

# Effect of ionic composition in water: oil interactions in adjusted brine chemistry waterflooding: preliminary results

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## Abstract

Low salinity or adjusted brine composition waterflooding (LSW or ABCW) is considered a promising improved/enhanced oil recovery (IOR/EOR) method. Despite the large number of studies documented in the literature, there are contradictory results and a lack of consensus regarding the mechanisms that operate in this recovery process. The proposed fluid:rock and fluid:fluid mechanisms are still under discussion and investigation. However, the impact of oil geochemistry and its importance on the fluid:fluid interactions that can occur with brines during LSW or ABCW have been overlooked and studied in a lesser extent. The scope of the present study is to preliminary evaluate crude oil:brine interactions to validate the influence of its compositions. These interactions were evaluated at static conditions for a week and reservoir temperature (60°C) using two oil samples from different Colombian basins and brine solutions of different composition at a constant ionic strength ( $I = 0.086$ ). Specifically, this investigation evaluated the effect of the type of cation ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) and anion ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) on crude oil:brine interactions. The results of these experiments were compared with tests using distilled water (DW). Although a basic characterization of brines (i.e. pH, alkalinity and ionic composition) and oil (oil viscosity) was performed, the main objective of this study is the analysis of water-soluble organic compounds (WSOC) using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). The results demonstrate that water:oil interactions are dependent on brine and crude oil compositions. The main changes observed in the aqueous phase were the increase in inorganic components (desalting effects) and organic compounds soluble in water. Only the system crude oil A and NaCl (5,000 ppm) showed the formation of a micro dispersion. Negative electrospray ionization (ESI (-)) FT-ICR MS data shows that WSOC's identified in DW and  $\text{Na}_2\text{SO}_4$  after the interaction with crude oil A belongs to similar classes but there is marked selectivity of species solubilized with different brines. The relative abundance of classes  $\text{O}_x$ ,  $\text{O}_x\text{S}$  and  $\text{NO}_x$  ( $x > 2$ ) decreases while  $\text{O}_x$ ,  $\text{O}_x\text{S}$  and  $\text{NO}_x$  ( $x \leq 2$ ) increase their solubility in the presence of  $\text{Na}_2\text{SO}_4$  compared to DW. The analysis of O2 and O3S classes using double bond equivalence (DBE) vs. carbon number (CN) contour plots shows that the isoabundance of water-soluble species are within the range of DBE  $\leq 10$  and CN  $\leq 20$  regardless the brine used in the experiments. Finally, the method of solvent extraction in silica columns used in this investigation for the analysis of WSOC using FT-ICR MS represents a powerful and new approach to study LSW and ABCW.

**Keywords:** Low Salinity Waterflooding (LSW), Adjusted Brine Composition Waterflooding (ABCW), Improved Oil Recovery (IOR), Enhanced Oil Recovery (EOR), Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS), Electrospray Ionization (ESI).

## Efecto de la composición iónica en interacciones crudo: salmuera en la inyección de agua de composición química controlada: resultados preliminares

## Resumen

La inyección de agua de baja salinidad (LSW) o de composición química modificada (ABCW) ha generado un gran interés como método de recobro mejorado (IOR/EOR). A pesar de múltiples estudios documentados en la literatura, se destaca que no existe un acuerdo respecto a los mecanismos que operan en este proceso de recobro e incluso se evidencian resultados contradictorios.

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Lo anterior se valida con el aumento del interés de investigar los posibles mecanismos a través de estudios de interacciones fluido:fluido y fluido:roca. Sin embargo, el impacto de la geoquímica de crudos y su importancia durante las interacciones fluido:fluido que pueden ocurrir durante LSW y ABCW no han sido estudiadas en profundidad. El presente estudio consiste en evaluar interacciones crudo:salmuera para validar la influencia de sus composiciones. El estudio se basó en experimentos en condiciones estáticas por una semana a temperatura de yacimiento (60°C) utilizando dos muestras de crudos colombianos y salmueras de diferentes composiciones a fuerza iónica constante ( $I = 0,086$ ). Específicamente, esta investigación evaluó el efecto del catión ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) y del anión ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) en las interacciones crudo:salmuera. Los resultados de estos experimentos fueron comparados con pruebas realizadas con agua destilada (DW). Aun cuando se desarrolla una caracterización básica de las fases acuosas (p.e. pH, alcalinidad y composición iónica) y oleica (viscosidad), el objetivo principal de este estudio es el análisis de compuestos orgánicos solubles en agua (WSOC) utilizando la técnica de Petroléomica (FT-ICR MS). Los resultados demuestran que las interacciones crudo:salmuera dependen de la composición de cada una de las fases. Los mayores cambios observados en la fase acuosa fue el incremento de especies inorgánicas (desalado de crudo) y de compuestos orgánicos solubles en agua. Solo el sistema crudo A y NaCl (5000 ppm) mostró la formación de una micro-dispersión. Los resultados de FT-ICR MS en modo de ionización negativa (ESI (-)) muestran que los WSOC transferidos de la fase oleica a la acuosa con DW y  $\text{Na}_2\text{SO}_4$  después de la interacción con el crudo A pertenecen a las mismas clases. Sin embargo, se evidencia una clara selectividad de las especies solubilizadas con las diferentes soluciones acuosas. La abundancia relativa de las clases  $\text{O}_x$ ,  $\text{O}_x\text{S}$  and  $\text{NO}_x$  ( $x > 2$ ) disminuyen mientras que las de las clases  $\text{O}_x$ ,  $\text{O}_x\text{S}$  and  $\text{NO}_x$  ( $x \leq 2$ ) aumentan su solubilidad en presencia de  $\text{Na}_2\text{SO}_4$  comparado con DW. A partir del análisis de las clases  $\text{O}_2$  y  $\text{O}_3\text{S}$  empleando mapas de contorno de Equivalencia de Doble Enlace (DBE) vs. Número de Carbono (CN) muestran que la iso-abundancia de especies solubles en agua se encuentra en el intervalo DBE  $\leq 10$  y CN  $\leq 20$  independientemente de la salmuera empleada. Finalmente, el método de extracción por solventes en columnas de sílice empleado en esta investigación para el análisis de WSOC utilizando la técnica de FT-ICR MS representa un nuevo y poderoso enfoque para el estudio de procesos LSW y ABCW.

**Palabras clave:** Inyección de agua de baja salinidad (LSW), inyección de agua de composición química controlada (ABCW), recuperación mejorada (IOR/EOR), Petroléomica, Transformada De Fourier-Resonancia de Ciclotrón Iónica- Espectrometría de Masas (FT-ICR MS), Electro Pulverización Iónica (ESI).

## Introduction

The injection of Low Salinity Water (LSW) is considered a promising method for improving oil recovery. This injection technique is gaining attention based on the multiple research documented in the literature. LSW is also referred in the literature as Advanced Ion Management, Designer Water Flood, Engineered Water Flooding, LoSal™ and Smart Water Flood, among others (Al-Shalabi & Sepehrnoori, 2016) (Kilybay, Ghosh & Thomas, 2017). For simplicity and integrate different concepts and approaches, in this paper authors will use the term Adjusted Brine Chemistry Waterflooding or ABCW (Alvarado, Garcia-Olvera & Manrique, 2015).

The increase of oil recoveries using low (fresh) salinity waters was first reported at lab scale by Bernard (1967). Incremental oil recoveries were attributed to fluid:rock interactions, specifically due to clay migration and/or swelling. As of today, there is no consensus regarding the mechanisms operating during ABCW. In fact, there are conflicting results between different studies that explains the difficulties to interpret existing experimental results (Skauge, 2013) (Fjelde, Polanska, Taghiyev & Asen, 2013) (Al-Shalabi & Sepehrnoori, 2016) (Martin & Páez, 2017). It is clear that both, fluid:rock and fluid:fluid interactions play a key role in ABCW. Hence and given the nature of each reservoir,

ABCW mechanisms are reservoir dependent making difficult to propose a general screening criteria for this recovery method.

It is important to mention that most of ABCW research have been mainly focused on the fluid:rock interaction. However, the impact of the oil geochemistry/composition on fluid:fluid interactions during ABCW have been overlooked and studied in a lesser extent. This is somehow surprising based on the evidences of organic compound transfer from the oil to the water phase in different processes well documented in the literature. Some examples include but are not limited to:

- Willey, Kharaka, Presser, Rapp & Barnes (1975) and Palandri & Reed (2001) reported the importance of the presence of organic acid anions (OAA) in the total alkalinity of oilfield waters. They also report that the OAA are potential sources of  $\text{CO}_2$  (thermal decarboxylation) and buffering agents in reservoir waters. The presence of OAA can also explain the super saturation of aluminum, calcium and iron (among others) in reservoir waters due to the capacity of OAA to form complexes with these cations in aqueous solutions.
- Fisher (1987), Surdam & MacGowan (1987), MacGowan & Surdam (1988) and Helgeson, Knox, Owens & Shock (1993) reported studies evaluating

the origin, distribution and types of low molecular organic acids soluble in formation waters of sedimentary basins for oil and gas exploration, the interpretation of geologic systems and to interpret fluid:rock interactions in oil reservoirs such as mineral dissolution (i.e. porosity increase) during diagenetic processes.

- Lafargue & Barker (1988) and Larter & Aplin (1999) reported the importance of water washing effects in organic geochemistry and its potential applications for exploration, reservoir characterization and monitoring. Water washing is the stripping of water-soluble organic compounds from the oil into the aqueous phase. Additionally, Lafargue & Barker (1988) concluded that water washing was more effective in fresher waters and higher temperatures.
- Khatib & Salanitro (1997) proposed the mechanisms of reservoir souring and suggested that the main variables responsible of these souring effects appears to be the sulfate concentration, organic acid content (i.e. low molecular weight carboxylic and fatty acids) and the salinity of produced waters.
- Kaasa & Østvold (1997) and Wang et al. (2014) also demonstrated the influence of the presence of organic acids naturally present in formation waters on water total alkalinity. In simple terms the alkalinity of produced waters can be expressed with the following equation:  $\text{Alkalinity} \approx [\text{HCO}_3^-] + \Sigma [\text{organic acid anions}]$ .

However, most recently the effect of fluid:fluid (crude oil:brine) interactions on the recovery mechanisms of ABCW have been recognized. Some studies addressing the importance of water-soluble organic anions in ABCW are summarized below:

- Wang & Alvarado (2011) report that in general low ionic strength brines favors the formation of stable water-in-oil emulsions. They also found that as the oil-to-water ratio increase emulsion stability also increase suggesting that the interfacial-active fractions from the oil plays an important role on emulsion stability.
- Fjelde et al., (2013) reported that the retention of polar compounds present in the crude oil onto minerals and sandstone rock depend on brine composition. Additionally, the retention of these polar compounds onto sandstone rock increased with the increasing total concentration of divalent cations onto clay surfaces.
- Mahzari & Sohrabi (2015) documented the contribution of the formation of micro-dispersions on incremental oil recoveries at lab scale. This

study concluded that the incremental oil recoveries recorded during Low Salinity Water Injection (LSWI) experiments decreased when the micro-dispersions were removed from the oil.

- Chakravarty, Fosbøl & Thomsen (2015) demonstrated that the brine solution can alter the micro forces at the oil-water interface. This research found that the brine concentration has a significant effect on the amount of emulsion formed and that its formation significantly depends on the crude oil composition.
- García-Olvera, Reilly, Lehmann & Alvarado (2016) reported that the emulsion stability is a complex function of the dynamic interfacial properties and does not correlate to oil recovery. They also observed that the organic acids present in oil play an important role in the values of the viscous and elastic components of the interface rheological characteristics. Additionally, and as expected, the organic acid distribution was found to be oil specific based on <sup>1</sup>H NMR (Proton Nuclear Magnetic Resonance) data summarized in this study.
- Ayirala, Li, Saleh, Xu & Yousef (2018) studied the effects of salinity and water ions on crude oil-Water Interface identifying that higher interfacial tensions (IFT) were obtained with deionized (DI) water vs. brines at elevated temperature. They also found that the IFT in the same brine were generally higher at ambient temperature compared to elevated temperature. Finally, DI and sulfate-rich brine showed a delayed coalescence of crude oil droplets with respect high salinity multivalent brine containing calcium and magnesium.

Collins et al., (2018) reported the changes of crude oil composition during low salinity waterflooding (LSW) using High Resolution Mass Spectrometry (HRMS). The results of this research confirmed the changes in composition of the produced oil during the low salinity brine injection. This study also reports that the release of fatty acids is consistent with LSW mechanisms involving wettability changes due to binding of polar molecules, especially carboxylic acids, at the rock surface.

The main objective of this work is to preliminary evaluate crude oil:brine interactions to validate the influence of its compositions. This study will summarize preliminary results of a larger research program evaluating ABCW. The study was developed by means of static experiments using two oil samples from different Colombian basins and brine solutions of different composition at a constant ionic strength. Specifically, this investigation evaluated the effect of the type of cation ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) and anion

(Cl<sup>-</sup> and SO<sub>4</sub><sup>=</sup>) on crude oil: brine interactions. The results of these experiments were compared with tests using distilled water (DW). The evaluation of the crude oil:brine interactions was performed by measuring possible changes in the water (i.e. pH, alkalinity, ionic composition and water-soluble organic compounds) and the oil (i.e. viscosity) phase. Finally, the analysis of water-soluble organic compounds transferred from the crude oil were analyzed using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS).

## Experimental Study

Table 1 summarizes the main properties of crude oils used in this investigation. Oil sampling procedures were performed in separator tests after few days flowing without any chemical treatment. The oil:water interfacial tension (IFT) of both oil samples were measured to discard possible contaminants with chemicals. The IFT measured for crude oils A and B in DW water was 30.2 dynes/cm and 31.2 dynes/cm, respectively. These values are considered reasonable and within the acceptable ranges for laboratory experiments. No further treatment were performed to the oil samples avoiding any possible alteration compared to current oil properties at reservoir conditions, except for the gas in solution liberated during the sampling.

**Table 1.** Main properties of Colombian crude oils evaluated.

| Property              | Oil A | Oil B |
|-----------------------|-------|-------|
| Viscosity @ 60°C (cp) | 11.5  | 31.6  |
| Oil Gravity (°API)    | 26.6  | 21    |
| TAN (mg KOH/g oil)    | 0.68  | 0.42  |
| Saturates (%)         | 41.8  | 23.6  |
| Aromatics (%)         | 44.2  | 42.1  |
| Resins (%)            | 10.8  | 28.2  |
| Asphaltenes (%)       | 3.2   | 6.1   |

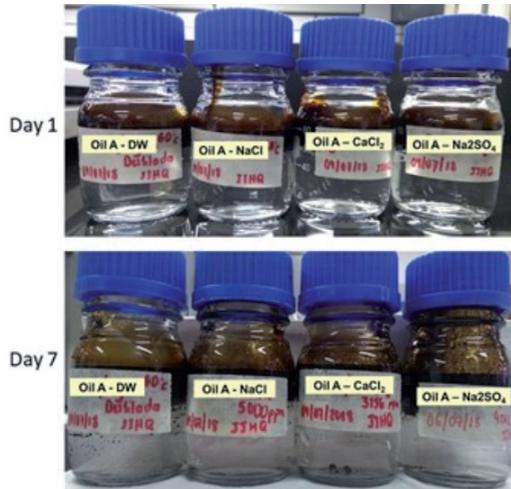
Crude (dead) oil:brine interactions were studied at reservoir temperature (60°C) in batch experiments for a period of one week. The oil:brine systems were stirred periodically to promote the contact between both phases. However, most of the interactions occurred at static conditions. DW and brine solutions of NaCl, CaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> were used in these experiments. Brine solutions were prepared using reagent grade chemicals and DW. The effect of the type of cation (Na<sup>+</sup> and Ca<sup>2+</sup>) and anion (Cl<sup>-</sup> and SO<sub>4</sub><sup>=</sup>) on crude oil: brine interactions were tested at a constant ionic strength (I = 0.086) that is equivalent to a NaCl concentration of 5,000 ppm. The oil-to-water ratio used in these experiments was 50:50 using a total volume of fluid of 80 cc.

After one week of interaction, fluids were separated to perform the characterization of both phases. The pH, alkalinity (ASTM D 1067-92) and ionic composition of DW and brine solutions were measured before and after the interaction. Calcium was measured by titration method (ASTM D 511-92) and Chloride and Sulfate were measured using the Mohr (SM 4500-Cl D) and turbidity (ASTM D4130-82) methods, respectively. The type and distribution of water-soluble organic compounds (WSOC) transferred from the oil to the water phase were analyzed using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). WSOC were first extracted from water following established protocols well described in the literature (Kujawinski, Kido Soule, Valentine, Boysen, Longnecker & Redmond, 2001) (Stanford, Kim, Klein, Smith, Rogers & Marshall, 2007) (Sleighter & Hatcher, 2007) (Bae, Yeo, Jeong, Shin, Shin & Kim, 2011) (Kellerman, Dittmar, Kothawala & Tranvik, 2014) (Gonsior et al., 2016) (Rojas, Gómez, Pachón, Villar & Orrego, 2016). As described earlier, the oil characterization only included viscosity measurements before and after the interaction.

## Results and Discussions

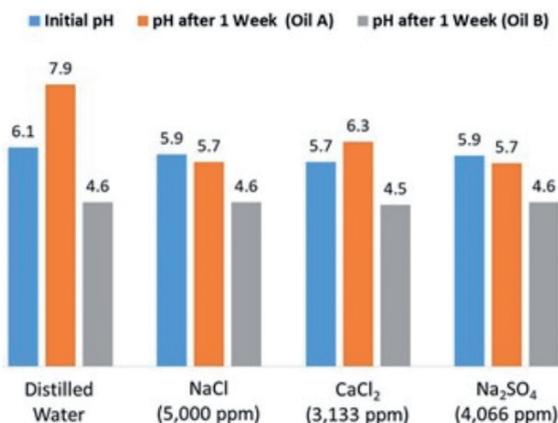
After seven day of interaction no major evidences of dispersions in the water phase or in the oil:water interface were observed in all experiments. Figure 1 shows a picture of the crude oil A and brine systems tested after 1 and 7 days interacting at reservoir temperature (60°C). Despite the apparent low reactivity of crude oils (A and B) evaluated, the pH of the water phase after interacting with both oils suggest that these interactions are oil dependent (Figure 2).

Both oils showed the largest pH changes when interacting with distilled water. However, trends in pH resulted completely opposite. Crude oil A increased and crude oil B decreased the pH with respect the initial pH of the DW (Figure 2). This result suggest that the crude oil composition plays an important role in low salinity waters as reported by Lafargue and Barker (1988). Based on the pH changes measured, crude oil A seems to show higher reactivity with DW and CaCl<sub>2</sub> compared to NaCl and Na<sub>2</sub>SO<sub>4</sub>. For the brines evaluated, final pH are similar or higher when interacting with oil A for 7 days at 60°C. On the contrary, oil B shows a similar pH reduction behavior regardless the brine used in the experiments. These differences in pH trends observed with oils A and B can also suggests that the nature of the organic compounds transferred from the oil to the water phase should be different and dependent on the crude oil geochemistry or molecular composition.



**Figure 1.** Picture of oil A:brine systems after interacting for 1 and 7 days at 60°C.

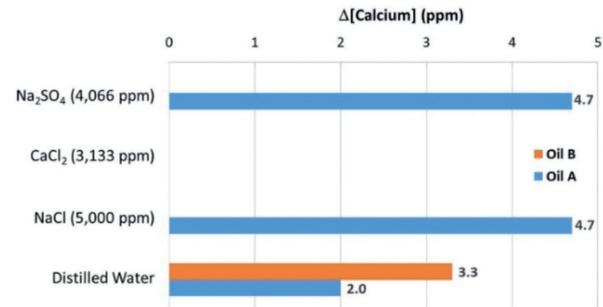
Regarding the alkalinity of the brines after interacting with both crude oils, the changes were minor except in the system oil A and  $\text{CaCl}_2$ . This system reported an increase in alkalinity with respect the initial  $\text{CaCl}_2$  solution. Overall, oil A did not change the alkalinity of DW, NaCl and  $\text{Na}_2\text{SO}_4$  solutions after interacting for a week. On the other hand, all brine solutions tested decreased its alkalinity after the reaction with oil B. However, these changes were within the experimental error and are not considered conclusive. Nevertheless, due to the minor changes measured in the alkalinity of the brines the analytical method (ASTM D 1067-92) used seems to be inadequate for the experimental conditions used in this study.



**Figure 2.** pH changes before and after the interaction of oil:brine systems evaluated for a week at 60°C.

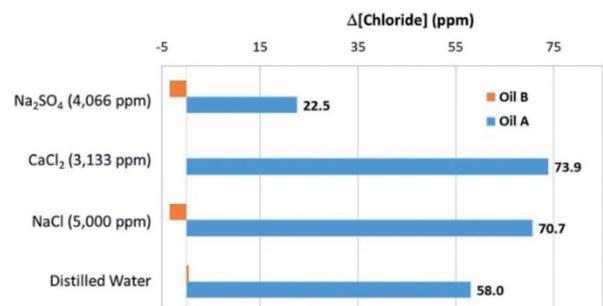
The potential effects of brine composition on crude oil:brine interactions was also evaluated. Sodium concentration were not measured after the experiments. Moreover, no major changes were evidenced in

sulfate concentrations before and after the interaction of both oils (A & B) with  $\text{Na}_2\text{SO}_4$ . However, calcium concentrations showed a small increase (2.0 to 4.7 ppm) in the water phase after the interaction of oil A and different brines (DW, NaCl and  $\text{Na}_2\text{SO}_4$ ). A similar increase in calcium concentration (3.3 ppm) was observed during the interaction of oil B and DW. Due to the small increase in concentrations, calcium was not measured in  $\text{CaCl}_2$  brines (Figure 3).



**Figure 3.** Changes in calcium concentrations after the interaction of oil:brine systems evaluated for a week at 60°C.

Changes in the chloride concentrations were also observed with both oils showing different behavior (Figure 4). All brines evaluated (DW, NaCl,  $\text{CaCl}_2$  and  $\text{Na}_2\text{SO}_4$ ) showed an increase in chloride concentration after the interaction with oil A. However, oil B did not generated changes in chloride concentration. The reduction in chloride concentrations reported after the interaction of oil B with NaCl and  $\text{Na}_2\text{SO}_4$  are within the experimental error and will not be discussed in this paper.



**Figure 4.** Changes in chloride concentrations after the interaction of oil:brine systems evaluated for a week at 60°C.

The importance of these simple static experiments demonstrates that crude oil:brine interactions are specific for each oil and reservoir system. For example, the transfer of calcium from the oil to the water phase (Figure 3) can be explained due to the presence of oil in contact with carbonate cement in sandstone reservoirs and hardness of formation and/or injection brines (i.e.

oil A). In this particular case calcium can be present either as an inorganic salt (i.e. calcium chloride) or in the form of organometallic compounds (i.e. calcium naphthenates).

Furthermore, the increase in chloride concentration in the aqueous phase after the interaction of oil A:brine systems (Figure 4) strongly suggest that in presence of lower salinity brines oil A suffer a desalting process. The desalting process is a well-known operation performed to remove salt and water from crude oils before sending a stream of oil to the refining process because of their negative effects in downstream processes such as corrosion and catalyst deactivation (De Oliveira et al., 2015) (Forero et al., 2001) (Manning & Thompson, 1995). De Oliveira et al. (2015) recently demonstrated that most of the salts identified in different crude oils were sodium (Na), calcium (Ca), magnesium (Mg), strontium (Sr) and iron (Fe) chlorides. The results of this study are in agreement with the desalting effect observed during the experiments using oil A (Figures 3 & 4). If the effects of desalting of crude oils with low salinity brines (ABCW) are present during coreflood experiments, it may lead to misinterpretation of oil recovery mechanisms (i.e. double layer and ionic exchange). Therefore, desalting effects of crude oils must be validated before evaluating possible oil recovery mechanisms of ABCW at laboratory scale.

Regarding the oil phase viscosity, minor changes were observed but within the experimental error except for the oil A after interacting with NaCl (Figure 5). All viscosities were measured at a shear rate of  $7.33 \text{ s}^{-1}$  and reservoir temperature ( $60^\circ\text{C}$ ). Oil A increased 2.6 cp after interacting with the NaCl solution.

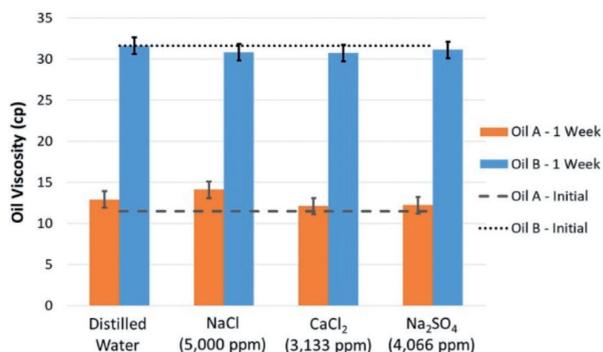


Figure 5. Changes oil viscosities (shear rate of  $7.33 \text{ s}^{-1}$  and  $60^\circ\text{C}$ ) after the interaction of oil:brine systems evaluated for a week at  $60^\circ\text{C}$ .

Analyzing a sample of the oil:water interface of this system (Oil A:NaCl) using an optical microscope confirmed the presence of a micro-dispersion (Figure

6). The presence of this micro-dispersion (water-in-oil emulsion) can explain the increase of the oil viscosity measured after the experiment. This result agrees with the study reported by Mahzari & Sohrabi (2015) that demonstrated the formation of micro-dispersions in LSW and its importance on incremental oil recoveries observed at laboratory scale. Wang & Alvarado (2011) also reported that low ionic strength favored the formation of stable water-in-oil emulsions using oil samples from Wyoming reservoirs at different salinities and water:oil ratios at  $25^\circ\text{C}$ . Additionally, their study also found that calcium played a key role in emulsion stability compared to sodium. However, these results differ from those observed in this study where sodium (NaCl) was the only brine that formed a stable micro-dispersion with oil A. The later represents another evidence that mechanisms of LSW or ABCW are oil/reservoir specific. Therefore, propose general screening criteria for this recovery process represents a difficult task.

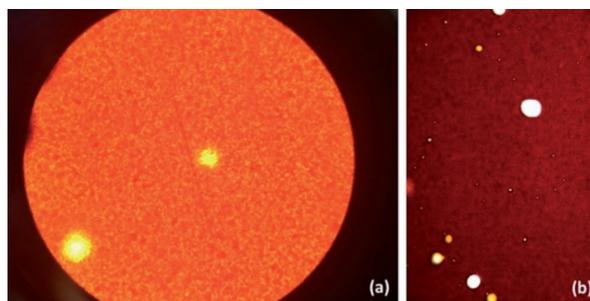


Figure 6. Optical micrograph of the micro-dispersion sampled at the Oil A:NaCl interface: a) 40x and b) 5x.

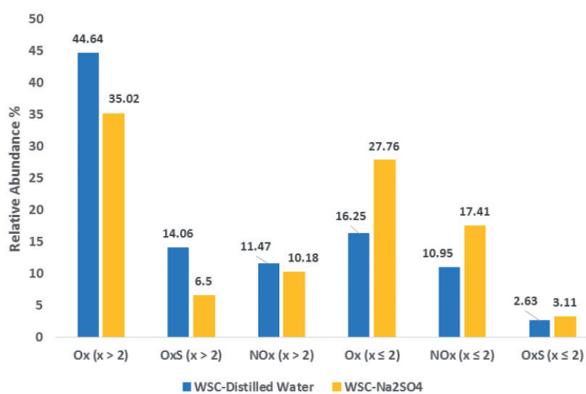
The molecular level composition of the WSOC transferred from Oil A was analyzed throughout ESI(-) FTICR MS and compared with the classes detected for crude Oil A. Table 2 lists the relative abundance percentage for these classes. Compound classes  $\text{O}_x$  ( $X = 2, 3, 4$  and  $5$ ),  $\text{O}_x\text{S}$  ( $X = 1, 2, 3$  and  $4$ ) and  $\text{NO}_x$  ( $X = 1, 2, 3, 4$  and  $5$ ) were the most abundant water-soluble classes. Thus, as it is expected, oxygen containing functional groups appear to promote aqueous solubility of organic matter. In contrast, other NSO classes (N, N<sub>2</sub>, NS and O) were only detected in the parent oil.

Considering that highly oxygenated ( $\text{O}_x$  and  $\text{NO}_x$ , for  $x > 2$ ) species were not detected in Crude Oil A, there was no direct relationship between the relative abundance of heteroatomic classes in Oil A and its corresponding watersoluble organic compounds (Distilled water and Na<sub>2</sub>SO<sub>4</sub> brine). It can be noticed that WSOC identified are from similar classes regardless the brine used in the experiment (Table 2). However, there is a marked

selectivity for species solubilized with different brines (DW or Na<sub>2</sub>SO<sub>4</sub>). The results show that the relative abundance (%RA) of classes O<sub>x</sub>, O<sub>x</sub>S and NO<sub>x</sub> (x > 2) decrease while O<sub>x</sub>, O<sub>x</sub>S and NO<sub>x</sub> (x ≤ 2) increase their solubility in presence of Na<sub>2</sub>SO<sub>4</sub> compared to DW (Figure 7).

**Table 2.** Relative abundance of classes detected in Crude Oil A and Water-Soluble Fractions WSOC in DW and Na<sub>2</sub>SO<sub>4</sub>.

| Class                    | Crude Oil A | WSOC-DW | WSOC-Na <sub>2</sub> SO <sub>4</sub> |
|--------------------------|-------------|---------|--------------------------------------|
| N                        | 56.54       | 0.00    | 0.00                                 |
| N <sub>2</sub>           | 0.55        | 0.00    | 0.00                                 |
| NS                       | 0.59        | 0.00    | 0.00                                 |
| O                        | 29.67       | 0.09    | 0.00                                 |
| O <sub>2</sub>           | 8.51        | 16.16   | 27.76                                |
| O <sub>3</sub>           | 0.00        | 18.87   | 19.3                                 |
| O <sub>4</sub>           | 0.00        | 15.63   | 11.87                                |
| O <sub>5</sub>           | 0.00        | 10.14   | 3.85                                 |
| OS                       | 0.10        | 0.00    | 0.00                                 |
| O <sub>2</sub> S         | 0.00        | 2.63    | 3.11                                 |
| O <sub>3</sub> S         | 0.00        | 10.78   | 5.53                                 |
| O <sub>4</sub> S         | 0.09        | 3.28    | 0.97                                 |
| NO                       | 3.91        | 2.6     | 0.13                                 |
| NO <sub>2</sub>          | 0.04        | 8.35    | 17.28                                |
| NO <sub>3</sub>          | 0.00        | 9.13    | 9.09                                 |
| NO <sub>4</sub>          | 0.00        | 1.87    | 0.98                                 |
| NO <sub>5</sub>          | 0.00        | 0.47    | 0.11                                 |
| O <sub>x</sub> (x = 2)   | 38.18       | 16.25   | 27.76                                |
| O <sub>x</sub> (x > 2)   | 0.00        | 44.64   | 35.02                                |
| O <sub>x</sub> S (x > 2) | 0.09        | 14.06   | 6.50                                 |
| O <sub>x</sub> S (x = 2) | 0.10        | 2.63    | 3.11                                 |
| NO <sub>x</sub> (x > 2)  | 0.00        | 11.47   | 10.18                                |
| NO <sub>x</sub> (x = 2)  | 3.95        | 10.95   | 17.41                                |



**Figure 7.** Summed relative abundances of oxygenated classes detected in Water Soluble Fractions of Oil A.

ESI (-) FT-ICR MS data were further analyzed using isoabundance double bond equivalence (DBE) vs. carbon number (CN) contour plots. Figure 8 shows these plots (classes O2 and O3S) based on the mass spectra of the parent oil A, the distilled water WSOC, and the Na<sub>2</sub>SO<sub>4</sub> brine WSOC. The color intensity scale of the plot represents the relative abundance observed in the spectra. The DBE values of the compounds were calculated by the expression  $DBE = c - h/2 + n/2 + 1$ , for neutral molecules having a generic composition C<sub>c</sub>H<sub>h</sub>N<sub>n</sub>O<sub>o</sub>S<sub>s</sub> (Muller, Hajji, & Koseoglu, 2007).

For these samples, DBE vs CN plots help illustrating how the aromaticity extent (number of rings and double bonds) and the number of carbon atoms influence segregating of organic matter into water. For instance, Oil A exhibit a widely variable distribution of compounds for the O2 class, showing DBE 040 and CN 1850, with higher abundance around C25 DBE 3. In contrast, its water-soluble fractions show species with lower CN range (C10 - C20) and higher DBE (110), in both distilled water and Na<sub>2</sub>SO<sub>4</sub> brine. The most abundant species in each water-soluble fraction correspond to C16 and DBE 1 (exact mass 255.2329 Da, MF C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>). As it is well known, aqueous solubility is inversely related to hydrophobic surface area (Turner, 2003). For instance, polar functional groups, alkyl branching, and aromatization decrease hydrophobic surface area, whereas alkyl chains increase hydrophobic surface area. This effect is more noticeable for the Na<sub>2</sub>SO<sub>4</sub> brine, where electrostriction decreases the area into which hydrophobic moieties may solvate between more ordered water molecules. As a result, relatively shorter, less aromatic and less oxygenated polar molecules are present in water when Na<sub>2</sub>SO<sub>4</sub> is present. In its place, relatively larger, more aromatic and more oxygenated compounds are dissolved in distilled water (see figure 7 to compare). These results agree with previous reports where sea water-soluble organic species were studied (Stanford et al., 2007).

## Conclusions

The water:oil interactions indicate that the composition of brines changes during the Adjusted Brine Chemistry Waterflooding (ABCW). The main changes observed were the increase in inorganic components (desalting effects) and organic compounds soluble in water.

This study strongly suggests that water:oil interactions are dependent on brine and crude oil compositions. Preliminary results also suggest that oil properties such as TAN and SARA can't be used to predict the potential transfer of organic compounds from the oil to the water

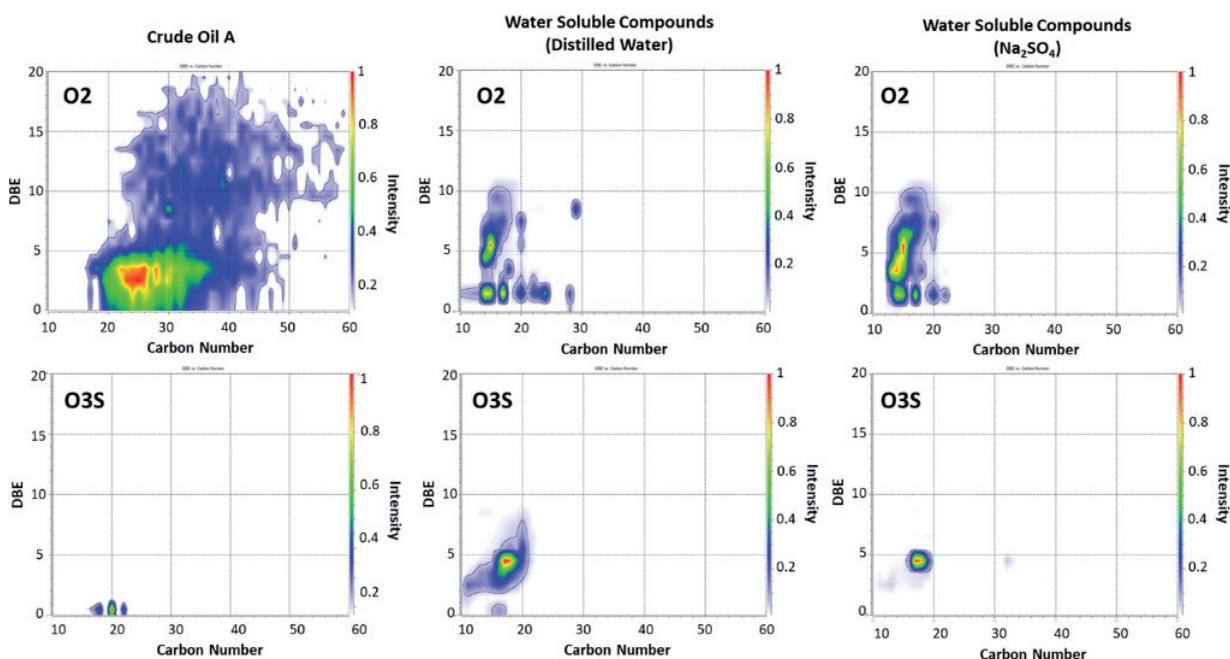
phase during ABCW. Therefore, greater efforts to understand oil geochemistry will contribute explaining the possible mechanisms that operate during the ABCW.

Of the systems evaluated (two oil samples and four different brines) only the crude oil A and NaCl (5,000 ppm) formed a micro dispersion. These results represent additional evidence of the influence of oil and brine compositions on water:oil interactions during ABCW.

The enrichment of the water-soluble organic compounds (WSOC) transferred from the oil to the aqueous phase during ABCW can be detected and identified by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS).

ESI (-) FT-ICR MS data shows that WSOC's identified in distilled water (DW) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) belongs to similar classes. However, a marked selectivity was observed for species solubilized with different brines. The relative abundance of classes  $\text{O}_x$ ,  $\text{O}_x\text{S}$  and  $\text{NO}_x$  ( $x > 2$ ) decreases while  $\text{O}_x$ ,  $\text{O}_x\text{S}$  and  $\text{NO}_x$  ( $x \leq 2$ ) increase their solubility in the presence of  $\text{Na}_2\text{SO}_4$  compared to DW.

Based on isoabundance double bond equivalence (DBE) vs. carbon number (CN) contour plots it was found that O2 and O3S classes are characteristic for each brine (DW and  $\text{Na}_2\text{SO}_4$ ), however, WSOC were consistently identified within the range of DBE  $\leq 10$  and CN  $\leq 20$ .



**Figure 8.** DBE vs. CN for classes O2 and O3S detected in parent Oil A, the distilled water WSOC, and the  $\text{Na}_2\text{SO}_4$  brine WSOC.

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