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● *Short Communication*

SUSCEPTIBILITY EFFECTS IN UNSATURATED POROUS SILICA

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Nuclear magnetic resonance proton line widths have been studied as the saturation level of water in a porous silica system is varied. Two silica samples were used with nominal pore sizes of 60 and 140 Å. It was found that the line width increased with saturation level for both systems; this is consistent with the saturation process suggested by Allen et al. At low saturation levels the peak shift, from bulk water, increased with the saturation level reaching a maximum at filling factors of approximately 40% and 20% for the 60- and 140-Å samples, respectively, after which point it began to decrease. Analysis is currently under way to try to model this system to determine whether these results are also consistent. It is anticipated that further analysis will give information on the pore morphology of the system.

Keywords: **Porous media; Susceptibility; NMR; Water.**

INTRODUCTION

This work involves a nuclear resonance imaging study of water confined within unsaturated porous media. There has been much previous work[1,2] on the study of water in porous materials, but it has generally involved completely saturated systems. It is also expected that this technique will provide information on the morphology of the confining pores. There are at present few techniques available for this. Related work has recently been published by Allen et al.[3] that used nuclear magnetic resonance relaxation measurements to study the location of water in unsaturated porous silica.

MATERIALS AND METHODS

Experimental

The proton line width and peak shift were measured as a function of saturation level for water confined within a porous silica sample. The work was carried out on a Bruker (Karlsruhe, Germany) MSL300 at a proton resonance frequency of 300 MHz. A single 90° pulse was applied, and an free induction decay (FID) was acquired. After Fourier transforming, the line width was measured as the width at half-height. The peak shift was measured relative to bulk water.

Two silica samples were used in this work. According to the manufacturer's specifications they had nominal pore diameters of 60 and 140 Å, and specific pore volumes of 0.7 and 1.15 $cm^3\ g^{-1}$. These samples were supplied by Unilever and Aldrich, respectively. The samples were first dried then a known volume of water was added, and a measurement was taken at each different level of saturation (the percent saturation is defined as $100 \times$ [volume of water added/the total pore volume]).

Theory

Line widths are due to the observed nuclei having a range of resonant frequencies, i.e., being in a range of local magnetic fields. Variations in local fields can be caused in several different ways: 1) different chemical environments; 2) inhomogeneities in the main magnetic field B_0; and 3) different magnetic susceptibilities within heterogeneous materials. The main magnetic field B_0 in this work is very homogeneous. On our equipment the line width of a stationary bulk water sample can be shimmed down to less than 20 Hz. The lines observed in this work are at least 500 Hz wide. The cause is unlikely to be chemical environment effects as the chemical shift range for ^1H is known to be very small. It can therefore be concluded that it is susceptibility effects that are causing this line broadening.

There are three different materials present in our pore

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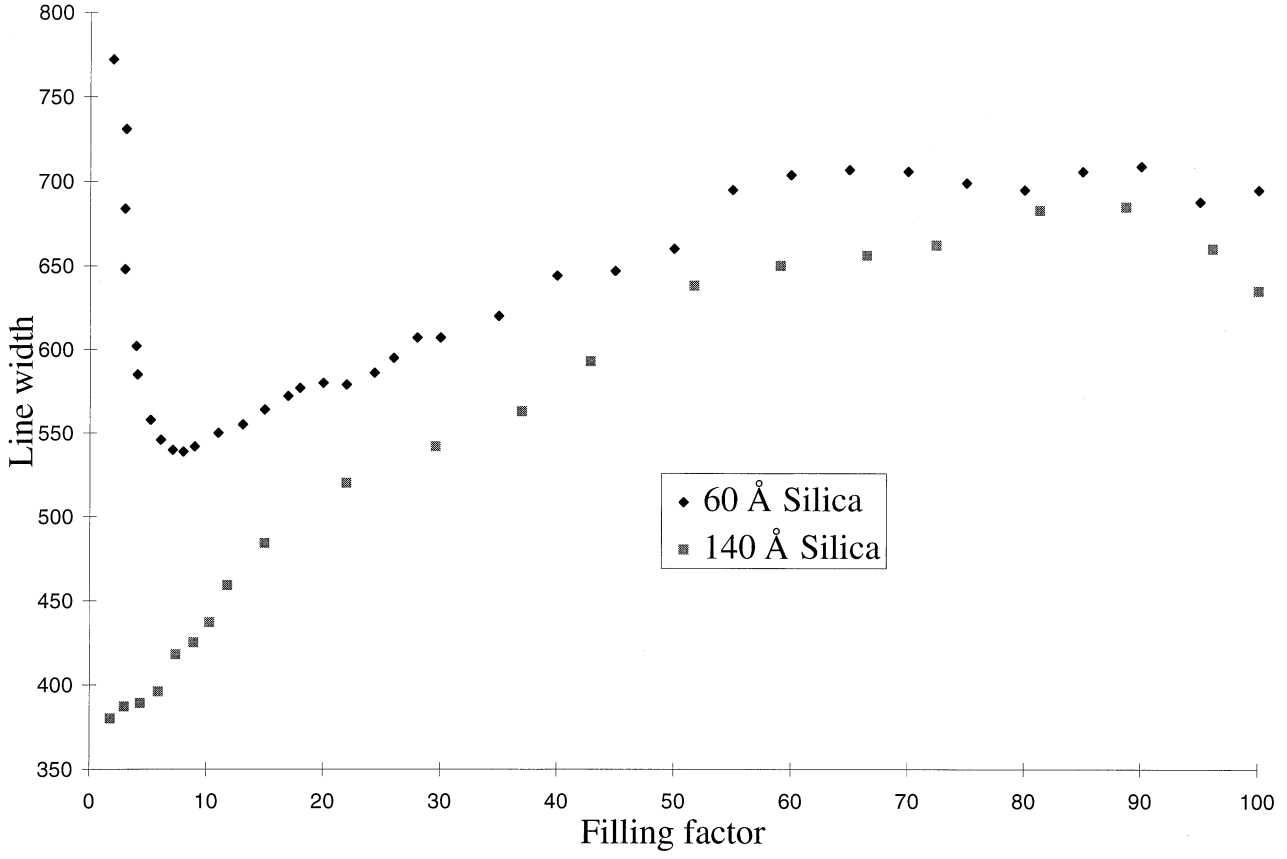

Fig. 1. A plot of proton line width against saturation level for water in 60 and 140 Å porous silica.

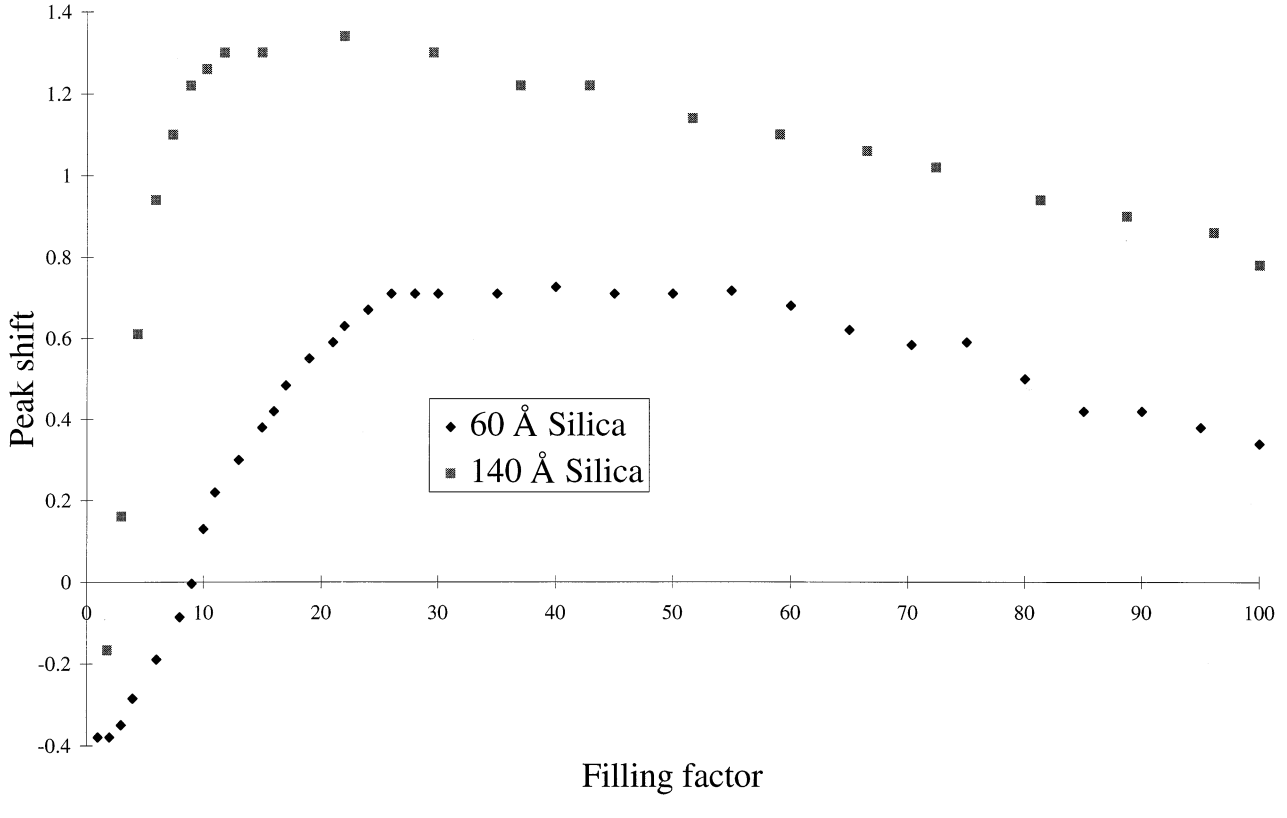

Fig. 2. A plot of peak shift relative to bulk water for water confined in 60- and 140-Å porous silica.

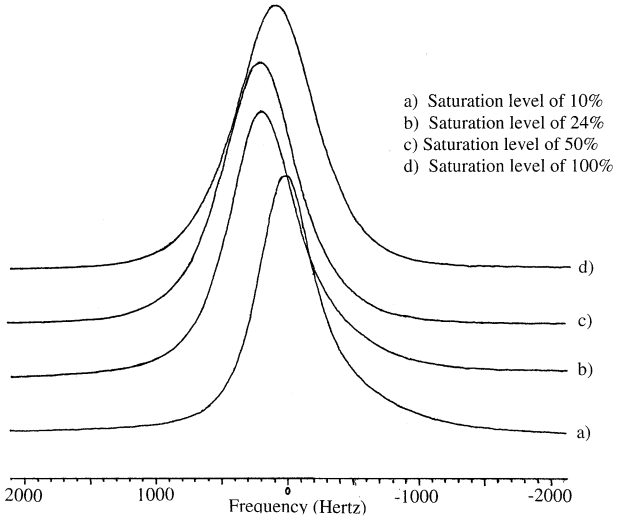

Fig. 3. Proton line shapes for water in 60 Å silica at different saturation levels. (a) 10%; (b) 24%; (c) 50%; (d) 100% saturation.

system, silica, water, and air, each with different susceptibility. The morphology of the pores and the location of the water will also affect the internal field gradients and hence the line width and peak shift.

RESULTS

The results are illustrated in the three figures.

DISCUSSION

Consider first the line width. Above a saturation level of 10%, the line width increases with saturation. Below 10%, a very broad line is observed for the 60-Å sample (but not for the 140-Å sample). This broad line is thought to arise from unevaporable hydroxyl groups that are bound to the surface of the silica.

The peak shift increases at low saturation levels until it flattens at approximately 30% and eventually begins to drop as filling is increased beyond 60%.

It has recently been suggested[3] that the hydration process occurs as shown in Fig. 4. The water first fills the cracks and interstices within the pore. As more water is added, it covers the surface, and the pores fill from the outside of the pore inward.

This filling process would also explain the line broadening with increased saturation. As the saturation level increases, water occupies different regions of the pore, thus experiencing different fields. The water as a whole will experience a greater range of fields, and so a broader line will be observed.

The results for the peak shift are harder to explain. The shift indicates a change in average field seen by the water which is certainly to be expected. Further analysis is needed to model different possible pore morphologies.

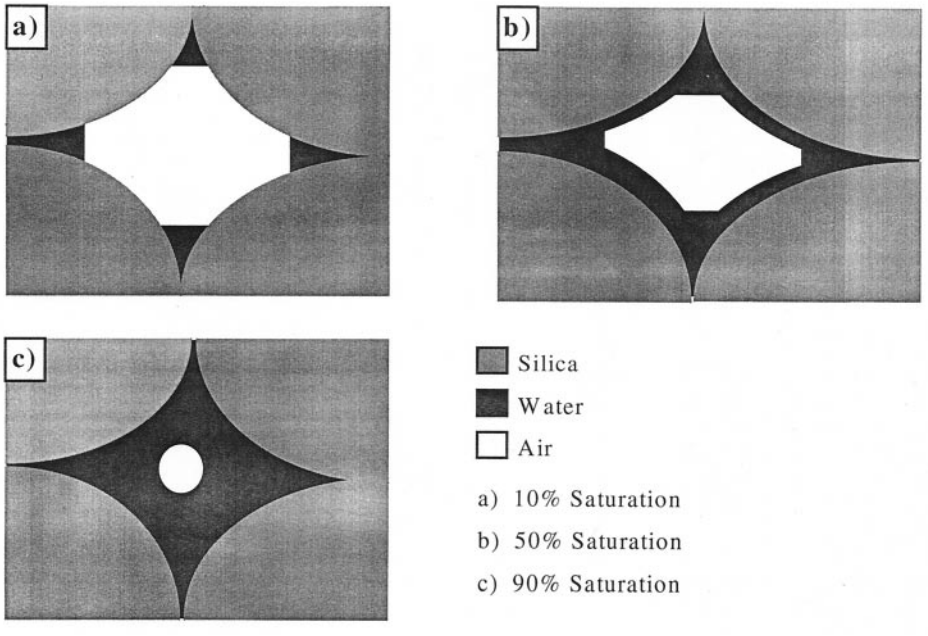

Fig. 4. The saturation process suggested by Allen et al.[3] for water in silica. This process appears to be consistent with our results.

CONCLUSIONS

The results from this work are consistent with the filling processes suggested by Allen et al. and illustrated in Fig. 3. Further analysis is currently being performed to obtain information on the morphology of the pores.

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