INSTITUTE OF PHYSICS PUBLISHING PHYSICA SCRIPTA
Phys. Scr. **74** (2006) 531–534 doi:10.1088/0031-8949/74/5/006

Energy absorption of nanoporous silica particles in aqueous solutions of sodium chloride

Xinguo Kong, Falgun B Surani and Yu Qiao

Department of Civil Engineering, University of Akron, Akron, OH 44325-3905, USA

E-mail: yqiao@uakron.edu

Received 7 December 2004
Accepted for publication 11 August 2006
Published 3 October 2006
Online at stacks.iop.org/PhysScr/74/531

Abstract
An experimental study is carried out on the effect of chemical admixtures, particularly sodium chloride, on the energy absorption behaviour of a hydrophobic nanoporous silica. As the pressure increases, once the capillary effect is overcome, the liquid is forced into the nanopores; and when the pressure is reduced, outflow is difficult, resulting in a pronounced hysteresis. The inflow pressure and the specific absorbed energy are strongly dependent on the sodium chloride concentration, providing a promising way to adjust the system performance.

PACS number: 61.43.Gt

1. Introduction

In the past decade, processing techniques for nanoporous materials have been well established [1, 2]. Commonly used synthesis methods include the templating technique, in which the network surrounding the template is produced first through phase separation or nanocasting, and then the template is removed by etching or heating. Among the few network materials suitable for mesoporous processing, silica is probably the most important one. Silicas with various pore sizes in the range of 2–80 nm, pore shapes, pore volume fractions, pore distributions, pore connections, as well as surface properties have been produced [3–6]. The mesoporous silicas can be either in powder form with the particle size ranging from 0.1–100 μm or in monolith form as large as 100 mm. They have been widely used in catalysis, absorption, and purification processes [7, 8].

Recently, a novel application of mesoporous materials in advanced energy absorption systems (EAS) has been noticed by several research teams [9–12]. As pressure increases, in a system consisting of hydrophobic mesoporous particles immersed in water, forced inflow can occur once the capillary effect is overcome. As the pressure is reduced back to atmospheric pressure, the outflow, on the other hand, can be difficult. Thus, a considerable amount of energy is ‘absorbed’ during this loading–unloading process. Due to the ultrahigh specific area, the energy absorption efficiency can be higher than that of conventional energy absorption materials, such as composites or shape memory alloys, by an order of magnitude [10–12]. However, research in this area is still at a very early stage. The reason for the non-outflow is quite inadequately understood. It is not clear what the confinement effect of the nanopores on the interfacial properties is, and whether this is a more important factor than its influence on the molecular mobility. Currently, most of the data in the open literature are for systems based on pure water. In order to gain a deep insight into the solid–liquid interaction in the nanoenvironment, and to develop systems of higher energy absorption efficiency, it is imperative to understand the effects of admixtures.

In this paper, we study the behaviour of mesoporous silica particles in sodium chloride solutions. It is known that the addition of aqueous electrolytes such as NaCl can increase the surface/interfacial tension, and thus would have a beneficial effect on the energy absorption efficiency. Furthermore, the NaCl admixture can serve as an anti-freezing agent such that the system can be used at temperatures lower than 0 °C. Since the change in pH value is negligible as the NaCl concentration, c, varies, the acid and base terms, γ^+ and γ^-, in the van Oss–Chaudhury–Good (VCG) equation are quite constant [13]. As a result, at a macroscopic level, the relationship between the interfacial energy and the NaCl content is nearly linear [14–16].

0031-8949/06/050531+04$30.00

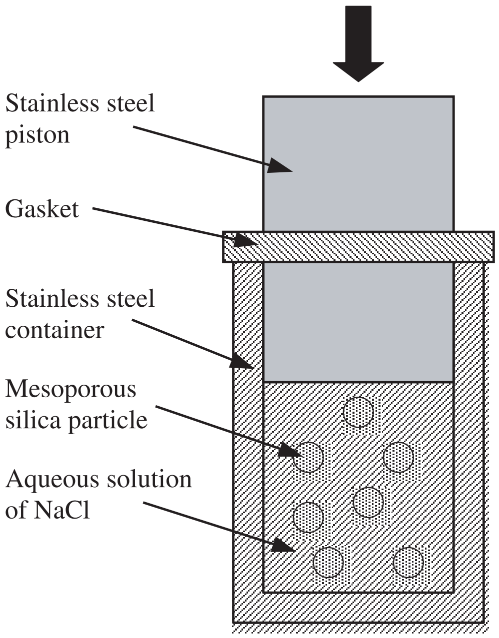

Figure 1. A schematic diagram of the nanoporous EAS.

2. Experimental

Figure 1 depicts the EAS consisting of end-capped Fluka 100 C_8 reversed phase mesoporous silica particles immersed in an aqueous solution of NaCl. The surface coverage was 10–12%. The particle size ranged from 15–35 μm. The average pore size, $\bar{r}$, was 7.8 nm, and the standard deviation was 2.4 nm. The specific area was 287 $m^2\,g^{-1}$. The specific pore volume was 0.55 $cm^3\,g^{-1}$. The Barrett–Joyner–Halenda (BJH) measurements were performed at the Quantachrome Instruments. Prior to the experiment, the particles were calcinated at 250 °C in vacuum for 6 h.

The mixture of the silica particles and the NaCl solution was sealed in a 304 stainless steel container with the cross-sectional area of 286.3 mm^2. By using a type-5569 Instron machine in displacement control mode, the system was compressed through a sliding steel piston at a constant rate of 1.0 $mm\,min^{-1}$. The friction force between the piston and the container was in the range of 20–30 N, which was negligible compared with the peak loading. When the applied pressure exceeded 50 MPa, the crosshead was stopped and then moved back at the same rate of 1.0 $mm\,min^{-1}$. The amount of the mesoporous silica particles used in each test was 0.5 g.

Altogether, eight systems of different NaCl concentrations were studied. For each system, 4–7 samples were tested. The typical sorption isotherm curves are shown in figure 2. The specific volume change is defined as the ratio of the system volume change to the amount of mesoporous particles. The area enclosed by the loading–unloading loop indicates the specific absorbed energy, E^*, which is shown in figure 3 as a function of c. The inflow pressure, P_{in}, is taken as the pressure at the centre point of the plateau region of the loading curve (see figure 4), which will be discussed in detail shortly. The liquid–silica interfacial energy can be estimated through $\Delta\gamma = p_{\text{in}}\bar{r}/2$ [9, 10], and the result is also shown in figure 4.

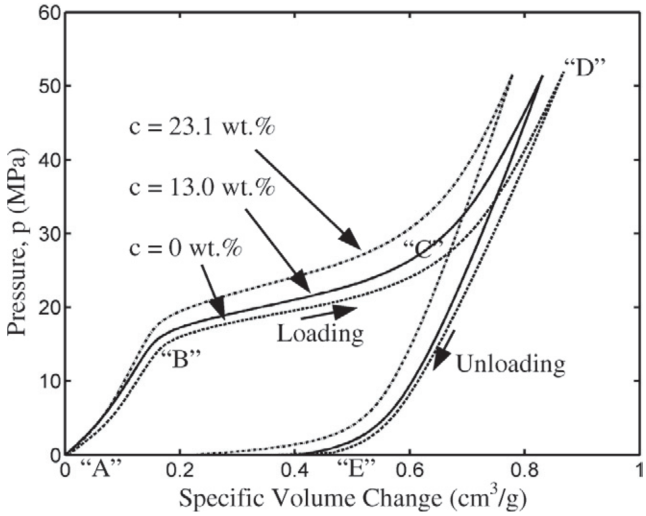

Figure 2. The sorption isotherms of mesoporous silica particles immersed in aqueous solutions of NaCl.

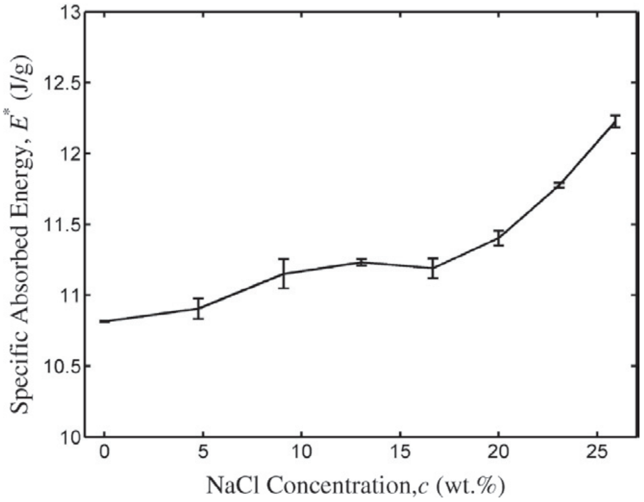

Figure 3. The energy absorption efficiency, E^*, as a function of the NaCl concentration.

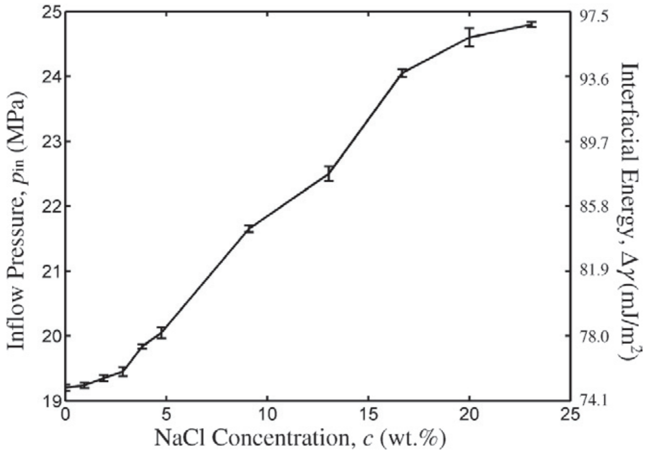

Figure 4. The measured inflow pressure, p_{in}, and the calculated interfacial energy, $\Delta\gamma$, as functions of the NaCl concentration.

3. Results and discussion

Through figure 2, it can be seen that, in the EAS based on pure water, initially as the volume variation increases from point 'A' to 'B', the pressure rises rapidly. The effective bulk modulus, $p/(\Delta V/V)$, is about 2.5 GPa, where ΔV is the volume change under pressure p, and V is the initial volume. This value is somewhat different from the literature data for water, which is about 2.2 GPa, primarily due to the presence of the silica particles. When the pressure exceeds about 15 MPa, from point 'B' to 'C', there is a plateau region, which should be attributed to the forced inflow of water in the nanopores. In the ideal case where all the nanopores are identical, the pressure should be constant in this region. In the current study, since the pore size distribution is relatively broad, the slope is of a finite value. The volume variation associated with the plateau region is in the range of 0.5–0.55 $\mathrm{cm^3\,g^{-1}}$, close to the specific pore volume fraction measured by the BJH technique, as it should be.

As most of the pores are filled, from point 'C' to 'D', the water phase becomes a load-bearing component again, and the system stiffness converges to that of section 'AB'. When the pressure reaches around 50 MPa, the crosshead is stopped and moved back, resulting in the rapid decrease in pressure. The unloading curve is quite linear when the pressure is higher than 5 MPa, indicating clearly that the confined water in the nanopores is unable to come out. Under low pressures, outflow starts to occur; but until p is reduced to 0 the system volume is still not fully recovered. Due to the non-outflow, the increase in interfacial energy associated with the forced inflow can be considered as being 'absorbed'. The energy absorption efficiency $E^* = 10.7\ \mathrm{J\,g^{-1}}$.

As the NaCl concentration increases, the system stiffness becomes higher. When c is changed from 0 to 30 wt%, the effective bulk modulus rises by about 20%. This is consistent with the literature data of the bulk moduli of NaCl solutions [17]. The specific volume change associated with the plateau region, however, remains the same, as it should, since it reflects the pore volume fraction. The value of the inflow pressure, p_{in}, increases with c, i.e. with the addition of the NaCl, the inflow is more difficult, which should be attributed to the increase in $\Delta\gamma$ [18].

As shown in figure 4, unlike in the macroscopic cases where the surface energy varies linearly in a broad range of NaCl concentration [14–16], for the mesoporous silica the $\Delta\gamma$–c relationship is quite nonlinear. When $c > 20$ wt%, the nonlinearity may be related to the saturation effect. When c is lower than 5 wt%, the nonlinear behaviour cannot be captured by the conventional interfacial energy theories, which are usually based on the calculations of the change in chemical potentials associated with the ion distribution in the interfacial zone. In the nanopores, the confinement effect of the pore walls must be taken into account. Since the pore radius is comparable with or even smaller than the interfacial zone, a 'bulk liquid' phase does not exist, and thus the molecular interaction can be significantly affected. However, currently there is still no satisfactory model that can capture the details of this size effect.

Comparison between figures 3 and 4 shows that, while both E^* and p_{in} increase with c, the former is less sensitive to c. As the NaCl concentration increases from 0 to 23.1 wt%, p_{in} increases by about 30% and E^* increases by only about 15%. This is because that when p_{in} increases, p_{out}, the critical pressure at which the outflow starts to occur, also rises (see figure 2), and therefore the beneficial effect of increasing p_{in} on E^* is lowered. Thus, the mechanisms of the NaCl concentration effects on the inflow and outflow processes must be different. The inflow can be discussed in the framework of surface flow processes, in which the dominant factor is the balance of the surface and interface forces. The outflow, on the other hand, may be considered as an equilibrium phase transformation [10–12], for which the key factors are still under investigation.

4. Conclusions

To summarize, the effects of addition of NaCl in nanoporous EAS is investigated through loading–unloading experiments. As the pressure increases, the capillary effect can be overcome and the liquid is forced into the hydrophobic nanopores. When the pressure is reduced, the liquid cannot completely come out, leading to a significant hysteresis behaviour. Through this process, a considerable amount of energy is absorbed. The following conclusions are drawn.

1. In the nanoenvironment, the relationship between the interfacial tension and the NaCl concentration is highly nonlinear.
2. The addition of NaCl leads to higher inflow and outflow pressures.
3. Increasing NaCl concentration is beneficial to the energy absorption efficiency.

Acknowledgments

This study was supported by the Army Research Office under grant W911NF-04-1-0244, for which we are grateful to Dr D M Stepp. Special thanks are also due to Dr M Jaroniec and Dr B Z Newby for valuable suggestions and useful discussions.

References

[1] Terasaki O *et al* 2002 *Studies Surf. Sci.* **141** 27
[2] Polarz S and Smarsly B 2002 *J. Nanosci. Nanotech.* **2** 581
[3] Lin Y S, Kumakiri I, Nair B N and Alsyouri H 2002 *Separ. Purif. Method* **31** 229
[4] Hayashi J, Watada Y and Muroyama K 2001 *Mater. Lett.* **50** 87
[5] Stout R W, Cox G B and Odiorne T J 1987 *Chromatographia* **24** 601
[6] Kralj S, Ziedansek Z, Lahajnar G, Zumer S and Blinc R 2000 *Phys. Rev.* E **62** 718
[7] Dabrowski A 2001 *Adv. Colloid Interface Sci.* **93** 135
[8] Pandey P and Chauhan R S 2001 *Prog. Polym. Sci.* **26** 853
[9] Borman V D, Grekhov A M and Troyan V I 2000 *J. Exp. Theor. Phys.* **91** 170
[10] Han A and Qiao Y 2006 *J. Am. Chem. Soc.* **128** 10348
[11] Han A, Kong X and Qiao Y 2006 *J. Appl. Phys.* **100** 014308
[12] Qiao Y and Kong X 2005 *Phys. Scr.* **71** 27

[13] van Oss C J 1994 *Interfacial Forces in Aqueous Media* (New York: Marcel Dekker)

[14] Matubayasi N, Matsuo H, Yamamoto K, Yamaguichi S and Matuzawa A 1999 *J. Colloid Interface Sci.* **209** 398

[15] Levin Y and Flores-Mena J E 2001 *Europhys. Lett.* **56** 187

[16] Weissenborn P K and Pugh R J 1996 *J. Colloid Interface Sci.* **184** 550

[17] Lane C D, Hathcock D J, Leavitt A J, Khan F A and Hansen J E 2001 *Chem. Edu.* **6** 4

[18] Churaev N V 1990 *Liquid and Vapor Flows in Porous Bodies—Surface Phenomena* (The Netherlands: Gordon and Breach)