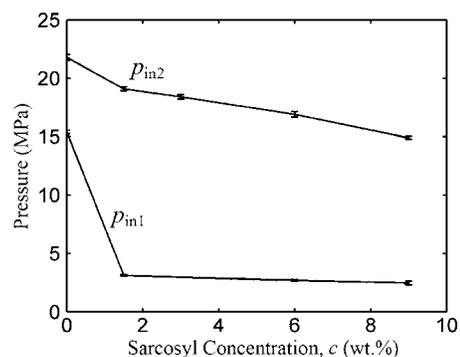


FIG. 4. The stage-I and the stage-II infiltration pressures as functions of the sarcosyl concentration.

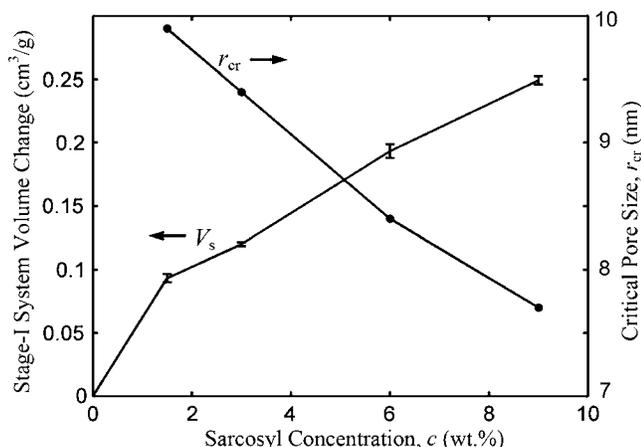


FIG. 5. The stage-I infiltration volume and the critical pore size as functions of the sarcosyl concentration.

the onset of the infiltration of sarcosyl and water molecules, their distributions are nonuniform.

Note that the decrease in sarcosyl content outside the nanopores is dependent on the initial sarcosyl concentration, which is probably caused by the increase in stage-I infiltration volume,  $V_s$ . Figure 5 shows the influence of  $c$  on  $V_s$ , which is the specific volume of the large pores that can be infiltrated by sarcosyl molecules. If we assume that the pore size follows a normal distribution function, the  $V_s/V_0$  ratio can be related to the critical pore size between stages I and II,  $r_{cr}$ , as shown in Fig. 5. The value of  $r_{cr}$  is much larger than the molecular size of sarcosyl, which is compatible with the molecular dynamics simulation result that, even when a nanoenvironment is nominally energetically favorable, the repelling effect is significant unless the pore size is several times larger than the molecules.<sup>12</sup> That is, a sarcosyl molecule needs a “free volume” to enter the nanopore. It is remarkable that  $r_{cr}$  is not a material constant. Rather, it is highly dependent on the sarcosyl concentration. As  $c$  increases from 1.5 to 9.0 wt.%,  $r_{cr}$  decreases from

9.9 nm to 7.7 nm. Accordingly, the free volume is reduced by a factor of 2. The relationship between  $r_{cr}$  and  $c$  is quite linearly, the reason of which is still unclear.

To summarize, with the addition of sarcosyl, the sorption isotherm of the silica based nanoporous energy absorption system becomes two-staged. Both of the activation pressure and the staged specific infiltration volume vary as the sarcosyl concentration changes, which is caused by the difficulty in infiltration of sarcosyl molecules in relatively small pores. The critical pore size of infiltration is much larger than the sarcosyl molecule, suggesting that there exists a free volume as the molecule enters a nanopore. The size of the free volume is dependent on the sarcosyl concentration, and the  $r_{cr}$ - $c$  relation is nearly linear.

The experimental work was supported by The Army Research Office under Grant No. W911NF-05-1-0288, for which we are grateful to Dr. D. M. Stepp; and the analysis was supported by The National Science Foundation under Grant No. CMS-0503910. Special thanks are also due to Dr. C. Wesdemiotis for the help with the sarcosyl concentration measurement.

<sup>1</sup>B. Lefevre, A. Saugey, J. L. Barrat, L. Bocquet, E. Charlaix, P. F. Gobin, and G. Vigier, *J. Chem. Phys.* **120**, 4927 (2004).

<sup>2</sup>V. Eroshenko, R. C. Regis, M. Soulard, and J. Patarin, *J. Am. Chem. Soc.* **123**, 8129 (2001).

<sup>3</sup>X. Kong and Y. Qiao, *Appl. Phys. Lett.* **86**, 151919 (2005).

<sup>4</sup>F. B. Surani, X. Kong, D. B. Panchal, and Y. Qiao, *Appl. Phys. Lett.* **87**, 163111 (2005).

<sup>5</sup>X. Kong and Y. Qiao, *J. Mater. Res.* **20**, 1042 (2005).

<sup>6</sup>T. Martin, B. Lefevre, D. Brunel, A. Galarneau, F. Di Renzo, F. Fajula, P. F. Gobin, J. F. Quinson, and G. Vigier, *Chem. Commun. (Cambridge)* **2002**, 24.

<sup>7</sup>J. M. Wightman and S. L. Gladish, *Ann. Emerg. Med.* **37**, 664 (2001).

<sup>8</sup>X. Kong, F. B. Surani, and Y. Qiao, *Philos. Mag. Lett.* **85**, 331 (2005).

<sup>9</sup>K. R. Lange, *Surfactants: A Practical Handbook* (Hanser Gardner, New York, 1999).

<sup>10</sup>X. Kong, F. B. Surani, and Y. Qiao, *Phys. Rev. E* (unpublished).

<sup>11</sup>G. D. Christian, *Analytical Chemistry* (Wiley, New York, 2003).

<sup>12</sup>D. T. Wasan and A. D. Nikolov, *Nature (London)* **423**, 156 (2003).