

Wettability Alteration in Carbonates: The Effect of Water-Soluble Carboxylic Acids in Crude Oil

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Acidic components in crude oil influence the wetting condition through their effect on electrostatic interactions with the mineral surfaces. In this paper, we have extracted water-soluble acids from a crude oil with a high acid number (AN) to study the effect of these acidic materials on the wetting condition. The AN for the original oil was 1.8 mg of KOH/g, while the AN for the oil depleted in water-soluble acids was 1.5 mg of KOH/g. Two crude oils have been studied by a chromatographic wettability test and spontaneous imbibition using seawater as imbibing fluid to determine the differences in the wetting condition and oil recovery. In a spontaneous imbibition process at 110 °C, both the imbibition rate and ultimate recovery were higher in the cores saturated with the oil depleted in water-soluble acids. The difference in the imbibition rate and also ultimate recovery indicates that the carboxylic material from the oil depleted in water-soluble acids can be displaced easily compared to the original oil. The difference in wetting properties was also confirmed by chromatographic wettability tests. The water wetness appeared to be lower for the original oil compared to that for the treated oil. These crude oils were also investigated with respect to interfacial tension. Even though the strength of the bonding of carboxylic material onto the calcite surface is mostly dictated by the carboxylic group, the organic structure of the carboxylic material will have an influence on the wettability alteration process as well.

Introduction

The carboxylic group adsorbs very strongly onto the positive sites of a calcite surface.¹ Therefore, the carboxylic material quantified as the total acid number (AN) is the most important wetting parameter for carbonates.^{2,3} Natural bases, in the presence of carboxylic acids, appeared to increase the water wetness, probably because of the formation of acid–base complexes in the crude oil, which prevents the acid from adsorbing onto the carbonate surface.^{3,4} The carboxylic acids in crude oil have often been termed naphthenic acids because the carboxylic group is mostly linked to cyclic organic material. Even though naphthenic acids are more prevalent, it is also known that aliphatic acids are present in crude oil. It is believed that acids with fewer than eight carbon atoms are almost entirely aliphatic in nature. Monocyclic acids begin at C6 and predominate above C14.⁵ Thus, the structure of the carboxylic acids appears to correspond with those of the hydrocarbons with which they are associated in the crude oil. The fact that the oxygen content of crude oil increases with the boiling point of the fraction examined also indicates that

the carboxylic materials are mostly located in the heavy end fraction of crude oil, i.e., in the resins and asphaltenes.

A wider range of acidic compounds have been investigated, especially with the use of mass spectrometric techniques,^{6–8} and it has been reported that the major types of acidic compounds in 10 high-boiling crude oil distillates were identified as carboxylic acids, phenols, carbazoles, and amides.⁹ The type of acid compounds in Wilmington crude oil is 28% carboxylic acids, 28% phenols, 28% pyrroles (indoles and carbazoles), and 16% amides. These results show the complexity of the acidic fraction of crude oils and that phenols and carboxylic acids comprise the major portion of the acidic species.

The water-soluble components of the carboxylic material are therefore believed to be a small fraction of the total amount of acids present. They may, however, play an important role in establishing the initial wetting conditions because they can contribute toward destabilizing the water film between the rock and oil.

At high temperatures, seawater is able to change the wetting conditions of chalk toward higher water wetness, which favors improved oil recovery by spontaneous imbibition (SI). It has been documented that the interactions between the chalk surface and the ions Ca²⁺, Mg²⁺, and SO₄²⁻ present in seawater are responsible for the wettability modification of chalk.¹⁰ Even though the strength of the bonding of carboxylic

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(1) Thomas, M. M.; Clouse, J. A.; Longo, J. M. *Chem. Geol.* **1993**, *109*, 201–213.

(2) Standnes, D. C.; Austad, T. *J. Pet. Sci. Eng.* **2000**, *28* (3), 111–121.

(3) Skauge, A.; Standal, S.; Boe, S. O.; Skauge, T.; Blokhus, A. M. Effects of organic acids and bases, and oil composition on wettability. Presented at the 1999 Society of Petroleum Engineers (SPE) Annual Technical Conference and Exhibition, Houston, TX, 1999; Paper SPE 56673.

(4) Puntervold, T.; Strand, S.; Austad, T. *Energy Fuels* **2007**, *21* (3), 1606–1616.

(5) Speight, J. G. *The Chemistry and Technology of Petroleum*, 2nd ed.; Marcel Dekker: New York, 1991.

(6) Seifert, W. K.; Teeter, R. M. *Anal. Chem.* **1970**, *42*, 750–758.

(7) Tomczyk, N. A.; Winans, R. E.; Shinn, J. H.; Robinson, R. C. *Energy Fuels* **2001**, *15*, 1498–1504.

(8) Quian, K.; Robbins, W. K.; Hughey, C. A.; Cooper, H. J.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2001**, *15*, 1505–1511.

(9) McKay, J.; Cogswell, T. E.; Weber, J. H.; Latham, D. R. *Fuel* **1975**, *54*, 50–61.

(10) Zhang, P.; Tweheyo, M. T.; Austad, T. *Colloids Surf., A* **2007**, *301*, 199–208.

Table 1. Crude Oil Properties^a

	density (g/cm ³)	AN (mg of KOH/g)	BN (mg of KOH/g)	viscosity (cp)
base oil (Heidrun crude oil)	0.893	2.82	1.13	24.4
OO	0.812	1.8	0.51	3.38
TO	0.814	1.5	0.53	3.01

^a Density and viscosity determined at room temperature.

material onto the calcite surface is mostly dictated by the carboxylic group, it is not unreasonable that the organic structure of the carboxylic material will have influence on the wettability alteration process. Consequently, the question asked is what is the impact of water-extractable acids in crude oil on wettability and wettability alteration in carbonates? One way to achieve this information is to compare oil recovery and wetting properties of oils with and without the presence of water-extractable acids.

Materials and Methods

Crude Oils. The biodegraded Heidrun crude oil with AN = 2.82 and base number (BN) = 1.13 mg of KOH/g was used as the base crude oil, which was sampled from a new well during a well test. The original test oil (OO) was made by diluting the base oil, Heidrun crude oil, with 40 vol % heptane. After acidic material was extracted from the Heidrun oil, it was also diluted 40 vol % with heptane and the oil was termed treated oil (TO). Both crude oils were centrifuged and filtered through a 5 μm Millipore filter. No precipitation of asphaltenic material was observed during storage. The OO is a crude oil with a high AN ~ 1.8 mg of KOH/g of oil, and the AN of the crude oil depleted in water-soluble acids (TO) was determined to be AN ~ 1.5 mg of KOH/g of oil. The oil properties are presented in Table 1. The density and viscosity of the crude oils were measured using an Anton Paar DMA 4500 density meter and a Physica UDS 200 viscometer, respectively.

Rock Materials. Outcrop Stevns Klint chalk from a quarry nearby Copenhagen, Denmark, was used as porous medium. This is a highly porous (45–50%) and low-permeable (2–5 mD) chalk, with a specific surface area of about 2.0 m²/g.^{11,12}

Brines. Valhall formation brine (VB) was used as the initial formation water. During SI, VB and synthetic seawater (SW) were used as imbibing fluids. Artificial seawaters with and without tracer, SW1T and SW0T, respectively, were used during the chromatographic wettability test, as described later in this section. All brine compositions are given in Table 2.

Core Preparation. The chalk cores were prepared according to the method described by Puntervold et al.¹³ The cores were flooded with 250 mL of distilled water at 50 °C to remove soluble salts, especially SO₄²⁻. After the cores were dried at 90 °C to a constant weight, the cores were evacuated and saturated with formation water and the pore volume was determined. The initial water saturation (*S*_{wi}) of 10% was obtained by draining the cores on a porous plate using water-saturated N₂ gas. The pressure was increased gradually to ~10 bar. The cores were then saturated and flooded with the actual crude oil: 1.5 pore volume (PV) of oil in each direction at 50 °C using a Hassler core holder with a confining pressure not exceeding 25 bar. Prior to aging, the cores were wrapped in Teflon tape to avoid unrepresentative adsorption of acidic material onto the core surface. The cores were aged in the actual crude oil at 90 °C for 4 weeks. The core data are given in Table 3.

Table 2. Brine Compositions (mol/L)

	VB	SW	SW0T	SW1T
HCO ₃ ⁻	0.009	0.002	0.002	0.002
Cl ⁻	1.066	0.525	0.583	0.492
SO ₄ ²⁻		0.024		0.024
SCN ⁻				0.024
Mg ²⁺	0.008	0.045	0.045	0.045
Ca ²⁺	0.029	0.013	0.013	0.013
Na ⁺	0.996	0.450	0.460	0.393
Li ⁺				0.024
K ⁺	0.005	0.010	0.010	0.034
total dissolved solids (TDS) (g/L)	62.8	33.4	33.39	33.39
ionic strength	1.112	0.657	0.643	0.647

Extraction of Water-Soluble Carboxylic Acids. A procedure for the extraction of the total acid fraction has been described previously.^{14,15} An indication of the amount of easily extractable water-soluble acids was obtained by a two-phase titration. Oil and distilled water (DW) were mixed at predetermined volume ratios and titrated with NaOH at preset pH values. The crude oil used was Heidrun oil diluted with 40 vol % *n*-heptane, giving an oil with AN = 1.80 mg of KOH/g. The titration was performed at room temperature, and the results were reported as the decrease in AN versus the W/O volume ratio at pH 10 (Figure 2) and as a function of pH at the given W/O ratio of 4.0 (Figure 3). At sufficiently high pH, unstable emulsions can be produced, while at low pH, stable emulsions are formed.¹⁶

Thereafter, preparative extraction of carboxylic acid was performed using pure Heidrun oil, AN = 2.82 mg of KOH/g, and DW in the W/O volume ratio of 2.0. The pH was kept at 10 by adding small amounts of a concentrated NaOH solution. The mixture was stirred vigorously on a magnetic stirrer while adjusting the pH of the mixture for more than 24 h. An emulsion was formed because of the strong mixing of oil and water. The mixture was centrifuged to separate the oil and water phases. The oil phase was extracted and centrifuged with DW until neutral pH was obtained. Titration showed that the AN of the TO had decreased by 17%. It is important to note that the intention is not to have a quantitative extraction of acids into the water phase. It is only the most water-soluble acidic material that is of interest. Finally, the oil was filtered through a 5 μm Millipore filter and diluted with 40 vol % *n*-heptane, and the AN and BN were determined to be 1.50 and 0.51 mg of KOH/g, respectively. The oil was then mixed with Valhall formation water in the same ratio as the initial saturations, i.e., ~10 vol % water. After equilibrating the solution under stirring for 24 h, the pH was determined to be 7.17.

AN and BN Measurements. A Mettler Toledo DL55 autotitrator was used to determine AN and BN by potentiometric titrations using an internal standard. The methods used were developed by Fan and Buckley¹⁷ and are modified versions of the standard methods ASTM D2896 for BN titration and ASTM D664 for AN titration.^{18,19} Measured AN and BN are given in Table 1.

(14) Hoeliland, S.; Barth, T.; Blokhuis, A. M.; Skauge, A. *J. Pet. Sci. Eng.* **2001**, *30*, 91–103.

(15) Constantinides, G.; Arich, G. Non-hydrocarbon compounds in petroleum. In *Fundamental Aspects of Petroleum Chemistry*; Nagy, B., Colombo, U., Eds.; Elsevier: Amsterdam, The Netherlands, 1967; pp 109–175.

(16) Omole, O.; Falode, O. A. *J. Appl. Sci.* **2005**, *5* (5), 873–877.

(17) Fan, T.; Buckley, J. Acid number measurements revisited. Presented at the 2006 Society of Petroleum Engineers (SPE) Improved Oil Recovery (IOR) Symposium, Tulsa, OK, 2006; Paper SPE 99884.

(18) American Society for Testing Materials (ASTM) International. ASTM 2896-88. Standard test method for base number of petroleum products by potentiometric perchloric acid titration. In *Annual Book of ASTM Standards*; ASTM: West Conshohocken, PA, 1988.

(19) American Society for Testing Materials (ASTM) International. ASTM 664-89. Standard test method for acid number of petroleum products by potentiometric titration. In *Annual Book of ASTM Standards*; ASTM: West Conshohocken, PA, 1989.

(11) Frykman, P. *Mar. Pet. Geol.* **2001**, *18* (10), 1041–1062.

(12) Røgen, B.; Fabricius, I. L. *Pet. Geosci.* **2002**, *8* (3), 287–293.

(13) Puntervold, T.; Strand, S.; Austad, T. *Energy Fuels* **2007**, *21* (6), 3425–3430.

Table 3. Core Properties

core ID	L (mm)	D (mm)	PV (cm ³)	ϕ (%)	S_{wi} (%)	S_{oi} (%)	remarks	crude oil
SK#11	69.3	38.1	36.28	46	9	91	SI at 110 °C and wettability test after SI	
SK#1	69.9	38.1	36.40	46	9	91	SI at 110 °C	saturated with OO
LSSK#5	70	38.1	36.64	46	9	91	initial wettability test	
SK#5	71.0	38.0	36.65	45	9	91	SI at 110 °C and wettability test after SI	
SK#3	69.7	38.1	35.32	44	9	91	SI at 110 °C	saturated with TO
LSSK#6	70	38.1	35.64	45	10	90	initial wettability test	
SFK#1	70	38.1	36.11	45	10		reference core	clean core

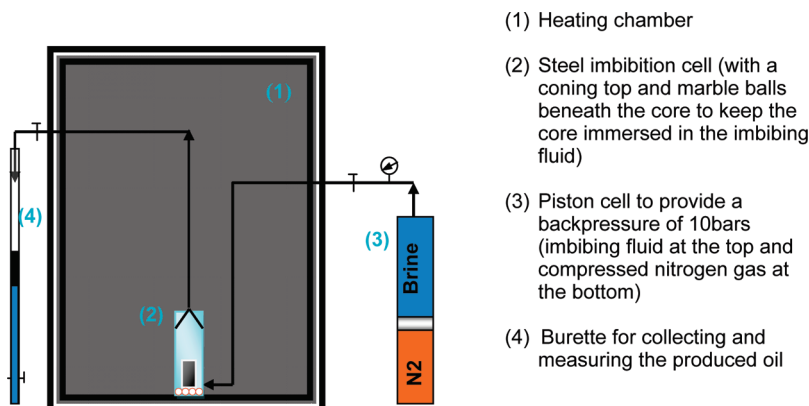


Figure 1. Schematic diagram of SI at high temperatures.

Interfacial Tension (IFT) Measurements. IFT between the crude oil and SW was measured at ambient temperature using a drop volume tensiometer DVT30. The measurements were performed at injection rates between 40 and 3 $\mu\text{L}/\text{min}$ to reduce the sensitivity of measurements to the injection rate. The IFT values varied more with the flow rate for the OO compared to that for the TO, while at low flow rates, the IFT values converged to the same value, about 11 mN/m.

SI. After aging, the core was placed in a sealed, steel cell and surrounded by the imbibing fluid using a back pressure of 10 bar. The SI tests were performed at 110 °C. The cores were first imbibed with VB until the production plateau was reached, and then the imbibing fluid was switched to SW. The amount of produced oil was collected in a graded buret, and the oil recovery was recorded as a function of the time and presented as a percent of original oil in place (% OOIP). A schematic diagram is given in Figure 1.

Chromatographic Wettability Test. The water-wet fraction of the rock surface after aging, initial condition, and after SI was measured using the chromatographic wettability test described by Strand et al.²⁰ The initial wetting property of the core after aging was determined by flooding the core with 2.0 PV of the SW0T brine at a rate of 0.20 mL/min, followed by another PV of the brine at a rate of 0.40 mL/min, to obtain residual oil saturation. SW0T brine contains neither SO_4^{2-} nor tracers (SCN^- and Li^+) (Table 2). Next, the core was flooded with at least 2.0 PV of SW1T brine (containing SO_4^{2-} and the tracers SCN^- and Li^+) at the rate of 0.20 mL/min. The effluent was collected in fractions of 1–4 mL by use of a fraction collector. The fractions were analyzed for the concentration of SO_4^{2-} and tracers (SCN^- and Li^+) using a Dionex ICS-3000 ion chromatograph. The concentration relative to the initial concentration was plotted against the injected pore volume. Chromatographic separation between the non-adsorbing tracers (SCN^- and Li^+) and the adsorbing SO_4^{2-} takes place at the water-wet sites of the chalk surface, and the area between the elution curves of the two components is directly proportional to the water-wet area inside the core.

After SI, the core was flooded at room temperature with SW0T to remove seawater and movable oil, first at a rate of

0.20 mL/min and afterward at 0.40 mL/min, to obtain S_{or} . Then, the chromatographic wettability test was performed by flooding the core with SW1T.

The area ratio between the tracer and sulfate curves of the sample (A_{wet}) and between those of a completely water-wet reference core (A_{ref}) is a measure of the water-wet fraction of the core (WI)

$$WI = \frac{A_{wet}}{A_{ref}}$$

where WI = 0 is completely oil-wet, WI = 0.5 is a neutral wetting state, and WI = 1 is completely water-wet.

The reproducibility of the calculated area between the tracer and sulfate curve was less than 5% between different cores as reported by Strand et al.¹¹

Results and Discussion

Extraction of Carboxylic Acids. The amount of carboxylic acids in the crude oil that can be extracted from the oil into the aqueous phase is dependent upon the volumetric water/oil ratio (W/O) as well as the pH. To quantify the amount of extractable acids in the crude oil, an autotitrator was used in a two-phase titration mode. Oil and distilled water at the predetermined volume ratio were added to the titration beaker, and titration with NaOH was performed at a preset pH value. The amount of carboxylic material that was dissolved in the aqueous phase at the specific titration conditions was then calculated. When using the OO with AN = 1.8 mg of KOH/g of oil and a predetermined pH 10.0, the decrease in the AN of the crude can be determined as a function of the volumetric W/O ratio, as shown in Figure 2. It can be seen that the AN of the crude oil decreased as the W/O volume ratio increased and the variation was greater at low values of the W/O ratio. A variation in the W/O ratio from 3.0 to 16.0 caused a decrease in the AN of the crude oil by 30–40%. At a given W/O ratio of 4.0, the amount of extractable carboxylic acids can be determined at different pH values. As shown in Figure 3, the AN decreased 5–30% when the pH increased from 8 to 10.

(20) Strand, S.; Standnes, D. C.; Austad, T. J. *Pet. Sci. Eng.* 2006, 52, 187–197.

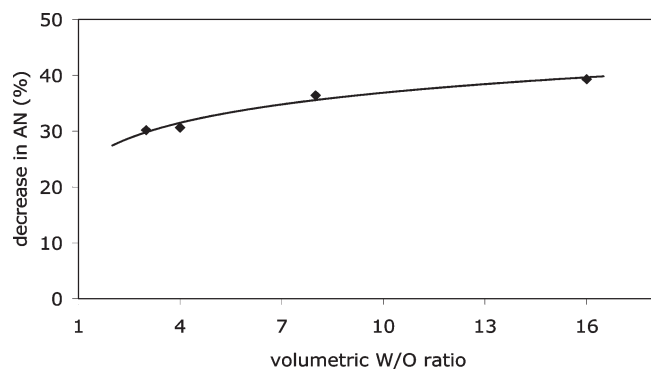


Figure 2. Acid extraction at different W/O ratios at pH 10.0.

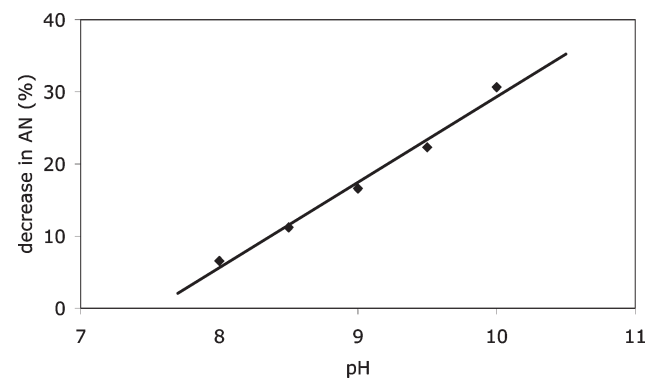


Figure 3. Percent decrease in AN as a function of pH at W/O = 4.0.

The oil used in these experiments was biodegraded, thereby containing a significant amount of water-extractable carboxylic acids. As pointed out by Barth et al.,²¹ the amount of extractable acids is greater for biodegraded oils compared to that for non-biodegraded oils. It was also confirmed that the average molecular weight of the extractable acids from biodegraded oils was significantly lower than that of non-biodegraded oils. An infrared spectrum also showed clear distinctions between the chemical properties of extractable acids from the two types of oils; i.e., biodegraded crude oils contained carboxylic acids of more saturated structure compared to the acids in non-biodegraded oil, which are more phenolic in structure.

The preparative extraction of water-soluble carboxylic acids was performed at pH 10. After the OO and TO (depleted in water-soluble carboxylic acids) were diluted with 40 vol % *n*-heptane, the final ANs were determined to be 1.8 and 1.5 mg of KOH/g of oil, respectively. The BNs remained the same for both crude oils.

As noticed, there is a difference in the decrease in AN when using the titrator and preparative extraction at W/O ratio of 2.0 and pH 10. The reason is that two different crude oils have been used. In the titrator test, the crude oil was Heidrun oil diluted with 40 vol % heptane or OO, but in the preparative test, pure Heidrun oil was used. It is therefore expected that the decrease in AN is different.

SI. Two parallel SI tests were performed at 110 °C for both crude oils after the cores had been aged in the respective crude oils at 90 °C for 4 weeks. As seen in Figure 4, there is a significant difference in the oil recovery for the two test series when using initial VB as the imbibing fluid. The oil recovery

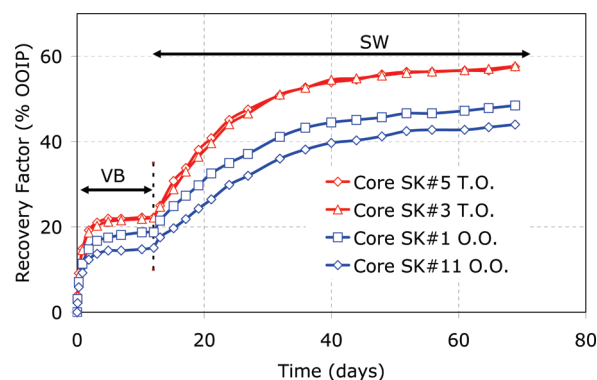


Figure 4. SI into chalk cores saturated with different crude oils, OO and TO. SI was performed by VB, followed by SW as the imbibing fluid at 110 °C, $S_{wi} = 10\%$.

from the cores containing TO (depleted in water-extractable acids) was about 22% OOIP after 12 days, and the imbibition curves were very reproducible. The imbibition curves for the cores containing the OO were less reproducible, but the oil recovery was well below the recovery from the cores containing TO. After 12 days, the average recovery was about 16% OOIP.

Because of the lack of SO_4^{2-} in the formation water, it is not able to induce wettability modification during the imbibition process.¹⁰ The oil recovery is therefore related to capillary forces and initial wettability conditions. By experience, for a completely water-wet system, the oil recovery would be in the range of 60–65% OOIP for this outcrop chalk material. In both cases, the AN of the crude oils is quite high, 1.8 and 1.5 mg of KOH/g of oil, and previous studies have indicated that it is very difficult to see any experimental differences in the wetting conditions as the AN increases beyond 1.0.²⁰ The apparently lower water wetness of the OO, from an imbibition point of view, may indicate that the water film between the rock and oil is more easily broken with water-soluble acids present in the crude oil.

After 12 days, the imbibing fluid was changed to SW. This caused an immediate increase in oil recovery for both series. The slope of the imbibition curve for the cores containing the TO was higher than that for the cores with the OO. The increased oil recovery by SW is related to the ability of SW to improve the water wetness, which increases the capillary forces. The difference in the imbibition rate can indicate that the carboxylic material from the TO is more easily displaced than that from the OO. The oil recovery after about 70 days is also different, about 56 and 43% of OOIP for the TO and OO, respectively.

Under constant wetting properties and similar fluid viscosities, the difference in imbibition rate is usually related to differences in IFT. The imbibition rate decreases as the IFT decreases, but the ultimate recovery usually increases as the IFT decreases. The IFT value between the Heidrun oil (base oil) and SW and both of the diluted oils appeared to converge to the same value as the flow rate decreased, ≈ 11 mN/m (Figure 5). The Heidrun oil should not be contaminated by production chemicals because the well was newly drilled and only used for a well test. The rather low IFT value may indicate that the naphtenic acids of the biodegraded oil are very surface-active.

The viscosities of the two oils are also quite similar at room temperature, 3.38 and 3.08 cP for the OO and TO, respectively. Thus, the difference in the imbibition rate and ultimate

(21) Barth, T.; Høiland, S.; Fotland, P.; Askvik, K. M.; Pedersen, B. S.; Borgund, A. E. *Org. Geochem.* **2004**, *35*, 1513–1525.

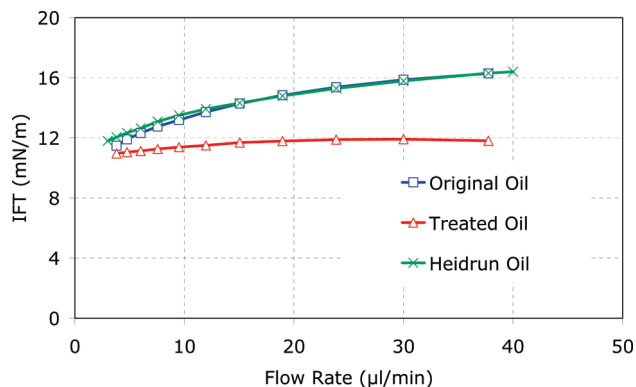


Figure 5. IFT for different crude oils and SW at ambient temperature and different rates of injection using a drop volume tensiometer.

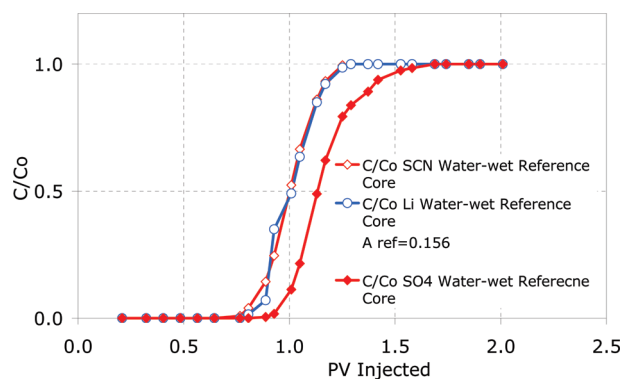


Figure 6. Chromatographic wettability test on a completely cleaned and water-wet core using two tracers (SCN^- and Li^+), core SFK#1. The chromatographic separation area was used as the reference area (A_{ref}) to calculate the water-wet fraction for the chromatography analysis.

recovery between the two oils is most likely related to differences in wetting properties.

Chromatographic Wettability Test. The water-wet fraction of the chalk surface was determined by using the chromatographic wettability test method developed by Strand et al.²⁰ The water-wet fractions of a core initially saturated with OO and another core initially saturated with TO were determined after (1) aging to describe the initial wetting property and (2) SI by SW to describe the final wetting conditions.

Figure 6 shows the chromatographic analysis on a clean core as a reference core, i.e., a core flooded with distilled water to remove dissolvable inorganic salts. The area between the sulfate and the tracer curves is proportional to the water-wet area inside the core. The two tracers (SCN^- and Li^+) eluted from the core simultaneously, which indicated no interaction with the rock from either the positively or negatively charged tracer. The area between the tracer and sulfate curves was determined to be 0.150 and 0.156 for Li^+ and SCN^- , respectively. The value for the SCN^- tracer was used as the reference value for a completely water-wet system when calculating wetting indexes.

On the basis of the chromatographic data from the completely water-wet core, the initial water-wet fraction of the cores containing the OO and TO can be calculated from the areas determined from the chromatographic tests shown in Figures 7 and 8, respectively. The chromatographic separation area between the tracer and sulfate elution curves for the OO and TO was 0.083 and 0.098, respectively, and the

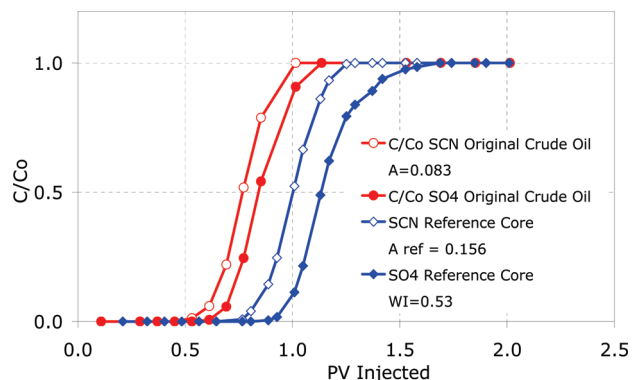


Figure 7. Initial wetting condition of a core saturated with the OO, core LSSK#5, $S_{wi} = 10\%$. The water-wet fraction was calculated with respect to the chromatographic separation area for the reference core (A_{ref}), $WI = 0.53$.

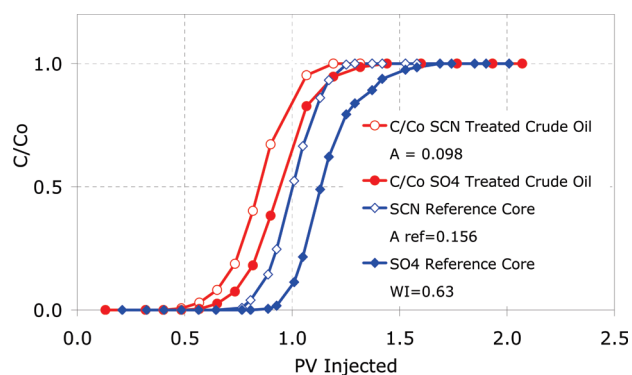


Figure 8. Initial wetting condition of a core saturated with the TO, core LSSK#6, $S_{wi} = 10\%$. The water-wet fraction was calculated with respect to the chromatographic separation area for the reference core (A_{ref}), $WI = 0.63$.

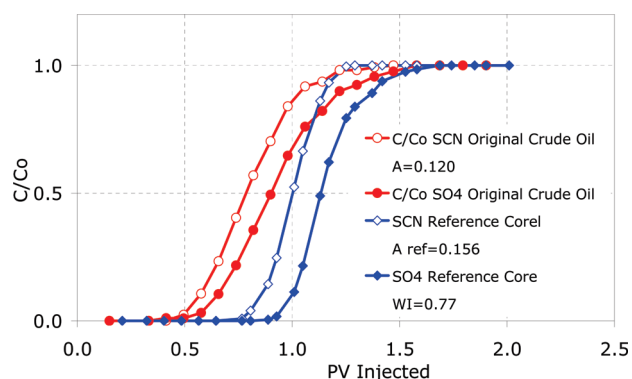


Figure 9. Wettability test after SI with SW at $110\text{ }^\circ\text{C}$. The core was saturated with OO, core SK#11, $S_{wi} = 10\%$. The water-wet fraction was calculated with respect to the chromatographic separation area for the reference core (A_{ref}), $WI = 0.77$.

corresponding water-wet fractions were calculated to be 0.53 and 0.63, respectively. This is in line with the observed difference in SI using formation water as initial imbibing fluid; i.e., the OO made the chalk less water-wet than the TO.

The wetting properties of the cores after SI with formation water and SW at $110\text{ }^\circ\text{C}$ were determined from the tests shown in Figures 9 and 10. The area between the tracer and the sulfate elution curves for the core containing the OO and TO was 0.120 and 0.148, respectively, and the corresponding

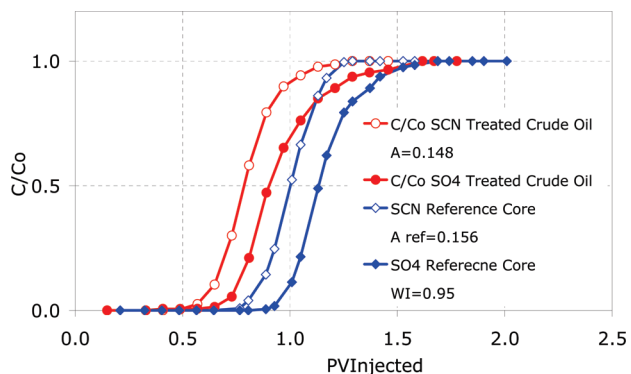


Figure 10. Wettability test after SI with SW at 110 °C. The core was saturated with TO, core SK#5, $S_{wi} = 10\%$. The water-wet fraction was calculated with respect to the chromatographic separation area for the reference core (A_{ref}), $WI = 0.95$.

Table 4. Water-Wet Fraction (WI) and Difference in Water-Wet Fraction (ΔWI %) at Initial Conditions and after SI with SW at 110 °C

water fraction	OO	TO
WI (initial)	0.53	0.63
WI (after SI)	0.77	0.95
ΔWI (%)	24	32

water-wet fractions were determined to be 0.77 and 0.95, respectively. In line with the SI data, the water-wet area increased by 32% for the core containing the TO depleted in soluble acidic material compared to an increase of 24% for the core containing the OO. A summary of the water-wet fraction calculations is given in Table 4. These observations indicate that it is easier to remove adsorbed organic material from the TO compared to that from the OO. Thus, the molecular nature of the carboxylic material will both affect the initial wetting properties and also the wettability alteration process using SW.

Conclusion

This study has shown that the chemical properties of the acids present in the crude oil have impact on the wetting properties of chalk. The tests have been performed to compare the wetting properties of chalk resulting from treatment with an OO with $AN = 1.80$ mg of KOH/g of oil and with a TO with $AN = 1.50$ mg of KOH/g of oil that has been depleted in water-soluble acids at pH 10. The results are summarized below: (1) The amount of organic acid extracted into the

aqueous phase from a crude oil is a function of the W/O and pH. (2) Chromatographic wettability tests and SI confirmed that cores saturated with oil depleted in water-soluble acids were somewhat more water-wet, indicating that water-soluble acids may affect the stability of the initial water film between the rock and oil. (3) In a SI process by wettability alteration using SW, both the rate and ultimate oil recovery were systematically higher for the cores saturated with oil depleted in water-soluble acids. (4) During SI of SW, the water-wet fraction increased from 0.53 to 0.77 and from 0.63 to 0.95 for the cores initially saturated with OO and TO, respectively. (5) Cores saturated with TO appeared to undergo wettability alteration more easily compared to the cores saturated with the OO.

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Nomenclature

A = adsorption area
 AN = acid number (mg of KOH/g)
 BN = base number (mg of KOH/g)
 C/C_o = relative concentration of ions
 D = core diameter (cm)
 DW = distilled water
 IFT = interfacial tension (mN/m)
 L = core length (cm)
 $OOIP$ = original oil in place
 OO = original crude oil
 PV = pore volume
 S_{wi} = initial water saturation (%)
 S_{oi} = initial oil saturation (%)
 S_{or} = residual oil saturation (%)
 SI = spontaneous imbibition
 SW = synthetic seawater
 $SW0T$ = synthetic seawater without SO_4^{2-}
 $SW1T$ = synthetic seawater where the concentration of SCN^- and SO_4^{2-} is 0.024 mol/L
 TO = treated crude oil
 TDS = total dissolved solids (g/L)
 VB = Valhall formation brine
 WI = water-wet surface fraction
 W/O = water/oil ratio
 Φ = porosity (%)
 μ = viscosity (cp)
 ΔWI = change in the water-wet surface fraction