

## Detecting Gas Hydrate Behavior in Crude Oil Using NMR

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Received: September 6, 2005; In Final Form: January 30, 2006

Because of the associated experimental difficulties, natural gas hydrate behavior in black oil is poorly understood despite its grave importance in deep-water flow assurance. Since the hydrate cannot be visually observed in black oil, traditional methods often rely on gas pressure changes to monitor hydrate formation and dissociation. Because gases have to diffuse through the liquid phase for hydrate behavior to create pressure responses, the complication of gas mass transfer is involved and hydrate behavior is only indirectly observed. This pressure monitoring technique encounters difficulties when the oil phase is too viscous, the amount of water is too small, or the gas phase is absent. In this work we employ proton nuclear magnetic resonance (NMR) spectroscopy to observe directly the liquid-to-solid conversion of the water component in black oil emulsions. The technique relies on two facts. The first, well-known, is that water becomes essentially invisible to liquid state NMR as it becomes immobile, as in hydrate or ice formation. The second, our recent finding, is that in high magnetic fields of sufficient homogeneity, it is possible to distinguish water from black oil spectrally by their chemical shifts. By following changes in the area of the water peak, the process of hydrate conversion can be measured, and, at lower temperatures, the formation of ice. Taking only seconds to accomplish, this measurement is nearly direct in contrast to conventional techniques that measure the pressure changes of the whole system and assume these changes represent formation or dissociation of hydrates — rather than simply changes in solubility. This new technique clearly can provide accurate hydrate thermodynamic data in black oils. Because the technique measures the total mobile water with rapidity, extensions should prove valuable in studying the dynamics of phase transitions in emulsions.

### Introduction

When natural gases come into contact with water under high pressures and low temperatures, they form ice-like crystalline compounds called gas hydrates, which are composed of nano-scale water cages that enclose gas molecules of appropriate diameters.<sup>1</sup> Hammerschmidt<sup>2</sup> first realized it was gas hydrates, not ice, that were plugging natural gas pipelines. This marked the beginning of the industrial interest in gas hydrates for flow assurance, i.e., assurance of unrestricted flow of fluids through pipelines. Due to the frequent presence of water and light hydrocarbons, such as methane, during oil production, hydrate plug formation is a serious concern in deep-water flow-assurance of oil and gas flow lines, where high pressures and low temperatures are often encountered. To prevent hydrate plugging, appropriate amounts of chemical hydrate inhibitors are often added into the pipelines or thermal insulations are installed to prevent heat loss. It was estimated that industry is spending over 500 million dollars on hydrate inhibitors annually.<sup>3</sup> The dose rates of hydrate inhibitors and thermal insulation designs are all based on the expected pipeline conditions relative to the hydrate phase diagram.<sup>4</sup> Therefore, accurate phase diagrams of gas hydrates are essential to safety and economic considerations. Equally important are hydrate formation and dissociation kinetics, key factors in hydrate management. Unfortunately, current models for predicting hydrate phase behavior show considerable discrepancy with experimental data for black oil

systems.<sup>5</sup> The differences can be as much as 5–6 degrees,<sup>5</sup> which will either invoke unnecessary expense or put the operation at great risk. New, accurate experimental data are needed to test and tune phase behavior models.<sup>5</sup> However, hydrate phase behavior in black oil, particularly with emulsions, is poorly understood due to the associated experimental difficulties. No kinetic data on gas hydrates in black oil has been reported in the literature.

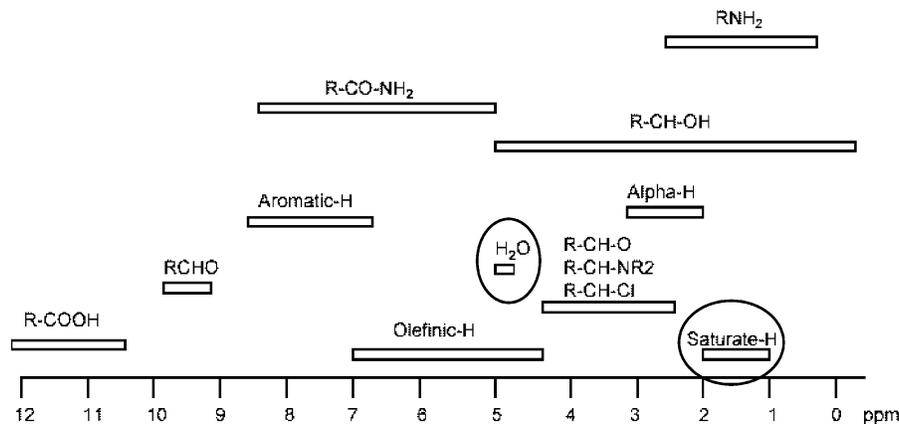
In multihydrate-former systems, such as natural gas and black oil, the hydrate thermodynamic point is defined as the equilibrium condition at which the last hydrate crystal dissociates.<sup>6</sup> Because the nature of black oil deters direct visual observation, traditional attempts to characterize hydrate behavior in black oil have frequently depended on monitoring system pressure changes.<sup>6</sup> In this method, water, black oil, and gas are charged into a high-pressure cell. The pressure is monitored as this closed system is ramped in temperature. Because the gases have to transport through the liquid oil and water phase, some means of mechanical stirring are often employed to facilitate the gas mass transfer. Pressure drops dramatically upon hydrate formation because hydrate formation consumes large quantity of gas. After hydrate formation, the temperature is raised to dissociate the hydrate. As hydrate dissociates, gases are released and pressure increases significantly. The transition point that indicates complete hydrate dissociation (normally where pressure and temperature return to the original  $P$ ,  $T$  curve before hydrate formation) is identified as the hydrate thermodynamic point.

This traditional pressure–temperature monitoring technique is widely used but has some inherent limitations. For example, it can be troublesome in obtaining accurate hydrate thermody-

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**Figure 1.** Proton NMR chemical shifts for common functional groups.<sup>7</sup>

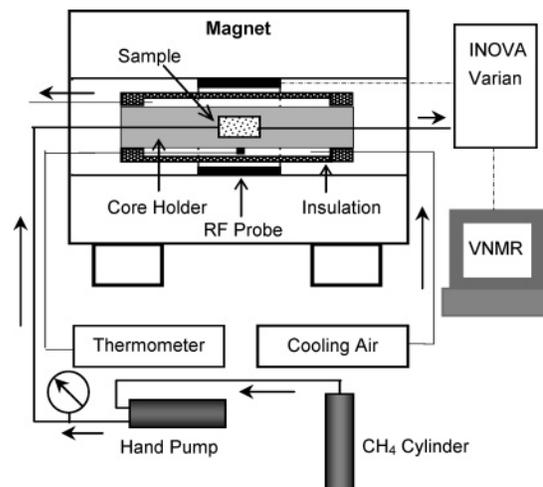
namics and kinetics when the oil phase is too viscous. Because gas diffusion rates in the oil are small, a long delay between hydrate behavior and pressure response is to be expected.<sup>6</sup> Because the dissociation of a small hydrate crystal in black oil is not likely to cause much pressure change, it is very challenging to locate accurately the hydrate thermodynamic equilibrium point. The traditional technique also has difficulties in very low water-cuts. If the amount of water is too small, hydrate formation may not cause enough pressure change for accurate hydrate point measurements. Further complications arise when the pressure is above the oil bubble point where the gas phase disappears.

To overcome these limitations, in this work, we demonstrate the viability of employing proton nuclear magnetic resonance (NMR) spectroscopy to directly and accurately observe in situ hydrate behavior in black oil. In a proton NMR spectrum, different hydrogen functional groups have different chemical shifts, as shown in Figure 1. The chemical shifts of water and saturated hydrocarbons, the dominant component in the black oil and natural gas, are about 3 ppm apart.<sup>7</sup> Thus, the water and oil components should be distinguishable in a high field NMR with sufficient magnetic field homogeneity. The water peak area in the NMR spectrum is directly related to the amount of liquid water in the sample. Because the free induction decay of water in gas hydrates at these fields is so short, and their spectral line so broad, they cease to contribute to the liquid water peak, and consequently the water peak decreases. We can immediately detect and easily quantify hydrate formation and dissociation from the changes of water peak area, instead of depending on pressure responses such as in the traditional method. Using this method, we can dynamically and accurately measure when hydrates nucleate or dissociate, their concentration in the system, and how fast hydrates are forming or dissociating, and therefore obtain accurate hydrate thermodynamic and kinetic information in black oil.

### Experimental Details

The experimental scheme is depicted in Figure 2. The magnet for NMR measurements is an 85 MHz Oxford horizontal 32 cm wide bore NMR with imaging capability. The probe is a LITZ RF volume coil (with 14 cm internal diameter) from Doty Scientific, Inc. NMR data were acquired and processed using Varian VNMR software and INOVA hardware systems.

To mimic the situation during oil production,<sup>8</sup> black oil and pure water were mixed in a 1:1 volume ratio and manually shaken to make a stable water-in-oil emulsion. Baker Petrolite generously provided the black oil samples. The pure water was from Aldrich Chemical Co. Inc. and used without further

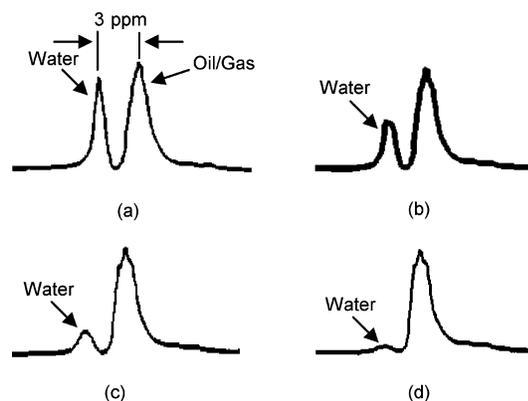


**Figure 2.** Schematic of the experimental setup.

processing. The 16 mL water-in-oil emulsion sample was contained in a Teflon bottle and then placed in a core holder from Temco Inc., which is made of strong nonmetal composite material and specially designed for NMR experiments. The core holder is capable of handling pressures up to 2500 psi. It has an outer diameter of 5.6 cm, enclosing the sample itself of 2.7 cm diameter and 3.1 cm height. Ultrahigh purity (UHP) grade methane from Airgas was used as the gas phase. A Ruska positive displacement hand-pump controlled the pressure. Its maximum pressure capability is 4000 psi. The gas pressure was accurately measured by a Heise high precision dial pressure gauge with 2.5 psi resolution.

An Air-Jet temperature controller blew dry air to control the core holder temperature. It is capable of controlling temperature from  $-40$  °C to  $100$  °C with  $\pm 0.1$  °C stability. Styrofoam material was placed around the core holder for insulation. A LUXTRON fluoroptic thermometer with resolution of  $0.1$  °C was mounted onto the core holder to monitor the temperature. Temperature of the core holder itself was measured at the same axial location of the sample (a radial distance of 2.8 cm). The temperature difference between sample volume and core surface was measured in a separate measurement at room pressure after a  $5$  °C step and found to be less than  $0.1$  °C after 2 h of equilibration. During hydrate measurements (at 2000 psi density methane) temperature gradient should be less.

With the emulsion sample inside and insulation outside, the core holder was placed into the NMR probe. Magnetic resonance imaging (MRI) techniques were utilized to ensure the sample was located in the center of the magnet, the spot that has the most homogeneous magnetic field. The more homogeneous the



**Figure 3.** NMR spectra at different stage of hydrate formation. From (a) to (d), as less mobile water is present, the water peak diminishes.

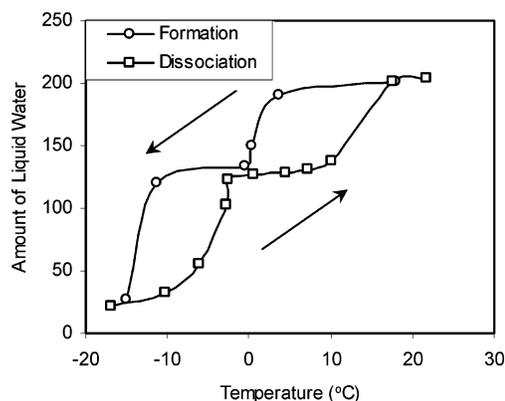
magnetic field, the better are the spectral resolution and signal-to-noise ratio. The core holder was then slowly pressurized to 2000 psi with methane at room temperature. The system was allowed to stabilize at room temperature and 2000 psi for 1 day to allow as much as gas as possible to dissolve into the oil/water phases. Over this period the consumption of gas required to maintain the pressure diminished to zero. The NMR system was fine-tuned to yield a spectrum in which the water peak was easily distinguishable from oil/gas peaks.

After the pressure was stabilized, indicating the system had reached equilibrium, the temperature control was turned on to slowly cool the core holder in steps. To ensure maximum hydrate formation before the sample went into the subzero region where ice may form, the system was held at  $\sim 2$  °C for two weeks. The temperature was then further cooled to the extent where most of the water peak disappeared. After the disappearance of the water peak, the core holder was heated in steps to dissociate the solid phases. Under all conditions, the pressure was kept constant at 2000 psi through the Ruska hand-pump. The temperature was held constant at each step for over 12 h before each measurement. An NMR spectrum was collected at every temperature step to detect any change in water peak area, i.e., the indication of hydrate formation or dissociation in black oil.

## Results and Discussion

Figure 3 shows the NMR spectrums of the water/black oil emulsion sample with different degrees of hydrate formation. Oil and gas components form a single broad peak. The water peak and oil/gas peak are nicely separated and are about 3 ppm apart, just as expected.<sup>7</sup> The hydrate was assumed to be structure I methane hydrate. However, it was possible that some amount of other hydrate structure also existed due to the complexity of the black oil. There are some possible components in petroleum, such as, methylcyclopentane, methylcyclohexane, neohexane, and adamantane, which can form some structure H hydrate with the help of methane.<sup>9</sup> Of course the current technique described here is indifferent to the specific type of hydrate structures involved.

As mentioned before, the water peak area is linearly correlated with the amount of liquid water in the sample. As water turned into hydrate (and possibly also ice when the temperature was below zero), the water peak area decreased, as shown from Figure 3a to Figure 3d. Peak areas were reproducible experimentally with an error of less than 1%. By measuring the change in peak area above the ice point, we can calculate exactly how much water in the emulsion has formed hydrate. From the rate of change of peak area, kinetic information can be obtained.



**Figure 4.** Amount of liquid water in the sample as a function of temperature during hydrate formation and dissociation in black oil at 2000 psi.

To our knowledge, this is the first time that in situ hydrate behavior in black oil has been directly and so accurately measured.

The data for the experimental protocol described are shown in Figure 4 where the liquid water in the emulsion is plotted as a function of temperature. The liquid water content was obtained from the water peak areas after compensating for the general decrease in bulk magnetization due to the decrease in temperature. With reference to Figure 4, as the temperature of observation was decreased, no significant change in water content occurred until  $\sim 1$  °C. It should be noted that at 2000 psi, the methane hydrate equilibrium temperature in bulk water predicted by CSMHYD<sup>1</sup> is 16.34 °C. Interestingly, after this initial onset, no more hydrate formed for 2 weeks at  $\sim 0$  °C, even though 70% of the water was still in the liquid state. A tempting explanation is that gas hydrate first occurred at the oil/water interface of the emulsion droplets. Because the diffusion rate of gas in hydrate solid is very slow, formation of hydrate shells around the droplets would keep gas from reaching the droplets' wet interiors and prevent further hydrate formation.

Further cooling had no effect on the liquid water content until  $-15$  °C, at which another drop occurred. About 10% of water still produced liquid signal, even at  $-17$  °C. This second disappearance of liquid water was probably due to the formation of ice. Support for this conjecture was found when warming up: the lost liquid reappeared before the temperature reached zero. Ice formation/melting temperatures in water/oil emulsions are subject to Rayleigh depressions and are dependent on droplet sizes.<sup>10</sup> The melting temperature of ice crystallites in an emulsion would then be expected to span some range related to the droplet size distribution. The amount of hydrate formation at subzero temperatures can be calculated from the difference between the formation and dissociation curves around  $-1$  °C. Subsequently, the amount of ice formation can be estimated by the total disappearance of liquid water at subzero temperatures deducted by the amount of hydrate formation at these temperatures. The water peak area reached a plateau above  $-2$  °C. Hydrate started to show significant dissociation around 12 °C, which is lower than predicted. This suggests the hydrate thermodynamic melting point was depressed by the same emulsion size considerations as for ice.

This experiment clearly demonstrates that NMR spectroscopy can directly detect and accurately measure hydrate behavior in black oil. Therefore, hydrate thermodynamics and kinetics can be obtained through this new technique. Using this technique and its extensions, future work will quantify the relations between hydrate behavior and emulsion droplet sizes and water

cuts. This technique measures the conversion of liquid water within the emulsion in comparatively real time. By combining the technique with conventional pressure measurements, future studies will reveal information on the time lags inherent in pressure measurements and provide data on gas migration.

### Conclusions

In this work, it was demonstrated that with adequate magnetic homogeneity the water peak can be distinguished from the black oil and gas peaks in proton NMR spectra. Because water in the solid hydrate phase is invisible to liquid state NMR, hydrate formation and dissociation in black oil were directly and accurately observed for the first time by tracking the change of water peak area. Results illustrated that emulsion formation depresses both the ice point and the hydrate point in black oil. By providing a direct measure of hydrate information in black oil, this new technique offers great potential for equilibrium and kinetics studies that will benefit deep-water flow assurance.

**Acknowledgment.** The authors gratefully acknowledge the financial support of the Robert A. Welch Foundation (grant

C-1241 at Rice University) and the Livermore Chair and MRI-PAC at TTU.

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