

● *Short Communication***FIELD-CYCLING NMR RELAXOMETRY OF MOLECULES UNDERGOING
LÉVY WALKS AT THE SURFACE OF FINE PARTICLES
AND POROUS GLASS**

TATIANA ZAVADA,* SIEGFRIED STAPF,* UWE BEGINN,† AND RAINER KIMMICH*

*Sektion Kernresonanzspektroskopie and †Abteilung Organische Chemie III, Universität Ulm, Ulm, Germany

Slow surface dynamics of solvents confined in the pore space of porous glass and fineparticles was studied by proton field-cycling relaxometry. Molecular reorientations mediated by translational displacements are shown to be an important low-frequency T_1 -relaxation mechanism in porous media at low nuclear magnetic resonance (NMR) frequencies in the strong adsorption limit. This is revealed by the pronounced T_1 -dispersion in this case while a flat one is observed for weak adsorption. The following nanoporous materials were examined in this respect: fineparticles of ZnO, TiO₂, porous glass. Silanized surfaces lead to a somewhat steeper T_1 -dispersion of non-polar cyclohexane than the native, i.e. polar, surfaces. On the other hand, there is no strong influence of the surface groups on the $T_1(\omega)$ slope of (polar) acetone. The results are discussed with reorientations mediated by translational displacements enhanced by Lévy walks on the surface. © 1998 Elsevier Science Inc.

Keywords: Porous media; Field-cycling; Reorientations mediated by translational displacements; Lévy walks.

INTRODUCTION

The low-frequency spin-lattice relaxation behavior of various liquids confined in the pore space of porous glasses and fineparticles is studied in order to probe the influences of the matrix surface geometry and adsorption properties on the adsorbate dynamics. It was experimentally found that the net effect of geometrical confinements reduces the translational mobility of molecules¹ but is of little influence to molecular reorientations unless strong adsorption bonds cause the preferential orientation of molecules relative to the adsorption sites on the surface. In this case, reorientations through molecular rotations are hindered near the surface. This situation is monitored by the frequency dependence of the spin-lattice relaxation: all polar liquids capable of forming strong bonds with the surface show a steep and all non-polar liquids a flat T_1 -dispersion. The former was shown^{1,2} to arise from the reorientation mediated by translational displacements (RMTD) mechanism.

RMTD appears as a consequence of the preferential orientation of adsorbate molecules relative to the surface and frequent desorption/readsorption events as soon as

the particle is once trapped by the surface. Surface diffusion develops in the form of Lévy walks³ through the bulk liquid from one surface site to another. This process persists a certain retention time until the particle tends to escape to the bulk. Large jumps lead to superdiffusive time scaling of the mean surface displacements $r \propto t$ which is typical for the Lévy-statistics. The corresponding waiting-time distribution of this process as well as a high molecular order relative to the surface leads to a much longer orientation correlation than that for rotational diffusion in the free liquid. The correlation gets gradually destroyed as the particles spread out along the curvature of the pore surface. This mechanism was recently corroborated with the aid of a Monte-Carlo computer simulation.⁴ In this work we extend our investigation to further systems (ZnO and TiO₂ fineparticles as well as porous glass with the modified surface).

EXPERIMENTAL

The field-cycling experiments were carried out with a home-built spectrometer. The detection magnetic-flux density was up to 1.5 T. Porous glass with a mean pore

Address correspondence to Tatiana Zavada, Sektion Kernresonanzspektroskopie, Universität Ulm, 89069 Ulm, Germany.

many. E-mail: tatjana.zavada@physik.uni-ulm.de

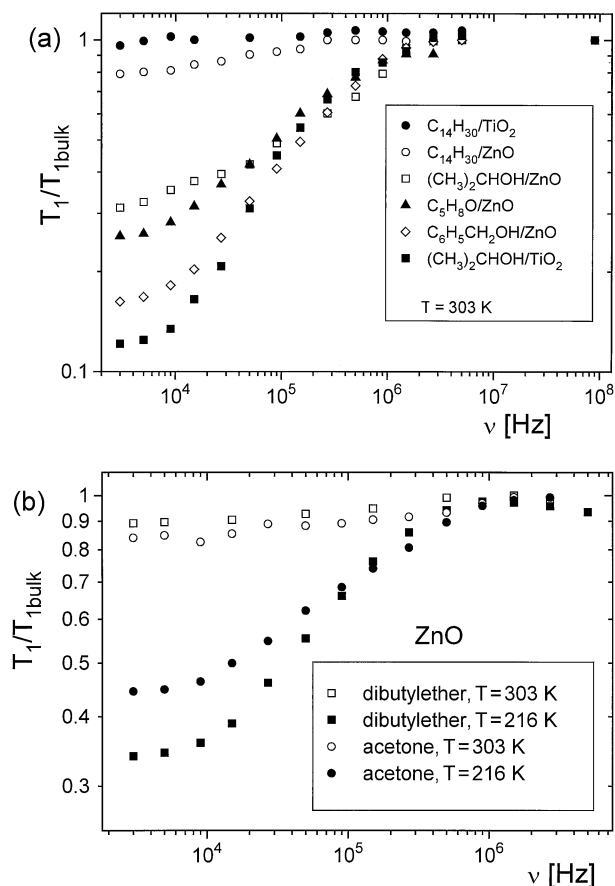


Fig. 1. Frequency dependence of the proton spin-lattice relaxation of organic liquids in the pore space of fineparticles: (a) polar and non-polar adsorbates in ZnO and TiO₂ particles; (b) polar adsorbate molecules with a symmetrical structure in ZnO particles. The data are plotted relative to the values measured in the bulk liquids.

diameter of 30 nm was purchased from Schott Glaswerke, Mainz, Germany. The ZnO and TiO₂ particles were obtained from Sigma-Aldrich, Steinheim, Germany. Using scanning electron microscopy the distribution of the particle sizes was specified by the range 200–800 nm (ZnO) and 200–500 nm (TiO₂). The pore surface of silica glass was treated by placing the predried porous glass directly in $(\text{CH}_3)_3\text{SiCl}$. The glass was then dried at 80°C under high vacuum. The polar hydroxyl groups were at least partially replaced by (non-polar) $\text{OSi}(\text{CH}_3)_3$ groups.

RESULTS AND DISCUSSION

Figure 1 shows the proton T_1 -dispersion for various liquids in ZnO particles. The efficiency of the RMTD low-frequency relaxation mechanism depends on both the polarity of the adsorbate and its molecular structure.

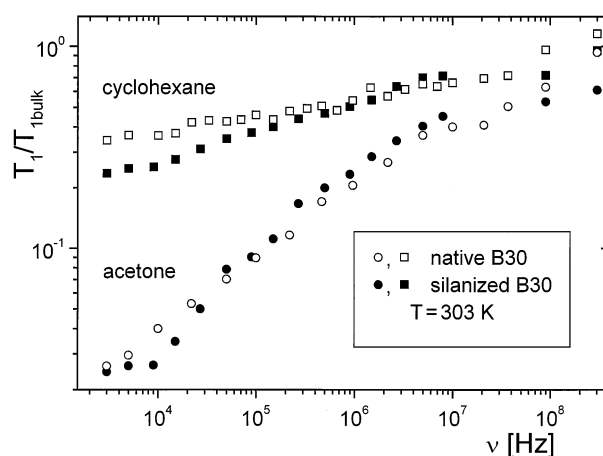


Fig. 2. Frequency dependence of the proton spin-lattice relaxation times of cyclohexane and acetone in porous glass B30 with native and silanized surfaces, respectively.

Polar molecules on a polar surface show a strong T_1 -dispersion in contrast to non-polar adsorbate species. On the other hand, linear molecules such as acetone and dibutylether having a polar group in the middle are capable of forming strong adsorption bonds with Zn^{2+} of the surface but nevertheless show a flat T_1 -dispersion at room temperature. This indicates the lack of any orientational order on the surface because the rotational barriers are low. That is, the high symmetry of these molecules prevents establishing a preferential orientation relative to the surface. However, at temperatures below 250 K, the intensity of rotational motion decreases so that RMTD becomes an important relaxation mechanism, as can be seen from the steeper T_1 dispersion curve (Fig. 1b).

In contrast, non-symmetrical linear polar molecules (hexanol, isopropyl alcohol) and rigid molecules with a ring structure (benzyl alcohol, cyclopentanone) have high rotational barriers. Therefore, a certain molecular order is expected on the surface as revealed by the steep T_1 -dispersion (Fig. 1a).

Figure 2 shows the T_1 -dispersions of cyclohexane and acetone in porous glass B30 for native as well as silanized surfaces. In the latter case the frequency dependence of the spin-lattice relaxation time of cyclohexane turned out to be steeper. The (slight) difference in the slope of $T_1(\omega)$ can be traced back to the better adsorption conditions for a non-polar molecule on the silanized surface. However, the non-polar cyclohexane is still incapable of strong adsorption bonds with the surface. For this reason, molecular dynamics of C_6H_{12} on native and silanized silica surfaces is not drastically different. In neither case is RMTD as efficient as for polar adsorbates on a polar adsorbent. On the other hand, no significant

influence of the surface modification on the slope of $T_1(\omega)$ was found for polar acetone in porous glass. This suggests that the protons in the surface hydroxyl groups do not participate in establishing the anomalous surface dynamics in this case.

CONCLUSIONS

Reorientation Mediated by Translational Displacements is the dominant low-frequency spin-lattice relaxation mechanism for most polar molecules confined in the pore space of polar fineparticles as well as in porous glasses. The symmetry of polar adsorbate molecules strongly influences the rotational dynamics in the bound state and, hence, the efficiency of the RMTD process. In the cases of acetone and cyclohexane, silanization of porous glass turned out to be of little influence on the surface dynamics.

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