Philosophical Magazine Letters,
Vol. 86, No. 4, April 2006, 253–260

Pressure-induced infiltration of an epsomite–silica system

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(*Received 24 October 2005; in final form 8 February 2006*)

The pressure-induced infiltration of hydrophobic nanoporous silica gel immersed in epsomite solutions or mixed with epsomite crystals is investigated. Owing to the hysteresis of sorption isotherm curves, these systems are energy absorbing. In the liquid system, as the epsomite concentration increases, both the first-cycle infiltration pressure and the system recoverability increase. The energy-absorption properties of the saturated-solution- and the solid-crystal-based systems are quite similar. The experimental data suggests that, while the solid–liquid interfacial energy dominates the infiltration behaviour, the defiltration process is somewhat independent of it.

1. Introduction

Energy absorption efficiency is an important factor in design and selection of materials for protection and damping systems, such as car bumpers, protective layers, mounting stages, etc. Many energy-absorbing materials are particulate and/or fibre-reinforced composites, in which, under external loadings, the filler–matrix interface areas can vary significantly, resulting in energy dissipation [1, 2]. To increase the dissipated energy density on a weight or volume basis, the size of fillers should be minimized, desirably down to the nanometer level, so as to maximize the filler–matrix interface area. However, very often as the filler size is reduced, the degree of ductility of the material is lowered considerably [3–5], so that the utility factor of the interface area becomes much smaller.

According to recent proof-of-concept research [6–10], a promising method for direct utilization of the large surface/interface area of a nanostructured material for energy absorption is to use liquid-based nanoporous systems, e.g. hydrophobic nanoporous silica particles immersed in water. The mechanism of energy absorption is related to the well-known capillary phenomenon: external work must be done to spread a non-wetting liquid on a solid surface. This effect is greatly amplified by the large specific area of nanoporous material, typically around 100–1000 m^2/g, as water is forced into the nanopores. Indeed, the energy absorption efficiency of a nanoporous system can be as high as 10–100 J/g.

As will be discussed shortly, in a pure water-based nanoporous silica system, owing to the hysteresis of sorption isotherm, the energy absorption capacity is

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Philosophical Magazine Letters
ISSN 0950-0839 print/ISSN 1362-3036 online
http://www.tandf.co.uk/journals
DOI: 10.1080/09500830600678862

reduced significantly after the first loading–unloading cycle, so the system is only suitable for one-time protection applications. In a previous experimental study, it was noticed that system recoverability can be improved by using sodium chloride as the chemical admixture [10], the reason for which is still unclear. On the one hand, the infiltration pressure increases slightly as the sodium chloride concentration rises, compatible with literature data of silica/sodium chloride solution interfacial energy. On the other hand, the defiltration pressure also increases with sodium chloride content, which is difficult to relate to macroscopic phenomena. The dominant process may be associated with the confinement effect of pore walls and the complicated interactions among gas, liquid, solid and interface phases. Currently, theoretical analysis and basic testing data in this field are scarce.

In the current study, we investigate the influence of the addition of magnesium sulfate hydrate, $MgSO_4 \cdot 7H_2O$ (epsomite), on the sorption isotherm of nanoporous silica. It is well known that, compared with sodium chloride, magnesium sulfate has a more pronounced effect on surface/interface tension [11]. Testing data show that the infiltration pressure, indeed, increases more rapidly with the addition of epsomite; however, recoverability is about the same as that of the sodium chloride-modified system, suggesting that the solid–liquid interaction may not be essential to defiltration. Furthermore, as a ‘side-product’, it is discovered that large energy dissipation can be achieved by using epsomite crystals, providing a promising way for developing solid-like nanoporous energy absorbing ‘composites’.

2. Experimental

The nanoporous material analyzed in this investigation was a hydrophobic Fluka 100 C_8 reversed phase silica gel, the same as that used for the sodium chloride-modified systems [10]. The pore size was 7.8 nm, with a standard deviation of 2.4 nm. The particle size was 15–35 μm and surface coverage 10–12%.

The epsomite crystals were produced by dispersing 40 wt.% VWR 7487 anhydrous magnesium sulfate in distilled water. At room temperature, the solubility of magnesium sulfate is about 26% and, thus, epsomite crystals could be formed rapidly. As long as the magnesium sulfate content is lower than 48 wt.%, no hexahydrite should co-exist [12]. The epsomite crystals were dried in an open container in air at ambient temperature for more than 72 h.

Both liquid and solid samples were tested. The liquid sample contained 0.5 g silica gel immersed in 7 g of aqueous solution of epsomite. It was sealed in a steel container by a piston fitted with a gasket. The epsomite concentration was in the range from 0 (pure water) to 54.2 wt.% (the saturated solution). Using a type 5569 Instron machine, the piston was compressed into the container. The crosshead speed was set to 0.5 mm/min. The force acting on the piston, F, was measured by an Instron 50KN load-cell, and the pressure inside the container was calculated as $p = F/A_0$, where the cross-sectional area of the piston $A_0 = 286\,\mathrm{mm}^2$. Once the pressure reached about 50 MPa, the crosshead was move back at the same speed of 0.5 mm/min, and the system volume partially recovered, as demonstrated in figures 1 and 2. The specific system volume variation was defined as the system

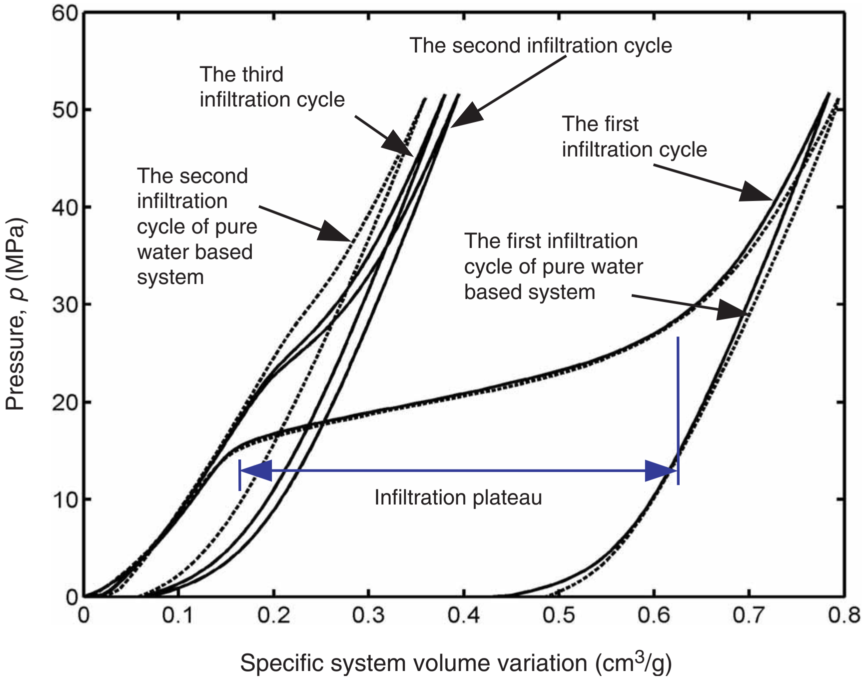

Figure 1. Sorption isotherm curves of the nanoporous system based on 20.8 wt.% epsomite solution. The dashed lines indicate the behaviour of a pure-water-based system. The curves have been shifted along the horizontal axis.

volume change normalized by the silica gel content. The loading–unloading cycle was repeatedly performed until the sorption isotherm curves converged.

The solid system was produced by mixing 0.5 g of silica gel with 8.5 g of epsomite crystals (see figure 3). It was then sealed in the same steel container used for liquid samples and tested through a similar procedure. Sorption isotherm curves are shown in figure 4. In figures 1, 2 and 4, the behaviour of silica gel in pure water is indicated by dashed lines.

3. Results and discussion

All the systems investigated are energy absorbing. For instance, in figure 1, as the pressure increases from 0 to 14 MPa, the sorption isotherm is linear, with the slope close to the compressibility of water. From 14 to 25 MPa, the system compressibility decreases significantly, leading to the formation of a plateau region, which could be attributed to the pressure-induced infiltration, i.e. the capillary effect is overcome and the liquid is forced into the nanoporous silica gel. Infiltration starts in relatively large pores and ends with relatively small pores. Once most of the porous space is filled, the system becomes incompressible again. As the pressure is lowered, owing to

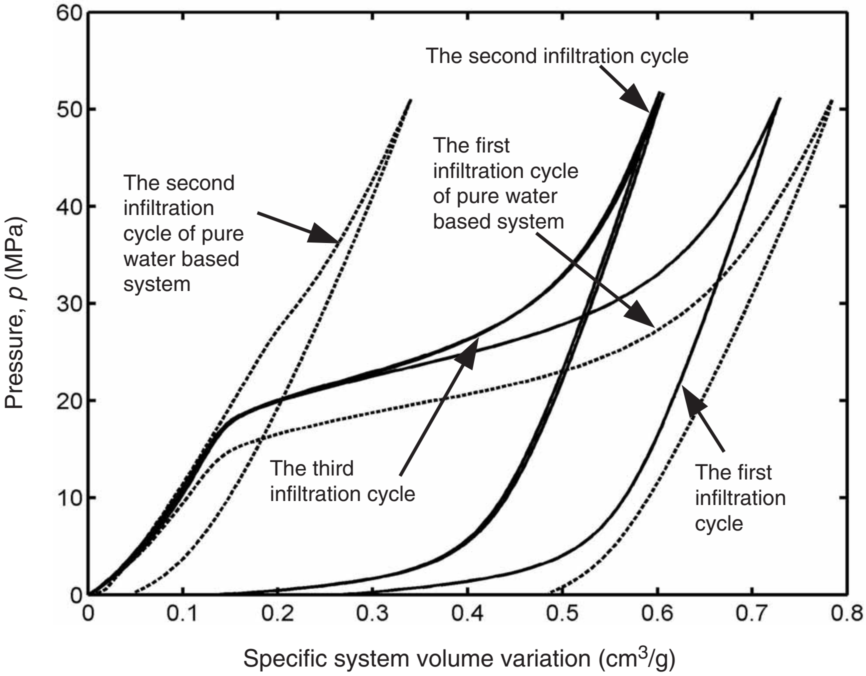

Figure 2. Sorption isotherm curves of the nanoporous system based on saturated epsomite solution. The dashed lines indicate the behaviour of a pure-water-based system. The curves have been shifted along the horizontal axis.

Figure 3. Photograph of the solid-like system containing epsomite crystals and nanoporous silica gel.

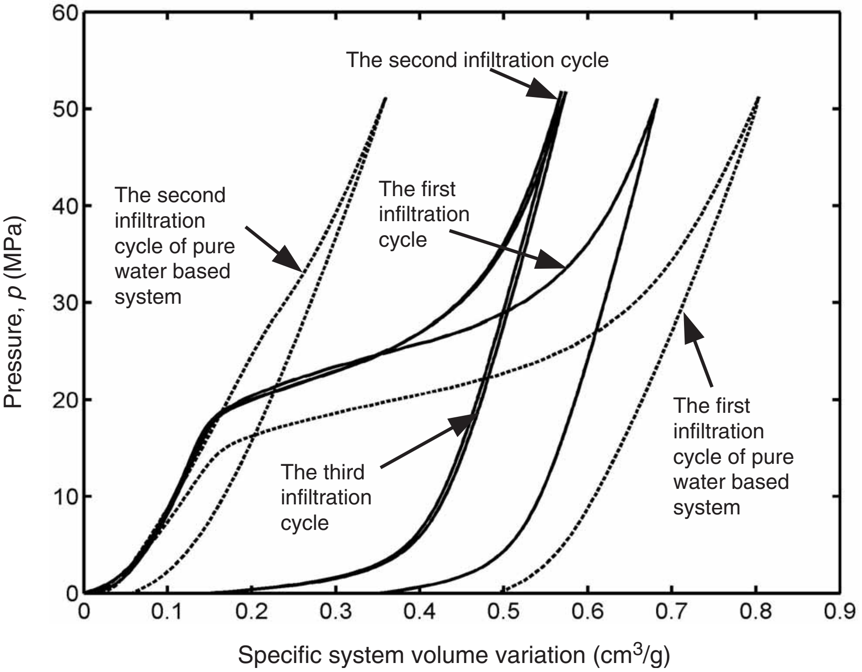

Figure 4. Sorption isotherm curves of the nanoporous system based on epsomite crystals. The dashed lines indicate the behaviour of a pure-water-based system. The curves have been shifted along the horizontal axis.

either kinetic or thermodynamic factors, or both, it is difficult for the confined liquid to exit the nanopores [13]. Hence, the infiltration–defiltration loop is hysteretic and the enclosed area represents the dissipated energy, which is ~14 J/g. Since most of the pores are filled after the first loading–unloading cycles, the energy absorption efficiency decreases from the second cycle. In a pure water-based system, recoverability is only ~10%. Here, recoverability is defined as the ratio of the width of the infiltration plateau of the second cycle to that of the first cycle, and the plateau is taken as the area between the two turning points where the slopes of sorption isotherm curve are 50% of that of the initial linear compression stage. Note that the infiltration plateau width reflects the accessible specific pore volume.

As the epsomite concentration increases, the shape of the first infiltration–defiltration cycle does not vary much, while the first-cycle infiltration pressure, p_{in}, the pressure at the middle point of the infiltration plateau, rises, as shown in figure 5, with the data scatter reflected by the error bars. When the liquid phase is pure water, $p_{\mathrm{in}} = 20.3$ MPa. If the epsomite concentration is relatively low, p_{in} increases gradually. As the epsomite concentration is relatively high, p_{in} becomes sensitive to it. Eventually, when the liquid phase is saturated, p_{in} rises by ~20% to 25.4 MPa. As a first-order estimation, p_{in} can be related to pore size, r, and the excess silica–$MgSO_4$ solution interfacial energy, $\Delta\gamma$, by $p_{\mathrm{in}} = 2 \cdot \Delta\gamma / r$. The epsomite concentration affects $\Delta\gamma$, and the testing results fit the literature data well [11].

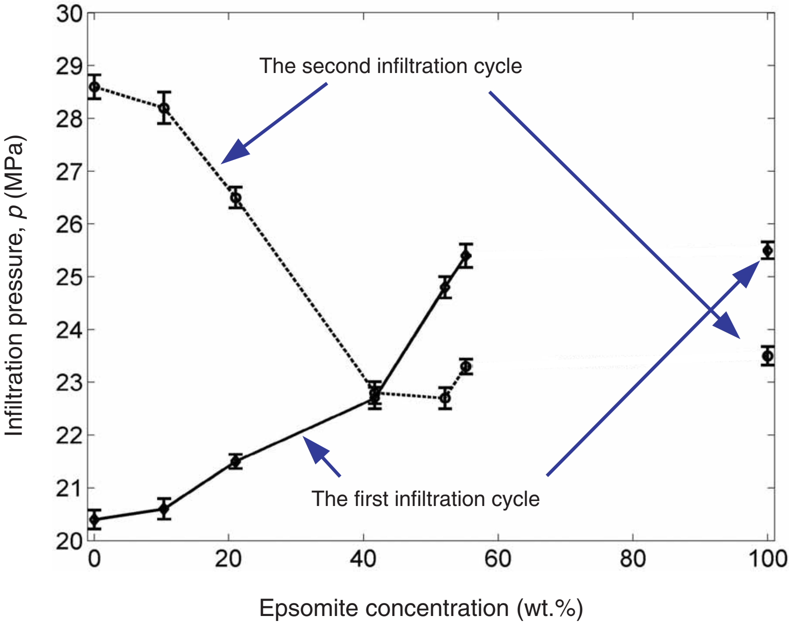

Figure 5. Infiltration pressure as a function of epsomite concentration.

The shapes of subsequent infiltration–defiltration cycles, on the other hand, are highly sensitive to epsomite concentration. In particular, the width of the infiltration plateau increases considerably with the addition of epsomite. As the epsomite concentration is low, the width is similar to that of a pure water-based system. As shown in figure 6, when the epsomite concentration reaches saturation level, the width rises to ~0.3 cm^3/g, nearly one-order of magnitude higher than that of pure water and about 75% of that of the first cycle. Note that the infiltration plateau width of the first loading–unloading cycle is insensitive to the epsomite concentration. After the second cycle, system behaviour stabilizes. The variations in infiltration pressure and infiltration plateau width are negligible; that is, the infiltration process is repeatable from the third cycle.

These phenomena must be related to the defiltration behaviour of the confined liquid in nanopores. The addition of Mg^{2+} and/or SO_4^{2-} ions promotes defiltration, i.e. the confined liquid is less stable under reduced pressure and, as a result, more liquid can exit the pores when the external loading is removed. Thus, more porous space is available for infiltration in the next loading–unloading cycle, and after the second cycle the process becomes nearly reversible. Compared with data from sodium chloride-modified systems [10], system recoverability of the epsomite-modified systems is about the same, i.e. the defiltraion process is insensitive to solid–liquid interfacial energy.

The infiltration pressure in the second loading–unloading cycle, p_{in2}, tends to be higher than that in the first cycle, as indicated in figure 5. The second cycle is actually similar to the high-pressure portion of the first cycle, which is associated with the liquid motion in smaller pores, indicating that defiltration in smaller pores is easier

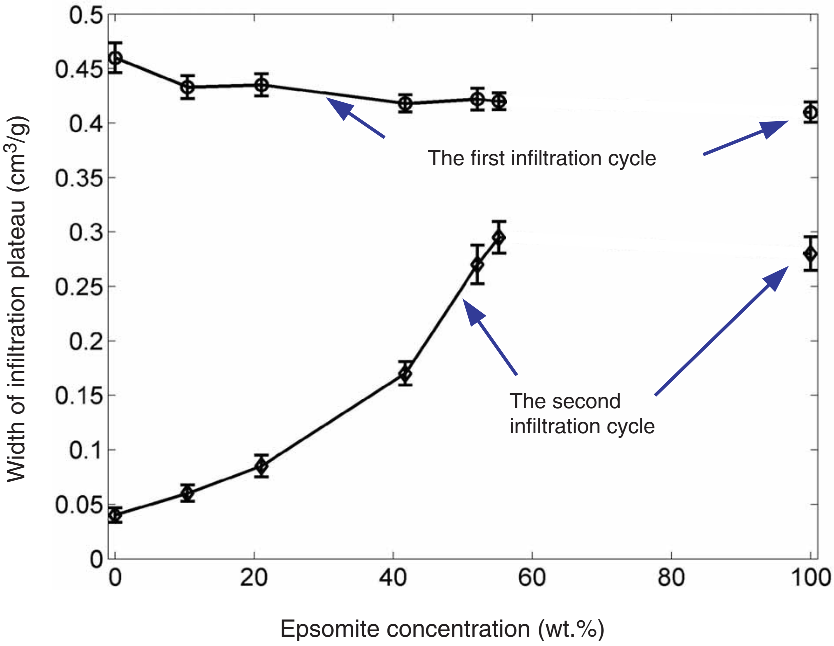

Figure 6. System recoverability as a function of epsomite concentration.

than in larger ones. Consequently, as system recoverability increases, the width of the infiltration plateau becomes larger and p_{in2} decreases. As the epsomite concentration reaches ~40%, p_{in2} is close to p_{in}. However, when the epsomite concentration is further increased, the second cycle is more similar to the low-pressure portion of the first cycle.

Figure 4 shows the infiltration behaviour of the mixture of epsomite crystals and nanoporous silica gel. It can be seen that the performance of this solid 'composite' is similar to that of the liquid system based on saturated epsomite solution (see also figures 5 and 6). Since in the pressure range of the current study, the crystallographic structure of epsomite should be stable [12], it is likely that the infiltrated liquid comes from surface moisture. Because epsomite is highly soluble in water, its surface layer can absorb a large number of water molecules. As the pressure increases, it becomes energetically favourable for the water molecules to diffuse into the nanopores, leading to the observed infiltration–defiltration phenomenon. The ion concentration in the mobile water should be saturated.

4. Conclusions

To summarize, the pressure-induced infiltration of epsomite-modified nanoporous silica systems is investigated experimentally. The sorption isotherm curves are highly hysteretic and, therefore, these systems can be used for energy-absorption applications. The following conclusions are drawn:

- Excess solid–liquid interfacial tension is dominant in the infiltration process, while the defiltration process is independent of it.
- Addition of Mg^{2+} and SO_4^{2-} ions can increase infiltration pressure and promote defiltration.
- Defiltration in smaller pores is easier than in larger pores.
- The energy absorption behaviour of the epsomite crystal-based system is similar with that of the saturated epsomite solution-based system.

Acknowledgements

This study was supported by The Army Research Office under Grant No. W911NF-05-1-0288, for which we are grateful to Dr David M. Stepp.

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