

Effect of Water-Extractable Carboxylic Acids in Crude Oil on Wettability in Carbonates

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ABSTRACT: The acidic components of the crude oil have a profound effect on the initial wetting conditions and possible wettability alteration by seawater in carbonates. In this work, three types of crude oils with different concentrations of water-extractable acidic components were prepared from a base oil: (1) a reference oil, RES-40 [acid number (AN) = 1.90 mg of KOH/g and base number (BN) = 0.51 mg of KOH/g], (2) a treated oil depleted in water-extractable acidic components, termed treated oil (TO) (AN = 1.50 mg of KOH/g and BN = 0.53 mg of KOH/g), and (3) a crude oil containing only water-extractable acidic components, termed EWS-oil (AN = 1.90 mg of KOH/g and BN < 0.01 mg of KOH/g). Outcrop chalk cores were used as the porous medium, and the difference in oil displacement efficiency and wettability was compared. The spontaneous imbibition (SI) process was performed in two steps: first imbibing with formation water without any wettability modification and then with seawater, which acted as a wettability modifier. The oil recovery decreased as the content of water-extractable acidic material in the crude oil increased, for both formation water and seawater as imbibing fluids. The difference in wetting properties was also confirmed by chromatographic wettability analysis. The water wetness appeared to be lower for the cores saturated with the crude oil containing only water-extractable acids. It was concluded that water-extractable carboxylic acids present in crude oil have a great impact on the stability of the water film between the carbonate surface and the oil and seawater was less efficient as a wettability modifier when the extractable acids were adsorbed onto the carbonate surface. Observations from both SI and chromatographic wettability tests emphasize the importance of acid structures or acid types present in the crude oil compared to the acid concentrations.

INTRODUCTION

The mixed-wet or oil-wet character of carbonate reservoirs can be ascribed to the adsorption of carboxylic material from the crude oil onto the positive calcium sites on the calcite surface.^{1,2} Mechanisms by which crude oil components may adsorb on high-energy mineral surfaces include polar interaction that predominates in the absence of a water film between oil and solid, acid–base interaction, which controlled the surface charge, and ion-binding interactions between charged sites and high valent cations.^{3,4} Surface precipitation of asphaltenic material can further alter the surface wetting.^{3–6}

Both the interfacial tension (IFT) and contact angle experiments indicate that the chemical structure of the acidic material may be more important than the concentration in the oils.⁷ It is reported that crude oils with a high content of phenolic compounds and alkyl and cyclopentane/cyclohexane acids seemed to have the greatest impact on the wetting behavior of the silicate surface, whereas more complicated high-molecular ring-structured acids did not affect the wetting behavior significantly.^{7,8}

The differences between the organic acids of biodegraded and non-biodegraded oils have been studied previously.⁸ The biodegraded oils have higher total acid and total base content, by both titration and extraction. The molecular-weight ranges of the extracted acids are lowest in the biodegraded oils, and the equivalent weight calculations indicated a dominance of multifunctional molecules. The extracted acids from biodegraded oils were more carboxylic and aliphatic, while the non-biodegraded oils were more phenolic. A wider range of acidic compounds in the crude oil has been investigated, especially with the use of mass

spectrometric techniques,^{9,10} 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.¹¹

The basic material in crude oils has a minor effect on wetting properties, but it was observed that the presence of natural basic material increased the water wetness of chalk. It was suggested that the basic components formed an acid–base complex in crude oil and, in that way, partly prevented adsorption of carboxylic material onto the carbonate surface.¹²

Dependent upon the oil properties, the water-extractable carboxylic acids are usually a small fraction of the total amount of the acidic material present in the crude oil. It is reported that chalk cores saturated and aged with the crude oil depleted in water-extractable carboxylic acids, resulting in a high water-wet fraction using a chromatographic wettability test.¹³ Furthermore, in a spontaneous imbibition (SI) process by wettability alteration using seawater, both the rate and ultimate oil recovery were systematically higher for the cores saturated with oil depleted in water-extractable acids. The observations indicated that water-extractable acids may affect the stability of the initial water film between the rock and oil.

In this work, carboxylic acids were extracted from a crude oil with a high acid number. The crude oil, which was depleted in polar components by silica, was spiked with the water-extractable

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Table 1. Crude Oil Properties

	density ^a (g/cm ³)	AN (mg of KOH/g)	BN (mg of KOH/g)	viscosity ^a (cp)	remarks
base oil	0.8856	2.82	1.13	20.47	recently sampled crude oil
RES-40 oil	0.8087	1.90	0.51	3.38	diluting base oil with 40 vol % <i>n</i> -heptane
EWS-oil	0.8094	1.90	>0.01	3.01	containing only water-extractable acidic components
RES-40 oil silica	0.8013	>0.01	>0.01	2.44	depleted in polar components by active silica gel
TO	0.814	1.5	0.53	3.01	depleted only in water-extractable acids

^a Density and viscosity were determined at room temperature.

acids. The behavior/property of this new crude oil was then compared to the original crude oil with regard to wetting properties and oil recovery by SI from chalk cores. Furthermore, the results were compared to a previous study on the same crude oil, which was depleted in water-extractable acids. The objective of the investigation is to obtain a better understanding of the impact of acidic material on wetting properties and water-based oil recovery by wettability alteration.

MATERIALS AND METHODS

Rock Material. Outcrop Stevns Klint chalk from a quarry near Copenhagen, Denmark, was used as the porous medium. The Stevns Klint is of Maastrichian age and is a soft and highly porous material. The porosity is about 45–50%, and the permeability is low, in the range of 1–3 mD. The chalk materials have a specific area of about 2.0 m²/g.^{14,15}

Crude Oils. A biodegraded crude oil with an initial acid number (AN) = 2.78 mg of KOH/g and a base number (BN) = 1.13 mg of KOH/g was used as the base oil. The oil was sampled from a new well during a well test. Two types of test oils with different concentrations of water-extractable acidic components were prepared, RES-40 and EWS-oil. The RES-40 oil was made by diluting the base oil with 40 vol % *n*-heptane. The mixture was centrifuged and filtered through a 5 μm Millipore filter. No precipitation of asphaltic material was observed during storage. The EWS-oil was prepared by adding water-extractable acidic material from the base oil into a RES-40 oil sample depleted in polar components. The RES-40 oil depleted in polar components was prepared by adsorbing the polar components onto an active silica gel, termed RES-40 silica.¹⁶ About 10 wt % of silica gel was added to the original crude oil, RES-40, and the mixture was stirred at room temperature for 3 days. Then, a similar amount of silica gel was added to the mixture, and it was stirred for 2 more days. The testing oil was then centrifuged and filtered through 0.65 Millipore filter, and it was confirmed that the AN and BN were <0.01 mg of KOH/g.

The treated oil (TO) was the RES-40 oil depleted in water-extractable acids, which was used in a previous study.¹³ The crude oil was prepared by extracting the water-extractable acidic components from the original RES-40 oil. Density and viscosity of the crude oils were measured at room temperature using a DMA 4500 density meter and a Physica UDS 200 viscometer. The properties of the crude oils are given in Table 1.

AN and BN Measurements. A Mettler Toledo DL55 auto-titrator was used to measure the AN and BN for the different crude oils. This method involves potentiometric titrations using an internal standard. The method used was developed by Fan and Buckley,¹⁷ which is a modified variation of ASTM D2896 for the BN and ASTM D664 for AN titration.^{18,19}

Brines. Formation brine and seawater were made and termed VB and SW, respectively (Table 2). The chromatography wettability tests were performed using the brines termed SW0T and SW1/2T. During the SI process, both VB and SW were applied as the imbibing fluids. The brines were made by adding different salts to distilled water, and prior to use, the brines were filtered through a 0.22 μm filter and degassed.

Table 2. Brine Compositions (mol/L)

	VB	SW	SW0T	SW1/2T
HCO ₃ ⁻	0.009	0.002	0.002	0.002
Cl ⁻	1.066	0.525	0.583	0.538
SO ₄ ²⁻		0.024		0.012
SCN ⁻				0.012
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	0.427
Li ⁺				0.012
K ⁺	0.005	0.010	0.010	0.022
total dissolved solids (TDS) (g/L)	62.8	33.4	33.39	33.39
ionic strength	1.112	0.657	0.643	0.647

Core Preparation. The cylindrical cores were drilled out from the same chalk block by an oversized bit, shaved in a lathe to a diameter of ~38.1 mm, and cut to a length of ~70 mm. The cores were placed in a Hassler core holder and cleaned according to the method described by Puntervold et al.²⁰ The cores were flooded by 250 mL of distilled water at a rate of 0.2 mL/min at 50 °C to remove soluble salts. 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 core data are given in Table 3.

The initial water saturation, *S*_{wi}, of 10% was obtained by draining the cores saturated with VB on a porous plate using water-saturated N₂ gas. The cores were then placed in a Hassler core holder with a confining pressure not exceeding 25 bar and flooded with 1.5 pore volume (PV) of crude oil at a rate of 0.2 mL/min in each direction at 50 °C. 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.

Extraction of Water-Soluble Acids from the Crude Oil. Water-extractable acids are defined in this study as a small fraction of the carboxylic acids in the crude oil that can be extracted from the oil into the aqueous phase at a volumetric water/oil ratio (W/O) of 2.0 and pH of 10. The procedure for the extraction of the acid fraction has been described previously.^{8,10,13,21} The alkaline extraction of carboxylic acid was performed using the base oil, with AN = 2.82 mg of KOH/g and BN = 1.13 mg of KOH/g. The volume ratio of distilled water and oil was 2.0. The pH was increased to 10 by adding small amounts of a sodium hydroxide solution (1.0 M NaOH). The mixture was stirred in the air-tight condition vigorously on a magnetic stirrer, and the pH of the mixture was kept constant (pH 10) for 24 h. An emulsion was formed as a result of the strong mixing of oil and water, and the mixture was centrifuged to separate the oil and water phase. The aqueous phase, containing the water-extractable acids, was separated, and the pH was adjusted to 2 by adding a hydrochloric acid solution (3.0 M HCl). The acidic material was extracted into dichloromethane, CH₂Cl₂, using a mixing ratio of 1:1. The dichloromethane was evaporated, and the water-extractable acidic material was added to the RES-40 oil depleted in polar

Table 3. Core Properties

core ID	L (mm)	D (mm)	pore volume (mL)	Φ (%)	S_{wi} (%)	S_{oi} (%)	crude oil
MH#1	70.2	38.1	36.08	45	11	89	EWS-oil
MH#2	70.6	38.0	36.40	45	11	89	EWS-oil
MH#3	70.2	38.1	35.93	44	11	89	RES-40 oil
MH#4	70.2	38.1	36.45	45	10	90	RES-40 oil
MH#5	70	38	36.0	45			clean reference core

components to prepare the EWS-oil with AN similar to the AN of the RES-40 oil (1.90 mg of KOH/g). The EWS-oil was treated with distilled water in two steps at a ratio of 50:50 vol % to remove inorganic acidic material. The testing oil was filtered through a 5 μ m Millipore filter, and the AN and BN were determined to be 1.90 and <0.01 mg of KOH/g, respectively. The oil was then mixed with the VB formation water in the same ratio as the initial core saturations, i.e., \approx 10 vol % water. After equilibration, the solution was stirred for 24 h and the pH was determined to be close to 7.

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 μ L/min to reduce the sensitivity of measurements to the injection rate.

SI. The aged cores were immersed in the imbibing fluid in sealed steel cells. The SI tests were performed at 110 $^{\circ}$ C, with a back pressure of 10 bar to avoid boiling of the fluids. The cores were first imbibed with VB until the production plateau was reached, and then the imbibing fluid was switched to SW. The produced oil during the test was collected in a buret, and oil recovery was determined versus time and calculated as a percentage of original oil in place (% OOIP).

Chromatographic Wettability Test. The chromatographic wettability test for carbonates, described previously by Strand et al., was used to determine the water-wet fraction of the rock surface.²² The principle of the test is based on a chromatographic separation between a tracer (SCN^- or Li^+) and sulfate (SO_4^{2-}).

The core was flooded with SW0T at a rate of 1 PV/day, followed by a rate of 0.20 mL/min to establish residual oil saturation. Next, the core was flooded with at least 2.0 PV of SW1/2T brine (containing SO_4^{2-} and the tracer SCN^-) at a rate of 0.20 mL/min. The effluent was collected in fractions of 1–4 mL using a fraction collector. The fractions were diluted 200 times by a Gilson Gx-271 liquid handler and analyzed for the concentration of SO_4^{2-} and tracer, SCN^- , using a Dionex ICS-3000 ion chromatograph. The concentration relative to the initial concentration was plotted against the injected pore volume. The area between the tracer curve and the sulfate curve is directly proportional to the water-wet area inside the core because the chromatographic separation only takes place at the water-wet sites. The area ratio between the tracer and sulfate curve for the sample at residual oil saturation, A_{wet} , and the corresponding area for 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 the neutral wetting state, and WI = 1 is completely water-wet.

The error in the reproducibility of the calculated area between the tracer and sulfate curve was less than 0.5% between different cores, as reported by Strand et al.²²

RESULTS AND DISCUSSION

Water-Extractable Acids in Crude Oil. The water-extractable components in the crude oil are believed to be a small fraction of

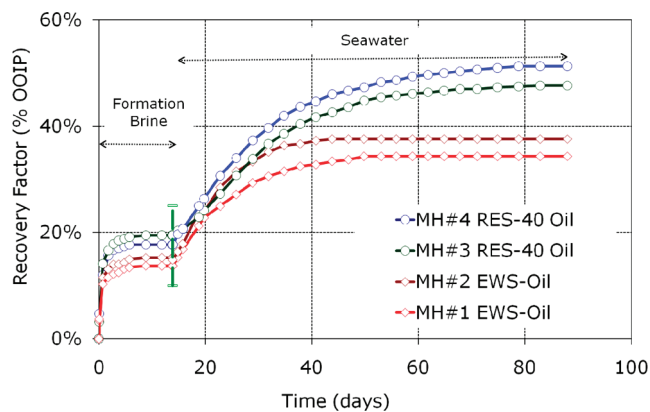


Figure 1. SI into chalk cores saturated with different crude oils, RES-40 oil and EWS-oil. SI was performed by VB followed by SW as the imbibing fluids at 110 $^{\circ}$ C and $S_{wi} = 10\%$.

the total amount of acids present in the crude oil. The amount of extractable water-soluble acids in the crude oil is quantitatively studied previously using an auto-titrator in a two-phase titration mode and is a function of pH and the W/O. In a mixture of aqueous phase and crude oil, the amount of water-extracted acids decreased as the pH and W/O decreased.¹³

In the present study, the extraction was performed at pH 10 at a W/O of 2.0. The acids were back-extracted from the aqueous phase according to the procedure described in the experimental description. The extracted acids were recovered by back-extracting into dichloromethane at pH 2 and evaporating the solvent. The EWS-oil was prepared by adding extractable acids to the crude oil, which was depleted in polar components by active silica gel. Therefore, EWS-oil contained mainly water-extractable acids as polar components. The EWS-oil was then mixed with the VB in the same ratio as for the initial core saturation, i.e., \approx 10 vol % water. After equilibration of the solution for 24 h, the pH was determined to be close to 7, confirming that the presence of HCl was negligible.

SI. The oil recovery by SI of VB and SW was compared for the cores containing the original oil, RES-40, and the EWS-oil containing only water-extractable acids as the polar components. The imbibition was performed at 110 $^{\circ}$ C with a back pressure of 10 bar. Two parallel cores were prepared for each of the crude oils to confirm the experimental reproducibility of the results.

When formation water was used as the imbibing fluid, the oil recovery from the cores containing the original oil was systematically higher than the oil recovery for the cores containing the EWS-oil, at about 19 and 14% of OOIP, respectively (Figure 1). The difference in the recovery from the two test series was about 5% of OOIP, and the imbibition curves were very reproducible for each of the test series. Because the imbibing fluid was the same as the VB, no wettability alteration is supposed to take place

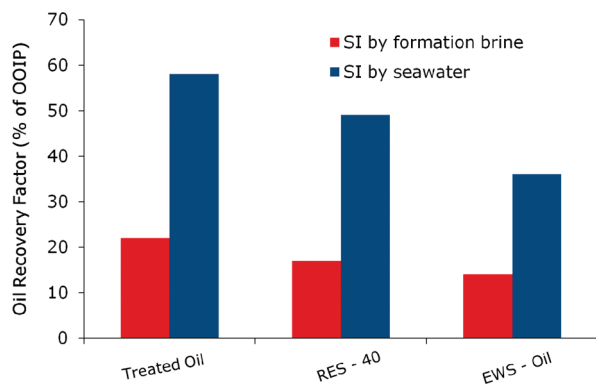


Figure 2. Effect of water-extractable acidic components in the crude oil on the oil recovery during SI by VB and SW, with $T = 110\text{ }^{\circ}\text{C}$ and $S_{wi} = 10\%$. Crude oils: TO, depleted in water-extractable acids, RES-40 oil, and EWS-oil containing only water-extractable acids.

during the oil displacement process. The difference in the oil recovery by VB is directly related to the initial wetting condition, resulting from the adsorption of the polar components on the positively charged rock surface.

After 14 days of imbibition with VB, the imbibing fluid was changed to SW. A dramatic increase in oil recovery was observed in both systems (Figure 1). The average oil recovery after 88 days was 49 and 36% of OOIP for the cores saturated with the RES-40 and EWS-oil, respectively. The difference in the oil recovery factor was about 13% of OOIP. The increase in oil recovery is related to the properties of SW to increase the water wetness of the rock surface.²³ The potential determining ions present in the SW, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , have great influence on the surface charge of chalk. The interactions between the chalk surface and these potential determining ions are responsible for the wettability modification of the chalk.

Previously, we have discussed the difference in oil recovery from chalk cores saturated with the original RES-40 oil and the RES-40 oil depleted in water-extractable acids, termed TO.¹³ The AN and BN of the TO was 1.50 and 0.53 mg of KOH/g, respectively, as shown in Table 1. The tests were performed under the same conditions as for the present study. The results of the imbibition studies are summarized in Figure 2. In all cases, the SI was performed using VB followed by SW as the imbibing fluids. The oil recovery from imbibition studies using the VB and SW was in the following order: TO > RES-40 > EWS-oil. Figure 2 shows the relative dependence of the displacement efficiency related to the amount of the water-extractable components in the crude oil. The highest oil recovery was achieved for the crude oil depleted in water-extractable acidic components.

The difference in oil recovery between TO, RES-40, and EWS-oil using VB as the imbibing fluid is related to the difference in initial wetting conditions, resulting from the different polar components in the crude oils. The AN was lower for the TO because it was depleted in the water-extractable acids (1.50 mg of KOH/g). By experience, as the AN of the crude oil increased above 1 mg of KOH/g, the wetting properties were not changed very much.²⁴ The BN for the TO and RES-40 was quite similar, 0.53 and 0.51 mg of KOH/g, respectively. The basic material in crude oils has a minor effect on wetting properties, but it may increase the water wetness a little probably because of complex formation between acids and bases in the crude oil, which will partly prevent adsorption of carboxylic material onto the carbonate

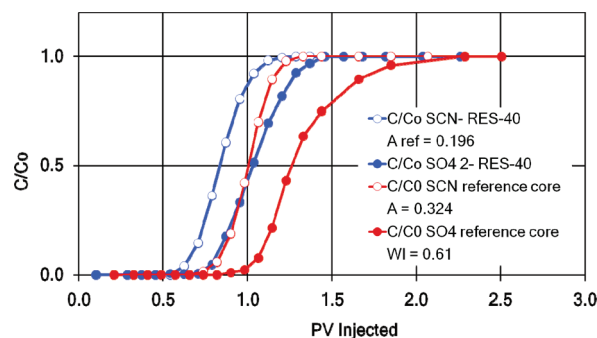


Figure 3. Chromatographic wettability test after SI with VB and SW at $110\text{ }^{\circ}\text{C}$. The core was saturated with RES-40 crude oil, core MH#3, at $S_{wi} = 10\%$. The water-wet fraction was calculated with respect to the chromatographic separation area for the reference core, A_{ref} at $WI = 0.61$.

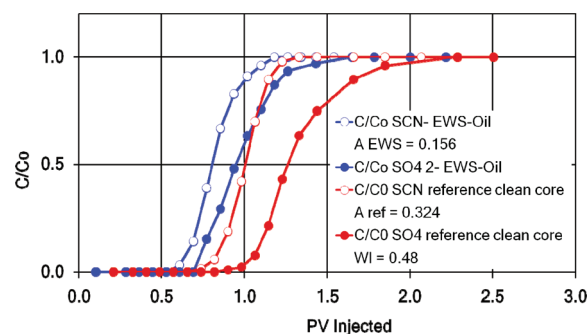


Figure 4. Chromatographic wettability test after SI with SW at $110\text{ }^{\circ}\text{C}$. The core was saturated with EWS-oil crude oil, core MH#2, at $S_{wi} = 10\%$. The water-wet fraction was calculated with respect to the chromatographic separation area for the reference core, A_{ref} at $WI = 0.48$.

surface.¹² Because of the fact that the BN is the same in the TO and RES-40 (about 0.51 mg of KOH/g), it is suggested that the difference in oil recovery was mainly related to a different initial wetting condition.

The lowest oil recovery, using both VB and SW as the imbibing fluids, was observed for the core containing the oil spiked with water-extractable acids, the EWS-oil (Figure 2). The amount of basic material in this crude oil was negligible ($\text{BN} < 0.01$ mg of KOH/g), which caused the acidic material to be more reactive toward the chalk surface. Furthermore, the strong affinity of water-extractable acids toward the chalk surface also resulted in the lowest recovery of oil by wettability alteration using SW.

The difference in oil recovery by wettability alteration using SW was discussed in relation to different affinities of carboxylic material toward the carbonate surface; i.e., it appeared to be more difficult to remove water-extractable acidic material from the surface (Figure 2).

Wettability Analysis. The water-wet fraction of the rock surface after the SI process was determined using chromatographic wettability tests. The water-wet fraction is the ratio of the chromatographic separation area between the effluent curves (SCN^- and SO_4^{2-}) at the residual oil saturation divided by the chromatographic separation area for a completely clean reference core.

Chromatographic wettability tests after the SI process for the core containing the original oil, RES-40, and EWS-oil are shown in Figures 3 and 4. From the chromatographic analysis on a clean reference core, i.e., a core flooded with distilled water to remove

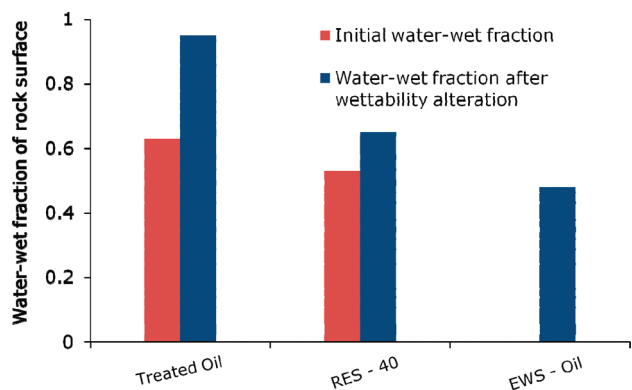


Figure 5. Water-wet fraction of the rock surface at the initial conditions and after wettability alteration by SW at 110 °C. Crude oils: TO depleted in water-extractable acids, RES-40 oil, and EWS-oil containing only water-extractable acids.

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

water fraction	original RES-40 oil	TO	EWS-oil
WI (initial)	0.53	0.63	
WI (after SI)	0.61	0.95	0.48
Δ WI (%)	8	32	

dissolvable inorganic salts, the area between the tracer and sulfate curves was measured to be 0.324. On the basis of the chromatographic data from the reference core, the water-wet fraction of the cores containing RES-40 and EWS-oil was calculated. The chromatographic separation area between the tracer and sulfate curves was 0.196 and 0.156 for cores containing RES-40 and EWS-oil, and the corresponding water-wet fraction was calculated to be 0.61 and 0.48, respectively.

The results of the wettability analysis together with the corresponding data for the TO, depleted in water-extractable acidic components, are summarized in Figure 5. The initial water-wet fraction of the core containing the TO was about 0.63, while the corresponding value for the core containing the RES-40 oil was 0.53 (Figure 5 and Table 4). Thus, it appeared that water-extractable acids in the crude oil have a greater tendency to break the water film at the carbonate surface, resulting in a decreased water wetness of the rock.

The water wetness of the cores after the imbibition process was in the order of TO > RES-40 > EWS-oil. The water-wet fraction after imbibitions was 0.95, 0.61, and 0.48 for the cores containing TO, RES-40, and EWS-oil, which is also reflected in the difference in oil recovery by SI (Figures 1 and 2). The neutral wetting condition of the cores containing EWS-oil (WI = 0.48) after the imbibition process supported the fact that the water-extractable acidic material was more difficult to remove from the chalk surface in a wettability alteration process.

IFT and Viscosity. The IFT between the crude oil and water will also affect the oil recovery in a SI process. There was a small difference in the IFT values at high rates of injection, but the IFT values appeared to converge to the same value at low rate of injection, at about 12 mN/m (Figure 6). Thus, the small differences in IFT cannot explain the observed difference in oil recovery. The base oil should not be contaminated by the

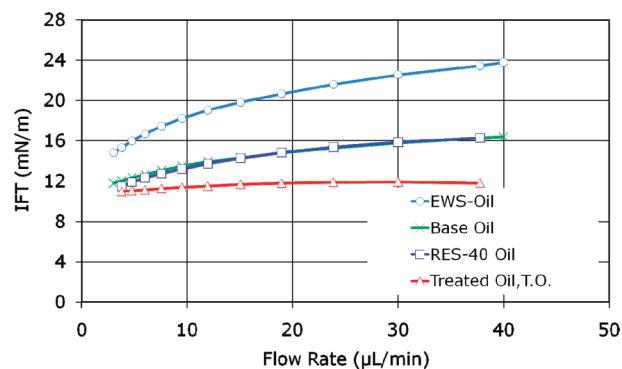


Figure 6. IFT between different crude oils and SW at ambient temperature and different rates of injection using the drop volume tensiometer. Crude oils: EWS-oil containing only water-extractable acids, base crude oil, original RES-40 oil, and TO depleted in water-extractable acids.

production chemicals because the well was newly drilled and only used for the well test.

Viscosity will always play an important role in oil displacement by water. Low viscosity oil is easily displaced from the porous medium than high viscosity oil. The viscosity of the RES-40 crude oil is slightly higher than the viscosity of the EWS-oil, 3.38 and 3.01 cP, respectively, at room temperature (Table 1). Therefore, the difference in oil recovery between the test series cannot be a viscosity effect.

The results from this work together with the previous study¹³ indicate that the chemical properties of the acids present in the crude oil are very important with regard to wetting conditions of carbonates. Thus, 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 has also influence on the initial wetting and the wettability alteration process.

CONCLUSION

Water-extractable acids in the crude oil will have impact on initial wetting conditions as well as the efficiency of SW to act as a wettability modifier in a SI process. The wetting condition and oil recovery from chalk cores saturated with (1) a reference oil RES-40 (AN = 1.90 mg of KOH/g and BN = 0.51 mg of KOH/g), (2) a treated oil depleted in water-extractable acidic material, TO (AN = 1.50 mg of KOH/g and BN = 0.53 mg of KOH/g), and (3) an oil containing only water-extractable acidic material, termed EWS-oil (AN = 1.90 mg of KOH/g and BN < 0.01 mg of KOH/g) were compared. The experimental results are summarized as follows: (1) The oil recovery by SI of VB without wettability alteration at 110 °C decreased in the order of TO > RES-40 > EWS-oil. The oil recovery was in the range of 14–22% of OOIP. (2) In the tertiary imbibition process using SW as imbibing fluid, the oil recovery increased dramatically but the order of recovery was the same: TO > RES-40 > EWS-oil. The oil recovery was in the range of 36–58% of OOIP. (3) Chromatographic wettability tests after the SI tests confirmed that the water wetness of the cores was in the order of TO > RES-40 > EWS-oil. The water-wet surface fraction of the cores varied between 0.48 and 0.95. (4) As a general conclusion, it appeared that the presence of water-extractable acids in the crude oil has a significant influence on both the initial wetting conditions and

also the effect of SW to act as a wettability modifier. Water-extractable acids appeared to break the water film between the rock and the oil more easily, which decreased the water wetness of the rock. SW, as a wettability modifier, appeared to be less efficient on carbonate cores containing oils with water-extractable acids.

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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)

EWS-oil = crude oil containing only water-extractable acidic components with $AN = 1.9$ mg of KOH/g

DW = distilled water

L = core length (cm)

OOIP = original oil in place

PV = pore volume

RES-40 = original RES-40 oil with $AN = 1.9$ mg of KOH/g

RES-40 silica = RES-40 oil depleted in polar components by silica gel, AN and $BN < \text{mg of KOH/g}$

S_{wi} = initial water saturation (%)

S_{oi} = initial oil saturation (%)

S_{or} = residual oil saturation (%)

SW = synthetic seawater

SW0T = synthetic seawater without SO_4^{2-}

SW1/2T = synthetic seawater where the concentration of SCN^- and SO_4^{2-} is 0.012 mol/L

TO = treated crude oil that is depleted in water-extractable acidic components

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

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