

NMR wettability indices: Effect of OBM on wettability and NMR responses

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Abstract

Wettability and NMR surface relaxation are related to each other. Wettability controls the fluid distribution in porous media. NMR surface relaxation dictates that the fluid in contact with the mineral surface has a relaxation time shorter than its bulk value. In this study, first, the nature of wettability effect on NMR responses was demonstrated by a parameter $\rho_{2, \text{eff}}$, the effective surface relaxivity. Quantitative changes of $\rho_{2, \text{eff}}$ of water or oil for unconsolidated silica flour and calcite were shown to be consistent with the expected wettability alteration based on the contact angle measurements. Based on the concept of effective surface relaxivity, a novel NMR model was then proposed to quantify rock wettability by two NMR wettability indices from either water or oil responses. This model was tested with water/oil partially saturated Berea cores at different wettability conditions. Correlations show that both NMR indices agree well with the Amott–Harvey wettability index, suggesting that quantitative information of reservoir rock wettability can be gained from NMR measurements. Finally, the effect of oil base mud (OBM) surfactants on wettability alteration and NMR responses was systematically investigated with Berea cores. Results show that the originally strongly water-wet Berea cores are altered to be intermediate-wet or oil-wet by OBM surfactants. As a result, the irreducible water saturation from NMR interpretation assuming water-wetness when wettability alteration occurs generally underestimates the measured value. The magnitude of underestimation correlates well with the Amott–Harvey wettability index.

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1. Introduction

Wettability, one of the important factors affecting NMR surface relaxation, has been investigated using NMR techniques. Brown and Fatt (1956) started the pioneering work using uncoated sand as water-wet porous media and Dri-film treated sand as oil-wet porous media. They found that water relaxed faster in

the water-wet system than in the oil-wet system. Later works (Devereux, 1967; Saraf et al., 1970; Williams and Fung, 1982; Borgia et al., 1991; Hsu et al., 1992; Howard, 1994; Straley et al., 1995; Daughney et al., 2000; Zhang et al., 2000; Al-Mahrooqi et al., 2003; Manalo et al., 2003) confirm that NMR technique can give qualitative information about wettability. However, the quantitative connection between wettability and NMR characteristic parameter has been investigated by only a few studies (Howard, 1998; Guan et al., 2002; Fleury and Deflandre, 2003). Howard (1998) proposed a quantitative estimate of porous media wettability

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from proton NMR measurements by a normalized relaxation time versus water saturation. Guan et al. (2002) found good linear relationships between Amott–Harvey index and two groups of NMR quantities; one is the “differences” and the other is the “ratios” between the arithmetic mean relaxation time at residual oil saturation and that at irreducible water saturation. Fleury and Deflandre (2003) proposed a NMR wettability index based on fluid distributions. This study proposes a NMR model to quantify rock wettability by two NMR wettability indices from either water or oil responses based on the concept of effective surface relaxivity.

Oil base mud drilling fluids have surfactant additives such as emulsifiers and oil-wetting agents. These OBM surfactants are mainly the wettability alteration material (Yan et al., 1993). An excess amount of emulsifiers and oil wetting agents is often added to maintain the stability and rheological properties of the mud system (Ballard and Dawe, 1988; McKinney and Azar, 1988). Potentially, these OBM surfactants may invade the near-well-bore formation and induces wettability alteration toward more oil-wetness. As a result, the estimation of NMR derived parameters for the formation evaluation such as permeability and irreducible water saturation may not match the true values if the wettability alteration is not taken into account (Marschall and Coates, 1997; Zwaag et al., 2001). This study quantitatively examines the effect of OBM surfactants on wettability and NMR estimated irreducible water saturation.

The layout of this study is as follows. First the nature of the wettability effect on the NMR response was demonstrated by a parameter $\rho_{2, \text{eff}}$, and then quantitative changes of $\rho_{2, \text{eff}}$ were shown to be directly related to wettability alteration. Next two NMR wettability indices were defined based on the concept of effective surface relaxivity. This NMR wettability model was then tested with Berea cores. Finally, the effect of OBM surfactants on wettability and NMR estimated irreducible water saturation was systematically examined with Berea cores.

2. Methods

2.1. Materials

Unconsolidated silica flour (U.S. Silica, mean diameter: 1.5 μm , BET surface area: 2.1 m^2/g) and calcite (Solvay Minerals, mean diameter: 0.07 μm , BET surface area: 21.8 m^2/g) particles were calibrated for the determination of surface relaxivity. The Berea

sandstones used (1 in. by 1 in.) were cored from a large slab and were similar in porosity (0.17–0.19) and permeability (81–147 md). Cationic surfactant dodecylamine (DDA) and anionic surfactant stearic acid (SA) were used to alter the wettability of the silica flour and calcite, respectively. The effect of OBM surfactants on the wettability of Berea cores was investigated with four systems of emulsifiers and oil-wetting agents: LLD, BOO, NOVA and VERSA. The OBM flushing fluid was simulated by mixing a specified amount of emulsifiers and oil-wetting agents with base oil and aging in an oven at 75 °C for 18 h. The ratio among the emulsifiers and oil-wetting agents was based on what was used in the whole mud. Base oils Escaid and SB were a light hydro-treated petroleum distillate and a mixture of internal olefins with C_{16} to C_{18} , respectively. The crude oil used was a North-Sea crude oil (29.2 API, 15 cp).

2.2. Sample saturation preparation, experimental procedures and Amott–Harvey wettability index measurements

For 100% water or oil saturation of the unconsolidated silica flour or calcite, the particles (oven dried to remove adsorbed water) were first slowly added into water or oil in a beaker and stirred with a bar magnet. The slurry was then centrifuged at 2800 rpm for 15 min and the supernatant liquid layer was removed. To reach water/oil partial saturation, 100% water saturated silica flour or calcite was further processed as follows. First the slurry was transferred to a large, flat Petri dish that was heated in an oven at 80 °C. The particles were stirred during heating to homogenize the sample. Agglomerated particles were disaggregated by grinding with a mortar and pestle before they were added to an excess amount of oil in a centrifuge tube. Ultra-sonication was used to further disaggregate the particles. Finally, the sample was centrifuged at 2800 rpm for 15 min and the supernatant liquid layer removed. The sample was weighed at each step to determine the porosity and water saturation.

The Berea cores were brine or oil saturated as follows. First, the dry core was evacuated for 8 h using a vacuum pump. Brine or oil was then introduced into the vacuum vessel and the core remained immersed in brine or oil for 8 h under vacuum. Finally, the core was placed in a bottle full of water with a loosely fitting rubber stopper and pressurized at 1000 psi for 8 h.

The brine saturation was reduced by centrifugation with air, base oil or crude oil in an L5-50P model

centrifuge. The core was centrifuged for 17 h at a rotational speed that corresponded to a capillary pressure of 100 psi (inlet face). The sample orientation was reversed after 16 h.

The “crude oil/brine” saturated cores were flushed with 10 or 15 PV OBM flushing fluid at a rate of 9 ml/h in a Hassler core holder. The flushing fluid is base oil plus OBM surfactants at a range of concentrations (0%, 0.5%, 1%, 2% and 3%, wt.%).

Amott–Harvey wettability index measurements followed the flushing process. For the Amott water index, the flushed core was immersed in brine in a standard imbibition cell for at least 48 h, and the volume of oil displaced by spontaneous imbibition of brine (V_{SI}) was recorded. Then the core was centrifuged under brine with capillary pressure of -25 psi, and the volume of oil displaced by forced imbibition of brine (V_{FI}) was recorded. The Amott water index was calculated as follows:

$$\delta_w = V_{SI}/(V_{SI} + V_{FI}) \quad (1)$$

After the Amott water index measurement, the Amott oil index was similarly measured:

$$\delta_o = V_{SD}/(V_{SD} + V_{FD}) \quad (2)$$

where V_{SD} is the water volume by spontaneous displacement of oil after at least 48 h. V_{FD} is the water volume by forced displacement of oil by centrifuging with a capillary pressure of 100 psi. The Amott–Harvey index was then calculated as follows:

$$\delta_{AH} = \delta_w - \delta_o. \quad (3)$$

2.3. NMR T_2 relaxation time and $D-T_2$ measurements

NMR T_2 relaxation time at each saturation stage and $D-T_2$ measurements at some selected stages (after forced imbibition and after forced displacement) were made at room temperature with a Maran-2 spectrometer (Resonance, Inc.). The sample was left in the spectrometer for 15 min with a cover on the top of the probe to reach temperature equilibrium before NMR measurements. T_2 was measured by the CPMG pulse sequence with a small echo spacing (0.32 ms) to minimize relaxation due to diffusion. The signal to noise ratio of all the T_2 measurements was set to be 100. A non-negative non-linear least square inversion method developed in our laboratory was used to estimate the multi-exponential T_2 relaxation time distributions (Chuah, 1996). $D-T_2$ measurements (Hürlimann and Venkataraman,

2002) were carried out at 9 diffusion lengths. 3000 echoes with echo spacing of 400 μ s and 400 scans were collected at each diffusion length. In this study, $D-T_2$ measurements were used to obtain separate T_2 relaxation time distributions for water and oil after forced imbibition and after forced displacement for the calculation of NMR wettability indices. This separation of T_2 relaxation time distributions for water and oil greatly helps the study of wettability from NMR methods (Freedman et al., 2003; Flaum et al., 2005).

3. Results and discussion

3.1. Wettability alteration of silicate and calcite surface by DDA and SA

Contact angle measurements (captive drop method adapted by Yang, 2000) of “brine/glass slide/oil” and “brine/marble/oil” systems were performed to investigate the wettability alteration of silicate and calcite surfaces by DDA and SA, respectively. Fig. 1(a) shows that the glass surface is preferentially water-wet when the oil phase is pure Escaid or Escaid plus 0.5% SA, and that the glass surface becomes oil-wet when the oil phase is Escaid plus 0.74% DDA. On the

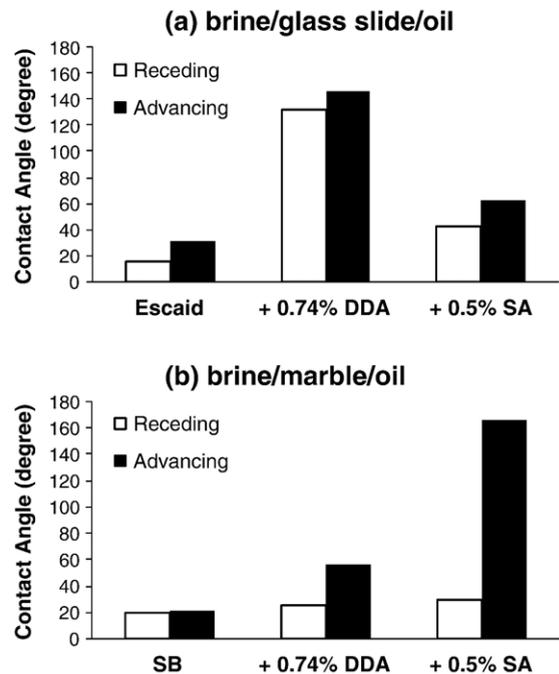


Fig. 1. Contact angle measurements of brine/glass slide/oil (a) and brine/marble/oil (b) systems.

contrary, Fig. 1(b) shows that the marble surface is preferentially water-wet in both receding and advancing directions when the oil phase is pure SB or SB plus 0.74% DDA, and that the marble surface becomes oil-wet in the advancing direction when the oil phase is SB plus 0.5% SA. Here “advancing” and “receding” refer to water phase and all these wettability alterations refer to the surface which is in contact with the oil.

The wettability alteration shown above is due to surfactant adsorption. Because cationic surfactant DDA has a positively charged head group, it can adsorb onto the negatively charged silicate surface but not onto the positively charged calcite surface. On the contrary, SA is an anionic surfactant with a negatively charged head group, which adsorbs onto the calcite surface but not onto the silicate surface.

3.2. Effect of wettability alteration on surface relaxivity for water/oil partially saturated silica flour and calcite

For 100% S_w or 100% S_o , surface relaxivity ρ_2 is calculated by Eq. (4), assuming that relaxation due to diffusion is negligible:

$$\rho_2 = \frac{V_p}{A_T} \left(\frac{1}{T_2} - \frac{1}{T_{2,B}} \right) \quad (4)$$

where V_p and A_T are the total pore volume and surface area, respectively.

Similarly, for water/oil partial saturation, surface relaxivity of water and oil are calculated as follows:

$$\rho_{2,w} = \frac{V_w}{A_w} \left(\frac{1}{T_{2,w}} - \frac{1}{T_{2,w,B}} \right) \quad (5)$$

$$\rho_{2,o} = \frac{V_o}{A_o} \left(\frac{1}{T_{2,o}} - \frac{1}{T_{2,o,B}} \right) \quad (6)$$

$\rho_{2,w}$ and $\rho_{2,o}$ are based on the actual surface area (A_w, A_o) and pore volume (V_w and V_o) covered by water and oil phase, respectively.

To demonstrate the effect of wettability on NMR response, Eqs. (5) and (6) are rearranged as follows:

$$\rho_{2,w,\text{eff}} = \rho_{2,w} \frac{A_w}{A_T} = \frac{V_p}{A_T} S_w \left(\frac{1}{T_{2,w}} - \frac{1}{T_{2,w,B}} \right) \quad (7)$$

$$\rho_{2,o,\text{eff}} = \rho_{2,o} \frac{A_o}{A_T} = \frac{V_p}{A_T} S_o \left(\frac{1}{T_{2,o}} - \frac{1}{T_{2,o,B}} \right) \quad (8)$$

where S_w and S_o are water and oil saturation, respectively. Qualitatively speaking, since wettability determines both the surface coverage of the pore fluid and its affinity with the mineral surface (Hirasaki, 1991), it affects A_w/A_T (A_o/A_T) and $\rho_{2,w}$ ($\rho_{2,o}$). Therefore, the product of surface relaxivity and surface coverage of the corresponding phase is combined as an effective surface relaxivity.

The quantitative effect of wettability on surface relaxivity was investigated with water/oil partially saturated silica flour and calcite. Two cases were

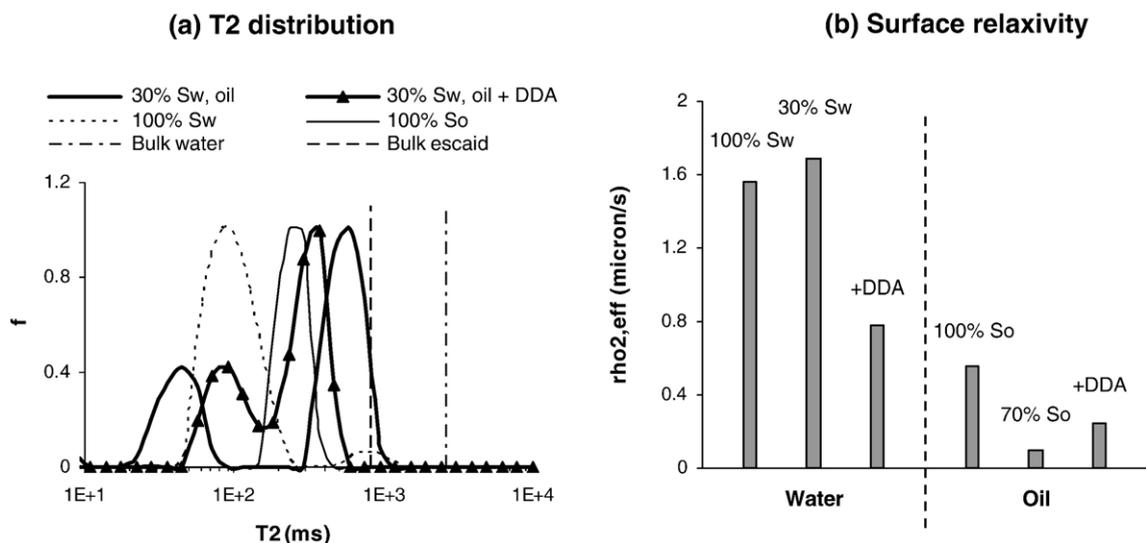


Fig. 2. T_2 relaxation time distributions (a) and the effective surface relaxivity of water and/or oil (b) at 100% S_w , 100% S_o , 30% S_w with pure oil (Escald) and 30% S_w with oil plus DDA (0.74% wt), silica flour.

compared with the oil phase being pure base oil in one case and base oil plus a small amount of DDA or SA in the other case.

Fig. 2 shows that for silica flour partially saturated with water and pure Escaid, $\rho_{2,w,eff}$ is about the same as that of 100% S_w , and $\rho_{2,o,eff}$ is much less than that of 100% S_o . This is because the silica flour is still preferentially water-wet (Fig. 1(a)). Therefore, the affinity of the water phase with the surface is about the same as that of 100% S_w , and almost all the surface area of the silica flour particles is covered by water, which means that $A_w \approx A_T$ and $A_o \ll A_T$ (Eqs. (7) and (8)). In comparison, for silica flour partially saturated with water and Escaid plus 0.74% DDA, $\rho_{2,w,eff}$ decreases and $\rho_{2,o,eff}$ increases. This is because the silica flour surface changes to partially oil-wet or locally oil-wet (Fig. 1(a)) due to DDA adsorption. Therefore, both the surface coverage by water and its affinity with the surface decrease, resulting in decreased $\rho_{2,w,eff}$ according to Eq. (7). For the oil phase, both the surface coverage and affinity increase, leading to increased $\rho_{2,o,eff}$ according to Eq. (8).

For the same reason, Fig. 3 shows that for calcite partially saturated with water and pure SB, in which the calcite is still preferentially water-wet (Fig. 1(b)), $\rho_{2,w,eff}$ is about the same as that of 100% S_w , and $\rho_{2,o,eff}$ is much less than that of 100% S_o . However, for calcite partially saturated with water and SB plus 0.5% SA, in which the calcite surface becomes partially or locally oil-wet (Fig. 1(b)) due to SA adsorption, $\rho_{2,w,eff}$ decreases and $\rho_{2,o,eff}$ increases.

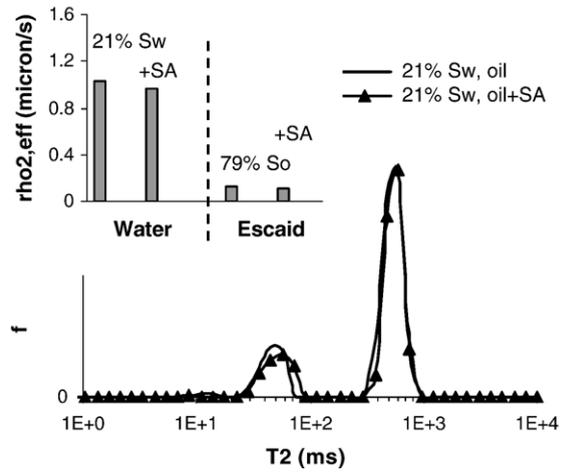


Fig. 4. T_2 relaxation time distributions and the effective surface relaxivity of water and oil at 21% S_w with pure oil (Escaid), and 21% S_w with oil plus SA (0.5% wt), silica flour.

Without wettability alteration, surface relaxivity of either water or oil is unchanged, as shown by two cases. One case is for water/oil partially saturated silica flour with the oil phase being pure Escaid versus Escaid plus 0.5% SA (Fig. 4). The other case is for water/oil partially saturated calcite with the oil phase being pure SB plus 0.74% DDA (Fig. 5). In both cases, no wettability alteration occurs due to any surfactant adsorption (Fig. 1(a) and (b)). As a result, $\rho_{2,w,eff}$ and $\rho_{2,o,eff}$ is unchanged.

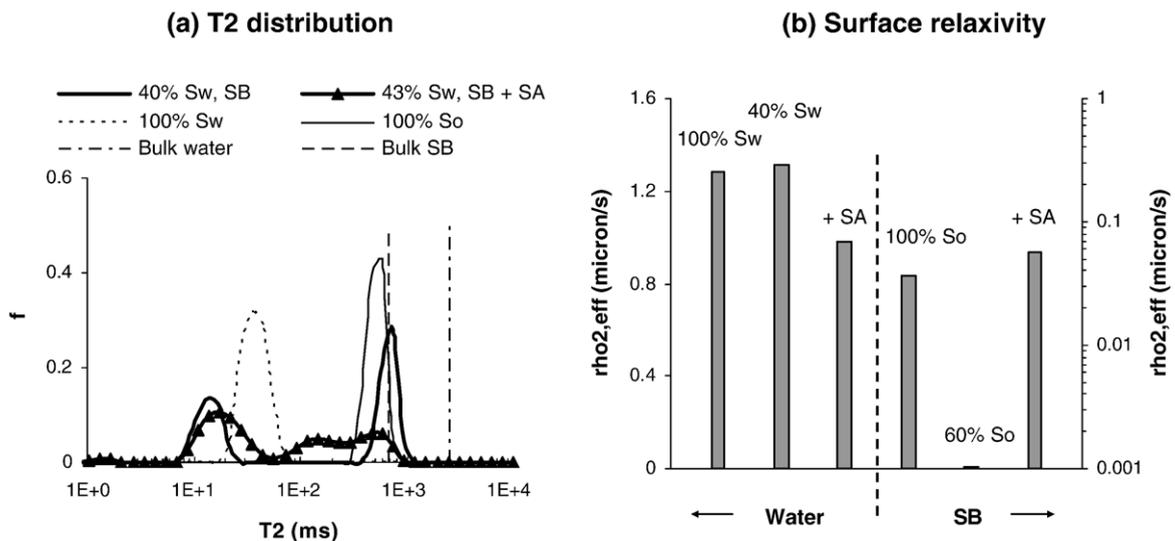


Fig. 3. T_2 relaxation time distributions (a) and the effective surface relaxivity of water and/or oil (b) at 100% S_w , 100% S_o , 40% S_w with pure oil (SB) and 43% S_w with oil plus SA (0.5% wt), calcite.

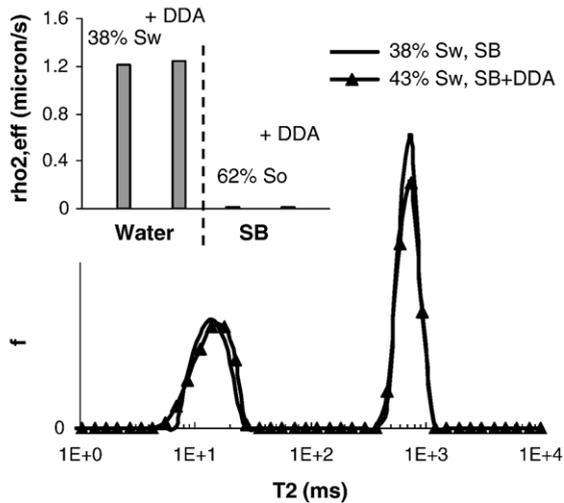


Fig. 5. T_2 relaxation time distributions and the effective surface relaxivity of water and oil at 38% S_w with pure oil (SB), and 43% S_w with oil plus DDA (0.74% wt), calcite.

3.3. Effects of OBM surfactants on wettability alteration of Berea cores

Effects of OBM surfactants on wettability alteration of Berea cores were systematically investigated. Amott–

Harvey wettability indices are summarized in Table 1. Core #44 is a base case of no fluid flushing before the Amott–Harvey measurement. It shows that the crude oil used does not alter the rock wettability. Cores #27, #30 and #72 are base cases of no OBM surfactants in the flushing solution. They show that originally the Berea cores are strongly water-wet. However, for all four OBM surfactant systems, when their concentrations in the flushing solution are as low as 0.5%, the strongly water-wet Berea cores were altered to intermediate-wet. With increase of the surfactant concentration in the flushing solution, the Berea cores were still intermediate-wet for OBM surfactant system VERSA. For LLD and NOVA, however, the Berea cores were more and more oil-wet with the concentration increase. For the same OBM surfactant system and concentration (3% NOVA), the Berea cores were slightly more oil-wet (Amott–Harvey: -0.58 to -0.67) when the flushing volume increased from 10 PV to 15 PV.

Other special cases were examined to investigate the effect of OBM surfactants on wettability alteration. Cores #51, #64, #69 and #96 were saturated with 100% S_o (SB+3% BOO for core #51 and SB+3% NOVA for core # 64, #69 and #96) to make the

Table 1
Amott–Harvey wettability indices and irreducible water saturation

Core #	OBM surfactants	Concentrations (wt.%)	δ_w	δ_o	$\delta_w - \delta_o$	S_{wir} weighing	S_{wir} $T_{2,cutoff}$
44 ^a			0.93	0	0.93		
27		0	0.95	0	0.95	0.220	0.214
30		0	0.92	0	0.92	0.211	0.204
72		0	0.93	0	0.93	0.215	0.213
56	VERSA	0.5	0.08	0	0.08	0.215	0.203
57	VERSA	1	0.05	0	0.05	0.219	0.199
107	VERSA	2	0.03	0	0.03	0.218	0.189
32	LLD	0.5	0.08				
28	LLD	1	0.04	0.14	-0.10	0.223	0.197
34	LLD	2	0.03	0.38	-0.35	0.217	0.177
16	BOO	0.5	0.08	0.20	-0.12	0.216	0.195
45	BOO	1	0.06	0.44	-0.38	0.221	0.172
58	BOO	2	-0.04	0.48	-0.52	0.223	0.143
66	BOO	3	0.05	0.56	-0.51	0.215	0.131
91	BOO	3	0.01	0.51	-0.50	0.230	0.134
26	NOVA	3	0	0.57	-0.57	0.233	0.121
77	NOVA	3	0.01	0.60	-0.59	0.212	0.127
80 ^b	NOVA	3	0	0.68	-0.68	0.211	0.136
40 ^b	NOVA	3	0	0.66	-0.66	0.218	0.142
69 ^c	NOVA	3	0	0.67	-0.67		
64 ^c	NOVA	3	0	0.72	-0.72		
96 ^c	NOVA	3	0	0.69	-0.69		
51 ^c	BOO	3	0	0.60	-0.60		

^a No flushing before Amott–Harvey measurement.

^b Flushing volume 15 PV.

^c Start with 100% S_o saturation.

mineral surface contact first with oil and OBM surfactants instead of water. Results show that the corresponding Amott–Harvey indices decrease only slightly (3% BOO: −0.51 to −0.60; 3% NOVA: −0.58 to −0.69). It suggests that about the same oil-wetness can be achieved by the adsorption of these OBM surfactant molecules even when the mineral surface was initially in contact with water.

3.4. NMR wettability indices and correlations with Amott–Harvey index

Based on the concept of effective surface relaxivity (Section 3.2), this study defines two NMR wettability indices as the effective surface relaxivity normalized with respect to the maximum surface relaxivity. By this definition their values range between 0 and 1.

$$I_w^{NMR} = \frac{\rho_{2,w,eff}}{\rho_{2,w,max}} \quad (9)$$

$$I_o^{NMR} = \frac{\rho_{2,o,eff}}{\rho_{2,o,max}} \quad (10)$$

Similar to the Amott–Harvey index, the difference between the NMR water index and the NMR oil index defines a combined NMR index:

$$I_C^{NMR} = I_w^{NMR} - I_o^{NMR} \quad (11)$$

For water, $\rho_{2,w,max}$ corresponds to 100% S_w at strongly water-wet condition. Substitute Eqs. (4) and (7) into Eq. (9), and we have:

$$I_w^{NMR} = \left(\frac{1}{T_{2,w}} - \frac{1}{T_{2,w,B}} \right) \cdot S_w / \left(\frac{1}{(T_{2,w,S_w=1})_{water\ wet}} - \frac{1}{T_{2,w,B}} \right) \quad (12)$$

Similarly, for oil, $\rho_{2,o,max}$ corresponds to 100% S_o at strongly oil-wet condition. Substitute Eqs. (4) and (8) into Eq. (10), we have:

$$I_o^{NMR} = \left(\frac{1}{T_{2,o}} - \frac{1}{T_{2,o,B}} \right) \cdot S_o / \left(\frac{1}{(T_{2,o,S_o=1})_{oil\ wet}} - \frac{1}{T_{2,o,B}} \right) \quad (13)$$

This definition cancels out other factors affecting the effective surface relaxivity such as mineralogy, pore structure, concentration of paramagnetic impurities on the surface and so on.

Quantitative correlations between NMR water and oil wettability indices and Amott–Harvey wettability indices are shown by water response after forced brine imbibition and oil response after forced oil displacement. The reasons for selecting these two cases are that the saturation for brine after forced imbibition and for oil after forced displacement is relatively higher, so that better resolution of the NMR measurements is gained for the corresponding water and oil phases.

For the NMR water wettability index (Eq. (12)), $(T_{2,w,S_w=1})_{water\ wet}$ and $T_{2,w}$ correspond to the log mean (Fig. 6(a)) or mode (Fig. 6(b)) value of the T_2 relaxation time distributions of water at 100% brine saturation and after forced brine imbibition, respectively. In both cases, the NMR water wettability index correlates well with the Amott–Harvey wettability index ($R^2=0.87$ (a) and $R^2=0.93$ (b)).

For the NMR oil wettability index (Eq. (13)), $(T_{2,o,S_o=1})_{oil\ wet}$ and $T_{2,o}$ correspond to the mode value of

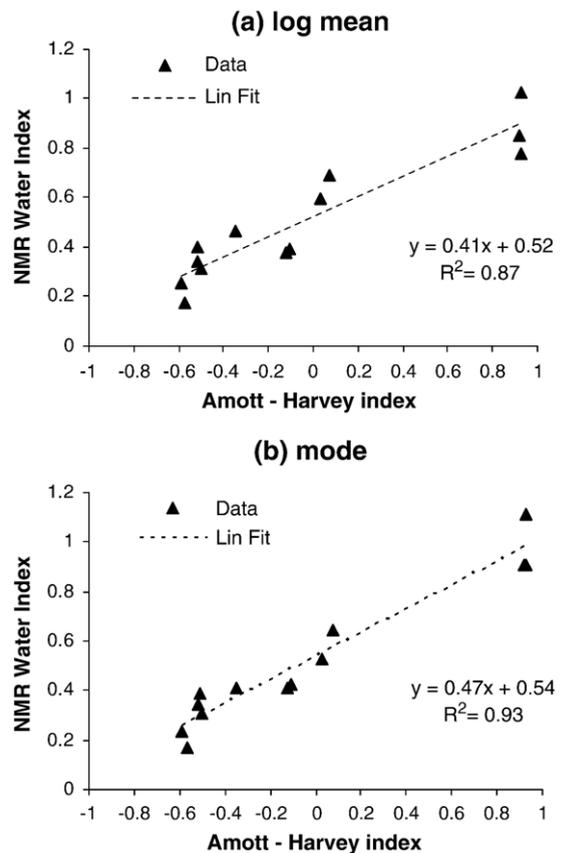


Fig. 6. Correlation between NMR water index and Amott–Harvey index, log mean (a) and mode (b) values of the T_2 relaxation time distributions of water are used.

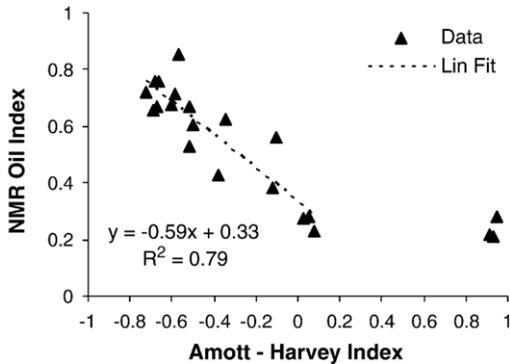


Fig. 7. Correlation between NMR oil index and Amott–Harvey index.

the T_2 relaxation time distributions of oil at 100% oil saturation (SB+OBM surfactants) and after forced displacement, respectively. Fig. 7 shows that in the intermediate-wet to oil-wet region, the NMR oil wettability index correlates well with the Amott–Harvey wettability index ($R^2=0.79$). The water-wet points do not follow the correlation well, but this limitation is probably due to the internal gradient effect of the Berea cores we used. T_2 of oil inside the rock is shorter than the bulk value even at water-wet condition due to the internal gradient effect, resulting in non-zero NMR oil wettability index (Eq. (13)).

For the combined NMR index (mode values of T_2 are used for both water and oil T_2), the cross plot (Fig. 8) shows that it also correlates well with the Amott–Harvey index ($R^2=0.80$). Good correlation between NMR wettability indices (either NMR water index, NMR oil index or combined NMR index) and the Amott–Harvey indices suggest that quantitative information about the reservoir wettability can be gained from NMR measurements.

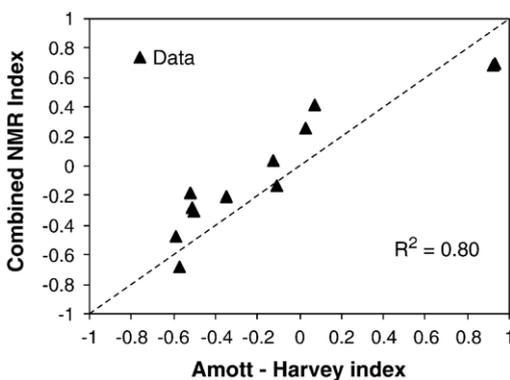


Fig. 8. Cross plot of combined NMR index and Amott–Harvey index.

3.5. Effect of wettability alteration on residual oil saturation of Berea cores

The residual oil saturation S_{or} after forced brine imbibition for these Berea cores depends on their wettability condition (Fig. 9). From water-wet to intermediate-wet, S_{or} decreases. This is because at intermediate-wet conditions the mineral surface forms a continuous path for the oil to flow through the pore space. From intermediate-wet to oil-wet, however, S_{or} increases. This is because more and more oil is trapped by the mineral surface when the oil-wetness increases. These observations are consistent with the literature (Jadhunandan and Morrow, 1995).

3.6. Effect of wettability alteration on NMR estimated S_{wir} of Berea cores

Effect of wettability alteration of Berea cores by OBM surfactants on NMR estimated S_{wir} was investigated. Fig. 10 shows an example of the normalized incremental and cumulative T_2 distributions at the following conditions: 100% S_w , S_{wir} of “air/brine”, S_{wir} of “crude oil/brine” and after flushing (core #30: 10 PV SB; core #66: SB+3% BOO). In this study, the $T_{2,cutoff}$ model is used to estimate S_{wir} from NMR, shown as the dashed line in the cumulative T_2 distributions. It shows that for core #30 which remains strongly water-wet after flushing (Table 1), the default $T_{2,cutoff}$ of 33 ms works well for both 100% S_w and after flushing. As a comparison, for core #66 which is altered to be oil-wet after flushing (Table 1), the default $T_{2,cutoff}$ of 33 ms works well for 100% S_w (water-wet), but underestimates the measured value after flushing.

Fig. 11 shows the correlation between the magnitude of underestimated S_{wir} (S_{wir} from weighing— S_{wir} from

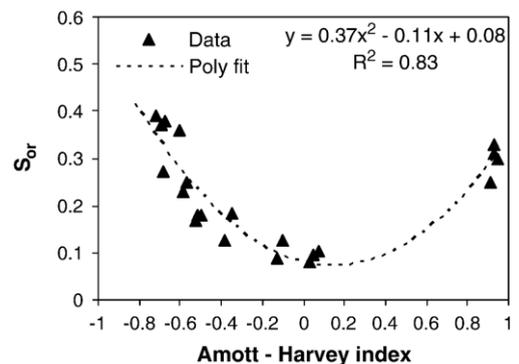


Fig. 9. Residual oil saturation after forced brine imbibition versus Amott–Harvey index.

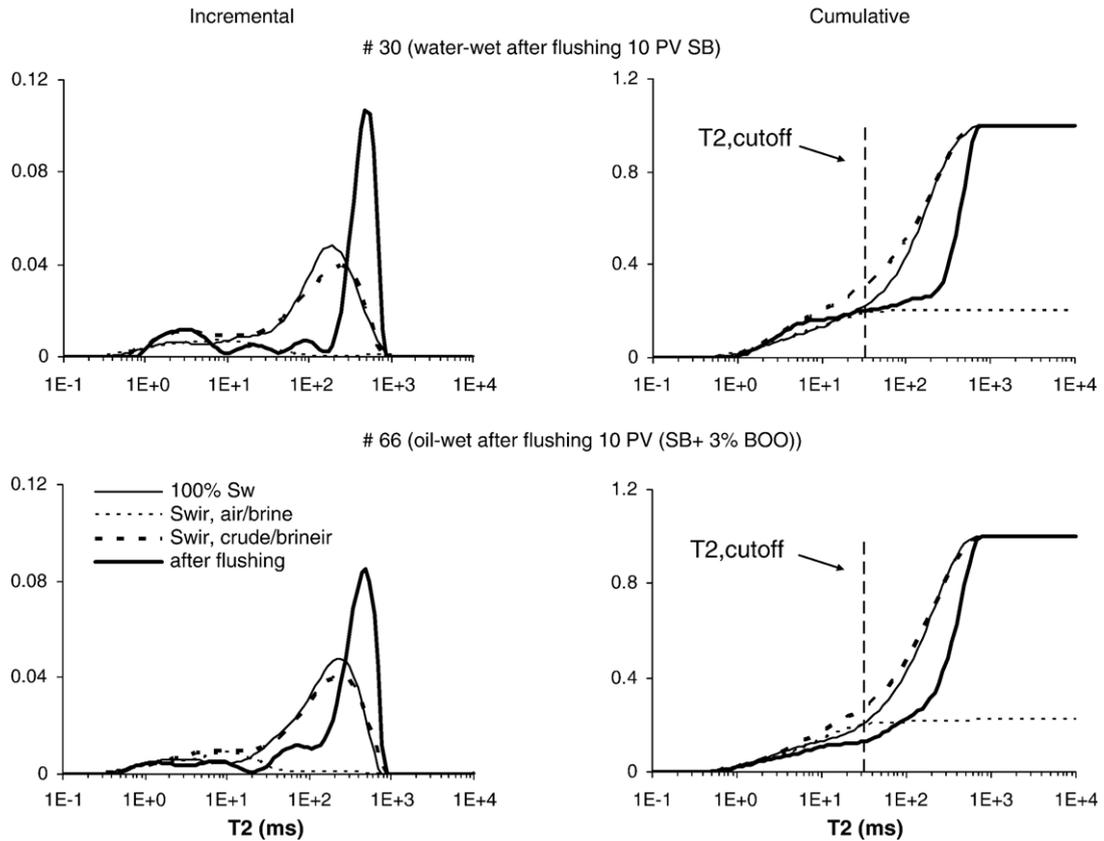


Fig. 10. Incremental and cumulative T_2 distributions for core #30 and #66 at the following conditions: 100% S_w , S_{wir} of air/brine, S_{wir} of crude oil/brine and after flushing.

$T_{2,cutoff}$) and the corresponding Amott–Harvey index. Here the four OBM surfactant systems were not differentiated. In the intermediate-wet and oil-wet region, the magnitude of underestimation increased linearly with the decrease of the Amott–Harvey wettability index. When extrapolated to Amott–Harvey

index of -1 , which corresponds to strongly oil-wet conditions, the magnitude of underestimation is about 0.128. This value is reasonable in the sense that it is smaller than S_{wir} measured gravimetrically (0.219 ± 0.006 for all the cores studied). It suggests that even when the core has been altered to be strongly oil-wet, there is still some water remaining in the small pores. In the water-wet region, there is no underestimation. The measured and estimated irreducible water saturation values for all the cases are summarized in Table 1.

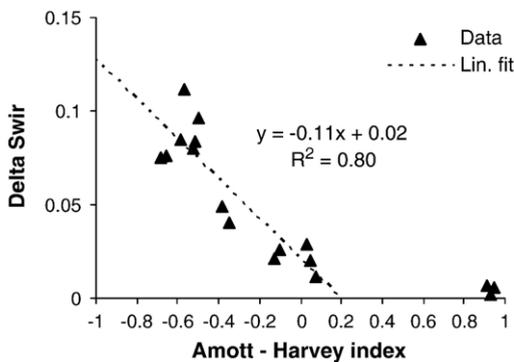


Fig. 11. Magnitude of S_{wir} underestimation versus Amott–Harvey index.

4. Conclusion

- (1) Cationic surfactant dodecylamine alters the wettability of glass slide surface. While anionic surfactant stearic acid alters the wettability of marble surface.
- (2) For water/oil partial saturation of silica flour or calcite, quantitative changes of the effective surface relaxivity of water or oil are consistent with the expected wettability alteration based on the contact angle measurements.

- (3) The originally strongly water-wet Berea cores are altered to be intermediate-wet or oil-wet by the OBM surfactants, depending on the type and their concentrations.
- (4) The proposed NMR wettability indices (either water index, oil index, or combined index) correlate well with the traditional Amott–Harvey indices, suggesting that quantitative information about rock wettability can be gained from NMR measurements.
- (5) After forced brine imbibition, residual oil saturation decreases from water-wet to intermediate-wet region, while it increases from the intermediate-wet to oil-wet region.
- (6) S_{wir} from $T_{2,\text{cutoff}}$ assuming water-wetness in cases where wettability alteration occurs generally underestimates the measured S_{wir} . The magnitude of underestimation correlates well with the Amott–Harvey indices.

Nomenclature

A	Surface area
I	NMR wettability index
R^2	Regression coefficient
S	Saturation
T_2	Relaxation time
V	Volume
δ	Amott wettability index
ρ_2	Surface relaxivity

Subscripts

AH	Amott–Harvey
B	Bulk
cutoff	Cutoff value
eff	Effective
FD	Forced displacement
FI	Forced imbibition
max	Maximum
o	Oil
or	Residual oil
p	Pore
SD	Spontaneous displacement
SI	Spontaneous imbibition
T	Total
w	Water
wir	Irreducible water

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