TOWARD A METHOD FOR MEASURING WETTABILITY IN POROUS MEDIA BY NMR WATER VAPOR ISOTHERM TECHNIQUE

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ABSTRACT

The wettability of reservoir rocks is one of the most important factors in evaluating hydrocarbon reserves and producibility. Reservoir rocks contain considerable amounts of pore spaces to trap and transport fluids including hydrocarbons and brine. Although those pore spaces are essential and beneficial for hydrocarbon production, the porous nature of reservoir rocks, on the other hand, poses difficulties for measuring the wettability. Macroscopic experiments, such as a contact angle determination, are of limited value because the wettability needs to be determined within the rock pore structure. Here, we propose a new method for measuring the wettability of porous media by Nuclear Magnetic Resonance (NMR) water vapor isotherm technique. It could provide insight into the molecular dynamics at the interface between fluids and surfaces by analyzing different total amount of adsorbed water vapor and shapes of the measured water vapor isotherm as a function of relative vapor pressure. Since the NMR water vapor isotherm is affected not only by water molecule affinity for the pore surface but also by other factors controls wettability of the surface, it could provide the wettability information of pore surface within porous materials. An additional advantage of NMR water vapor isotherm wettability measurement is it is able to measure the wettability of nano-sized pore surface since gas is injected instead of liquids in the case of other conventional wettability measurement methods.

In the current work, the isotherms taken on the soda lime glass beads with different wetting properties prove that our approach is indeed capable of distinguishing between hydrophobic and hydrophilic surface states which are directly related to the wettability. The consistency of the contact angle measurement is also discussed. The new NMR method can be further applied to

study reservoir core rocks, leading to new insights that are needed in optimize hydrocarbon production.

INTRODUCTION

The wettability of the porous structure within rocks is one of the key parameters that determine the fluid flow through those rocks. Consequently, it is one of the essential input variables for geophysical models that predict flow through reservoir rocks. Wettability is often used as a distinguishing characteristic of materials, designating them as hydrophobic (water fearing), or hydrophilic (water loving). However, it is not just a material parameter characteristic of a given rock but depends on other factors as well, such as surface roughness, surface size, existence of primary adsorption sites, and specific ion effect. Therefore, it is not sufficient to determine the wettability of an idealized surface by using a water drop and measuring the contact angle as a decisive indication of the ability of the surface to attain moisture. Moreover, in terms of rock pore structure, macroscopic experiments, i.e. contact angle determination, are of limited value. Other common wettability measurement methods for porous media, such as Amott-Harvey and USBM methods are indirect method which are prone to a considerable margin of errors from the unavoidable multiple experimental procedures. In addition, these methods only measure the global wettability which has is not sufficient for porous media with heterogeneous pore structures such as carbonate.

Two forces determine the wettability of solid surface, adhesion and cohesion force. The adhesion force is the tendency of liquid molecules to create an attraction to a different substances and the cohesion force is that of liquid to create the minimum possible surface area. The affinity of water molecule to the solid surface, which is the hydrophobicity (or hydrophilicity) of solid surface, is caused by the adhesive force between liquid and solid. Thus, the hydrophobicity is directly relate to the wettability of solid surface.

NMR has been proven to be a good technique to determine the hydrophobicity within porous materials. For example, using NMR, Wang et al. shows that the shape of water adsorption isotherm in micropore environments strongly depends on the surface hydrophobicity; hydrophobic surfaces produce a concave shape, while hydrophilic surfaces lead to a convex isotherm, corresponding to Type III and Type I, II, respectively of the IUPAC classification of isotherms [1]. In addition to the isotherms, NMR can also provide insight into the molecular dynamics at the interface by probing the relaxation processes (T_1, T_2) [2, 3]. This additional information sheds light on the interactions between the water molecules and the hydrophilic or hydrophobic surface [4].

In the current work, we focus on surfaces where external stimuli can trigger changes in surface hydrophobicity. The resulting change in surface wetting is observed by monitoring the change in the static contact angle and NMR-detected water vapor isotherm. Clear differences of the NMR water vapor isotherm curves from hydrophilic and hydrophobic porous materials has been observed and analyzed.

Methods
Materials

The soda lime glass beads and microporous silica beads (> 98% SiO_2 and < 2% B_2O_3) are purchased from Mo-Sci Corporation and used as purchased without further purification. The soda

lime glass beads are solid and nonporous; their morphologies are shown in Figure 2. Three different soda lime glass beads are used: 20, 40 and 400 μm in diameter, respectively. The diameter of microporous silica beads is 8 μm. Sulfuric acid solution (4N), glass wafers made of soda lime and Chloro(dodecyl)dimethylsilane (purity $> 95\%$) are purchased from Fisher Scientific.

Surface Wettability Modification

The surface hydrophobicity (or wettability) of glass beads and glass wafers are modified by two different chemical treatments. Hydrophilic surface is obtained through acid wash treatment. Clean glass beads or glass wafers are immersed in 2M sulfuric acid solution for 24 h. The acid-treated samples are subsequently rinsed with distilled water and dried in the lab for two days. Hydrophobic surface is obtained via the silane-coating method [6-8]. Clean glass beads or glass wafers are immersed in the Chloro(dodecyl)dimethylsilane for 24 h. The reaction can be represented as follows.

$$CH_3(CH_2)_{11}Si(CH_3)_2Cl + -Si-OH \rightarrow -Si-O-Si(CH_3)_2(CH_2)_{11}CH_3 + HCl \qquad (1)$$
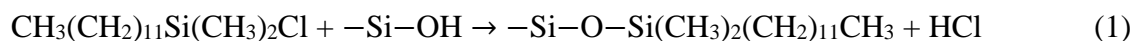
Following the silane coating, the treated sample is rinsed with ethanol to wash off any remaining organic materials.

Contact Angle Measurement

Static contact angles are measured using CAM 200 optical contact angle meter (KSV instruments). A water droplet of 2 μL is formed at the end of the syringe and carefully deposited onto the sample surface. The images of static contact angle are taken within 5s of water deposition by a charge coupled device (CCD) camera. Static contact angle is calculated by vendor-supplied software.

NMR-detected Isotherm

The water isotherms are measured at a home-made in situ NMR system on a 34 MHz magnet at 293 K. The in situ NMR isotherm system enables us to selectively detect the adsorbed water on the surface with high sensitivity. As illustrated in Figure 1a, the basic components are a vacuum chamber connected to a mechanical pump, a pressure gauge, the NMR sample tube, and the source of water vapor. Shown in the left figure of Figure 1b, in each measurement, equal amounts of treated 20-μm and 400-μm beads are first mixed thoroughly and then loaded into the sample tube. The inner diameter of the sample tube is 3.9 mm and the length (height) of packed sample is 5 cm. The sample tube with the loaded sample is then shaken carefully to get random close packing. The ^{1}H free-induction-decay (FID) signal of the dry sample is then acquired by a single-pulse excitation with pulse duration of 8 μs. The waiting interval between each repetition of the pulse sequence is set long enough, longer than $5T_1$, to ensure that the signal is fully recovered after each scan. A broad peak of 500 ppm (full width at half-maximum, FWHM) is observed in the background spectrum and is subtracted from subsequent spectra. Water vapor is then loaded to the sample at varying vapor pressures, and the NMR spectra of the hydrated samples are acquired. The intensity of the ^{1}H NMR signal is calibrated with a test tube of bulk water of known mass.
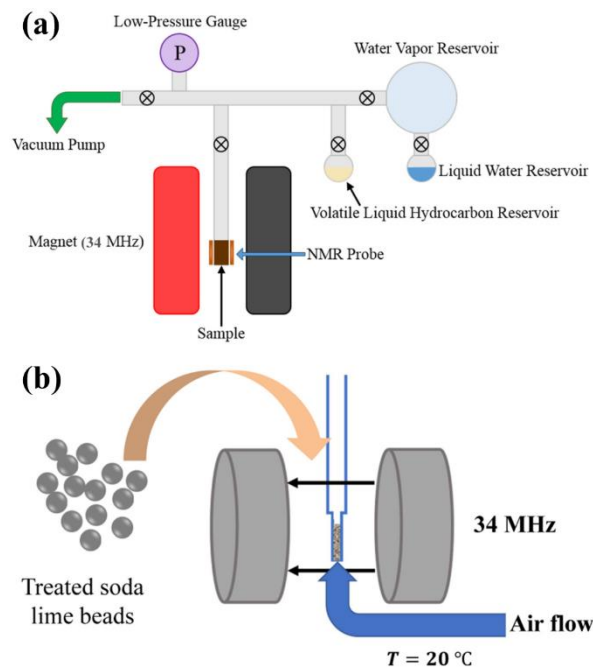
Figure 1. (a) 34 MHz magnet and water vapor delivery system with vapor expansion bulb, distribution chamber, pressure gauge, pump connection, and sample tube. (b) Treated glass beads are first loaded into the sample tube. The sample tube is subsequently attached to the water vapor delivery system and maintained at 20 ℃ by air flow.

Results and Discussion

Two different chemical treatments have been applied to modify the surface wettability. The morphology and particle size of soda lime glass beads before and after surface modifications are determined by scanning electron microscope (SEM). In Figure 2, SEM images show that the three representative samples, assigned as unmodified, hydrophilic and hydrophobic glass beads, have uniform spherical morphology in large domains. All three samples contain uniform spheres with a size of approximately 40μm, which agrees well with the supplier's characterization (particle size ranging from 38 to 45μm).
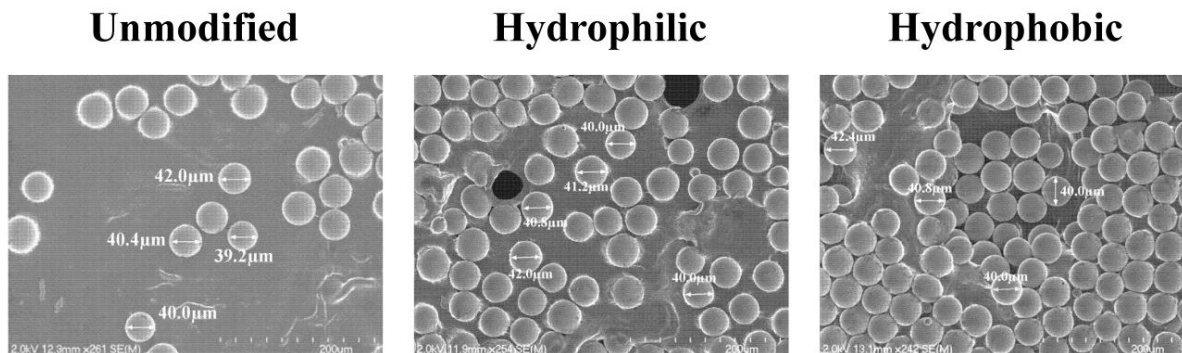

Figure 2. SEM images of soda lime glass beads with unmodified (left), hydrophobic (right) and hydrophilic (middle) surface, respectively.

The resulting change in surface wetting is characterized by monitoring the change in static contact angle and NMR-detected water isotherm. Figure 3 shows the static contact angles of water on

unmodified, hydrophilic and hydrophobic treated glass surfaces, respectively. The macroscopic contact angle of the unmodified glass surface is ~59°, indicating that soda lime glass surface is intrinsically mildly hydrophilic. After Silane coating, the contact angle increases to ~95° , indicating a much better degree of hydrophobicity compared to the unmodified surface. The strong hydrophobicity of the silane-coated surface comes from the outermost long alkyl chains ($-(CH_2)_{11}CH_3$), which is verified by the strong ^1H NMR signal in the dry sample (see Figure 4). Soda lime glass surface after acid wash is clearly tuned to hydrophilic with contact angle ~24°. Hence, through different chemical modification methods, the wetting behavior of the surface can be controlled from hydrophobic to hydrophilic. In the following isotherm measurements, identical chemical modification methods are applied to soda lime glass beads. Since the chemical composition of glass beads and glass surfaces are similar, it is assumed that the chemical treatments also work for glass beads, resulting similar surface wettability.
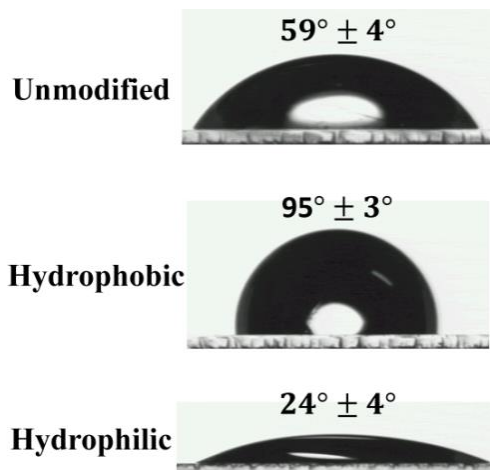

Figure 3. Images of water drops on glass wafers with unmodified, hydrophobic and hydrophilic treatment, respectively.
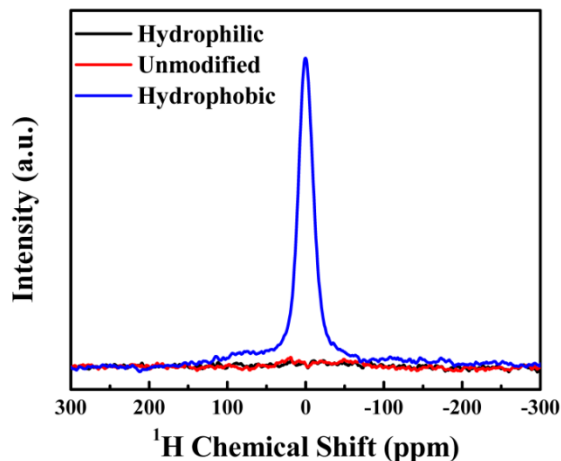

Figure 4. ^1H NMR spectra of dry glass beads after different chemical modifications. A strong ^1H signal is observed in the hydrophobic treated glass beads due to the long chained coating polymer ($-(CH_2)_{11}CH_3$). The ^1H peak of hydrophobic coated glass beads is set at 0 ppm. The bulk water proton peak is hence centered at 4.19 ppm.

NMR-detected water vapor isotherms of hydrophilic (red), hydrophobic (blue) and unmodified (black) soda lime glass beads at 20 ℃ are shown in Figure 5. For the hydrophobic treated glass beads, the water isotherm is nearly flat to the P/P_0 axis over its entire range and therefore demonstrates that the silane coated glass beads are more hydrophobic than the unmodified beads. This isotherm data is consistent with the contact angle result above. In contrast, compared with the hydrophobic treated glass beads, a significantly larger amount of water adsorption is observed on the hydrophilic-treated glass beads. Specifically, the amount of water adsorbed on the hydrophilic beads at the same relative pressure is larger than both the unmodified and hydrophobic sample, indicating a greater degree of hydrophilicity. As expected, the water vapor isotherm of unmodified glass beads lies between the hydrophilic and hydrophobic curves. The above isotherm results agree very well with the wetting properties obtained from the contact angle measurement. It demonstrates that water vapor isotherms can clearly distinguish between hydrophobic and hydrophilic surfaces embedded in a granular or porous structure, which the contact angle measurement cannot achieve. This is of particular importance in determining the wetting properties of rocks.
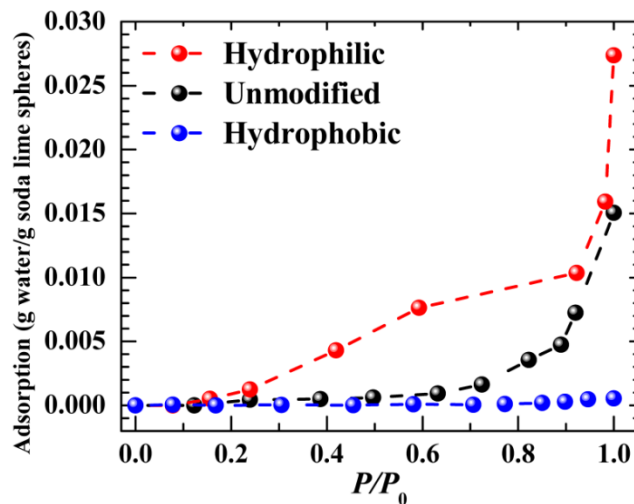

Figure 5. NMR-detected water isotherms of hydrophilic (red), hydrophobic (blue) and unmodified (black) soda lime glass beads at 20 ℃.

Figure 6 and 7 show NMR-detected water vapor isotherms of glass beads with 2 different sizes, 20 and 400 μm in diameter with different surface hydrophobicity. The pore sizes created by these glass beads when packed separately are similar to those of macro- and micropores of Middle East Arab formation carbonates, ~5 and ~100μm, respectively [9]. Figure 6 illustrates the mass ratio of adsorbed water to glass beads with respect to the relative pressure. Not surprisingly, the sample (black curve), consisting of hydrophilic treated 20 μm and hydrophilic treated 400 μm beads, adsorbs the largest amount of water. This is because all the exposed surfaces of this sample have been rendered hydrophilic, leading to strong water adsorption. The amount of adsorbed water on another sample (yellow curve), containing hydrophilic treated 20 μm and hydrophobic treated 400 μm beads, is close to the sample with both hydrophilic beads. In contrast, the sample (blue curve), consisting of hydrophobic treated 20 μm and hydrophobic treated 400 μm beads, adsorbs the least amount of water.
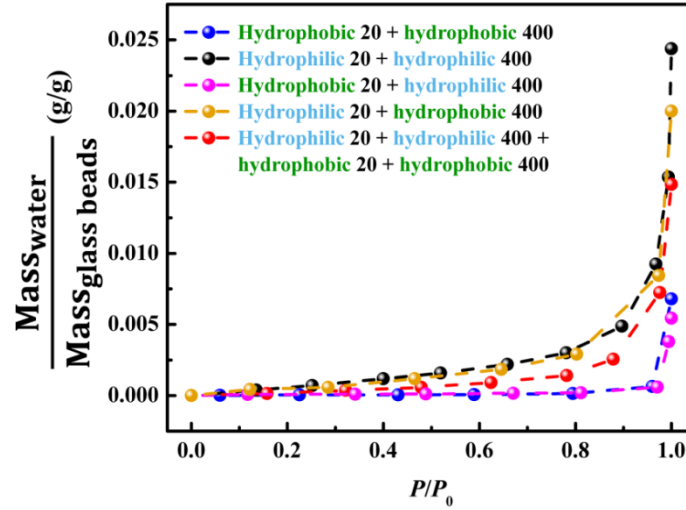
Figure 6. NMR-detected water vapor isotherms of glass beads with 2 different sizes, 20 and 400 μm diameter with different surface hydrophobicity.

In order to understand the adsorption mechanism, a quantitative relationship between the relative pressure and the ratio of water adsorption mass to the total hydrophilic surface area in each sample is analyzed. Figure 7 shows the $Mass_{water}/Area_{hydrophilic\ surface}$ vs. P/P_0. The total hydrophilic surface area is determined as follows, for example, for the hydrophilic 20 μm and hydrophilic 400 μm glass beads mixture sample,

hydrophilic surface area =

$$\frac{mass(20\ \mu m\ beads)}{\frac{4}{3}\pi*(10\ \mu m)^3*1.3g/cm^3} * 4\pi * (10\ \mu m)^2 + \frac{mass(400\ \mu m\ beads)}{\frac{4}{3}\pi*(200\ \mu m)^3*1.3g/cm^3} * 4\pi * (200\ \mu m)^2 \qquad (1)$$

,where mass(20 μm beads) and mass(400 μm beads) are the masses of the glass beads with diameter of 20 μm and 400μm, respectively. 1.3 g/cm^3 is the bulk Density of Dry Beads. Eq. (1) can be applied to all the samples. The sample, consisting of hydrophobic treated 20 μm and hydrophobic treated 400 μm beads, is not included in Figure 7 because it contains no hydrophilic surface area. Different from Figure 6, all curves in Figure 7 overlap with each other very well, indicating that the water vapor adsorption mainly depends on the total hydrophilic surface area. Moreover, it can be concluded that the water vapor adsorption in our glass beads sample is dominated by the surface adsorption. This conclusion is crucial for core rock surface modification and further analysis.
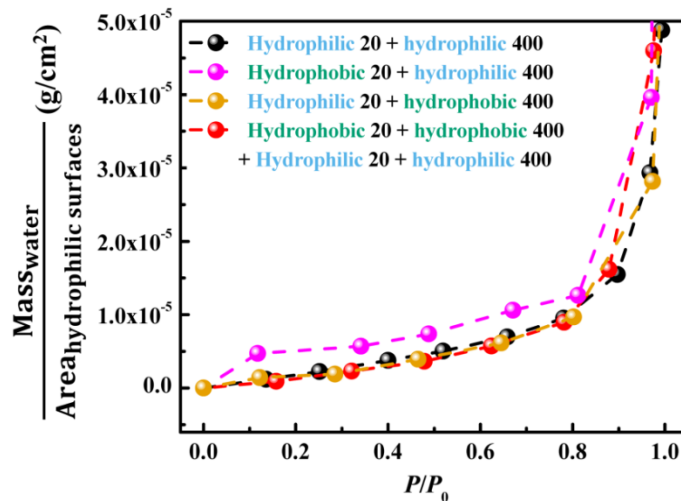
Figure 7. The quantitative relationship between the relative pressure and the ratio of water adsorption mass to the total hydrophilic surface area: $Mass_{water}/Area_{hydrophilic\ surface}$ vs. P/P_0.

To further elucidate the new water vapor isotherm technique, microporous silica beads of 8 μm in diameter are tested. In Figure 8, the isotherm obtained with the silica beads as received is shown in blue dots. Untreated beads adsorb water within the micropores, diameter about 5μm, at low relative pressure ($P/P_0 < 0.2$). Above $P/P_0 \sim 0.2$, water vapor starts filling the macropores, diameter about 100μm, between beads due to capillary condensation. A big difference in adsorption is observed for the hydrophobic treated surfaces. The red triangles show the isotherm after the beads are rendered hydrophobic via the silane coating. In the initial nanopores filling stage, $0 < P/P_0 < 0.2$, Silane coating has no influence on the water vapor adsorption. This is because the nanopores are too narrow to accept the long chained Chloro(decyl)dimethylsilane and remain uncoated, which allow the much smaller water molecules to adsorb. However, above $P/P_0 \sim 0.2$, water vapor adsorption occurs in the intergranular space between beads, which has been turned to hydrophobic via Silane coating. Thus, the isotherm changes to flat when $P/P_0 > 0.2$.
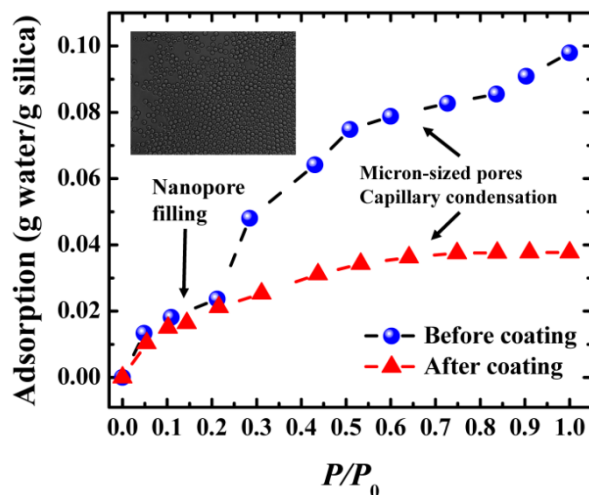

Figure 8. NMR-detected water isotherms of unmodified (blue) and hydrophobic treated (red) microporous silica beads at 20 ℃. Insert: SEM image of beads.

CONCLUSION
Wettability of reservoir rocks plays an important role in hydrocarbon recovery. However, characterizing the wettability of reservoir rock is particularly challenging due to the complex porous network inside the rock. In this paper, we propose a new method for measuring the wettability of porous media by NMR water vapor isotherm technique. The NMR-detected water vapor isotherms are taken on soda lime glass beads with different wetting properties vary from hydrophilic to hydrophobic, which are obtained through different chemical modifications. The contact angle measurements show that the silane coating can make water contact angle increase from 59° (unmodified surface) to 95°, indicating a stronger hydrophobicity; the acid wash can decrease the contact angle to 24°, indicating a stronger hydrophilicity. NMR-detected isotherms show that no water adsorbs on the hydrophobic glass beads. In contrast, a significantly larger amount of water adsorption is observed on the hydrophilic-treated sample. All of the isotherm data are consistent with contact angle measurements. The new NMR method can be further applied to study the wettability of core rocks, leading to new insights that are needed in improved oil production. Currently, we are further developing the current method to quantify the degree of pore surface hydrophobicity from reservoir rocks core sample, in the form of hydrophobicity index which is directly related to wettability index [10].

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