

● *Short Communication***A NMR INVESTIGATION OF ADSORPTION/DESORPTION HYSTERESIS IN POROUS SILICA GELS**P. PORION,* A.M. FAUGÈRE,* P. LEVITZ,* H. VAN DAMME,* A. RAOOF,† J.P. GUILBAUD,†
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The purpose of this study is to investigate possible differences in geometry and connectivity of the liquid phase in a partially water-saturated porous medium between the adsorption and the desorption branches, using a series of silica gels. This was done by comparing the T_1 and T_2 relaxation times (in ^1H and ^2H nuclear magnetic resonance (NMR) relaxation) as well as the water self-diffusion coefficient D (in ^1H) along the two branches of the adsorption/desorption isotherms. The results show that the two relaxation times and the diffusion coefficient are strongly dependent on the water content (saturation level). When plotted in normalized coordinates, the T_1 and T_2 vs. P/P_0 curves fit closely the adsorption/desorption isotherms, which validates the two-population, fast-exchange model. Furthermore, because at equivalent saturation levels, there is no difference between the relaxation times and diffusion coefficients obtained along the adsorption branch and those obtained along the desorption branch, one is led to the conclusion that despite different equilibrium conditions, the geometry and connectivity of the liquid phase are statistically the same along the two branches. © 1998 Elsevier Science Inc.

Keywords: Nuclear magnetic resonance relaxation; Silica gels; Diffusion coefficient; Porous media.

INTRODUCTION

The behaviour of confined liquids in porous silica gels is of both fundamental and practical interest. The purpose of our research is to investigate possible differences in geometry and connectivity of the liquid phase in a partially water-saturated medium between the adsorption and the desorption branches in such materials.

Some previous nuclear magnetic resonance (NMR) work^{1–5} on partially filled silica gels have been performed, but to our knowledge, it is the first time that the full hysteresis loop is studied.

In this present work, ^1H and ^2H NMR experiments have been performed to compare the T_1 and T_2 relaxation times as well as the water self-diffusion coefficient along the two branches of the adsorption/desorption isotherm. Using the results of adsorption/desorption isotherms experiments and within the framework of the fast exchange model,⁶ which was proved to be valid in our case, the relaxation rates should be sensitive to the solid/liquid

interface area, whereas the self-diffusion coefficient should depend on pore space tortuosity.

EXPERIMENTAL PROCEDURE

The study has been performed on a series of mesoporous (according to International Union of Pure and Applied Chemistry nomenclature) silica gels with pore diameters of 4, 6, and 10 nm, respectively (LiChroprep and/or LiChrospher from Merck, Rahway, NJ, USA). The adsorption/desorption water isotherms were obtained by applying the continuous inlet/outlet quasi-equilibrium gravimetric method.⁷ Type IV isotherms (Brunauer–Demming classification) were obtained in all cases (Fig. 1). The specific surfaces S_v have been calculated using the classical Brunauer–Emmett–Teller (BET) model.⁸

Two different NMR experiments have been used. All the NMR measurements were performed for different saturation levels by equilibrating the samples with a given water

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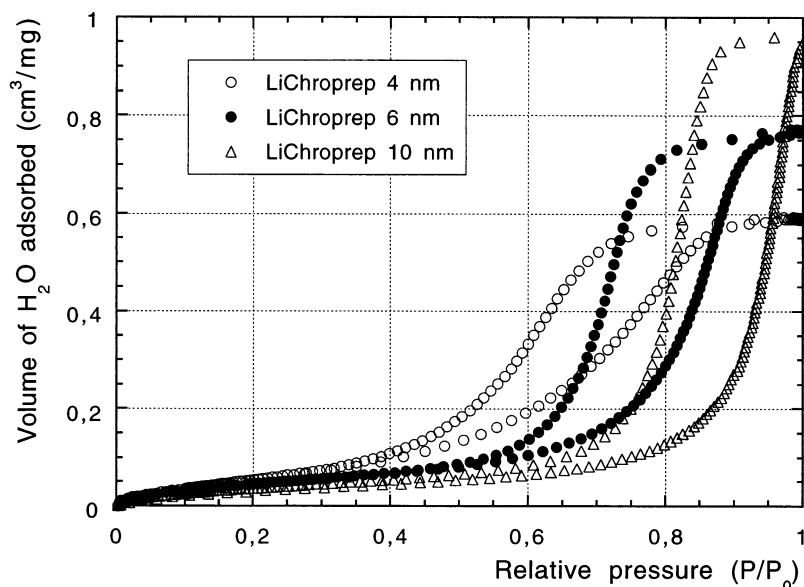


Fig. 1. Adsorption/desorption isotherms for water obtained by applying the continuous inlet/outlet quasi-equilibrium gravimetric method on different silica gels.

(or deuterated) vapor pressure at room temperature (23°C). In the first experiment, only the adsorption branch was investigated for all the samples filled with heavy water (D_2O). Deuterium T_1 relaxation times were measured at 55.28 MHz as function of the relative pressure P/P_0 (Fig. 2).

In the second experiment, the full hysteresis loop was explored only on the LiChroprep 10-nm samples by performing ^1H T_1 (inversion-recovery) and T_2 Carr–

Purcell–Meiboom–Gill sequence relaxation times (see Figs. 3 and 4), and diffusion coefficient D (pulsed field gradient Hahn sequence) measurements at 100 MHz.

RESULTS AND DISCUSSION

The results show that the two relaxation times (T_1 and T_2) are strongly dependent on the water content (satura-

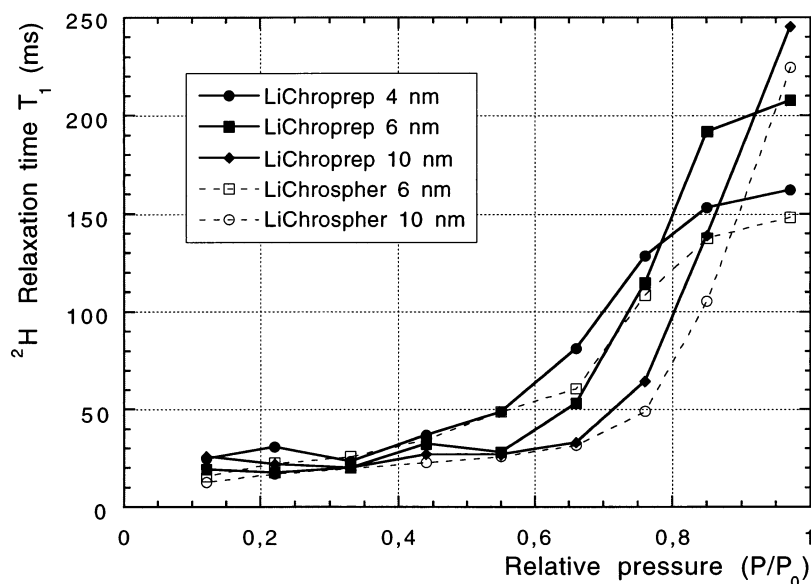


Fig. 2. ^2H relaxation time T_1 for different silica gels as a function of the relative pressure P/P_0 for the adsorption branch.

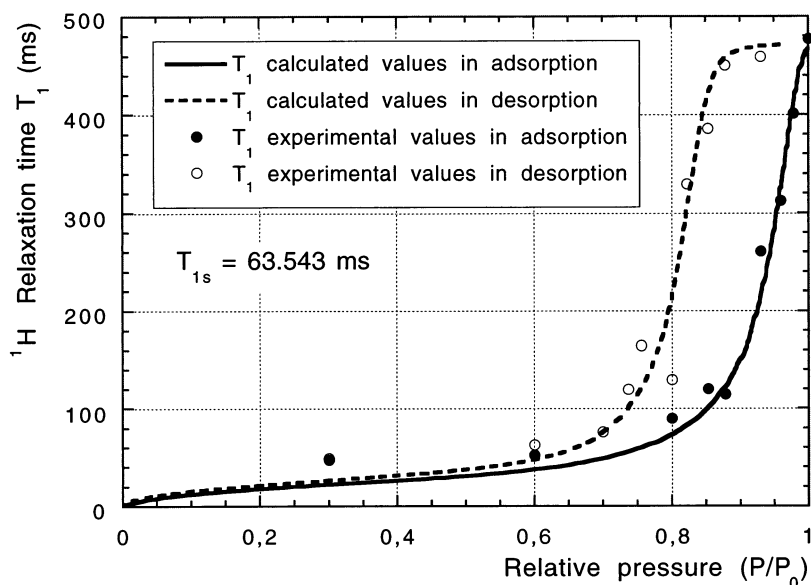


Fig. 3. ^1H relaxation time T_1 for the silica gels LiChroprep 10 nm as a function of the relative pressure P/P_0 for the adsorption and desorption branches. The solid and dashed lines represent, respectively, the fit of T_1 for the ad/desorption branches using the fast-exchange model with T_{1s} equal to 63.5 ms.

tion level). Indeed, when plotted in normalized coordinates, the T_1 and T_2 vs. P/P_0 curves fit closely the adsorption/desorption isotherms, which validates the two-population, fast exchange model and shows that T_1 and T_2 are only dependent on the water content and not

on whether this water content was reached on the adsorption or on the desorption branch. The same behavior, with a larger scatter of the data points, is obtained for the diffusion coefficient D . Concerning the ^2H data, for the smallest values of P/P_0 , we find that T_1 reaches to an

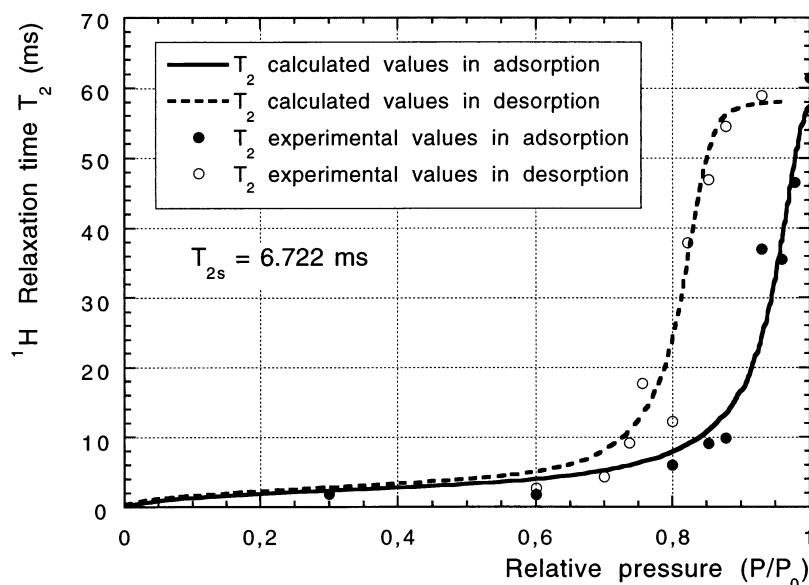


Fig. 4. ^1H relaxation times T_2 for the silica gels LiChroprep 10 nm as a function of the relative pressure P/P_0 for the adsorption and desorption branches. The solid and dashed lines represent, respectively, the fit of T_2 for the adsorption/desorption branches using the fast exchange model with T_{2s} equal to 6.7 ms.

asymptotic value (when P/P_0 reaches 0) equal to 20–25 ms, which can be defined as the T_{1s} (T_1 near the surface). It has been proved experimentally⁹ that this value does not depend on the paramagnetic centers in the deuterium NMR.

For the ^1H data, all of the hysteresis loop has been explored for the LiChroprep 10 nm. Using the results of the Brunauer–Emmett–Teller analysis and the experimental measurements of T_1 and T_2 , we have been able to calculate T_{1s} (63.5 ms) and T_{2s} (6.7 ms) assuming that the two-population, fast-exchange model is validated. The diffusion coefficient D has also been measured: it depends on the filling factor V/V_0 . Due to the tortuosity of our samples, we find values of D smaller than the bulk value ($D_{\text{H}_2\text{O}} = 2.3 \times 10^{-9} \text{ m}^2/\text{s}$). D varies in a range of 4.4×10^{-10} to $8.3 \times 10^{-10} \text{ m}^2/\text{s}$, depending on the V/V_0 values.

CONCLUSIONS

When taken together, our results did not allow us to detect any difference in NMR parameters between the adsorption and the desorption branches at equal water content. In other words, the geometry and connectivity of the liquid network at a given saturation level seems to be independent of whether this saturation level was approached from above or below. Whether this is general or restricted to the particular interface morphology of our samples remains to be established.

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