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● *Contributed Paper*

NMR CHARACTERIZATION OF HYDROCARBON GAS IN POROUS MEDIA

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Laboratory investigations of nuclear magnetic resonance (NMR) relaxation properties of methane gas in bulk and in porous media are reported. Measurements were performed for methane alone and together with water in glass bead packs and Bentheimer sandstone. Results indicate that surface relaxation effects can be significant and that diffusion effects dominate observed T_2 relaxation. © 1998 Elsevier Science Inc.

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INTRODUCTION

The relatively dense hydrocarbon gasses in underground reservoirs can contribute significantly to the signals detected by nuclear magnetic resonance (NMR) logging tools. Discrimination of the hydrocarbon gas is important for accurate determination of hydrocarbon reserves. Several methods[1,2] have been proposed to discriminate various fluids in reservoirs based on anticipated differences in relaxation and diffusion properties. However, little is actually known about NMR properties of gas in porous media. Here we report a laboratory investigation of NMR relaxation properties of methane gas, the major component of hydrocarbon gas in underground reservoirs.

EXPERIMENTAL METHODS

The experiments were conducted on a GE 2T OMEGA CSI operating at 85 MHz. Bentheimer sandstone and two different sized glass beads (B. Braun Melsungen AG, Melsungen, Germany) of nominal diameter 0.1 mm (0.10–0.11 mm) and 0.5 mm (0.45–0.50 mm), were used as the porous media. A cylindrical gas cell made of PEEK (Ensinger Special Polymers, Houston, TX, USA) was used, with a sample size 0.8 cm in diameter and 8–10 cm in length. Experiments were conducted at 295 K. Proton spin-lattice relaxation times T_1 were measured using the conventional inversion recovery method, and transverse relaxation times T_2 were obtained from the Carr–Purcell–Meiboom–Gill (CPMG) sequence. Aver-age relaxation times for fluids in porous media were calculated from the estimated relaxation distributions.[3]

NMR RELAXATION AND DIFFUSION PROPERTIES OF METHANE GAS

Properties of Bulk Methane

NMR relaxation properties of bulk methane have been reported for a range of temperatures and pressures.[4–6] It is known that T_1 relaxation of bulk methane is dominated by the spin-rotation mechanism,[4] and thus is sensitive to the pressure and temperature.

T_1 measurements of bulk methane at various pressures were conducted to provide a basis for investigating the relaxation properties in porous media. Figure 1 summarizes our T_1 measurements of bulk methane along with measurements from the literature. The results reported from the various investigations appear to be consistent; variations among them are to be expected due to differences in the temperatures.

Properties of Methane in Porous Media

Porous media has a profound effect on the relaxation properties of some saturating fluids, such as water. The degree to which surface relaxation may contribute to the relaxation of hydrocarbon gasses has not been established. Here, we investigate T_1 and T_2 relaxation of methane in porous media.

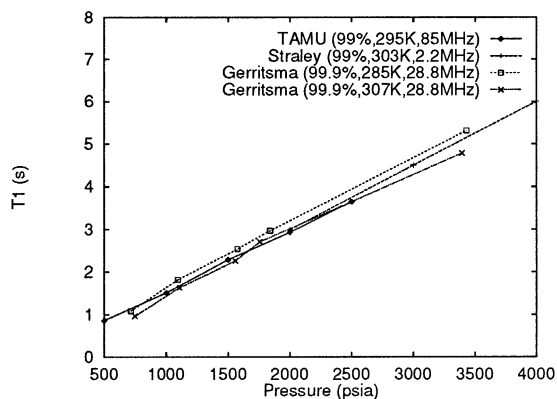*T_1 Properties.* Under the fast-exchange approxima-

Fig. 1. Measurements of T_1 vs. pressure for bulk methane by various groups are shown. The quantities in the parentheses are the purity of methane gas, temperature and the NMR frequency, respectively.

Fig. 2. Comparison of T_1 values of bulk methane to T_1 of methane in porous media with water and D_2O.

tion, the spin-lattice relaxation rate for an isolated pore can be written as:

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \frac{\rho S}{V}, \qquad (1)$$

where the subscript b refers to bulk conditions, ρ is the surface relaxivity, and S/V is the surface-to-volume ratio of the pore. The degree to which surface effects contribute to relaxation is important. If surface effects are not significant, the relaxation of methane in porous media is determined simply by the bulk properties. On the other hand, the contribution of surface relaxation will depend on the material with which the gas interfaces.

We investigated the role of surface relaxation by comparing the average T_1 of methane at various pressures for the following five cases: 1) bulk methane; 2) methane in 0.1-mm bead pack; 3) methane and water in 0.1-mm bead pack; 4) methane and D_2O in 0.1-mm bead pack; and 5) methane in Bentheimer sandstone. Our results are summarized in Fig. 2.

The results indicate that surface relaxation can be important. The average relaxation for methane in bead packs and in Bentheimer sandstone is faster than that for bulk methane. The relaxation of methane in the sandstone is considerably faster than in the glass beads, which is consistent with the sandstone having the greater surface relaxivity. These results indicate that surface effects can be important when the gas is in contact with sedimentary rocks.

When liquids are present with gas in the porous media, the liquids are expected to wet the surface of the media. Consequently, the gas interface will be with the liquid, and not the porous media. The average relaxation for methane when the bead pack also contains water is not significantly different from that of the bulk. This would indicate that
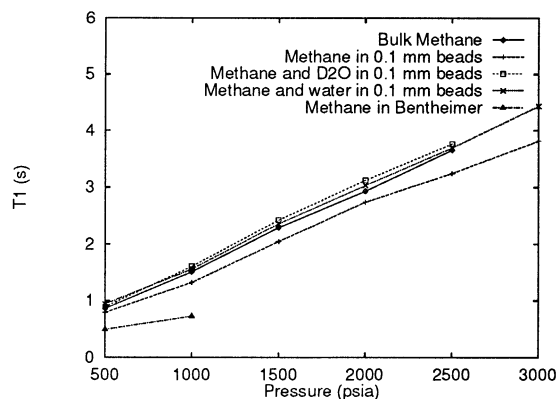
surface effects may not be important in reservoirs which contain liquid with the gas. If the spin-lattice relaxation of methane in the presence of water occurs via dipole-dipole exchange between gas molecules and water molecules, we should be able to see the differences in T_1 values when D_2O is substituted for water. As can be seen from Fig. 2, there is no significant difference in these two T_1 values. From these results, we conclude that there is no significant contribution to T_1 relaxation of methane from the dipole-dipole exchange between methane and water molecules.

T_2 Properties. T_2 is of particular interest for well logging because the CPMG sequence is normally used. The response of fluids in porous media can be complicated by the effects of diffusion within local magnetic field gradients. A measure of this effect is provided by the diffusion contribution, $1/T_{2d}$, for unrestricted diffusion in a magnetic field gradient G, which is given by:

$$\frac{1}{T_{2d}} = \frac{\gamma^2 G^2 D \tau^2}{3}, \qquad (2)$$

where γ is the gyromagnetic ratio, D is the diffusion coefficient and τ is half the echo spacing. Gasses typically have significantly larger diffusion coefficients than liquids, and the values are more sensitive to pressure. At constant temperature, the diffusion coefficient of methane has been found to be inversely proportional to the density up to the critical density.[7] Also, the magnetic field gradients are expected to be different due to differences of magnetic susceptibilities. Consequently, significantly different T_2 behavior may be encountered for gas compared to liquid.

We investigated the pressure dependence of T_2 of methane in 0.1- and 0.5-mm bead packs as a function of echo spacing. Average values of T_2 were determined and are plotted in Fig. 3. T_2 relaxation is seen to be quite sensitive to pressure. The initial slopes of $1/T_2$ vs. $(2\tau)^2$ are proportional to the diffusivity, D. That slope is in-
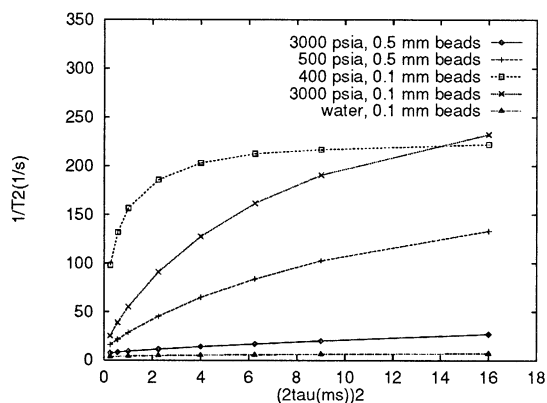
Fig. 3. $1/T_2$ vs. $(2\tau)^2$ in different bead packs.

Fig. 4. T_2 distributions of methane and water in 0.1-mm bead pack at 3100 psia as a function of echo spacing.

versely proportional to pressure, consistent with the dependence of gas bulk diffusion coefficients.[5]

Another important observation from Fig. 3 is that linearity is observed only up to very small values of echo spacing. The effect of restricted diffusion is apparent in these results, and it becomes more significant as the pressure decreases.

Comparing the average relaxations for the two bead packs at 3000 psia, we see that the contribution of diffusion effects to relaxation is greater for the 0.1-mm bead pack than the 0.5-mm bead pack. This is due to the greater internal gradient effect which arises from the smaller bead size. Its role is represented by G in Eq. (2). The increase in G with the decrease in bead size is consistent with the approximation of the internal field gradient reported by Glasel et al.:[8]

$$G \propto \frac{\Delta \chi H}{d}, \qquad (3)$$

where G is the internal field gradient, $\Delta \chi$ is the susceptibility contrast, H is the external field and d is the diameter of the beads.

Figure 4 shows T_2 distributions[3] of methane and water in a 0.1-mm bead pack at 3100 psia at various echo spacings. The large peaks corresponding to shorter T_2 are due to the methane gas, which has a large signal at high pressure. The water peaks are the small components of the spectra. As the echo spacing is increased due to the difference in diffusivity of the two fluids, the methane peak shifts significantly compared to the water peak and, thus, the two phases can be fully resolved by increasing the echo spacing.

SUMMARY OF RESULTS

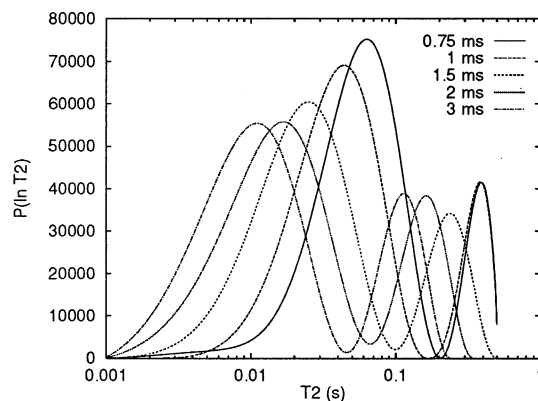We measured NMR properties of methane in bulk, in glass bead packs and in Bentheimer sandstone. For T_1, surface relaxation can be significant when gas interfaces with the porous media, but appears to be insignificant when water is present. The observed T_2 relaxation is very sensitive to echo spacing, which indicates a dominating diffusion effect. The behavior of $1/T_2$ was found to reflect the change in the diffusion coefficient with pressure as well as the change in internal field gradient with grain size. However, the effect of diffusion cannot be adequately represented by the expression for unrestricted diffusion in a constant field gradient.

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