

# Preliminary Evaluation of the Impact of Modified Injection Water Composition on the Oil/Water Separation in Produced Water Treatment Facilities

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The effect of the electrolyte composition of produced water in oil & gas production facilities was investigated by developing a laboratory scale oil/water separation setup and a related procedure, coupled with an analytical method based on the OSPAR reference method for oil-in-water measurement. The experimental plan was aimed at investigating the effect of the ionic strength, for a given electrolyte, and of different electrolytes, for a given ionic strength, on the separation of oil droplets from the aqueous phase. The oil-in-water concentration was reported against settling time, for a number of different ionic compositions. It was observed that increasing the ionic strength increases the separation efficiency, with more pronounced differences for settling times closer to those typical for the three phase separators in use in the field. For example, for a settling time of 5 min the increase in oil-in-water concentration caused by reducing the ionic strength from seawater level down to zero resulted in a reduction of the separation efficiency up to 37%. This result clearly shows the importance of the electrolytes in the kinetics of oil/water separation, for typical residence times in use in offshore production facilities. Changing the type of electrolyte for a given ionic strength gave results that are not conclusive and worth investigating further. In addition to the separation kinetics, the interfacial tension (IFT) between the crude oil and the different aqueous electrolyte solutions was measured. Only slight differences in the IFT were observed, thus suggesting that other parameters (e.g.  $\zeta$ -potential) are expected to be more relevant in explaining the observed differences in the separation kinetics. The developed experimental method for measuring the separation kinetics proved reliable and can serve as a basis for further investigations aimed at comparing the separation rate of actual brines vs. modified brines, i.e. brines with the composition that can be expected as a consequence of the application of enhanced oil recovery methods, such as SMART water injection.

## 1. Introduction

Water based enhanced oil recovery (EOR) methods are being researched in order to address the reducing oil production associated to conventional water-flooding. The injection of modified water (e.g. SMART water) is gaining potential as it seems to be a promising EOR method (Sheng, 2014). Such an implementation will evidently cause physico-chemical changes in the produced water that may affect the oil/water separation due to the alteration of water composition. Changes obtained by altering the water composition even to small extent “may cause unintended phase separation difficulties downstream” (Green and Perry, 2008). These compositional alteration effects can relate to the size distribution and surface electrical charge of the oil droplets in produced water, which are key factors for the oil/water separation kinetics.

The objective of this work was the preliminary evaluation of the effect that the modified injection water can introduce in the efficiency of the oil/water production separators and water treatment units. This objective was addressed by developing a laboratory setup and an experimental procedure, and by carrying out laboratory experiments focused on the kinetics of the oil/water separation during the gravimetric separation process, i.e. the primary oil/water separation process applied on oil & gas production facilities. The experiments consisted of studying the oil/water separation kinetics for different water compositions and for well-defined time intervals,

by accurately quantifying the oil content in aqueous samples. The time intervals and the oil/water ratio were inspired by typical field separator residence times.

A lot of research has been performed on the subject of modification of injection water and therefore it would be expected that there is a good base of knowledge with regard to oil/water interactions that could also serve as starting point for the present work. However, although experimental investigation showed promising results with respect to EOR, the involved mechanisms are still dubious because the interactions between oil, water and minerals are very complex and far to be fully understood (Lashkarbolooki et al., 2014). Additionally, most of the research is focused on the downhole interactions and the oil recovery, without taking into consideration the potential effect of the modified water to the separation processes that are taking place on production facilities (i.e. at conditions that are very different from the downhole conditions). Most of the already performed research focuses on the emulsions of water in oil (Liu et al. 2013; Lashkarbolooki et al., 2014), whereas much less information is available on oil in water emulsions. For example, it is considered that low ionic strength favours the stabilization of water in oil emulsions (Wang et al., 2012). In addition, it seems established that one important factor affecting the separation of the phases, and especially the emulsion behaviour between water and oil, is the presence of asphaltenes, resins and naphthenic acids in crude oil. These components can dramatically lower the interfacial tension (IFT) and therefore stabilize oil/water emulsions (Lashkarbolooki et al., 2014; Lee and Neff, 2011). This factor implies that relevant differences in the oil/water separation kinetics are expected, depending on the crude oil type.

Another important parameter of the oil/water emulsions is the electrical interactions between the two phases (Manning and Thompson, 1991; Stachurski and Michalek, 1996). In particular, the  $\zeta$ -potential, which appears to be correlated to the pH of the bulk phase, is a parameter that could shed some light in the interactions between oil and water. The presence of negative surface charge, which seems to be caused by the concentration of hydroxyl ions on the oil droplet surface, could dramatically change the oil/water interaction (Marinova et al., 1996) and create hindrances during the separation of the two phases. In this regard, and as an example, it is reported in the literature how the use of synthetic polymers in the injection water, as an EOR method, can cause a decrease in the efficiency in the oil/water separation which is related to IFT reduction and increase of  $\zeta$ -potential (Liu et al., 2013). It is therefore understandable that the modification of the water phase can have a great effect in the separation of oil and water.

## 2. Materials and methods

The experimental work consisted of the preparation of a number of brines with different ionic composition and the dispersion of crude oil in each of them. From the resulting Synthetic Produced Water (SPW) the oil was extracted and quantified by Gas Chromatography (GC). The quantitation of the oil-in-water concentration at different times was used to measure the separation kinetics, in order to understand the way the ionic composition affects the separation of the two liquid phases. In addition to the separation kinetics experiments, the oil/water IFT was measured. A detailed description of the experimental procedure is reported elsewhere (Kaprielian and Imrényi, 2016).

### 2.1 Chemicals

n-Pentane, NaCl and Na<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich, analytical grade,  $\geq 99.9\%$ ) and North Sea crude oil (Frederiksen Scientific A/S) were used for the main experiments; n-decane and n-hexane (Sigma-Aldrich, analytical grade,  $\geq 99.9\%$ ) were used as a substitute of oil and as an extraction agent, respectively, during the development of the experimental procedure. In addition to the chemicals, the water used for all experimental purposes was treated by reverse osmosis and distilled to ensure the same quality throughout the experiments.

### 2.2 Oil/water separation experiments

The SPW was prepared by diluting certain amounts of the relevant salts in distilled water. Crude oil in the ratio 0.2 to the brine (mass of oil / mass of brine) was added (Figure 1a). This ratio was inspired by typical values in current oil & gas production units connected to waterflooded fields. By mechanical dispersion for 2.5 minutes at 10000 rpm (IKA Ultra Turrax), oil/water dispersions were produced (Figure 1b). The dispersions were transferred to separating funnels (100 mL) and left to settle for different residence times (Figure 1c). At the end of the selected settling times, a large sample (30 mL) of aqueous phase, corresponding to approximately 60 % of the whole aqueous phase, was withdrawn from the bottom of the funnel.

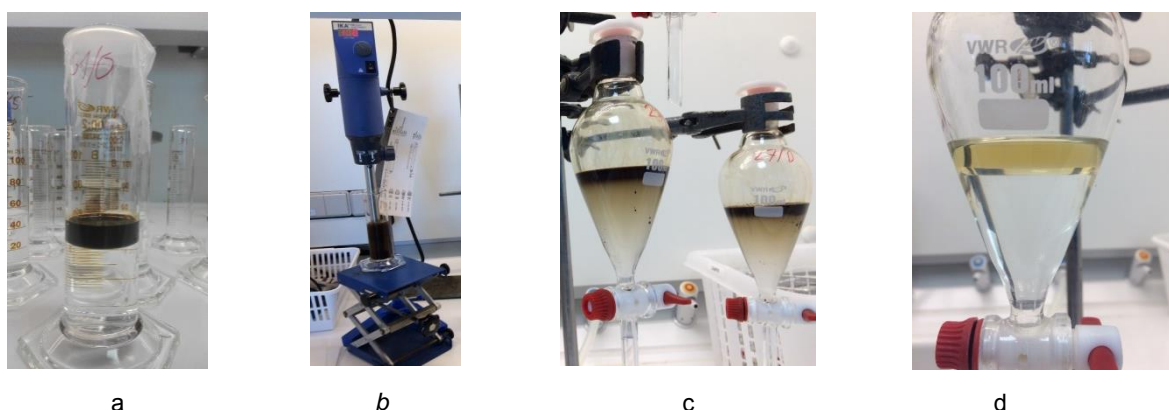


Figure 1: a) Oil/Water ratio, b) Dispersion, c) Settling, d) Oil extraction

### 2.3 Analysis

One of the most accepted compositional analysis methods for the produced water in the oil and gas industry is the use of GC coupled with Flame Ionization Detector (FID) (Lee and Neff, 2011). In order to measure the concentration of oil in water, the OSPAR method that is in use at the North Sea area was used as an inspiration (OSPAR 2011). The procedure consisted of two steps: 1) extraction of crude oil from the aqueous phase sampled at specified separation times; 2) GC-FID analysis. The extraction was carried out in a separating funnel using n-pentane as the extraction solvent, in a 0.2 ratio (mass of pentane/mass of aqueous phase). The separating funnel was vigorously shaken and left to settle. After the settling time, two liquid phases with a well-defined interphase existed in the separating funnel: the lighter organic phase (n-pentane rich) at the top; the heavier aqueous phase at the bottom (Figure 1d). Since the OSPAR reference method suggests that with a ratio of 0.1 of solvent to aqueous sample a complete extraction is achieved, it was assumed that all crude oil had been transferred from the aqueous phase to the organic phase in this work.

Following, the organic phase was sampled for analysis and both phases were weighted on an analytical balance (OHAUS Pioneer PA214C), as described in the following: from the top of the funnel, an appropriate amount (typically 2-3 ml) of the organic phase was withdrawn carefully using a syringe; the mass of the sample was measured and the sample was stored in a closed glass container for the analytical measurements; the entirety of the aqueous phase was discharged from the bottom of the funnel and the weight was measured; the remaining organic phase was discharged from the bottom of the funnel in a beaker in order to be weighted and then disposed. The weighting of the two liquid phases allowed checking the closure of the mass balances related to the whole procedure (maximum discrepancy < 3 %).

The quantitation of crude oil was performed by GC-FID (Perkin Elmer Clarus 500, column: 30 m x 320  $\mu\text{m}$ , temperature program: 50-275  $^{\circ}\text{C}$  by 10  $^{\circ}\text{C}$  per minute, injection volume: 1  $\mu\text{L}$ , injector temperature 250  $^{\circ}\text{C}$ , carrier gas He: 1 mL/min). The instrument was calibrated by the external standard method. Standard solutions at concentration range of 0.2-1.1 g/L were prepared with known concentration of the same crude oil that was used for the separation experiments. The oil was diluted in pentane and injected to the GC-FID to acquire an analytical response. An example of this response is shown in Figure 2. The calibration was carried out on the basis of the total chromatographic area in a certain retention time range (2.4-15 minutes). The repeatability of the results was tested by triplicate injections (relative standard deviation:  $\text{RSD} \leq 5\%$ ) of each standard and the response was regressed against the known oil concentrations. The calibration curves showed an acceptable linearity ( $\text{R-Squared} \geq 0.98$ ). Tests for the consistency of the results were performed daily by measuring the standards and the calibration was repeated when the test gave discrepancies higher than 3% or a new batch of crude oil was used. By using the calibration curve, the quantitation of crude oil in the samples of organic phase, obtained through the extraction step, was possible. The GC results were given in concentration basis of mg/L. This concentration was then converted to a mass fraction by using the mass of the organic phase and its density. For all experimental runs, the density of pure pentane was used at the laboratory temperature. The density of the organic phase was measured for some initial experiments and it proved that the use of the pure pentane density was accurate. A precision pipette (Gilson Microman) was used to ensure the accuracy of volume measurements and, in addition, the pipette was calibrated with the use of distilled water and the density value acquired from NIST in the measured ambient temperature.

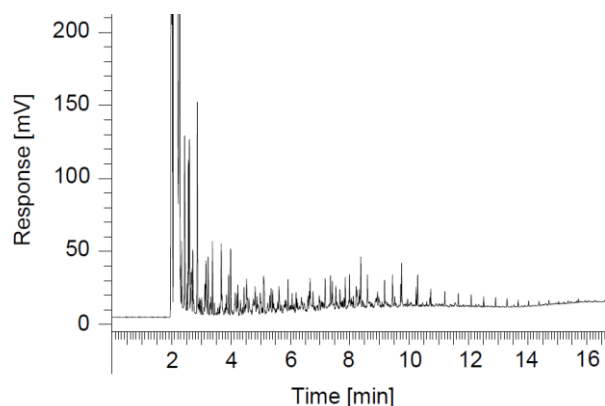


Figure 2: Example of GC response on the crude oil used in this work

With this conversion the crude oil concentration in the organic phase (pentane-rich) was calculated which enabled the calculation of the overall oil mass by using the weight of the organic phase. Since it was assumed that all crude oil was transferred to the organic phase, by using the calculated mass and the measured initial aqueous phase mass, the mass fraction of crude oil in the SPW was calculated.

## 2.4 Surface properties

The IFT was measured by the “pendant drop” method (Kruss DSA 100), which uses a small volume of medium (brine) and a droplet of oil hanging by the tip of an upside down needle submerged in the medium. The shape and size of the droplet is captured by a camera and in correlation to the gravitational forces acting on the system, the IFT is measured.

## 3. Results and discussion

The experimental work was planned in order to identify the significance of ionic concentration and possibly the effect of specific ions. The chosen electrolytes were NaCl and Na<sub>2</sub>SO<sub>4</sub> and four different brines were tested. The distilled water is abbreviated as DW; PW3 is the brine with the highest NaCl (35 g/L) concentration (ionic strength of seawater); PW1 (NaCl 6 g/L) and PW2 (NaCl 1.5 g/L and Na<sub>2</sub>SO<sub>4</sub> 3.6 g/L) were used as synthetic low salinity brines for which the specific ionic composition and the ionic strength were inspired by literature (Fathi et al., 2011). In this case, the introduction of Na<sub>2</sub>SO<sub>4</sub> while keeping the same ionic strength was chosen as a relevant parallel in order to study the effect of specific electrolytes.

Utilizing the experimental method that was reported in Section 2, a number of oil/water separation experiments were performed and the kinetic behaviour was studied against a few important parameters. The conditions that were varied during the experiments were the settling time of the oil/water separation and the brine compositions. In total, 16 experimental conditions were investigated by a repetition of 5 or 6 runs of the same conditions, giving a total of 94 separation experiments. The average RSD of the oil-in-water concentration measured in the experiments was 8 %, with a maximum RSD equal to 15 %.

### 3.1 Oil/water separation kinetics

With the quantitation of crude oil in the aqueous samples, the concentration of oil was plotted against the settling time for the distilled water and the two brines containing only NaCl. The results are shown in Figure 3. As expected, the oil concentration decreases with time. In addition, it can be seen that the oil-in-water concentration at any given settling time is much higher for distilled water with respect to the two brines. More specifically, the lower is the ionic strength the higher is the separation time.

Another noteworthy general observation is that the oil-in-water concentration differences are higher at lower settling times. That is particularly relevant since the residence times for the aqueous phase in oil/water separators at oil & gas production facilities are typically between 5 and 15 minutes. For example, the concentrations at a settling time of 5 minutes were: DW 1388 ppm; PW1: 1152 ppm; PW3 1010 ppm; PW2 932 ppm. Therefore, with a settling time of 5 min the increase in oil-in-water concentration caused by a complete electrolyte depletion (DW) is approx. 37% with respect to PW3 (simplified sea-water model). This result clearly shows the importance of the electrolytes in the kinetics of oil/water separation, for typical residence times in use at oil & gas production facilities. That is further observed comparing the difference in the results between PW1 and PW3 where partial electrolyte depletion (from PW3 to PW1) led to an increase of oil-in-water concentration equal to approximately 14 %. It is highlighted that the latter two brines (PW1 and

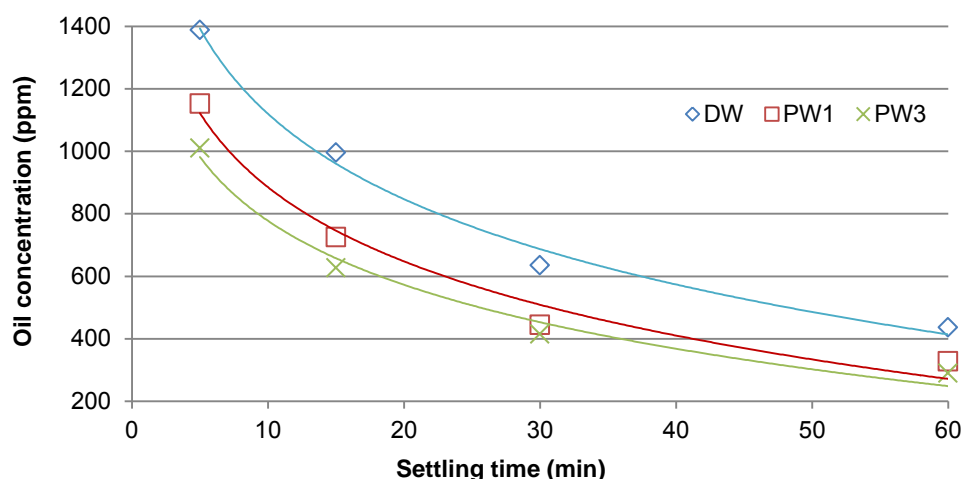


Figure 3: Oil/Water separation kinetic curves for DW, PW1 and PW3. Markers refer to experimental data (average of 5 or 6 measurements). Curves are obtained by regression of experimental data, using an empirical quadratic function.

PW3) were inspired by literature and prepared in order to contain NaCl similar to low salinity injection water and sea water, respectively (Fathi et al., 2011). The results clearly show that the potential modification of the salinity of produced water due to the use of low salinity injection water could result to lower separation efficiency.

The comparison of the results obtained using PW1 and PW2 refers to the potential effect of different electrolytes for a given ionic strength. The difference is not clear from the available data, even though the data at 5 minutes suggest a favourable effect of the divalent electrolyte  $\text{Na}_2\text{SO}_4$  (932 ppm), with respect to the case of a monovalent electrolyte NaCl (1152 ppm). These observations show that the presence of specific ions and their composition is a parameter which may affect the separation kinetics as it is probable that it changes the surface properties of the oil in water. Results are however not conclusive in this case.

As the settling time increases, the difference between the brines decreases and only the complete absence of ions seemed to maintain a pronounced difference even at long times. The kinetics shown in Figure 3 gives a clear indication that lower ionic strengths have a negative effect in the oil/water separation. That suggests that low salinity injection water, which may cause a shift in produced water towards lower salinity, can increase the needed residence times of oil/water separators in oil & gas production facilities, or, what is the same, for given residence time in existing separators, a worst separation is obtained, i.e. a water effluent with higher oil-in-water concentration.

### 3.2 Surface properties investigation

IFT measurements were carried out for the same oil/water systems for which the separation kinetics was investigated. The results were an average of 6 repetitions of each water/oil system with maximum average absolute deviations (AAD) of 0.04 mN/m. The values were for the four brines: DW 19.20 mN/m; PW1 18.51 mN/m; PW2 18.06 mN/m; PW3 17.62 mN/m. From these results, it is observed that the highest IFT value was obtained with distilled water. The presence of NaCl indicates a decrease of the IFT. Subsequently, the addition of  $\text{Na}_2\text{SO}_4$  and further depletion of NaCl, further decreases the IFT. Ultimately, with PW3, which had NaCl content similar to seawater, the lowest value of IFT is observed. Lashkarbolooki et al. (2014) observed a value of IFT with crude oil/deionized water equal to 22 mN/m, which is somewhat higher than the value found in the present work (19.20 mN/m). This difference can be related with the different crude oil. This is very much in line with the effect of natural surface active components (e.g. asphaltenes, resins) in the crude oil. This means that since different crude oils contain different surface active components and in different concentrations, process design studies on oil-in-water separation kinetics must be focused on the specific crude oil of interest in the production facility under investigation. Overall, the present results, together with those reported in the literature, indicate that: 1) IFT is influenced by the presence of specific ions, albeit to a small extent; 2) IFT is influenced by ionic concentration; 3) IFT is influenced by the type of crude oil. With regard to the electrolyte composition for a given oil, the observed IFT variations does not correlate with the observed kinetics differences in the oil/water separation, since lower IFT are typically associated with more stable emulsions, thus indicating that other factors are expected to be more relevant.

#### 4. Conclusions

The effect of the ionic composition that was observed during this experimental work indicated that a reduction of produced water ionic strength, that may result from continuous injection of low salinity water, is expected to reduce the oil/water separation kinetics and, therefore, to reduce the efficiency of the topside oil/water separators. The experimental results showed a clear trend of reduction of the separation efficiency as the ionic strength decreases from 0.6 M (approximate sea-water level) down to 0 M (distilled water). That was especially apparent for the lower settling times (e.g. 5 minutes), which are in line with the residence times for typical offshore production units and therefore this is a relevant issue to consider. More specifically, the increase in oil-in-water concentration at 5 min of residence time was 14%, when the ionic strength was reduced from 0.6 M to 0.1 M, and 37% when it was reduced from 0.6 M to 0 M. By investigating the synergistic behaviour of two ions with PW2 (0.1 M NaCl and Na<sub>2</sub>SO<sub>4</sub>), for a given ionic strength, it was observed that the presence of Na<sub>2</sub>SO<sub>4</sub> further complicates the process and the effect becomes unclear. That recommends further investigation. The IFT measurements that were performed showed that the ionic strength affects to a small extent the IFT of the specific systems. The observed differences in the separation kinetics are likely to be more strongly connected to other parameters, such as the  $\zeta$ -potential. This parameter may be a key factor to highlight the effect of the ionic interactions on the surface charge of the droplets and, therefore, on the kinetics of the coagulation of the oil droplets and ultimately on the oil/water separation kinetics.

#### Acknowledgements

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