IMPROVED METHOD FOR MEASURING SURFACE RELAXIVITY

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ABSTRACT

Surface relaxivity of both oil and water are important parameters in NMR logging. Correct values of these parameters are crucial when in situ wettability is to be determined. Literature values of surface relaxivity are encumbered with great uncertainty, even for model systems evaluated in the laboratory. The improved method for determining surface relaxivity is based on three main features: 1) Well defined surface composition, 2) Well defined pore geometry and 3) Improved temperature control. In this study we have used glass plates, which have a homogeneous composition. So far we have only used water, but any fluid can be used. Different glass types show variation in surface relaxivity due to varying iron content. The pore (slit) is constructed from two glass plates with a Teflon spacer in between. We therefore have a planar pore with constant spacing. This geometry is easy to model mathematically, and we can experimentally verify the fast diffusion region, proposed by Brownstein and Tarr. In this region the relaxation time is a linear function of the spacing, and the surface relaxivity can be calculated from the slope of the line. Our results extend this region to larger values than reported before. Improved temperature control is obtained by slightly adjusting the sample compartment to allow for better contact between the sample and the thermostat. Since the relaxation time of water is strongly temperature dependent, accurate values of both the bulk and the surface relaxation depends strongly on good temperature control. Our instrument can now keep the temperature stable within +/- 0.1°C for several days.

INTRODUCTION

One interesting feature with proton nuclear magnetic resonance (NMR) in porous media is that the relaxation rate is much faster at the surface than in bulk. This is caused mainly by the presence of paramagnetic ions in the surface region, but also by reduced rotational speed of the Hydrogen-protons at the surface. The relaxation rate in a pore is then the sum of the relaxation rate in bulk, the relaxation rate from the diffusion and the relaxation rate at the surface

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}, \tag{1}$$

where T_{2B} is the relaxation time in bulk, T_{2S} is the relaxation time contribution from the surface, T_{2D} is the contribution from diffusion in the gradient of the magnetic field B_0. We usually disregard the diffusion contribution T_{2D} since it is minimized in the measuring process. T_2 is the total relaxation time in the pore. If a pore is occupied by two fluids, as in an oil reservoir where oil and water can be present at the same time, a measurement of the effective relaxation time of oil and water can give us an indication of the wetting conditions in the pores. This requires that we know T_{2B} and ρ for both phases, in addition to the pore geometry, which gives us a ratio between the surface area and the volume occupied by the fluids *S/V*. In the so-called Fast Diffusion Regime (FDR) the surface relaxation is a linear function of this ratio. Determination of surface relaxivity of oil and water in reservoir rock is not an easy task, especially due to the problem of correctly estimating *S/V*. Even in laboratory clean systems this is difficult, and the estimated relaxivity can vary with a factor of 5, depending on what model that is used [2]. If the relaxivity in the reservoir is to be determined, the fact that both ρ and T_{2B} are temperature dependent has to be accounted for. Finally, reservoir cores are usually composed of several different minerals that have different surface relaxivities, and the relative amount of these minerals may also change with position.

The objectives of this work was
1) To see whether ρ could be determined accurately in a simple system in the laboratory.
2) To see if these measurements could be used to experimentally verify the FDR condition. That is: How much smaller than 1 does the dimensionless fraction $\rho a/D$ need to be for the system to behave according to the FDR. Earlier experiments [2] have shown that a value of 0.059 is sufficiently small [2]. Earlier calculations indicate that the dimensionless fraction should be smaller than 0.25 in order to be in FDR [3].
3) Finally we have modeled the experiments using a mathematical model based on the theory of Brownstein and Tarr [1].

THEORY

For nuclear magnetic decay between two parallel planes separated by distance $d = 2a$, the decay of the transversal magnetization can be described as a sum over eigenmodes, Brownstein and Tarr [1]:

$$M(t) = M(0)\left[e^{-t\left(\frac{1}{T_{2B}}+\frac{1}{T_{2D}}\right)} \sum_{n=0}^{\infty} I_n e^{-t/T_n} \right]$$

where:

$$T_n = a^2 \big/ DE_n^{\,2},$$

$$I_n = \frac{4Sin^2 E_n}{E_n\left(2E_n + Sin(2E_n)\right)}, \quad E_n = \frac{a}{\sqrt{T_n D}}, \quad \sum_{n=0}^{\infty} I_n = 1$$

where $E_n, n = 0,1,2,...$ are the roots of the transcendental equation: $E_n Tan(E_n) = \frac{\rho a}{D}$

Intensities I_n:
The lowest mode I_0 dominates (See Table 3). But when $\rho a/D$ is larger than 1 the other intensities start playing an increasing role and need to be considered when approximating the magnetic relaxation. At $a/D \leq 1$ it suffices to use the 0'th mode.

T_0 at Small a/D, The Fast Diffusion Regime (FDR).

A Taylor expansion of $E_n Tan(E_n)$ where we disregard the 2nd order and higher approximation, leads to the familiar result

$$T_0 = T_{2S} = \frac{a^2}{D}\frac{D}{\rho a} = \frac{a}{\rho}. \qquad (2)$$

This is the Fast Diffusion Regime where the surface relaxation T_{2S} is proportional to the distance between the plates $d = 2a$. Including the next order leads to

$$T_0 = T_{2S*} = \frac{1}{2}\frac{a}{\rho}\left[1+\sqrt{1+\frac{4}{3}\frac{\rho a}{D}}\right]. \tag{3}$$

Here we have lost the proportionality but we can still calculate the relaxivity from the decay curves as long as we know the distance a and the diffusion constant D. Relating this to the real world for a parallel pore, the average time for a molecule to diffuse from one wall to the other is given by $t_D=a^2/D$ and the average time to relax is $t = a/\rho$. If $t_D << t$ which is equivalent to saying that $\rho a/D << 1$, the time for a molecule to diffuse across the pore is less than the time it takes for the molecule to relax. The relaxation process is governed by the relaxation time and not the diffusion time. The magnetization and magnetic decay in the pore is uniform. A plot of T_0, T_{2S} and T_{2S*} (See Figure 6) shows that up to $\rho a/D = 0.1$ it is safe to use the T_{2S}-approximation, but for $0.1< \rho a/D< 1$ one should prefer the T_{2S*}. See Table 4 for calculated error. While T_0, T_{2S} and T_{2S*} vary depending on the values of a, D and , even if $\rho a/D$ is constant, the differences ΔT_{2S} and ΔT_{2S*} stay the same for each constant value of $\rho a/D$

For NMR measurements on parallel plates it is now possible to find the surface relaxivity using equations 1 and 5 when the system is in the FDR

$$\frac{1}{T_2} = \frac{1}{T_B} + \frac{1}{T_{2S}} = \frac{1}{T_B} + \frac{\rho}{a} = \frac{1}{T_B} + \frac{2\rho}{d}. \tag{4}$$

Plotting $1/T_2$ against the inverse of the distance 1/d gives a straight line with slope 2ρ and intersection point $1/T_{2B}$ in the FDR.

EXPERIMENTAL

Equipment

All measurements were performed at a stabilized temperature at 35 ºC by a Resonance Instrument MARAN 2 spectrometer which operates with a permanent magnetic field B_0 = 2 MHz. The T_2-values were measured by a CPMG pulse sequence. The dimensions of the cylindrical homogeneous magnetic field in the sample compartment are: height 6cm and diameter 5cm. The mapping of the decaying magnetization into relaxation time distributions was performed with the Resonance Instruments software WinDXP and WinFit.

Materials

The water used is purified by ion exchange, resulting in a resistance of 18 MW/cm. To remove oxygen we bubble Argon (99.999% purity) through the main water source (1 liter) for 10 minutes. The glass used is plain window glass and HSQ-300 Quartz glass. For measurements with quartz glass we do not degass the water. The HSQ-300 glass plates were manufactured, cut and polished by Heraeus Quarzglas, GmbH & Co. KG, Hanau, Germany. www.heraeus-quarzglas.com. See Table 6 for chemical composition of quartz glass.

Construction of Planar Glass Pores

Two pieces of 4cm x 5cm are cut from the main plate, and the surfaces are cleaned, first with soap, and then by storage in 25% hydrochloric acid for at least 24 hours. Two spacers of Teflon are then placed on plate 1 along the edge, leaving two small openings for injection of water. Plate 2 is then put on top, and they are glued together with epoxy while kept together in a vice. When the epoxy is almost dry, needles are injected into the openings, thus creating very small injecting holes for the water. For cells with spacings too small for the needles, the openings are not covered in epoxy. Instead, the opening is covered with tape. The epoxy-glued glass cells are left for approximately 24 hours to dry. The cell is filled with water and tape is used to seal off the openings.

RESULTS AND DISCUSSION

Measurement of T_2 Bulk

This, which was assumed to be an easy task, appeared to be most difficult. We are still fighting this problem, and have not yet seen accurate values in the literature for T_{2B} of water. The most important parameters that appear to affect T_{2B} are: temperature, oxygen content, ion content and the echo spacing time (τ). All T_{2B} values have been obtained using a mono-exponential fit. If nothing else is stated, the standard conditions for the NMR measurements are: number of echoes (NECH) = 34816, number of scans (NS) = 4 and $\tau =$ 300 ms.

Effect Of Temperature

Both literature values, Godefroy et. al. [2], and our own measurements, shows that when the temperature increases from 30 to 40°C, T_{2B} for water increases by approximately 0.6 seconds. Accuracy better than +/- 0.01 s requires that the temperature be kept within +/- 0.15°C. To check the stability of the temperature in the sample, we measured the temperature in the center of sample after having put it in the sample holder. The top of the sample holder was covered with a piece of carton. At first we saw a systematic drift in the temperature as shown in Figure 1. Even if the sample was thermostated in a waterbath at 33.8 +/- 0.1°C, which were believed to be the equilibrium temperature in the sample holder, the temperature dropped to 33.2°C, and then increased slowly to 33.6°C. This took approximately 24 hours. Suspecting that the sample holder prevented the air from the NMR instrument, holding 35.0°C, from effectively contacting the sample, we removed the sample holder. This resulted in a much faster attainment of equilibrium. Now only 5 hours are required, and the equilibrium temperature is 34.2°C. However, the accuracy is not good enough (+/- 0.2°C), probably due to air currents created by people entering and leaving the laboratory. This problem was dealt with by taping a piece of paper over the opening at the bottom of the sample compartment. The temperature was now kept between 34.5 and 34.2°C for several days. The error in T_{2B} for water caused by temperature fluctuations hence should be less than 0.01s.

Effect Of τ

Figure 2 and Table 1 shows the results of measurements of T_{2B} as a function of τ. From Figure 2 we see that T_{2B} increases from 3.7 s to 4.1 s. The fact that T_{2B} seems to depend on τ is as expected, since it is a result of diffusion of water in the gradient G of B_0. Thus the difference between the measured T_{2B} and the value obtained when extrapolating to $\tau = 0$ can be regarded as T_{2D}, which is defined by

$$T_{2D} = \frac{3}{\gamma^2 G^2 D \tau^2}, \tag{5}$$

where is the gyromagnetic ratio of the hydrogen proton and G is the gradient in the static magnetic field B_0.

Effect of Ion Content

Changing from distilled water to deionized water (18 MW/cm) led to an increase in T_{2B} of 0.33 s.

Effect of Oxygen Content

Degassing the water with argon for 10 minutes raised T_{2B} with another 0.33 s.

Effect of Baseline Contact

The measurements of T_{2B} seem to be remarkable robust regarding lack of baseline contact. As shown in Figure 3, measuring only the first 12% of the time for proper baseline contact only changes the value of T_{2B} by 0.02 s.

Effect of Signal-To-Noise Ratio (SNR)

The lower limit in SNR is important since it determines the lower limit of the sample volume that can be measured accurately and hence the lower limit in pore spacing. It seems possible to get fair accuracy at SNR = 10, which is in agreement with recommended values by Lewitt [4].

Measurement of ρ

Surface Relaxivity 1

In the first approach the glass pores were inserted into the sample compartment without the sample holder and without any preheating. T_2 is measured until a constant value is obtained, and the average of several measurements beyond this point is calculated. Then T_{2S} is calculated using equation 1. Since S/V for a planar glass pore is given by $2/d$, equation (4) gives the relation $T_{2S} = 2\rho/D$. If T_{2S} is plotted versus d, we then get a straight line when we are in FDR, and ρ can be calculated from the slope of the line. T_2 was determined using a mono exponential fit. The results from the first series of window glass plates, all cut from the same large plate are shown in Table 2. A straight line is shown to extend to $d = 135$ mm, which corresponds to a value of $\rho d/2D$ of 0.146. This extends the experimentally verified FDR by a factor of 3. Measurements of T_{2S} in pores with low content of paramagnetic ions show a value of about 1ms. This shows that the line in Figure 4 should pass through the origin. From Table 2 we see that is between 6.4 and 6.7 µm/s.

Surface Relaxivity 2

The quartz glass cells were preheated to approximately 35 °C, inserted into the sample compartment without the sample holder and left in the NMR spectroscope for 2 hours to reach thermal equilibrium. Measurements were performed with NECH = 30K, $\tau = 300$ and 1000 scans. We find from the fitted linear trend line (See Figure 5) of the plotted data that the non-polished quartz glass has a surface relaxivity of 6.8 μm/s and the polished quartz glass has a surface relaxivity of 0.9 μm/s (2.9 μm/s using mono exponential fit). It should be noted that we have ignored the "rogue" point on the non-polished curve and included the bulk measurement in both fitted trend lines.

Inversion method

We have 2 possibilities for finding T_2 measured from the magnetic decay curves. WinFit approximates the decay curves with a pre-selected number of exponential decay curves. WinDXP on the other hand finds a T_2 distribution. $T_{2\,Mono}$ is found by a mono exponential fit from the WinFit program. $T_{2\,Mean}$ is calculated from the T_2 distribution obtained from the WinDXP program. We disregard the short T_2's that can be representing anything from water between the Teflon spacers to rubble from the inversion process. The remaining peak is then used to calculate a $T_{2Mean} = \sum_i a_i T_{2i} \Big/ \sum_i a_i$. Comparing the two gives a relaxivity $_{Mono}$ of 2.9 μm/s and $_{Mean}$ of 0.9 μm/s for the polished quartz-glass. We also see that most of the T_2 points are fairly similar except the point representing the smallest separation distance d = 0.1 mm => 1/d = 0.01 μm^{-1} (See Figure 7). The reason for this difference is not fully known, but one reason might be that the before mentioned water between the Teflon spacers, signal noise and rubble from the inversion that is disregarded using $T_{2\,Mean}$ is included in the $T_{2\,Mono}$, and because the measured water volume is so small (approx. 0.2 cL), the effect of this inclusion is large. Another possibility is that the WinDXP program is constructed for distributions of T_2 and not single values, and that this shows when the pore distance becomes small.

The effect of surface roughness.

We compared NMR measurements of glass cells made quartz glass with different surface roughness. One set of plates were cut with wire saw, the other set was cut with wire saw and then fire polished. We observe that the unpolished glass has a surface relaxivity that seems to be 7.8 times larger (2.3 using mono exponential fit) than that of the polished glass (See Figure 5). AFM measurements (Atomic Force Microscopy) reveals that for a projected surface area of 9.0 μm^2 the polished glass has a surface area of 9.03 μm^2, while the unpolished glass has surface area measurements of 10.5 μm^2 and 11.3 μm^2.(See Table 5) This gives a maximum area difference of 25%, in other words this large difference cannot be explained by polishing only. Other factors such as how the surface composition has been changed by the fire polishing must have contributed. The pictures of the glass surfaces show that the polished glass is smooth, while the unpolished glass is so rough that the pictures become blurry. (See Figure 8)

CONCLUSIONS

T_{2B} of water has been measured. Water quality (ion and oxygen content) and temperature control are of crucial importance in order to get accurate results. Temperature control was improved by removing the sample holder. This allows for determining T_{2B} with an error less than 0.01 s. Determination of T_2 using planar pores seems convenient for determining both surface relaxivity and the range of the Fast Diffusion Regime. We found a surface relaxivity for the non-polished HSQ-300 quartz glass of 6.8 μm/s regardless of what inversion method was used. The fire polished glass had relaxivities of 0.9 μm/s ($T_{2,Mean}$) and 2.9 μm/s ($T_{2,Mono}$), depending on inversion method used. Atomic Force Microscopy revealed a difference in surface area of 25 % for the polished and non-polished glass. In other words, the difference in relaxivity for polished and non-polished glass is not only affected by the area difference. The relaxing properties of the glass surface must have been altered by the fire polishing. Our calculations for magnetic decay in a pore of parallel walls show that up to $\rho a/D$= 1, 98.6% of the decay signal stems from the 0'th mode. Thus the magnetic decay is approximately mono exponential with the form $M(t)=M(0)*Exp(-t/T_2)$, where $1/T_2 = 1/T_{2B}+1/T_{2D}+1/T_0$. For $\rho a/D \leq 0.1$ the approximation of T_0 with T_{2S} = a/   has an error ≤ 3.26%. For $\rho a/D \leq 1$ the approximation of T_0 with T_{2S*} has an error ≤ 6.46%. We suggest that for $\rho a/D \leq 0.1$ one should use the T_{2S} approximation and for $\rho a/D \leq 1$ one should use the T_{2S*} approximation.

NOMENCLATURE

d = pore diameter
D = self diffusion constant
T_{2D} = diffusion contribution to the relaxation time
T_{2B} = relaxation time in bulk
T_{2S} = surface contribution to the relaxation time in the pore
= surface relaxivity
= echo spacing time
$M(t)$ = Magnetization at time t
$M(0)$ = Initial magnetization, $t = 0$
I_n = n'th intensity
T_n = n'th relaxation time
E_n = n'th positive roots of the transcendental equation $E_n Tan(E_n)= \rho a/D$
I_0 = zero'th and dominating intensity
T_0 = zero'th relaxation time
a = $d/2$ =half distance between parallel relaxing surfaces
t_D = a^2/D =average time for molecule to diffuse between pore walls
t = $a/$ =average time for molecule to relax at pore wall.
T_{2S} = First order approximation of T_0
T_{2S*} = Second order approximation of T_0
ΔT_{2S} = Error in approximation of T_0 by T_{2S}
ΔT_{2S*} = Error in approximation of T_0 by T_{2S*}
$T_{2,Mono}$ = Relaxation time derived from magnetic decay curve using mono-exponential fit
$T_{2,Mean}$ = average T_2 from selection of T_2-distribution derived from magnetic decay curve
R_a = Root Mean Square of height of glass surface (AFM)
R_q = Average of height of glass surface (AFM)

ACKNOWLEDGEMENTS

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TABLES

Table 1. Effect of echo spacing time (τ) on bulk relaxation of water.

NECH	**τ (ms)**	**T_{2B}(s)**
34816	100	4.10
34816	200	4.06
34816	300	3.98
17408	600	3.70

Table 2. Effect of the glass surface on T_2 and T_{2S} as a function of the pore spacing.

d (mm)	**T_2 (s)**	**T_{2B} (s)**	**T_{2S} (s)**	**ρ (µm/s)**	**$\rho d/2D$**
44	1.84	3.95	3.44	6.4	0.048
135	2.84	3.95	10.11	6.7	0.146

Table 3. Intensities as function of $\rho a/D$.

a [cm]	**a/D**	**I_0**	**I_1**	**I_2**	**I_3**	**I_4**	**I_0-I_4**
0.02	0.1	0.999788	0.000195	1.27E-05	2.52E-06	7.99E-07	0.999999
0.1	0.5	0.995621	0.00398	0.0003	6.15E-05	1.97E-05	0.999982
0.18	0.9	0.988214	0.010557	0.000914	0.000194	6.28E-05	0.999942
0.2	1	0.986094	0.012409	0.001111	0.000237	7.73E-05	0.999928
2	10	0.874309	0.083924	0.023594	0.008981	0.004024	0.994832
20	100	0.818478	0.090767	0.032551	0.016513	0.009913	0.968222

Table 4.Error in estimates of T_0 as function of a/D. D=2*10^{-5} cm^2/s, =1*10^{-4} cm/s.

a/D	**T_0**	**T_{2S}**	**ΔT_{2S} [%]**	**T_{2S*}**	**ΔT_{2S*} [%]**
0,01	2006,67	2000	0,332	2006,64	0,001
0,1	20671,01	20000	3,246	20645,81	0,122
0,5	117160,98	100000	14,647	114549,722	2,229
1	270206,78	200000	25,983	252752,52	6,460

Table 5. Roughness and surface area of projected area for polished and non-polished HSQ-300 quartz glass. Measurements done at NTNU.

Projected Area 9 µm^2	Polished	Non-polished Test 1	Non-polished Test 2
R_q =	1.06 nm	105 nm	123 nm
R_a=	0.655 nm	77.6 nm	91.9 nm
Surface Area =	9.03 µm^2	10.5µm^2	11.3 µm^2

$R_q = \sqrt{\frac{\sum_{i=1}^{N}\left(Z_i - Z_{avg}\right)^2}{N}}$, where Z_i = measured Z value, Z_{ave} = average of Z and N equals number of measured points, $R_a = \frac{1}{L}\int_0^L f(x)dx$, where L is the length of the roughness curve and *f(x)* is the roughness curve.

Table 6. HSQ-300 quartz glass.Typical Trace Elements and OH Content (ppm by weight oxide)

Elements	AL	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ti	Zr	OH
	15	0,5	<0,05	<0,05	0,1	0,4	0,6	0,05	<0,05	0,3	1,1	0,7	<30

"Basic Materials Division" pamphlet from Heraeus Quarzglas.

FIGURES

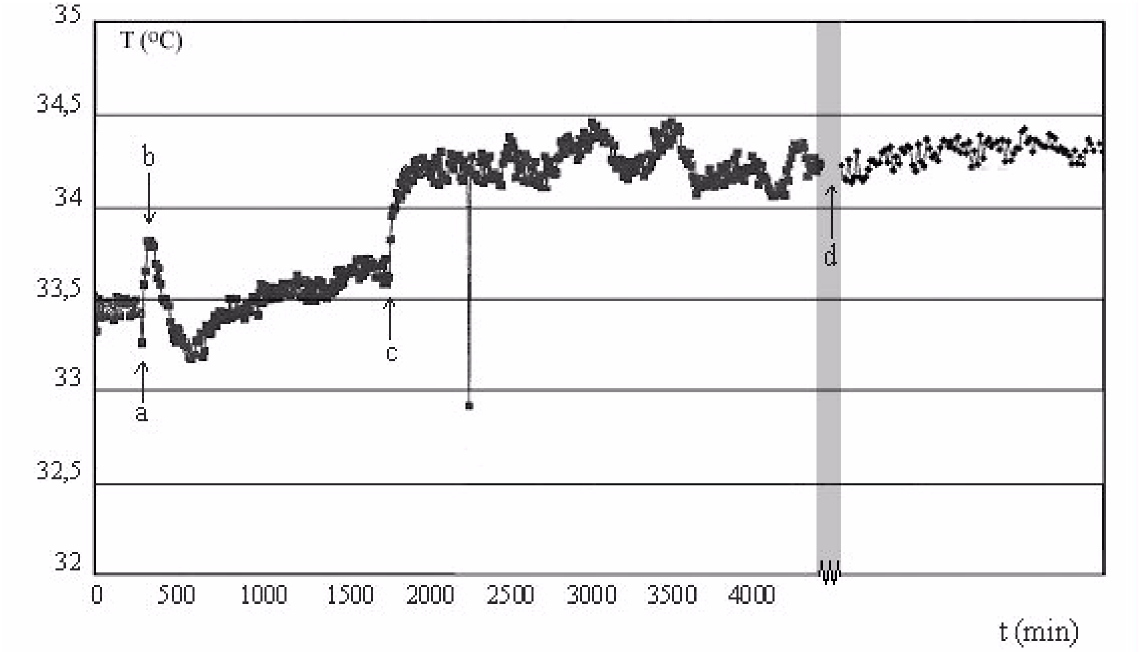


Figure 1. Evolution of the temperature measured in the middle of a bulk sample. a) Sample is put in a water bath at 33.8°C. b) Sample is put in the sample holder that is inserted into the open sample compartment surrounded by the magnet. Temperature of the air from the thermostat of the NMR instrument is 35.0°C. c) Sample holder is removed and the sample is only surrounded by the magnet. Top is covered with a piece of cartoon. d) A piece of paper covers the bottom of the sample compartment.

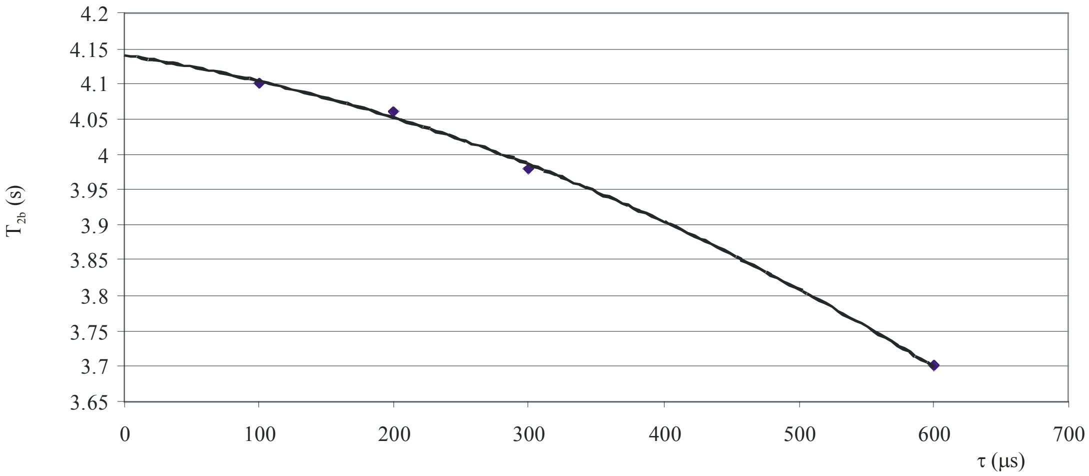


Figure 2. Effect of echo spacing time (τ) on bulk relaxation of water.

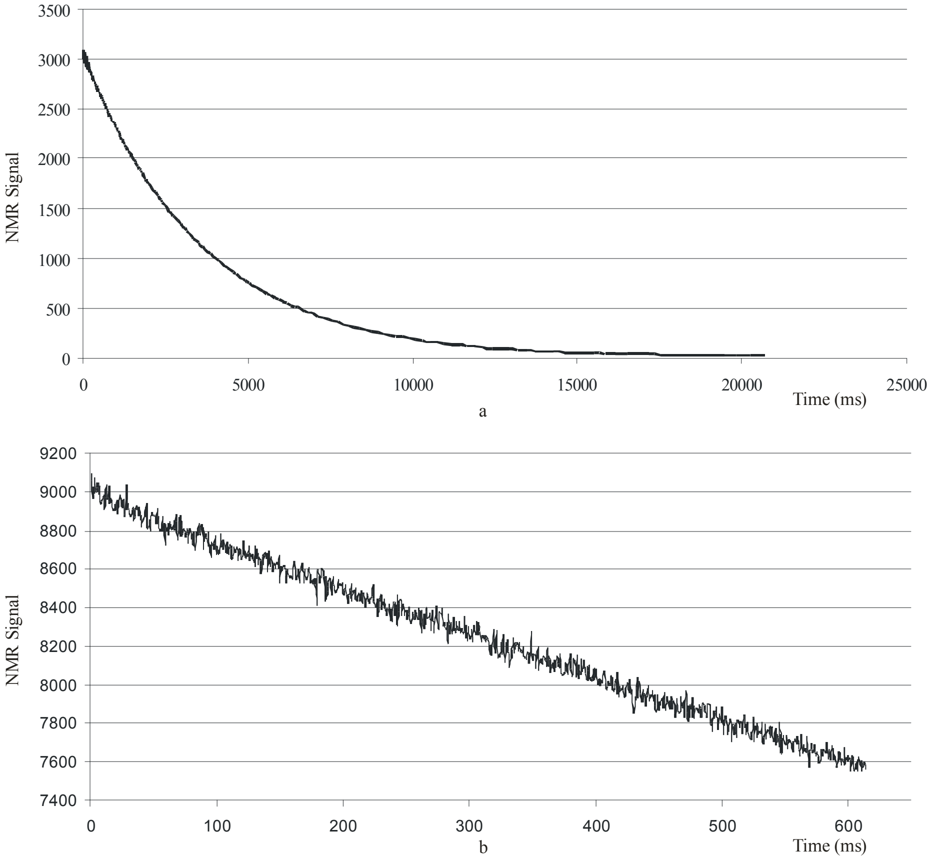


Figure 3 Effect of baseline contact on T_{2B}. a) T_{2B} = 3.62 s b) T_{2B} = 3.60 s (88 % away from baseline contact)

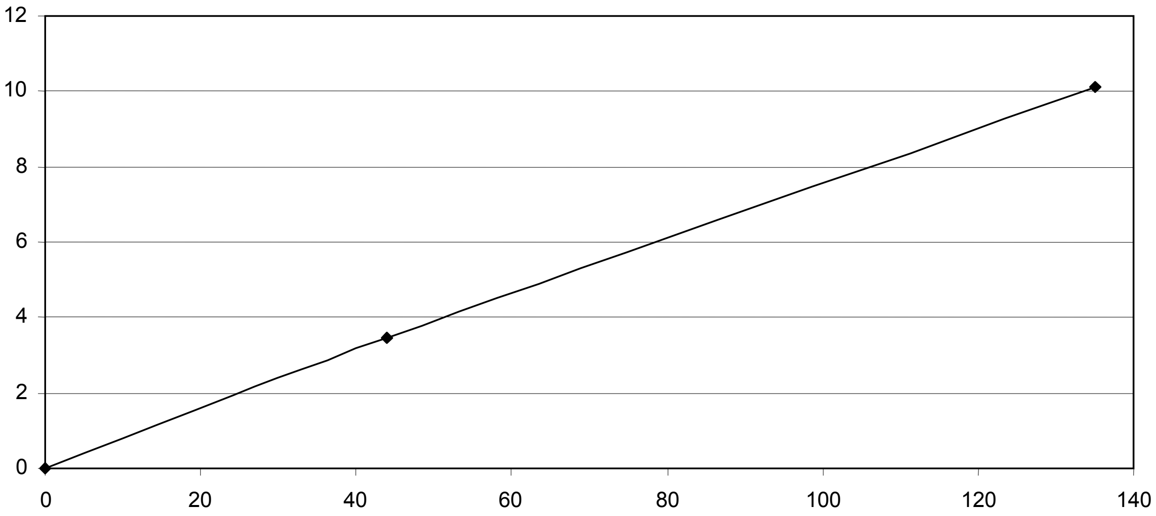


Figure 4. T_{2S} as a function of d for window glass. Mono exponential fit.   = 6.4-6.7 µm/s.

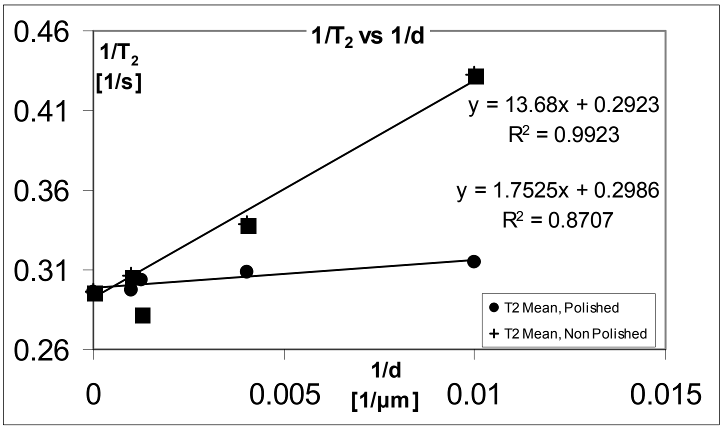


Figure 5. Measured relaxation rate plotted against inverse distance between plates for polished and non-polished quartz-glass.

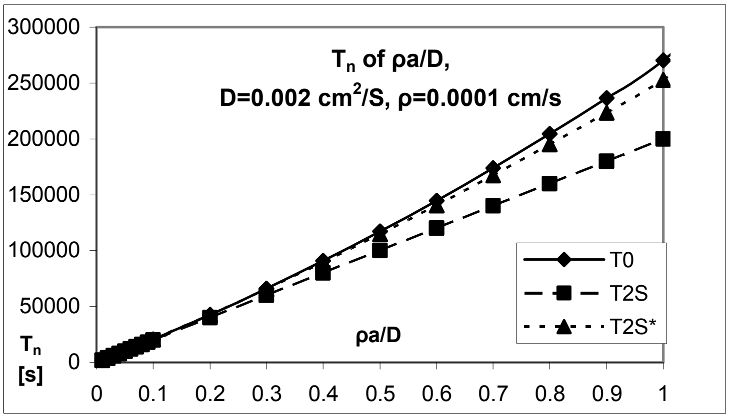


Figure 6. Calculated T_0 plotted with approximated T_{2S} and T_{2S*} against a/D.

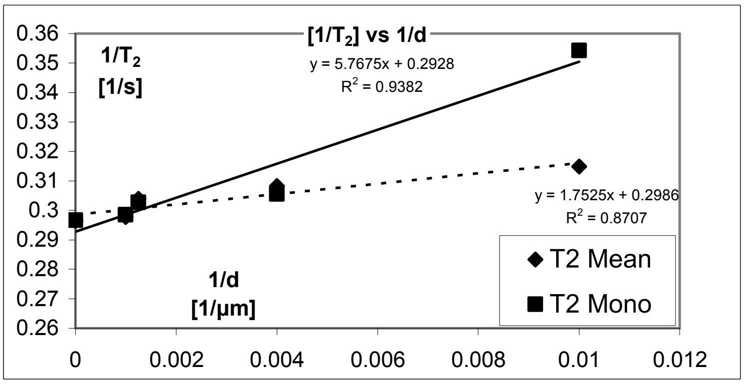
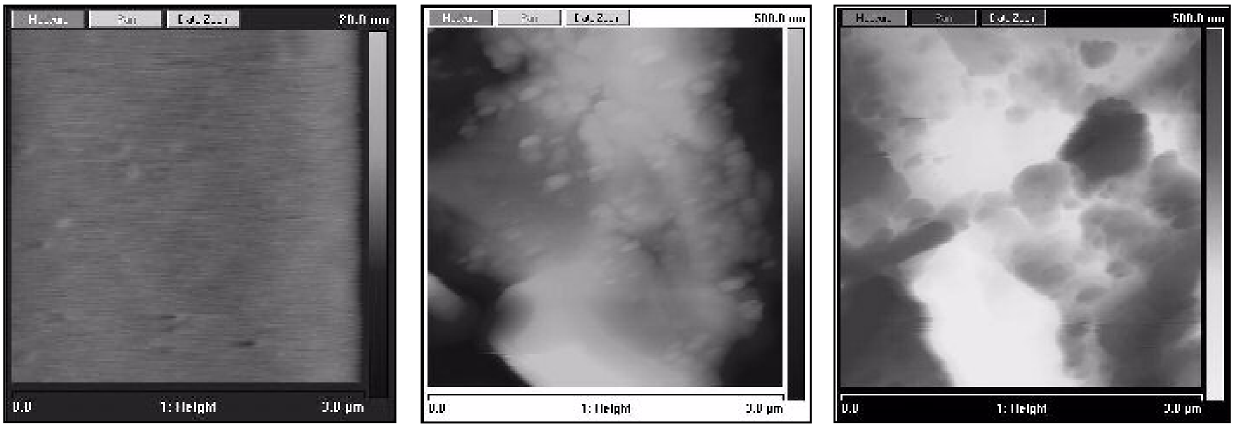


Figure 7. $T_{2\,Mean}$ and $T_{2\,Mono}$ obtained from same magnetic decay curve for polished quartz-glass.



Fire polished glass Non-polished glass Negative image, non-polished

Figure 8

AFM measurements of fire polished and non-polished HSQ-300 quartz glass.
The area measures 3.0 µm * 3.0 µm . Notice that the fire polished glass has a height range of 20 nanometers, while the non-polished has a range of 500 nanometers. The negative image seems to show the roughness better than the positive image. Note that the images are not from the same measurement.