

The Use of Dielectric And NMR Measurements To Determine The Pore-Scale Location of Organic Contaminants

Progress Report
15 July 1997

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Introduction

The objective of our three-year research project is to investigate the effect of adsorbed organics on the dielectric and nuclear magnetic resonance (NMR) response of porous geological materials. This will allow us to assess the use of dielectric and NMR measurements at a site to determine whether organic contaminants are present in the central volume of the pore space (in a water-wet system) or are adsorbed to the solid surface. In addition, we propose to use laboratory dielectric and NMR measurements to study the kinetics of the adsorption and desorption of organics by conducting experiments where we control temperature and vary fluid chemistry.

This project can be divided into three parts: sample preparation, NMR studies, dielectric studies. Over the past nine months we have made significant progress in sample preparation and NMR studies. As our plan is to conduct the NMR and dielectric measurements on the same set of samples, we delayed the start of the dielectric measurements until the first stage of NMR measurements were complete. Below we summarize our progress in sample preparation and NMR measurements, first briefly introducing the method used for the NMR measurements.

Method Used for Measurement of NMR Relaxation Times

One of the critical issues in our research is to understand how and why NMR measurements are affected by the wettability of the solid surface. Our approach is to conduct experiments on water-wet, hydrophobic and oil-wet systems with variation in the chemistry of the pore fluid.

The NMR measurements are made in collaboration with Dr. Alex Mackay in the Physics Department at UBC. We use a pulsed proton NMR spectrometer, with a Bruker iron-core electromagnetic and an S X P^TM probe with a dead time of 10 microseconds. The electromagnet has a magnetic field of 2.12 Tesla which translates into a Larmour frequency of 90 MHz for protons. Measurements are made of both T1 and T2 proton relaxation times. The actual measured data are magnetization as a function of time. To invert the data to obtain the distribution of relaxation times, we use the nonnegative least squares (NNLS) algorithm of Lawson and Hanson (1974) as implemented by Whittall and Mackay (1989). The sand samples are prepared using Teflon sample holders and are saturated when in the holders by using a high pressure saturation apparatus.

Sample Preparation

Our proposed research involves the study of three types of systems:

- 1) water-wet: water spontaneously coats and adsorbs to the solid surface. In this case any oil present in the pore space exists and moves through the central volume with minimal interaction with the solid surface.
- 2) hydrophobic: water is repelled from the solid surface through the adsorption of another phase.
- 3) oil-wet: oil coats the solid surface. This case represents the presence of an oil as the contaminant, which has become adsorbed to the solid surface, resulting in an oil-wet system.

Water-Wet Sands

We began our research by first determining whether any pre-treatment is required before starting experimental work with the water-wet sand. The purpose of this pre-treatment is to remove impurities within the surfaces of the sand grains and to ensure a known surface chemistry as a starting point. We tested various procedures, which involved washing of the sand with an acid or base. Measurement of the NMR T_1 relaxation time for the sand saturated with degassed distilled water was used as a way of comparing the various methods of sand washing; these T_1 values are listed in Table 1.

In previous experiments, conducted as part of W. Kanters M.Sc. thesis (Kanters, 1996), water wet sand was prepared by pre-treatment with hydrochloric acid followed by soaking in a pH 2.5, dilute brine solution according to the method of Dubey and Doe (1993). This was done to remove impurities and to obtain a known surface chemistry. The surface sites following this treatment are presumed to be Si-OH and Si-O⁺H₂ in a ratio of 3:2. This pre-treatment method resulted in an NMR relaxation time (T_1) of 0.8 s for water-saturated sand.

Our first measurement was made on water-wet sand, with no pre-treatment, but screened with a Frantz separator to remove ferromagnetic and paramagnetic particles. We found that this magnetically screened sand, saturated with degassed distilled water, had a T_1 of 1.2 +/- 0.1 s.

Our next series of experiments involved testing the effects of acid and base washing of sand. In the first experiment, the paramagnetically screened sand was treated by boiling and soaking overnight in either 2.0 M nitric acid or 2.0 M NaOH (a base), rinsed thoroughly with distilled water and dried overnight at 110°C. The measured NMR relaxation times for the samples are reported in Table 1. The T_1 for acid washed sand was 0.7 s while that for the base washed sand was 1.7 s. We assumed that treatment with nitric acid produced an electropositive quartz surface with 100 per cent Si-O⁺H₂ surfaces sites and the base treatment produced a negatively charged quartz surface with 100% Si-O surface sites. If this was the case, these treatments should be completely reversible, therefore, our next experiment tested the reversibility of the treatments.

The second experiment involved two steps of pre-treatment: acid wash followed by base wash or base wash following by acid wash. Base treatment following acid treatment produced a sand with the same T_1 (1.7 s) as the base-washed sand. However, when acid treatment followed base treatment, the T_1 increased to 2.1 s. Therefore, the acid-base pre-treatments are not completely reversible and the protonation or deprotonation of surface sites is not the only reaction occurring during these treatments.

This series of experiments showed that both acid and base washing can alter the state of the water-wet surface in ways that are not at present understood. One possible explanation for the unusually high T_1 after the two-step base-acid wash is the formation of silica polymers under basic conditions. While this will be a topic of ongoing research, we decided that it was best to use sand that was untreated except for paramagnetic screening as the standard for water wet sand. We have concluded that this gives us a material that is as close as possible to its natural state.

Hydrophobic Sands

The next phase of the project involved extensive testing of the various procedures that can be that can be used to obtain hydrophobic samples. The chemical treatment that we had used in the past involved adding a chromium complex to the system, which we have found can interfere with the NMR measurement. We are now investigating methods based on the silanization of silica by organosilanes

Bradford and Leiji (1996) prepared stable and reproducible hydrophobic surfaces on blasting sands using a 5% solution of octadecyltrichlorosilane in ethanol. Olsen and Crocker (1990) found that 10% solutions of octatrichlorosilane or dimethyldichlorosilane in toluene also prepared hydrophobic surfaces that were stable at room temperature but hydrolyzed within 48 hours with steam treatment. To prepare a completely stable hydrophobic surface they used a gas phase reaction at high temperature and pressure with bis(dimethylamino)dimethylsilane. We decided to investigate a variety of the liquid phase treatments before resorting to the complicated gas phase reaction.

The silanes chosen for these tests were dimethyldichlorosilane (MeSi) and octadecyltrichlorosilane ($C_{18}Si$) so that we would have both a long and a short carbon chain on the surface molecule. The length of the organic molecule has been shown to affect NMR relaxation times (Devereux, 1967). Both ethanol and toluene were tested for suitability as solvents and the effect of reaction temperature was also measured. It was found that the solubility of $C_{18}Si$ in ethanol was reasonably low, so 5% solutions of both silanes were used in all experiments. In fact, even a 5% octadecyltrichlorosilane solution was slightly supersaturated resulting in precipitation of some unreacted silane. All reactions were carried out for 48 hours with a 5% solution of the silane in either toluene or ethanol at room temperature or at the reflux temperature of the solvent. All eight sands prepared in this series were strongly hydrophobic. Although contact angles were not measured, water drops on a thin layer of each of these sands were tightly beaded. In addition, when exposed to a heptane-water mixture, each of these samples associated with heptane and avoided contact with water. This behavior did not change even after three months of continuous exposure to the solvent mixture.

The NMR relaxation times for the eight hydrophobic sands saturated with degassed distilled water are shown in Table 2; given in this table are the silane type, the solvent, the reaction temperature and the measured average T_1 value. All except three of the silane treatments resulted in T_1 values between 1.0 and 1.3 s. The similarity between the T_1 of hydrophobic sand and water wet sand is striking. This raises questions about the mechanism of surface relaxation. It was thought that silane treated sands and oil-wet sands would have similar T_1 values because they are both hydrophobic. Perhaps surface relaxation mechanism depends more on what is actually at the surface than the surface's wetting characteristics.

All three sands with a T_1 outside the 1.0-1.3 s range were prepared with octadecyltrichlorosilane. In the two cases where ethanol was the solvent, the T_1 was 1.7 s, which is as high as has been observed in oil-wet systems. In both cases white precipitate, assumed to be unreacted $C_{18}Si$, was mixed with the sand so these sands were subsequently rinsed with boiling toluene to remove any excess silane. Surprisingly, the T_1 after this treatment dropped to 0.9 s suggesting that it is the presence of excess silane, precipitated on the surface of the sand, that results in the high value of T_1 . This result has important implications for future studies concerning the mechanism of NMR relaxation.

The other unusual relaxation time was the value of 0.6 s, observed for refluxed $C_{18}Si$ in toluene at a temperature of 70°. In this case the T_1 was even lower than that observed for the water-wet sands. At this point we have no explanation for this anomalously low value for water in sands with a hydrophobic surface.

For pre-treatment to produce the oil-wet surfaces, we selected the longer chain silane ($C_{18}Si$) which we assumed would have a stronger association with oil. We also chose to

use the treatment which involves refluxing at high temperature; we presume that exposure to the higher temperature would create a more stable surface state. Thus all subsequent oil-wetting procedures used sand that was refluxed with $C_{18}Si$ in toluene. It is important to note that attempts to increase the scale of this reaction to treat large volumes of sand resulted in inconsistent results. The T_1 values of these reactions varied from 0.6 to 1.2 s. We are continuing to investigate this problem, but we found that this variation did not affect the oil-wetting procedure.

Oil-wet Sands

To prepare oil-wet sand from silanized sand, approximately 5 g of Cold Lake Crude (Alberta, Canada) were dissolved in 100 mL of 50:50 heptane:toluene. Fifteen grams of hydrophobic sand were mixed with the dissolved oil and allowed to sit overnight. Within 12 hours the solvent had evaporated leaving a tar-sand mixture that was then washed with the heptane-toluene mixture and vacuum filtered, leaving sand coated with a thin layer of oil. The sand was light beige in color, a lighter color than we expected. This suggested either that the layer of surface oil was very thin, or that a layer of oil was not covering all the grains. Measurement of the NMR relaxation of this sand, saturated with distilled water, showed an increase in T_1 to 1.4 s. This T_1 was low when compared to that obtained for oil-wet sands prepared by Kanters (1.8 s). Given the color and the low T_1 value, we decided to modify the oil-wetting procedure.

For subsequent preparations one additional step was added: the filtrate was collected and enough ethanol was added to make the solution opaque. This indicated the presence of micelles of suspended oil. This suspension was mixed with the sand and the mixture was vacuum filtered. The resulting oil-wet sand was a much darker brown than the original and the T_1 increased to 2.6 s. It was found that different shades of brown resulted when varying amounts of ethanol were added but the T_1 of each of these oil-wet sands was 2.5 +/- 0.1 s. It was decided to use the dark colors of sand for the NMR experiments; the T_1 was between 2.4 and 2.6 s for these samples. Experiments are currently in progress to quantify the exact ratio of heptane, toluene and ethanol required to produce a range of "sand color" which we assume is an indicator of the thickness and/or completeness of the surface oil film.

NMR Measurements

A complete set of experiments has been conducted on water- and oil-wet sands with variation in the pH and salinity of the pore fluid. The measured T_1 values for water-wet and oil-wet sands saturated with different solutions are shown in Figure 1. The first notable observation is that for all pore fluids tested, T_1 of the oil-wet sand is greater than T_1 of the water-wet sand. This is in agreement with previous work over a more limited range in salinity and pH and supports the idea that NMR is sensitive to the state of the solid surface.

Let us now consider the effect of pore fluid chemistry on the NMR relaxation. For both types of sand, at any given pH, there is almost no change in T_1 with variation in salinity. However, there are observed changes with pH. For the water-wet samples, T_1 is approximately 1.1 s within a pH range from 3 to 11. There is a sharp decrease in T_1 to 0.7 s as pH is reduced from 3 to 1.85. For the oil-wet sands, T_1 is constant at 2.5 s from pH 11 to 5 and drops to 1.5 s from pH 5 to 1.85. In both of these systems, we are currently investigating the way in which pH could affect the NMR relaxation through the effect of pH on the state of the solid/fluid interface. It is well known that pH will control the charge on solid surfaces and we suspect that the change in charge is indirectly responsible for the observed pH dependence. At pH equal to 2, the charge on quartz changes from positive at higher pH to negative at lower pH with pH of 2 being the point-of-zero charge for quartz

(Parks, 1990). A titration experiment will be done to determine the point-of-zero charge of the oil-wet sands.

Previous experiments have shown that the relaxation time of the bulk solutions used to saturate the samples is constant at approximately 3 s and does not vary with pH or salinity (Kanters, 1996). However, when these solutions are used to saturate sand samples, chemical reactions can occur between the solid and the fluid that can affect the T_1 of the solution. In particular, the relaxation time of a solution can be reduced by the addition of paramagnetic ions to solution. In order to quantify any changes in the NMR relaxation of the bulk fluid saturating the samples, a series of experiments was conducted in which we saturated samples of water-wet and oil-wet sand with 0.01 M NaCl over the range of pH, and measured T_1 of the extracted pore fluid. The samples were prepared in a syringe, making it very easy to extract the saturating solution after equilibration for 48 hours. As can be seen in Figure 2, we see a trend similar to what was observed for the sand samples, where there is little change in T_1 until pH is reduced from 3 to 1.85. We believe that the drop in T_1 of the bulk solutions is due to paramagnetic species going into solution.

Based on the data presented in Figures 1 and 2, we currently believe that there are two factors contributing to the observed changes in the NMR relaxation of saturated water- and oil-wet sand. We suggest that relaxation is occurring by a least two mechanisms in the sands: 1) surface relaxation (thus the observed differences between water-wet and oil-wet sands) and 2) relaxation due to paramagnetic ions being dissolved in the pore fluid. Both of these mechanisms appear to be affected by pH variation. Our ongoing research will continue to characterize the complex chemical nature of these solid/fluid systems in order to determine the key factors governing the NMR response.

Summary/Conclusions

We have made considerable progress to date in the initial stages of our research project. We have found a stable, reproducible method for creating hydrophobic and oil-wet surfaces. The NMR measurements on a set of sands have been completed with a variation in pore fluid chemistry; these data suggest that surface charge is a key parameter in governing the NMR response. Once we have an improved understanding of the main chemical factors influencing the NMR response of the sand samples, and determine how these can best be experimentally controlled, we will begin the parallel set of dielectric experiments.

Report on Budget and Anticipated Expenditures

Our expenditures in this first year will be very close to what was given in our initial budget. We anticipate that there will be no unexpended funds at the end of the first 12-month period in any of the budget items with the exception of salary. We have an under-expenditure in salary as there has been a delay in the arrival of the research associate, who will now arrive August 1997. In addition, given the September start date there was a four month delay in bringing students onto this project due to prior commitments to other ongoing projects.

References

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Table 1: Values of T_1 ave for different types of sand washing.

treatment of sand	T_1 ave
untreated	1.2 +/- 0.1 s
washed with 2.0 M HNO ₃	0.7 s
washed with 2.0 M NaOH	1.7 s
washed with 2.0 M HNO ₃ and then washed with 2.0 M NaOH	1.7 s
washed with 2.0 M NaOH and then washed with 2.0 M HNO ₃	2.1 s

Table 2: Values of T_1 ave for different types of silane treatments.

silane type	solvent	temp	T_1 ave
C ₁₈ Si	EtOH	~80°C	1.7 s
C ₁₈ Si	toluene	~70°C	0.6 s
C ₁₈ Si	EtOH	~25°C	1.7 s
C ₁₈ Si	toluene	~25°C	1.2 s
Me ₂ Si	toluene	~70°C	1.3 s
Me ₂ Si	EtOH	~80°C	1.2 s
Me ₂ Si	toluene	~25°C	1.0 s
Me ₂ Si	EtOH	~25°C	1.2 s

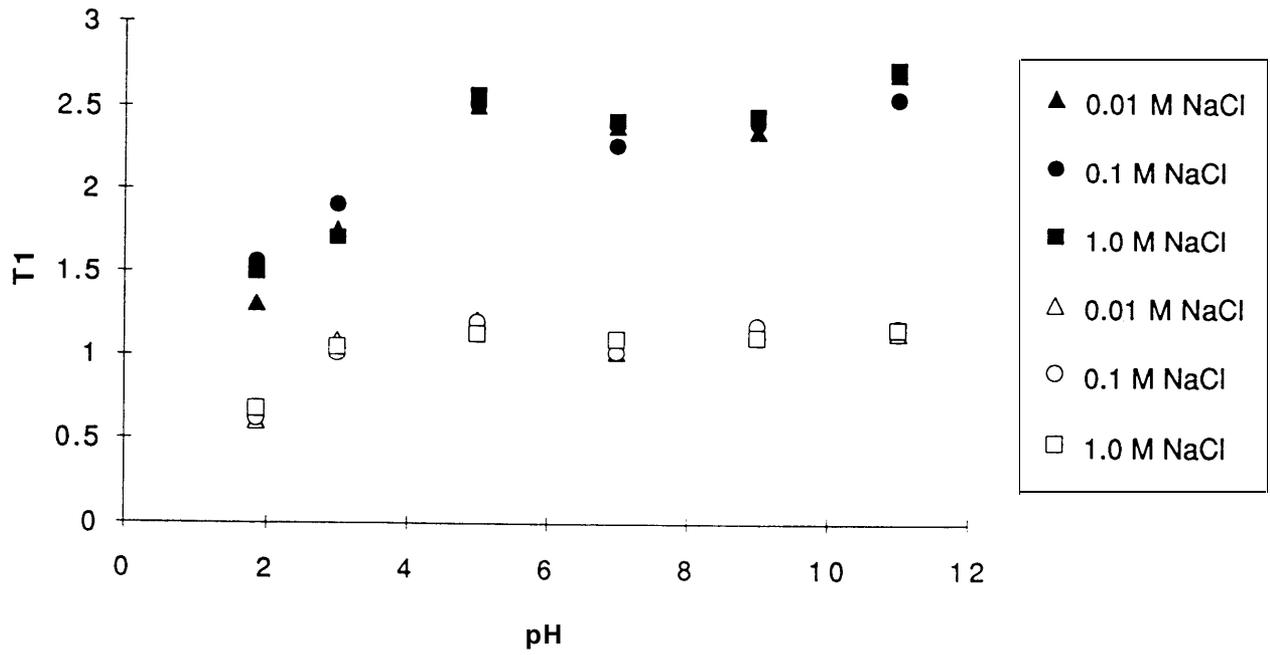


Figure 1. T₁ relaxation times for water-wet (open symbols) and oil-wet (solid symbols) sands saturated with fluids with variation in salinity and pH.

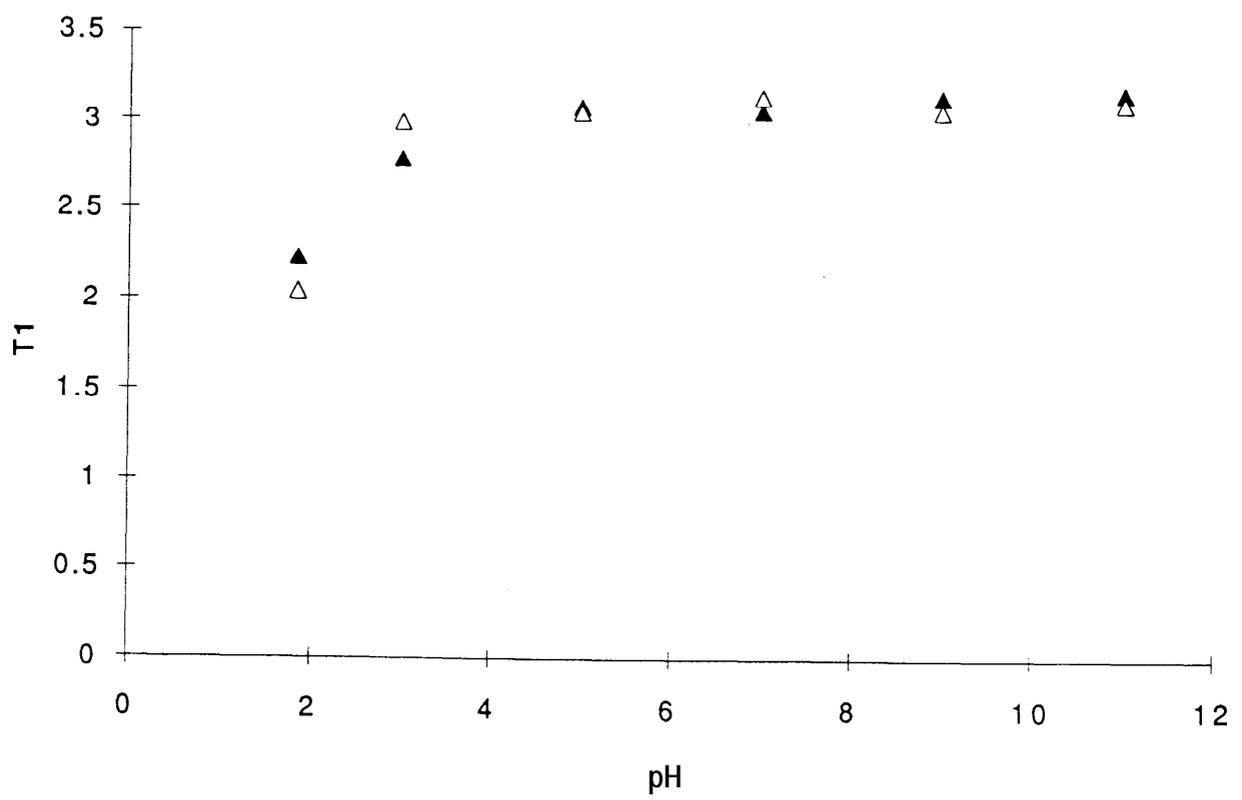


Figure 2. T₁ relaxation times for pore fluids after 48 hour equilibration with water-wet (open symbols) and oil-wet (solid symbols) sands. The fluids were 0.01 M NaCl.