A MECHANISM FOR THE TEMPERATURE DEPENDENCE OF THE SURFACE RELAXATION RATE IN CARBONATES

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ABSTRACT

Unexplained temperature dependence in some carbonate reservoir rock was reported recently, in which the mean log T_2 for the brine-saturated material increased with temperature [8]. For many years significant temperature dependence was not observed and was considered unlikely in rock materials based on a variety of evidence [5]. Some of the recently announced temperature dependence was explained. More efficient diffusive coupling between pores, which should occur with increased temperature, can shift the T_2 relaxation to shorter times. The examples that were reported to display an increase in relaxation time with increasing temperature were problematic and suggested that the surface relaxation rate weakened with temperature. Last year, new theory and experiments were introduced to explain temperature-dependent T_2-increases based on the surface diffusion in the vicinity of paramagnetic relaxation centers [4]. Our paper demonstrates that a complementary or possibly alternative mechanism for temperature dependence should be considered, too.

Brine in rock relaxes faster than in bulk. This augmented relaxation has been attributed to the presence of paramagnetic impurities in the rock, near the rock-water interface. Prior to the general acceptance of surface relaxation by paramagnetic centers as the dominant NMR relaxation mechanism for fluids in rock, hindered motion on the rock surface that caused enhanced *hh* (hydrogen-hydrogen) *dd*(dipole-dipole) relaxation was a competitive theory for the accelerated relaxation. The possibility of *hh* relaxation, which was provided for in the early theory for the relaxation of rock materials, eventually faded away because it did not seem relevant. Indeed, it was the failure to observe temperature-dependence in rock that led to the conclusion that only paramagnetic relaxation was important and that it was reasonable to exclude consideration of surface *hh* relaxation and further that only the temperature-independent scalar term for relaxation was important in the electron-proton interaction. In this paper, examination of a single carbonate rock, which has a previously documented temperature-dependence, indicates that the surface *hh* relaxation rate is comparable to the surface relaxation rate due to paramagnetic centers. Significant surface *hh* relaxation, relative to the total rate, could account for the observed temperature dependence of relaxation times in carbonates.

INTRODUCTION

Recent studies [8] have reported significant temperature dependence for the NMR relaxation of brine in some limestone reservoir rock[1], whereas an early study by Latour [7] observed weak temperature dependence for carbonates. Although Ramakrishnan et al. [8] quantified diffusive coupling between large and small pores to explain the decrease in relaxation time with increasing temperature, they did not explain a few observed cases in which the relaxation time increased with increasing temperature. This temperature dependence is not explained by the widely accepted mechanism of relaxation in rock [3, 5]. In fact, the picture of brine relaxation in rock assumes, based on a limited number of experimental observations, that the temperature dependence of the relaxation times for brine-saturated rock is insignificant. Kleinberg et al. [5] stated, ``The lack of strong temperature dependence of the rates indicates that diffusive motion of the fluid molecules or the on-off motion at a surface site do not enter into a determination of T_2 and T_1.'' This statement reflects the understanding that the paramagnetic relaxation of water at the rock surface is dominated by the abundance of paramagnetic sites and the electron's correlation time, not the water's correlation or residence times. Additionally, the paramagnetic relaxation has to take place primarily through scalar coupling to be independent of temperature. The results of the recent carbonate studies and the inability to reconcile those results using accepted theory require re-examination of the underlying assumption of domination by paramagnetic centers and re-evaluation of the significance of the water's correlation time or residence time in these unusual cases.

Theory of Korringa, Seevers and Torrey, 1962
Most theoretical discussions of relaxation in rock begin with the fundamental work by Korringa, Seevers and Torrey (KST) [6]. The KST model was very general and allowed relaxation at non-paramagnetic surface sites as well as relaxation at paramagnetic centers and a variable residence time on the surface. The anticipated relaxation mechanism at the non-paramagnetic centers was by *hh* (hydrogen-hydrogen dipole-dipole) interaction in the system, primarily the water. This mechanism is common. That relaxation is attributed to the inter-molecular and intra-molecular *dd* (dipole-dipole) interaction of the hydrogen nuclei during translation and rotation [1]. Furthermore, the *hh* relaxation rate is enhanced on surfaces because the motion of the absorbed molecule is slowed. For example, Woessner [10] found that the rotational rate of water on the surface of hectorite was about 1/5 of the value in the bulk fluid.

KST's general expression for relaxation in rock is

$$\frac{1}{T_{1,r}} = \frac{1}{T_{1,b}} + \frac{N_m}{N}\frac{1}{T_{1,e}+t} + \frac{N_n}{N}\frac{1}{T_{1,n}+t} \,, \qquad (1)$$

in which, $T_{1,r}$ is brine's relaxation time in rock, $T_{1,b}$ is the brine's bulk relaxation , N_m is the number of water molecules in the sphere of influence of a paramagnetic surface site,

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[1] This particular issue is discussed on page 8 of their text under the heading **Temperature Dependence** and illustrated with NMR logs, Figure 8. The author was provided additional data for those samples by Mr. Mark Flaum, a co-author of the referenced paper.

N is the total number of water molecules, $T_{1,e}$ is relaxation due to the interaction of the water's hydrogen and the paramagnetic center, τ is the average residence time of a water molecule in the sphere of influence, N_n is the number of water molecules in the sphere of influence on non-magnetic sites and $T_{1,n}$ is the relaxation time for a brine molecule at a non-magnetic site. Each relaxation time and the residence time in this equation are potentially temperature dependent.

Adaptation of KST by Kleinberg, Kenyon and Mitra, 1994
Because the observed temperature dependence in rocks was not considered significant and because *hh* relaxation is inherently weak, the terms for the non-paramagnetic sites in KST's equation were eventually dropped [5]. For the same reason, that it would necessarily be temperature dependent, the term for the residence time in the paramagnetic shell disappeared. It was also argued that the scalar term of the electron-proton paramagnetic relaxation interaction must dominate the dipolar term because the dipolar part would be temperature dependent. $T_{1,b}$, which is temperature dependent, remained but it is easily measured and removed from the calculation. The generally accepted functional form of KST became

$$\frac{1}{T_{1,r}} = \frac{1}{T_{1,b}} + \frac{N_m}{N} \frac{1}{T_{1,e}(scalar)} . \tag{2}$$

Godefroy, Fleury, Deflandre and Korb, 2001
Contemporary studies have been presented very recently that re-consider some of the basic issues that led to Equation (2). Godefroy et al. [4] demonstrated the temperature dependence of Lavoux limestone. They constructed a relaxation model to account for the temperature dependence. Their model allows for temperature dependent relaxation at paramagnetic surface sites in a manner similar to Korringa et al. but they do not incorporate the possibility of relaxation at non-paramagnetic sites.

Consideration of Surface Hydrogen-Hydrogen Interaction
The temperature dependence in carbonates observed by Ramakrishnan et al. [8] is significant when the carbonate's relaxation time is long, implying that the overall relaxation rate is small. It is probable that *hh* relaxation at the surface can only be a competitive mechanism under the condition of weak relaxation because *hh* relaxation is inherently limited to a small rate.

To evaluate whether *hh* relaxation contributes to the relaxation of brine in carbonates, a simple test can be devised. The relaxation of samples saturated with a small concentration of H_2O dispersed in D_2O (deuterium oxide) can be compared to the relaxation of the same samples saturated with pure H_2O. The *dd* relaxation due to DH (deuterium-hydrogen) interactions is roughly 1/40th of the comparable HH interactions. If the surface relaxation of hydrogen is purely due to interactions with paramagnetic impurities, the relaxation rate should remain unchanged in the two experiments; there should be no dependence on the concentration of hydrogen spins. On the other hand, if the relaxation

rate slows significantly for the H_2O/D_2O-saturated samples, *hh* interactions must have been important in the H_2O-saturated experiment.

Extracting $r_{2,p}$ and $r_{2,d}$

The observed rate, $\dfrac{1}{T_{2,obs}}$, in a uniform magnetic field should be the sum of the rates due to the specific interactions,

$$\frac{1}{T_{2,obs}} = \frac{1}{T_{2,p}} + \frac{1}{T_{2,d}} + \frac{1}{T_{2,b}}. \tag{3}$$

In this expression, $T_{2,p}$ is the surface paramagnetic relaxation time-constant, $T_{2,d}$ is the surface *hh* relaxation time-constant, and $T_{2,b}$ is the bulk relaxation time-constant for the fluid. There are no direct questions about temperature dependence of the relaxation times in this test because the two experiments are run at $30^{\circ}C$. The test is simply to determine whether *hh* relaxation is significant. If confirmed as a mechanism, *hh* relaxation must be temperature dependent.

In general, it is necessary to remove the fluid's bulk rate because the relaxation times for our samples are long (smaller but comparable to those for water itself) and the bulk rate can affect the result. The bulk rate is easily measured for the two saturating fluids and eliminated from the equation leaving a corrected rate, $\dfrac{1}{T_{2,corr}}$. This corrected rate includes the elimination of bulk fluid relaxation due to dissolved oxygen, which should be the same for all samples because they were in equilibrium with air. After correction for the bulk fluid relaxation,

$$\frac{1}{T_{2,corr}} = \frac{1}{T_{2,p}} + \frac{1}{T_{2,d}}. \tag{4}$$

When considering surface relaxation, the rate of diffusion to the surface and the rate of relaxation at the surface can lead to several different outcomes. Rock materials are generally considered to be in the fast diffusion limit ($\dfrac{rV}{SD} \ll 1$) for paramagnetic relaxation when the definitions of Brownstein and Tarr [2] are applied. In this limit,

$$T_{2,p} = \frac{V}{Sr_p}; \tag{5}$$

V is the pore volume, S is the pore surface area and r_p is the surface relaxation velocity due to paramagnetic relaxation. By analogy, since $T_{2,d}$ is a surface relaxation phenomenon, it should exhibit similar behavior if r_p and r_d are comparable, because the criterion for fast diffusion, $\dfrac{Vr_d}{SD} \ll 1$, would still be satisfied. In this expression, D

is the diffusion constant for the fluid and would be unchanged (or only slightly changed), just as V and S would be unaffected changing fluids from H_2O to HOD/D_2O. We can write,

$$T_{2,d} = \frac{V}{S r_d} . \tag{6}$$

The average value of $\frac{V}{S}$ for Equations 5 and 6 can be found from available physical measurements. When S_g is the specific surface area measured by BET, r_g is the grain density, and ϕ is porosity,

$$\frac{V}{S} = \frac{1}{r_g} \frac{f}{1-f} \frac{1}{S_g} . \tag{7}$$

3.82 s was taken as the relaxation time of oxygen-free water at 30^oC [8] and, experimentally, the oxygen-corrected bulk relaxation time for the HOD/D_2O was found to be 13.1 s. The hh surface rate was assumed to vary as the bulk rates. This is more realistic than assuming that the hh interaction is completely eliminated because 10% of the original hydrogen remains, enough that the hh rate cannot be zero. The HOD/D_2O is a mixture of isotopes of water and the diffusion should be essentially the same as water in bulk or on the rock's surface because the important van der Waals forces should be similar although the molecular masses are about 10% greater. If the effect of adding or removing hydrogen is a matter of superposition of magnetic effects, the surface rates should vary as the bulk rates,

$$\frac{r_{d,HOD}}{r_{d,H_2O}} = \frac{T_{2.b,H_2O}}{T_{2.b,HOD}}, \text{ or, } r_{d,HOD} = 0.29\, r_{d,H_2O} . \tag{8}$$

Combining Equations 4, 5, 6 and 8 we can write two equations,

$$\frac{1}{T_{2,obs}} = \frac{r_p S}{V} + \frac{r_{d,H_2O} S}{V}, \text{ and} \tag{9a}$$

$$\frac{1}{T_{2,obs}} = \frac{r_p S}{V} + \frac{0.29\, r_{d,H_2O} S}{V}, \tag{9b}$$

for the water-saturated and DOH/D_2O-saturated samples, respectively. These equations can be solved simultaneously to find the two surface rates.

$r_{2,d}$ and Consequences for Temperature Dependence

Consider what effect temperature variation should have on surface hh relaxation. With increasing temperature, the bulk water relaxation above ambient temperature is such that the relaxation time constant increases, that is, the hh mechanism is less effective because the water molecules are more energetic and the correlation times are shorter. Because the frequencies associated with the correlation times for the water molecules are further from

the Larmor frequency required for resonant interaction and relaxation rate is slowed. The temperature dependence for *hh* surface relaxation should be similar to the bulk relaxation using the same arguments. If the dominant relaxation process is paramagnetic, the weak surface *dd* relaxation and changes due to temperature may go unnoticed. If the *dd* relaxation is comparable or dominates, the measured relaxation times should increase with increasing temperature.

EXPERIMENTAL METHOD

Only two rocks were used in this study. One was from the Middle East, to be referred to as sample S, and the other was Leuder's limestone, sample L. The measured temperature dependences for samples S and L from a previous study [8] are shown in Figures 1 and 2, respectively. Sample S shows a substantial shift of the major peak to longer relaxation times when the temperature is increased, while the shift for L is more modest and appears to be a shift to slightly shorter relaxation time.   These contrasting samples were chosen as a representatives of a temperature dependent limestone, S, and a limestone apparently lacking temperature dependence, L.

The T_2-distributions are derived from the results of CPMG measurements, which were made using a Maran2 spectrometer operating at 2 MHz and observing the hydrogen NMR signal from the brine. The magnetic field for the Maran2 is relatively uniform and the echo spacing was chosen to accommodate the complete relaxation of the sample in 4096 echoes. The mean log T_2 of the distributions is used for the analysis. The porosity, grain density, BET surface area, and NMR T_2 relaxation times are listed in Table 1.

A 10% solution of distilled water in D_2O (99.9% purity) was made in a graduated cylinder. To work at low field with lower concentrations would have been extremely time consuming.   The hydrogen in water exchanges rapidly and should result in a fluid in which 20% of the molecules are HOD, an isomeric form of water with just one proton. The mass of HOD is slightly higher than for H_2O and the diffusion constant is probably slightly less than for H_2O but the intermolecular interactions are very similar. Of course, there is a 90% reduction in the total amount of hydrogen in the saturating fluid relative to pure water. The NMR bulk relaxation times for the water and the HOD solution were 2.7 and 5.4 sec respectively. Each of these fluids is in equilibrium with air and contains dissolved paramagnetic oxygen. The relaxation rate due to dissolved oxygen was measured as 0.11 s, which amounts to a relaxation time of 9.1 s for both fluids. The rocks were vacuum saturated each time they were impregnated with fluid. T_2-relaxations for the HOD/ D_2O-saturated samples are shown in Figures 3 and 4.

If the H_2O equilibrated with D_2O to form HOD, one in five molecules would have hydrogen. At that concentration all hydrogen would have one or more hydrogen neighbors and inter-molecular *hh* relaxation could still be effective. If the H_2O did not equilibrate, every hydrogen atom would have a neighbor in the same molecule and intra-molecular *hh* would be important. In bulk water at room temperature, the self-relaxation of the hydrogen on a molecule due to diffusional rotation accounts for about halve of the

total rate. In any event, the *hh* interaction is not completely eliminated despite being stongly reduced even when the amount of hydrogen is reduced by 90%.

RESULTS AND DISCUSSION

Figures 3 and 4 illustrate that changing the hydrogen concentration affects the relaxation time of the temperature dependent sample S as much as heating it to100^{o}C. Interestingly, there is a smaller but noticeable shift for Sample L.

The rates found from the application of Equations 9 and 9a to the experimental data are found in Table 2. Foley et al. [3], provide an estimate for the maximum theoretical value for r_d that is $0.6\,\mu m/s$. The estimate is based on the second moment of ice, a limiting case for the slow diffusion of water. The two measured values for r_d in this study are in the range from 0.2-0.3 $\mu m/s$, acceptable values in that they are less than the theoretical limit.   Another point should be made because it is well known that a measured value of r can vary depending on the method chosen to measure the surface area. BET provides the smallest *ruler* available for surface area measurements and therefore the largest surface area. Using BET provides the most appropriate measure of r for the comparison to the theoretical limit.

It is important to note that for sample S, the two estimated surface rates, r_p and r_d are similar, while for sample L, the two rates are different by factor of about ten. The relative values of these two rates explain why S shows noticeable temperature dependence when L did not. In Sample L the paramagnetic rate dominates and variation in r_d has only a small impact. For Sample S the two surface relaxation rates are comparable at 30°C and as the temperature increases, the *dd* rate should decrease and the overall relaxation time should increase noticeably until the relaxation is limited to the weak paramagnetic relaxation.

It is seductive that the measured r_d is comparable for both samples. The similarity could be an indication that the surface *hh* relaxation rate of all limestone is similar. In light of this, it is not unreasonable to hope that only a generalized temperature correction would be needed. By assuming a constant r_d for all limestone, $T_{2,d}$ can be estimated for the eleven samples from the Ramakrishnan et al. [8] study because surface areas, porosities and densities are available and r_p and $T_{2,p}$ can be calculated similarly. The estimates can be considered to ascertain whether the calculated $T_{2,p}$ falls below the highest value of $T_{2,obs}$ found at   the highest temperature.

For the eleven samples, assuming $r_d = 0.34$ $\mu m/s$, r_p is found to be in the range from 0.07 to 0.61 $\mu m/s$, with an average value of about 0.4 $\mu m/s$ (six of the samples are in

the range from 0.4-0.6 $\mu m/s$). Note that this average rate is similar to the assumed dipolar rate at 30°C, which means that both relaxation mechanisms are significant and temperature dependence would be expected. On average, the elimination of dipolar relaxation by these calculations accounts for 78% of the T_2 shift seen from 30°C to 130°C although for two of the eleven samples, a greater shift is calculated than is measured. For the other nine samples, the inability to account for the entire shift may indicate a limitation of the in the D_2O / H_2O experiment or analysis. Varying the value of r_d used for this calculation, shows that r_d would have to vary over a range from 0.34 to 0.48 $\mu m/s$ at 30°C to account for all the individual temperature dependent changes in T_2 for the members of the suite.

The failure to account for all the temperature dependence may indicate that the specific quantitative assumption about the relationship between the surface and bulk rates might be unrealistic (although it should create an upper bound on $\rho_{2,d}$). Accounting for only 80% of variation of ρ in the temperature range from 30-130°C also leaves open the possibility that the residual temperature dependence could be associated with the paramagnetic sites.

CONCLUSIONS

This study leads to several interesting observations.
1) In addition to paramagnetic surface relaxation, surface enhanced dipole-dipole relaxation between hydrogen pairs can be a mechanism for the relaxation of brine in the limestone matrix.
2) Surface enhanced *hh* relaxation should manifest itself through observable temperature dependence if the paramagnetic surface relaxation rate is small and the surface enhanced *hh* rate is comparable.
3) *hh* surface relaxation could account for about 80% the observed increases in relaxation time with temperature or the absence of temperature dependence for this limited suite.
4) The *hh* surface relaxation rate may be similar for all limestone with a value of about 0.3 $\mu m/s$. It is limited in range to the theoretical limit of 0.6 $\mu m/s$.
5) Ramakrishnan et al. [8] suggested that r might be changing to account for the shifts to longer time with increased temperature that were observed in logs and in the lab. This appears to be the case and the change is predominantly through the reduction of the strength of r_d. This conception of the mechanism provides a reasonable physical explanation that is consistent with other observations for sandstone and carbonate rock.

ACKNOWLEDGEMENTS

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NOMENCLATURE

D	diffusion constant
N	number of water molecules in sample
N_m	number of water molecules in sphere of influence of paramagnetic site
N_n	number of water molecules in sphere of influence of non-magnetic site
S	sample surface area
S_g	specific surface area

$T_{1,r}$	longitudinal NMR relaxation time in a rock matrix
$T_{1,e}$	T_1 relaxation in the sphere of influence of a surface paramagnetic site
$T_{1,n}$	T_1 relaxation in the sphere of influence of a surface non-magnetic site
$T_{2,obs}$	measured value of transverse NMR relaxation time
$T_{2,p}$	transverse NMR relaxation time due to surface paramagnetic sites
$T_{2,d}$	transverse NMR relaxation time due to surface dipole-dipole relaxation
$T_{2,b}$	transverse NMR relaxation time due for the bulk fluid
$T_{2,corr}$	transverse NMR relaxation time corrected to remove bulk water relaxation
V	sample pore volume
f	fractional porosity
r_p	transverse surface relaxation rate due to paramagnetic sites
r_d	transverse surface relaxation rate due to surface dipole-dipole relaxation
r_g	density

Table 1. The measured properties for the two carbonates used in this study.

Sample	ϕ fractional	density g/cc	Surface area m^2/g	$T_{2,HOD}$ s	$T_{2,H2O}$ s
S	0.252	2.736	0.547	0.630	0.370
L	0.185	2.720	1.400	0.0317	0.0296

Table 2. Surface relaxation times and rates for the two rocks.

Sample	$T_{2,p}$ s	$T_{2,d}$ s	r_p mn/s	r_d mn/s
S	0.978	0.762	0.230	0.295
L	.0328	0.340	1.803	0.174

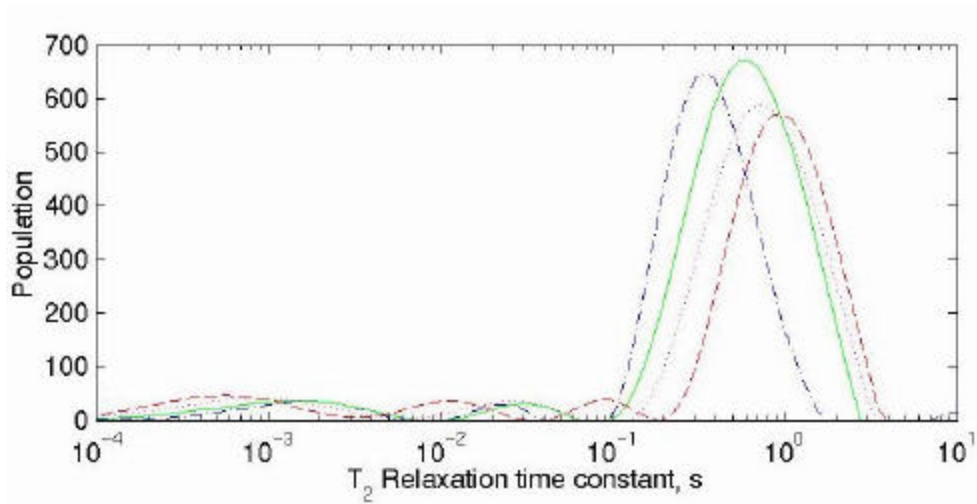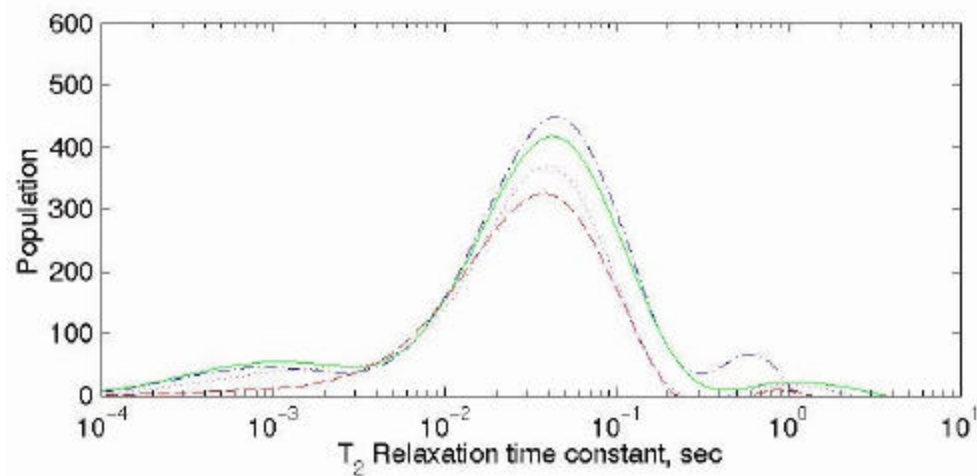**Figure 1.** T_2-distributions for Sample S at various temperatures. The dash-dot curve is for 30°C, the solid curve is at 70°C, the dotted curve is at 100°C, and the dashed curve is for 130°C. This data is from previous a study [8].

Figure 2. T_2-distributions for sample L at various temperatures. The dash-dot curve is for 30°C, the solid curve is at 50°C, the dotted curve is at 100°C, and the dashed curve is for 130°C. This data is from a previous study [8].
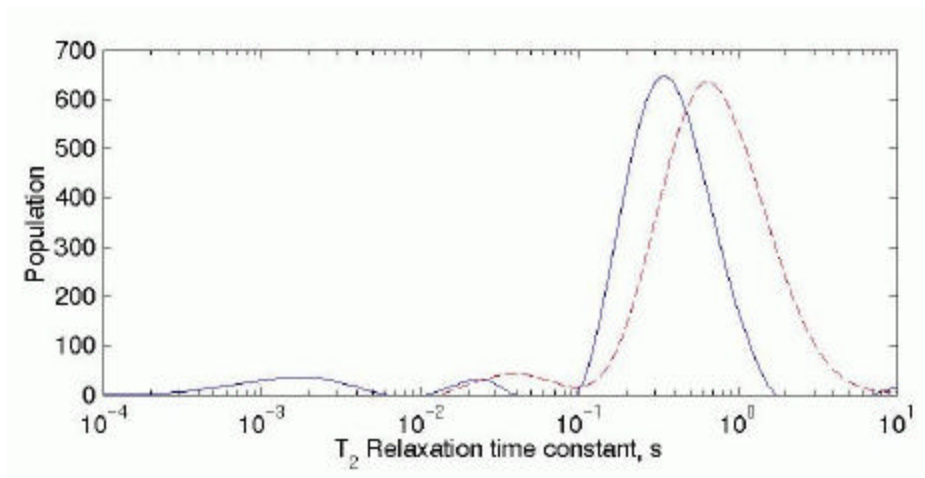
Figure 3. T_2-distributions are given for sample S at 100% and 10% H_2O concentration. If the relaxation were purely paramagnetic, the relaxation of both samples should be the same. The solid curve is the distribution for the sample saturated with pure water and the dashed curve is the HOD saturated measurement.
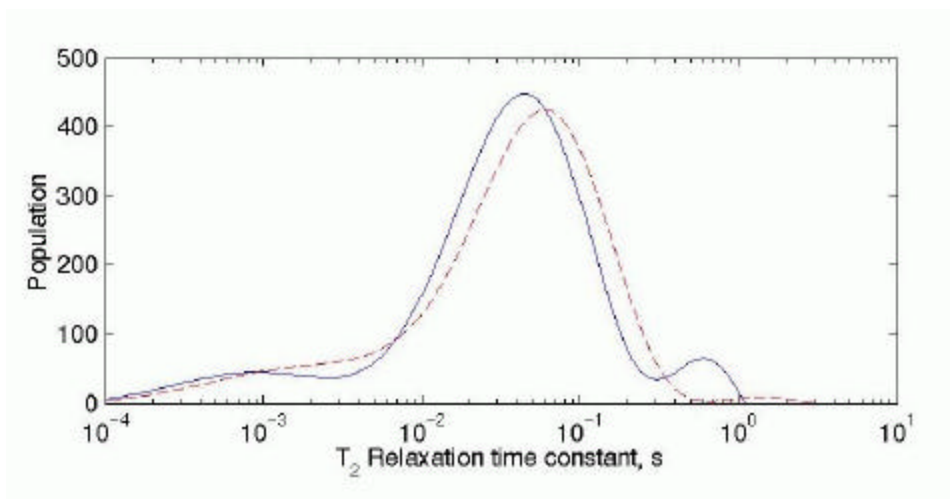

Figure 4. T_2-distributions for sample L at 100% and 10% H_2O concentration. If the relaxation were purely paramagnetic, the relaxation of both samples should have the same distribution of relaxation times. The solid curve is for the water saturated measurement and the dashed curve is for the HOD/H_2O saturated measurement. The shift of the mode of the distribution is compensated by some variation of the details and the change in mean log T_2 is small. See Table 2.