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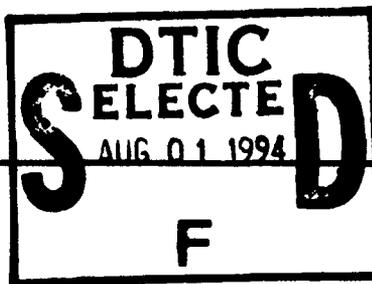
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As outlined in the original proposal our work deals with NMR and laser Raman scattering experiments on highly viscous liquids, including lubricants, both in bulk and confined geometries, over a wide range of pressures and temperatures. In a general sense we focus on the relationship between molecular level properties as obtained from our experiments and the macroscopic properties of the fluid studied, including fluids at the fluid-solid interface.

As continuation of our systematic efforts to improve the understanding of the dynamic behavior of confined fluids we carried out NMR relaxation experiments on a number of molecular fluids including model lubricants. Of particular interest are the unique experiments dealing with pressure effects on confined liquids.

As far as the development of new instrumentation is concerned we designed and fabricated NMR probes and pressure generating systems which allow measurements up to 10kbar pressures.

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## **SUMMARY OF RESEARCH PROGRESS**

**As outlined in the original proposal our work deals with NMR and laser Raman scattering experiments on highly viscous liquids, including lubricants, both in bulk and confined geometries, over a wide range of pressures and temperatures. In a general sense we focus on the relationship between molecular level properties as obtained from our experiments and the macroscopic properties of the fluid studied, including fluids at the fluid-solid interface.**

**As continuation of our systematic efforts to improve the understanding of the dynamic behavior of confined fluids we carried out NMR relaxation experiments on a number of molecular fluids including model lubricants. Of particular interest are the unique experiments dealing with pressure effects on confined liquids.**

**As far as the development of new instrumentation is concerned we designed and fabricated NMR probes and pressure generating systems which allow measurements up to 10kbar pressures.**

## **1.0 RESEARCH ACCOMPLISHMENTS**

### **1.1 LIQUIDS IN CONFINED GEOMETRIES**

#### **1.11 Confinement effects on dipolar relaxation by translational dynamics of liquids in porous silica glasses**

A theory of dipolar relaxation by translational diffusion of a *nonwetting* liquid confined in model porous media was presented. We obtained expressions of the rates of spin-lattice relaxation  $1/T_1$ , spin-spin relaxation  $1/T_2$ , and spin-lattice relaxation in the rotating frame  $1/T_{1\rho}$ , which depended on the average pore size  $d$ . The frequency variations of these rates were intermediate between the two-dimensional and three-dimensional results. At small frequency they varied logarithmically for small  $d$  and tended progressively to a constant with increasing  $d$ . For small pore sizes we obtained quadratic confinement dependences of these rates ( $\propto 1/d^2$ ), at variance with the linear ( $\propto 1/d$ ) relation coming from the biphasic fast exchange model usually applied for a *wetting* liquid in porous media. We applied such a theory to the  $^1\text{H}$  NMR relaxation of methylcyclohexane liquid in sol-gel porous silica glasses with a narrow pore-size distribution. The experiments confirmed the theoretical predictions for very weak interacting solvent in porous silica glasses of pore sizes varying in the range of 18.4-87.2 Å and in the bulk. At the limit of small pores, the logarithmic frequency dependencies of  $1/T_{1\rho}$  and  $1/T_1$  observed over several decades of frequency were interpreted with a model of unbounded two-dimensional diffusion in a layered geometry. The leveling off of the  $1/T_{1\rho}$  low-frequency dependence was interpreted in terms of the bounded two-dimensional diffusion due to the finite length  $L$  of the pores. An estimate of a finite size of  $L=100$  Å was in excellent agreement with the experimental results of the transmission electron microscopy study of platinum-carbon replicated xerogels.

#### **1.12 NMR Study of the Geometric Confinement Effects on the Anisotropic Rotational Diffusion of Acetonitrile- $d_3$**

The NMR spin-lattice relaxation times,  $T_1$ , of deuterium and nitrogen-14 of a symmetric-top molecule of acetonitrile- $d_3$  confined to sol-gel porous silica glasses were measured as a function of pore size over the temperature range 233-308 K. In agreement with our earlier results for other polar liquids we found the two-state fast-exchange model to be valid for both deuterium and nitrogen-14 spin-lattice relaxation data of acetonitrile- $d_3$ . The classical rotational diffusion equation was used to calculate the rotational diffusion constants,  $D_{||}$  and  $D_{\perp}$ , corresponding to motion about the main symmetry axis and motion about the axis perpendicular to the main symmetry axis, respectively. The rotational diffusion constant  $D_{||}$ , decreases dramatically with confinement to smaller pores, whereas confinement has a small effect on  $D_{\perp}$ . This experimental finding shows that confinement of liquid acetonitrile to porous silica glasses increases its motional anisotropy.

### **1.13 Pressure effects on the anisotropic rotational diffusion of acetonitrile- $d_3$ in confined geometry**

The NMR relaxation behavior of a polar molecular liquid, acetonitrile- $d_3$ , confined to porous silica glasses prepared by sol-gel process, was studied at pressures up to 5 kbar at 300K. Analysis of the relaxation data in terms of the two-state fast exchange model and the classical rotational diffusion equation allowed us to determine the pressure effects on the anisotropic rotational diffusion of acetonitrile- $d_3$  in confined geometry.

### **1.14 Relative role of surface interactions and topological effects in NMR of confined liquids**

We identified the relative roles of surface and topological effects on the nuclear relaxation rates  $T_1^{-1}$ ,  $T_2^{-1}$  and  $T_{1\rho}^{-1}$  of polar or non-polar liquids in porous silica glasses due to their very different pore size and frequency dependences. On the basis of a theory and molecular dynamics simulations for modelled porous systems, these rates  $1/T_1$

had been interpreted in terms of a linear combination of bulk, confinement and surface effects:  $1/T_1 = 1/T_{1\text{bulk}} + a_1/R^2 + b_1/R$ , where  $R$  was the average pore size and  $a_1$  and  $b_1$  were given in terms of the usual relaxation parameters of the studied molecular species. This simple expression had been used to fit the observed  $^1\text{H}$  relaxation rates as a function of pore size and frequency for methylcyclohexane, nitrobenzene, pyridine and toluene both for unmodified and surface modified porous silica glasses. Having used this method, the surface ( $\propto 1/R^2$ ) relaxation contributions were obtained and a quantitative estimation of the surface and translational correlation times were deduced. More generally, we explained the following seemingly paradoxical results obtained in confinements. (i) The pure confinement effect was independent of the polarities of the liquid molecules in pores and was very sensitive to the frequency. (ii) One had a logarithmic frequency variations of  $T_1^{-1}$  and  $T_1\rho^{-1}$  for small pores both for polar or nonpolar liquids, which showed that the geometrical confinement dominates over the surface interaction at low frequency and for small pores. In contrast to the bulk liquid behavior, the presence of a minimum of  $T_1$  in the temperature dependences of  $^1\text{H}$  relaxation rates of methylcyclohexane liquid at various conditions of pore sizes and frequencies and the absence of a phase transition in small pores, proved the existence of the anisotropic diffusion of this confined liquid.

## **1.2 STUDIES OF LUBRICANTS**

### **1.21 High resolution $^{13}\text{C}$ NMR study of liquid 2-ethylhexyl benzoate confined to porous silica glasses**

The natural abundance carbon-13 NMR spin-lattice relaxation times,  $T_1$ , and spin-spin relaxation times,  $T_2$ , of different carbons in the model liquid lubricant 2-ethylhexyl benzoate (EHB) confined to porous silica glasses prepared by the sol-gel process were measured as a function of pore size in the range of pore radii from 21 Å to 80 Å at 294 K. In agreement with our earlier results for other polar liquids we found that the two-state fast exchange model was valid for the  $^{13}\text{C}$  spin-relaxation data for liquid EHB, i.e., the

$(1/T_1)$  rates scale as  $(1/R)$  with the pore radius,  $R$ . The analysis of the  $(1/T_1)$  data for each carbon in confined EHB in terms of the two-state fast exchange model allowed us to calculate the relaxation rates  $(1/T_{1s})$  for each carbon of the EHB liquid in the surface layer. The comparison of  $(1/T_{1s})$  for each carbon with the  $1/T_1$  values for individual carbons in bulk EHB provided information on motional dynamics of EHB at the liquid/surface interface. The experimental  $^{13}\text{C}$  spin-spin relaxation rates  $(1/T_2)$  obeyed the quadratic power law  $(1/R^2)$  for confined EHB, which confirmed that at low frequency the pure geometric confinement effects dominate over surface interaction effects. Additional information on the EHB surface interactions was obtained by carrying out the NMR experiments with surface modified silica glasses.

## **1.22 Viscosity and density measurements of polyperfluoroethers**

Atmospheric pressure densities have been obtained for four Krytox® oils using a commercial Paar DMA45 Density Meter at a variety of temperatures. Viscosity measurements at high pressure have been obtained for Krytox® GPL 105, 143-AY, and 143-AX using a falling slug viscometer (slug coaxial hole ID=0.125") described previously. The scale is calibrated using anhydrous glycerol and the 500 cent and 1000 cent DCF 200 fluids at atmospheric pressure and a variety of temperatures.

## **2. WORK IN PROGRESS**

### **2.1 NMR Study of carbon-13 relaxation in di-(2-ethylhexyl)phthalate**

In continuation of the earlier experiments on 2-ethylhexyl benzoate(EHB) and 2-ethylhexyl cyclohexanecarboxylate(EHC)[1-4], natural abundance  $^{13}\text{C}$  NMR relaxation of di-(2-ethylhexyl)phthalate(DEHP) is now being studied. The choice of these liquids was motivated by a lack of understanding about the relationships between microscopic and macroscopic properties of elastohydrodynamic (ehd) lubricants. In the previous studies EHB was chosen as a model lubricants because it is complex enough to represent an actual lubricant yet simple enough to probe spectroscopically. As a next step of

systematic NMR relaxation experiments on complex fluids, we are investigating more complex and realistic lubricants, through which the understanding of dynamic behavior of highly viscous fluids including lubricants may be improved.

DEHP is widely used chemical compound in industry as a plasticizer for polymer processing, a diffusion pump fluid, or a synthetic lubricant. Due to the structural similarity between EHB and DEHP, the experimental and analytical methods for EHB study would be applied to the study of DEHP. These include natural abundance  $^{13}\text{C}$  spin-lattice relaxation time ( $T_1$ ) and Nuclear Overhauser Enhancement (NOE) measurements for individual carbon atom and analyze the relaxation data in terms of available theoretical models for liquid dynamics. However, the viscosity of DEHP is quite different from that of EHB in the investigated temperature region, and consequently the two liquids are in the different motional regime. Hence for the effective study of dynamic behavior of DEHP, the additional spin-lattice relaxation time in the rotating frame ( $T_{1\rho}$ ) and spin-spin relaxation time ( $T_2$ ) measurements need to be performed.

## 2.2 10 kbar Project

Two 10kbar NMR probes are currently awaiting testing, one for 300 MHz and one for 180 MHz( $^1\text{H}$ ). Pressures are to be generated using both a "large" and "small" pressure-generating system. The "large" system combines a relatively large intensifier along with a separator, and will be used primarily with the 300 MHz system. The "small" table contains a smaller intensifier and no separator. The small system will eventually be used exclusively with the 180 MHz probe, where high resolution proton studies ( $\text{CS}_2$  pressure transmitting medium) will not be required.

The initial probe design had used the "conventional" 5kbar design, which consists of a copper leadthrough, brazed stainless steel cone, and an SP-1 insulating cone. After the 9.2kbar pressurization, the copper leadthrough had become sheared at the tip of the SP-1 cone. With this development, attention has been focused on improving the

feedthrough design. Three possible variants have been chosen for testing, and are described in the following:

- a) Beryllium-copper feedthrough design
- b) Coaxial feedthrough design
- c) Boron nitride design

### **2.3 NMR measurements of $^{19}\text{F}$ relaxation times of perfluoromethylcyclohexane liquid and the liquid confined to porous silica glasses**

The theoretical interpretation of the NMR relaxation data for perfluoromethylcyclohexane liquid confined to porous silica glasses is in progress.

The  $^{19}\text{F}$  NMR relaxation times,  $T_1$  and  $T_2$ , of perfluoromethylcyclohexane liquid and the liquid confined to porous silica glasses were measured at the resonance frequency of 169.2 MHz over the temperature range from 0°C to 45°C. Several additional  $T_1$  measurements were made on bulk liquid at 376 MHz. A frequency dependence of  $T_1$  is observed due to the relaxation through chemical shift anisotropy. For the liquid in bulk and in large pores, the temperature dependence  $T_1^{-1}$  data show that the spin-rotation interaction is one of the main mechanisms dominating the spin-lattice relaxation at high temperatures. For the liquid in small pores and at low temperatures, the spin-rotation interaction becomes less important for the fluorine nucleus. The data for  $T_1^{-1}$  as a function of pore size shows a linear dependence on  $R^{-1}$  for most of the fluorine nuclei at lower temperatures. This indicates that the surface interaction between the liquid and the glass surface, and the intramolecular dipole-dipole interaction, may play an important role in the relaxation process. However, in contrast to the  $T_1^{-1}$  behavior,  $T_2^{-1}$  follows a linear dependence on  $R^{-2}$ . This means that the intermolecular dipole interaction, due to the logarithmic frequency enhancement of the spectral density, becomes a dominating mechanism to determine the relaxation time in the very low frequency regime.

### **2.4 NMR study of natural abundance $^{13}\text{C}$ relaxation of confined $\text{CS}_2$**

The final set of experiments to be discussed deals with our preliminary NMR study of liquid CS<sub>2</sub> confined to porous silica glasses. There were two main reasons for this study. In view of the referred literature data we wanted to find out whether confinement affects in a major way the dynamics of confined, non-polar liquid or CS<sub>2</sub>. In addition, it is well known that both chemical shift anisotropy and spin-rotation interactions contribute to the natural abundance <sup>13</sup>C NMR spin-lattice relaxation times, T<sub>1</sub>, in bulk liquid CS<sub>2</sub>. This offers an interesting opportunity to investigate the effects of confinement on angular momentum behavior in the simple fluid of CS<sub>2</sub>.

### 3. Recent Publications Acknowledging AFOSR Support

"NMR Study of the Geometric Confinement Effects on the Anisotropic Rotational Diffusion of acetonitrile-*d*<sub>3</sub>," J. Zhang and J. Jonas, *J. Phys. Chem.* **97**, 8815 (1993).

"Pressure effects on the anisotropic rotational diffusion of acetonitrile-*d*<sub>3</sub> in confined geometry," S. Xu, Y. J. Kim, and J. Jonas, *Chem. Phys.* **218**, 329-332 (1994).

"High Resolution <sup>13</sup>C NMR Study of Liquid 2-Ethylhexyl Benzoate Confined to Porous Silica Glasses," J. Zhang and J. Jonas, *J. Phys. Chem.*, in press.

"Relative Role of Surface Interactions and Topological Effects in NMR of Confined Liquids," J. P. Korb, A. Delville, S. Xu, Y. J. Kim, G. Demeulenaere, P. Costa, and J. Jonas, *J. Chem. Phys.*, submitted.

"Pressure as an Experimental Variable in NMR Studies of Molecular Dynamics" J. Jonas in *Nuclear Magnetic Resonance Probes of Molecular Motions*, Ed. R. Tycko Kluwer Publ., New York, 1994, in press.

### 4. Patents Pending

None.

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