WETTABILITY MEASUREMENTS IN MODEL AND RESERVOIR SHALE SYSTEMS

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ABSTRACT

We combined the equilibrium capillary pressure technique (ECPT) and NMR spectroscopy to characterize the wettability of model systems and selected shale samples. In ECPT, a liquid/gas interface moves through a packed bed of particles and the gas pressure ahead of it is monitored with a differential transducer. After a transient, the pressure stabilizes to a value representing the capillary pressure inside the packed bed. Measurements can also be made with water displacing oil and oil displacing water. In this way, effective contact angles in the immiscible displacements can be determined.

We placed the ECPT cell inside the NMR spectrometer, enabling measurements to be made during liquid penetration. Water and oil peaks can be identified in the NMR response and quantitative information about displacement and solid/liquid interactions can be obtained. Cleaned and chemically modified (methylated) quartz silt was used as a model system.

ECPT tests were complemented by water/oil contact angle measurement using the sessile drop, Wilhelmy plate and capillary tube techniques. These measurements achieved high accuracy, consistency and reproducibility for the model systems, and were adapted for shale surfaces in their native state, and after modification by oil compounds. We also report Environmental-SEM observations of wetting, swelling, and dehydration behaviour of shale fragments with and without large drops of oil and water present on their surfaces. ESEM observations are largely consistent with wettability and swelling tendencies measured macroscopically on the same samples.

INTRODUCTION

Caprocks act as seals to petroleum reservoirs because of their low permeability and high capillary entry pressure. Capillary sealing requires that the rock is substantially water wet. Typically, a zero contact angle of water is assumed for shales, though this is not usually confirmed by any measurements. There is some evidence that shales become (patchily) oil wet through in-situ maturation of organic matter – Boult et al (1997), or exposure to polar compounds in formation waters – Aplin et al (2005), Bennett et al (2004). Therefore it is worthwhile to test if shale caprocks are uniformly water-wet through controlled experiments. An ultimate aim of this project is to compile a database combining geological information about caprocks and their physico-chemical properties (assessed by XRD, SEM, CEC, bulk chemistry, and wettability tests). A further aim is to investigate which petrophysical methods may be used to predict these properties from downhole log data or rapid non-destructive tests on core samples. While we focus on topseals, we believe that the methods developed here will be useful also for formation evaluation of shaly sands, to give an indication of wettability at an early stage and/or to monitor wettability changes that may occur in the critical near-wellbore region during production of such clay-rich reservoirs.

Although cap and seal rocks are traditionally considered as strongly water-wet, they might exhibit moderate or even strong hydrophobicity at the liquid/liquid interface, when water comes into contact with oil in the pore space. Thus investigation of rock wettability in relation to the rock mineralogy becomes an important task.

To understand rock wettability we need to study several parameters of the system, such as surface texture, micromorphology of the porosity, oil composition and PVT state at the prevailing conditions, and brine composition. These primary parameters in turn affect macroscopic properties such as capillary pressure, water/oil adsorption and swelling. These physico-chemical interactions exert a combined effect on any technique of wettability measurement. As a result we had to break this study into several simple steps and build up knowledge of the individual phenomena. First the oil/water interface was studied in rather simple systems – a quartz plate or capillary, using the Sessile drop, Wilhelmy plate or pressure measurement techniques – Neumann et al(1979). Second the equilibrium capillary pressure technique (forced imbibition) was used on quartz powders. In the next step, NMR spectroscopy was applied to study in details the oil/water imbibition and displacement during the progress of ECPT. Clay was then added into the quartz powders and the ECPT-NMR measurements repeated on this simple mineral mixture. Finally we used ESEM and optical microscopy to investigate microscopic aspects of rock wettability on the actual shale samples.

PROCEDURES

Materials

We made the first set of measurements with the simplest model system – quartz. Samples with different geometry were chosen: (*i*) quartz plate (20×20 mm²); (*ii*) quartz capillary (ID 600 µm); and (*iii*) quartz powder (irregular quartz particles, size fraction 150-180 µm). It is the last type of samples that are of interest but most of the well-established methods for contact angle measurement are suited for flat surfaces only. A capillary was included to provide an intermediate situation. Our measurements were carried out with clean (i.e. hydrophilic) and methylated (i.e. hydrophobic) quartz. All quartz samples were thoroughly cleaned using sulphuric acid, hydrogen peroxide and potassium hydroxide to ensure a high level of surface cleanliness. Methylated surfaces were produced by reacting clean and dry samples with trimethylchlorosilane (Sigma-Aldrich, > 99%) at a temperature of 60 °C. TMCS reacts with the hydroxyl groups ("silanols") present on the surface of quartz. Trimethyl groups are thus chemically grafted onto the surface which then becomes hydrophobic. The methylated quartz surface (water contact angle ~ 80°) is less hydrophobic than wax (water contact angle ~ 110°) because the hydrophobic layer is patchy, i.e. full coverage of the surface is not achieved – Blake et al (1985). Experiments were also conducted with mineral samples: a quartz/smectite mixture (95:5) and sample shales.

Throughout this study we have looked at the water/hexadecane interface. Hexadecane was chosen as a model hydrocarbon liquid (against pure water) because it is immiscible with water, inert, non-polar (purely dispersive) and therefore an ideal model liquid for wettability measurements before complex mixtures such as crude oils are considered.

Experimental Methods

Sessile drop measurements were conducted on quartz plates and the contact angle was obtained by numerically drawing a tangent to the liquid/liquid interface at the solid surface (at 100× magnification). The Wilhelmy plate technique was also carried out with flat quartz samples. The samples were advanced/receded and the force trace recorded. The contact angle was obtained from the force trace interpreted in terms of capillary and buoyancy forces and extrapolated back to zero depth of immersion, as described at Neumann et al (1979).

The equilibrium capillary pressure technique (ECPT) is a type of imbibition test - Diggins et al (1990) & (1993) - that consists of measuring the gas pressure required to prevent liquid penetration in a porous medium. The setup is shown schematically in Fig. 1. The packing density of powder in the sample tube was constant (with an average value of about 0.58). The packed bed was fully saturated with hexadecane and then exposed to water from a constant-head reservoir. Water displaced the hexadecane under the combined action of capillary (spontaneous imbibition) and hydrostatic pressure. As the gas pressure above the bed increased liquid displacement slowed down and finally ceased. The capillary pressure determined under these static conditions was used to evaluate the contact angle.

The contact angle (always measured through the water) was an advancing one in this case. In the second stage of the experiment the gas pressure was increased by means of a screw activated syringe so that hexadecane pushed back the water. The pressure measured under these static conditions was used to calculate the receding contact angle - Stevens (2005).

Experiments showed that liquid displacement occurred reproducibly and reversibly under these conditions. A typical dependence of gas pressure versus time for water displacing hexadecane is presented in Fig. 1a (Right). The pressure increases initially due to the penetration of water into the hexadecane saturated porous bed. A constant value was achieved relatively quickly. After two steps of liquid (water or hexadecane) advancing

(Fig. 1 Right) we conducted the opposite displacement. The liquid/liquid interface was forced to recede through the powder under an excess gas pressure applied by a syringe. In this case we observed the gradual decrease of the pressure in the cell down to the level where the gas-pressure was equilibrated by liquid/liquid capillary and hydrostatic pressure.

The pressure plotted in Fig. 1 (Right) is the capillary pressure, P, which was obtained as the difference: $P_m - P_H$ (P_m - measured gas pressure, P_H - hydrostatic pressure of the water and hexadecane columns).

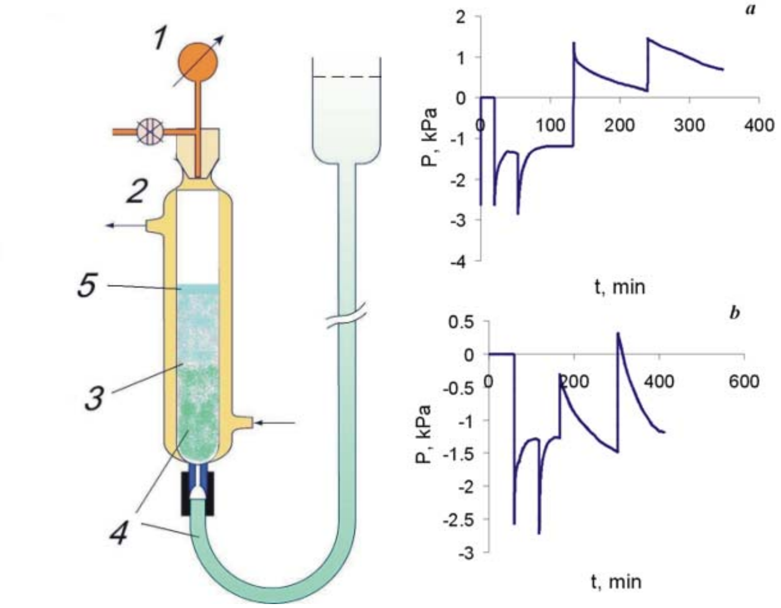

Figure 1. (Left) Equilibrium capillary pressure technique: 1) pressure sensor; 2) sample holder; 3) packed bed of particles; 4) water entering the packed bed; 5) hexadecane displaced by water; (Right) Capillary pressure versus time in quartz powder: (a) water displacing hexadecane; (b) hexadecane displacing water.

The contact angle, θ, was evaluated from the capillary pressure using Laplace equation - Adamson et al (1997):

$$\cos\theta = \frac{r_{eff}}{2\gamma} P_C \qquad [1]$$

The interfacial tension of the water/hexadecane interface was $\gamma = 53.3$ mJ/m² and r_{eff} was the effective capillary radius, which depends on particle size and packing density - Neumann et al (1979), Stevens et al (2006) & White et al (1982)

Pressure measurements were also conducted in single uniform capillaries as a means of calibrating the method. The methylated capillary tube was mounted instead of the sample holder in the ECPT setup (Fig. 1). The water/hexadecane meniscus was advanced (or receded), then stopped, and the dependence of pressure versus time was recorded.

The capillary pressure determined in packed beds was significantly higher in comparison to the pressure in a single capillary reflecting the significant difference in capillary radius: 300 µm (geometric radius) for the methylated capillary and 27 ± 5 µm for the quartz powder (effective radius obtained from a pressure measurement with a fully wetting liquid – cyclohexane).

Combined NMR/ECPT measurements were done in a specifically designed cell positioned in the homogeneous field region of an NMR spectrometer. The T_2 distributions were obtained using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (Table 1) for a mineral silt loaded into the ECPT cell. The mineral powder was packed between two glass wool plugs through which it was saturated with a liquid. We used a highly refined mineral oil with no polar or aromatic compounds (Ondina 15, Shell Lubricants) as the model hydrocarbon liquids in these tests. Ondina 15 is chemically similar to hexadecane in that it consists of alkanes, but is substantially more viscous, giving a bulk T_2 much shorter than water (Table 1).

Table 1. NMR Acquisition Parameters.

Instrument	Resonance Instruments Maran Ultra-2
Frequency of operation	1.95 MHz resonant frequency
Spins excited	Protons (^{1}H) in liquid phases
Fluid bulk relaxation parameters	Water: T_1 , T_2 = 2.98 s; Ondina 15: T_1 ,T_2 = 146 ms.
Fluid Hydrogen Index	Deionised Water, H.I. = 1.0; Ondina 15 oil H.I. = 1.09
Pulse sequence used	CPMG for transverse relaxation time- T_2
Relaxation delay (wait time, WT)	5 seconds with no bulk water up to 15 seconds for complete polarization of water in bulk
Spin refocusing delay, τ; (2τ = interecho spacing, TE)	120 microseconds
Number of echoes	4096
Number of scans (stacking level)	64 or 256

An investigation of the wettability of several shale samples was carried out as a starting point for the research of real minerals. Because of swelling and water adsorption the film flotation technique was used according to Fuerstenau et al (1987) and Williams et al (1987). Fine clay particles (1-10 µm) were carefully loaded on the surface of various water-methanol mixtures (having different surface tension) and the point where 50% of the particles float was determined. The contact angle was calculated from this value of the critical surface tension of wetting by using a calibration curve obtained for quartz particles methylated to a different degree.

In addition the shale samples were examined for swelling pressure and water adsorption. The shale sample was positioned in the cell (Fig. 1). Water was allowed to saturate the sample progressively. The adsorption was monitored via the changing level of water in the U-tube manometer. The swelling pressure was determined as the difference between the hydrostatic pressure of the water in the manometer and the gas pressure inside the sample holder.

Finally, observations of shale surfaces were made with a variable pressure scanning electron microscope at 1000× magnification and under conditions of varying humidity.

RESULTS AND DISCUSSION

Wettability Measurements in Model Systems

The results of contact angle measurement obtained with different techniques are compared in Fig. 2(Left). The difference between advancing and receding contact angles is known as contact angle hysteresis. It generally increases when the solid surface is rough and heterogeneous - Adamson et al (1997). The surface of methylated quartz is heterogeneous and the amount of hysteresis observed is not uncommon in such cases. In a solid/liquid/liquid system the advancing and receding of water can be performed in two ways: water displacing hexadecane (WH) and hexadecane displacing water (HW). Ideally the results obtained in both configurations should be the same but in fact we observe some differences (Fig. 2 Left).

The results from the sessile drop and the single capillary are in good agreement. The contact angles obtained with the sessile drop technique were θ_A = 123–127° and θ_R = 109–116° (Fig. 2 Left). These results are for a water droplet placed in a hexadecane environment but exchanging the two liquids had no influence on the measured values. In a methylated capillary tube we found similar values: 117–121° and 91–97°, respectively.

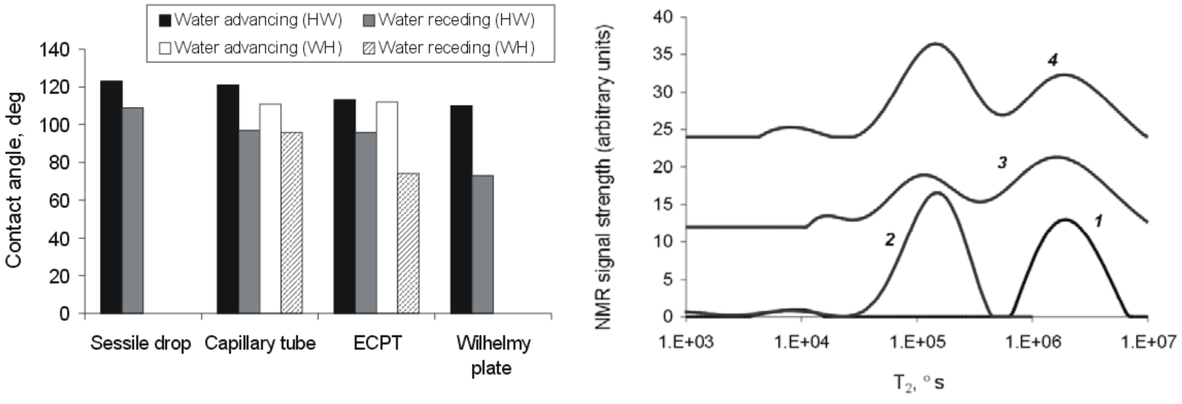

Figure 2. (Left) Advancing and receding contact angles: comparison of different techniques. (Right) T_2-distributions: (1) water alone in methylated quartz powder; (2) oil alone in methylated quartz powder; (3) Spectrum where water is displaced by oil in clean quartz silt; (4) water is displaced by oil in methylated quartz particle bed (150-180 µm grain size).

The advancing and receding angles obtained for the powder and with the Wilhelmy plate were smaller than those measured in the methylated capillary or with sessile drops. The values from the Wilhelmy plate were shown to be different because of a slightly different quality of the surface. The results from the ECPT were θ_A = 108–118° and θ_R = 91–101° on a methylated quartz powder. The reason for this discrepancy is that the penetrating liquid does not displace entirely the saturating liquid and the amount of retained liquid had to be accounted for, as shown at Stevens (2005) and (2006).

Thus we have successfully performed capillary pressure sessile drop and Wilhelmy plate measurement in a model solid/liquid/liquid system. The values of the contact angles (advancing & receding) are found to be in good agreement for all techniques used.

The equilibrium capillary pressure technique (ECPT) was successfully adapted for a solid/liquid/liquid system. Capillary pressure measurements are feasible, the overall reproducibility is good and the accuracy is acceptable. Consequently the ECPT is considered a reliable method for contact angle measurements in mineral/water/oil system.

Liquid/Liquid Displacement in Porous Media

In the next step we studied the liquid/liquid displacement and distribution in mineral porous media depending on the surface wettability. The process of oil and water penetration in mineral powders was studied using a combined ECPT/NMR technique. NMR spectroscopy is suitable for assessing rock wettability because spin relaxation measurements are sensitive to the state of the solid/liquid interface – Roussel et al (1992), Guan et al (2002) and Al-Mahrooqi et al (2003).

Our NMR T_2 spectrum measurements are presented in Fig. 2 (Right). The effect of surface hydrophobicity was studied for an oil/water interface on the surface of quartz powder. The oil/water interface was created by pushing oil into a water saturated particle bed. The oil/water T_2-distribution appeared to be a superposition of the signals for oil and for water on a quartz surface. The oil/water NMR response was different for clean (hydrophilic) and methylated (hydrophobic) quartz (see Fig. 2 Right). The water peak was higher for hydrophilic quartz. In hydrophobic quartz however, the oil peak exceeded the water peak showing that more oil entered. The position of the peaks also varies with the surface chemistry; water spreads to wider range of T_2 in the water wet quartz, whereas in the oil wet sample some of the oil resides in short T_2 positions. Thus nuclear magnetic resonance spectroscopy combined with the equilibrium capillary pressure technique can provide quantitative information on the water/oil distribution in porous materials depending on their surface wettability.

The NMR/ECPT technique was applied to a prototype mineral system – a mixture of quartz (95%) and smectite (5%). The pressure created in the cell due to liquid penetration was recorder over time – Fig. 3ab.

Simultaneously the T_2 distribution was acquired at different stages of liquid penetration (Fig. 3cd). A strong dependence of the T_2 distribution on the stage of liquid penetration in mineral porous media was observed.

Initially (0-100 minutes) the injected water was mostly taken up in a broad peak at 30-50 ms, with a substantial amount of water showing in between values from 3 ms to less than 100 µs. There was also some excess water with a near bulk T_2. That means water was occupying the inter-particle pores and also hydrating the clay. Later, after continuing water imbibition (100-240 minutes) the clay peak became distinct from the main larger pore mode.

Subsequent oil injection (> 240 minutes) made the main peak larger and also mitigated the excess water signal. The observed changes in the shape of the clay peak were consistent with oil penetration around and close to the clay surface with complete water displacement. Moreover we noted the high capillary pressure needed to inject the oil - it did not penetrate the sample at any appreciable rate.

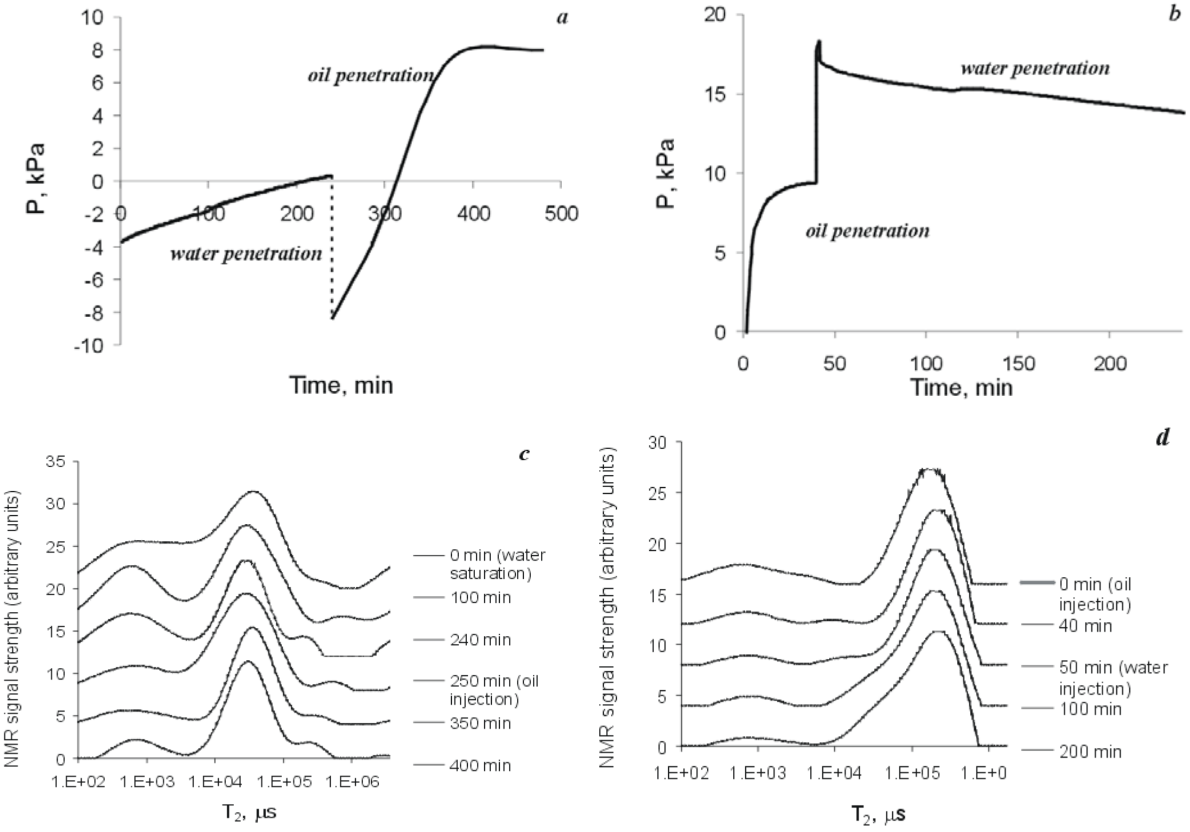

Figure 3. (a) Capillary pressure versus time for water imbibition followed by oil penetration into the 95% quartz plus 5% smectite mixture; (b) capillary pressure vs. time for oil penetration followed by water imbibition; (c) T_2 distribution monitored over time for the situation in (a); (d) T_2 distribution monitored over time for the situation in (b).

In the next step we performed the inverse experiment – oil was displaced by water. Initially oil entered the dry sample very freely and occupied a main peak at around 100 ms (smaller than bulk) and also showed a small signal at 100 µs to 10 ms. After water injection (> 50 minutes) the water occupied a T_2 slightly shorter than the original oil peak, and only a small amount imbibed. It seems to move into the clay region < 3 ms. We hypothesize that the oil has partly coated the clay, greatly reducing water relative permeability and thereby obstructing water adsorption onto the surfaces or absorption into the inter-layers. On the other hand, the pressure-time evolution – a slowly decreasing pressure – suggests a gradual process of water adsorption. However the pressure over time showed much higher values in the presence of montmorillonite clay in comparison to quartz powder. Such unexpectedly high value of pressure could not be interpreted as a capillary pressure. Thus we have to take into account water adsorption and swelling acting in parallel with capillary imbibition

Wettability and Swelling of Shale Minerals

The shale samples studied had contact angles ranging from 52 to 84°. The results of water adsorption and swelling pressure measurement are presented in Fig. 4. The rate of water adsorption was significantly higher for moderately hydrophobic samples (lower contact angles) in comparison to samples with higher contact angle. What is more, the swelling pressure is also in good correlation with the shale wettability. Thus significant swelling pressure was observed only for samples with higher values of the contact angle. In contrast, only a minor pressure growth was detected for samples with a contact angle of 52°.

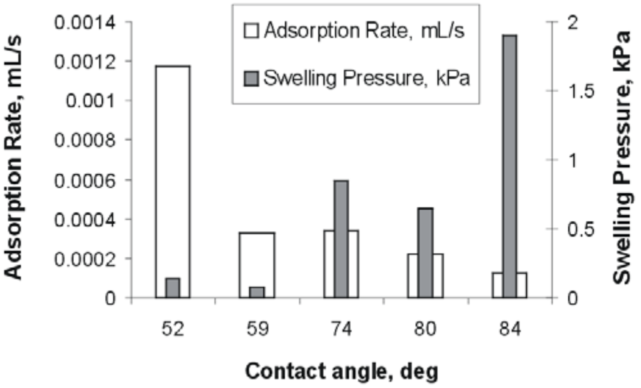

Figure 4. Water adsorption rate and swelling pressure versus contact angles for shale samples, with the corresponding water adsorption rates in the swelling test.

To observe the effect of water adsorption on the surface texture of shales, samples were studied using VPSEM and ESEM. Photos of the shale surfaces are presented in Fig. 5. These include dry, water saturated and dehydrated clay samples.

An increase in surface smoothness was observed after water saturation (Fig. 5b and 5e). Dramatic surface changes were observed after dehydration (Fig. 5c and 5f). Moreover surface degradation occurred differently for clays with moderate hydrophobicity (contact angle 52-59°) and higher hydrophobicity (contact angle ~ 80°). Although micro-pores appeared on both type of samples, the surface of the hydrophobic samples had smaller micro-pores (white spots on the picture). In addition, the appearance of long narrow micro-cracks was observed (Fig. 5c).

The study of oil penetration into a shale sample revealed the formation of a droplet on the surface of the dry clay sample with subsequent slow penetration and spreading on the surface without significant surface changes (Fig. 6a). A subsequent increase in humidity - up to 100% - lead to the formation of water droplets on top of the oil impregnated surface (Fig. 6b). In this case water neither penetrated nor affected the shale surface once oil had been adsorbed.

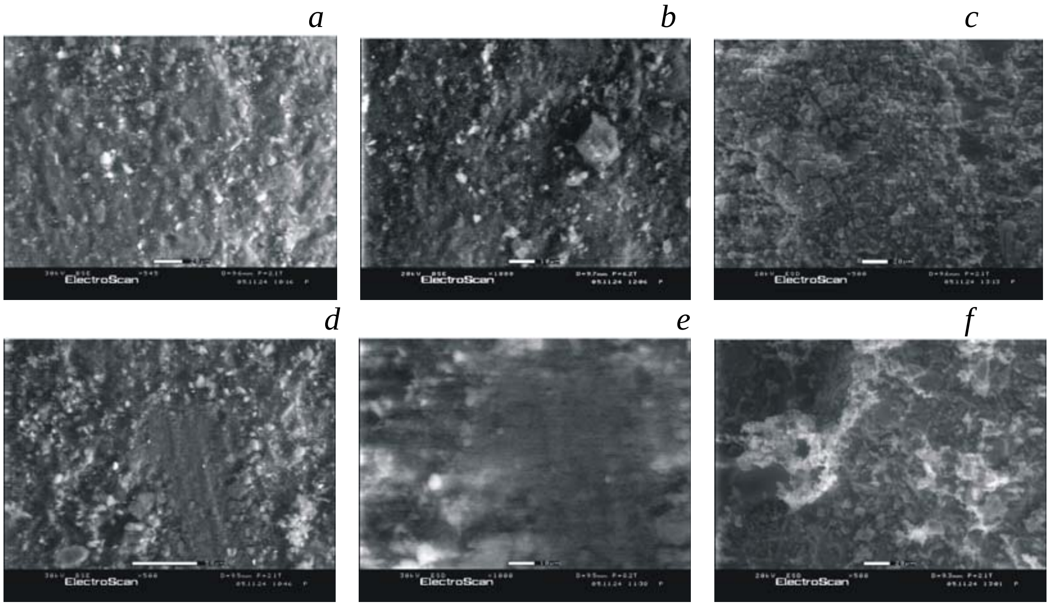

Figure 5. Hydrophobic shale sample L1-604m (a-c) and moderately hydrophobic shale L1-665m (d-f): dry (a & d); water wetted (b & e) and dehydrated (c & f).

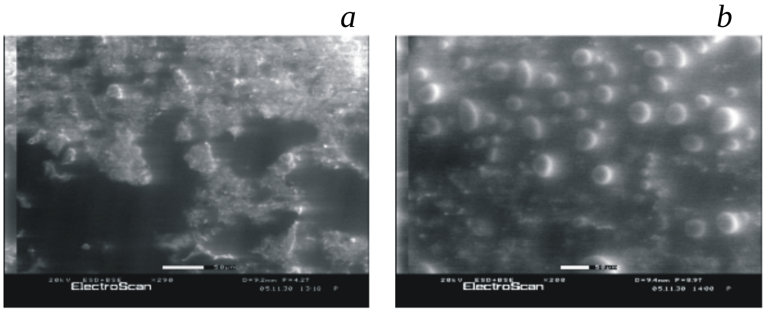

Figure 6. (a) The surface of kaolinitic North Sea shale S4 onto which oil has adsorbed and spread; (b) The droplets of water forming on the surface of the shale which has become oil-wet.

CONCLUSION

We have successfully performed capillary pressure, sessile drop, Wilhelmy plate and ECPT measurement in model solid/liquid/liquid systems. The values of the contact angles (advancing & receding) are found to be in a very good agreement for all techniques. A correlation between contact angle, swelling pressure and adsorption rate was found for clay minerals of different mineralogical and chemical structure.

ESEM observations showed the significant difference in surface modification under the action of water and oil, which also correlates with their macroscopic contact angles.

We have shown that the process of oil/water displacement in porous minerals can be thoroughly characterized and clarified using the combination of ECPT and NMR spectroscopy. The acquired information allows us to investigate the water/oil wettability (capillary pressure and contact angle) in mixed quartz and clay systems and real shale samples. That gives us the possibility to study the liquid behaviour in porous media depending on their mineralogical structure and wettability.

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Appendix

NATURAL SHALE PROPERTIES

The shales investigated in this study come from the Officer Basin onshore Western Australia, the Bass Basin offshore the southern Australia, and the North Sea. The Officer Basin shales are Proterozoic in age, sometimes laminated, rich in illite, quartz and orthoclase feldspar; they have moderate to low clay fraction and generally ~40-50% clay content (Table 2). They have a high capillary seal capacity, with air-mercury threshold pressures (derived from mercury porosimetry) in excess of 8500 psi (>300m gas column under in situ conditions). The Bass Basin shale O1A is of Palaeocene age and dominated by quartz and kaolinite with subsidiary micas and feldspar. Bass basin shales are siltier than the Officer Basin shales and the example used here has lower capillary seal capacity (~5000 psi). The North Sea shale sample S4 is highly kaolinitic, with abundant fine quartz, mica and pyrite.

Table 2. Major mineral composition and some physical properties of Officer Basin shales. Qz = quartz; Or = orthoclase; Kao = kaolinite; Chl = chlorite; Hem = haematite; Dol = dolomite; CC = clay content; CF = clay fraction (< 2 µm size fraction); CEC = cation exchange capacity; P_{th} = air-mercury threshold pressure.

Sample	**Qz**	**Or**	**Kao**	**Illite/Mica**	**Chl**	**Hem**	**Dol**	**CC**	**CF**	**CEC**	P_{th}
	%	**%**	**%**	**%**	**%**	**%**	**%**	**%**	**%**	cmol/kg	psi
L1-390	20	11	0	49	2	5	13	51	26	30	8479
L1-603	25	29	2	35	4	2	0	41	17	21	8486
L1-665	22	19	7	45	6	0	0	58	23	23	8519
L1-900	20	33	0	29	3	3	11	32	13	19	6965