



## The effect of organic acids and salinity on the interfacial tension of n-decane/ water systems

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### ABSTRACT

We have investigated how a homologous series of straight-chain carboxylic acids with a cyclohexyl substituent in the opposite end of the functional groups impacts the interfacial tension (IFT) between decane (oil) and water. The employed method was the pendant droplet technique. We do not observe any striking effect of expanding the chain length: all acids reduced the IFT compared to water by approximately 20 mN/m. Additionally, the effect of changing the chemical character and the concentration of the cation in a series of brines were studied too, and again we do not observe a significant IFT impact. The only modification that significantly reduces the IFT is the modification of the anion from chloride to carbonate, a change that results in an increased pH and thus a transformation of the constituent acids from their neutral to their anionic form. This is expected to result in a reduced IFT because of the polar end of the surfactant is even more polar which alleviates the stress on the surface.

### 1. Introduction

At present, most production of crude oil is based upon primary and secondary methods of recovery, both leaving behind considerable amounts of residual oil in the reservoir (Speight, 2014). This remaining oil is in many cases retained in the formation rock by capillary trapping mechanisms (Alyafei and Blunt, 2016). These are a consequence of the wettability of the rock, the size of the pore throat in the rock, and the interfacial tension between the reservoir fluids (Tiab and Donaldson, 2011). Reducing interfacial tension, or altering the wettability of the rock, allows the production of significant amounts of oil compared to normal water flooding methods (Strand et al., 2003; Wu et al., 2008). Amphiphile molecules (surfactants) are able to reduce the interfacial tension between the reservoir fluids and alter the wettability of the reservoir rock (Al-Sahhaf et al., 2005; Aveyard et al., 1985; Harkins and Humphery, 1916; Kumar and Mandal, 2016; Thomas et al., 1993). Thomas et al. (1993) confirmed the adsorption of several amphiphiles on calcite using thermogravimetry and contact angle measurements to demonstrate that the adsorption of fatty acids on clean calcite renders the surface oil-wet. Similarly, Wu et al. (2008) utilized a range of naphthenic acids to instantly alter the wettability of calcite from strongly water-wet to oil-wet. Also demonstrated by this group was the ability of surfactants to reverse this wettability change, thus improving oil-recovery by imbibition of a surfactant solution. Likewise, Schechter

et al. (1994) found that decreasing the interfacial tension between the non-wetting phase and the wetting phase increased the total percentage of recovered oil in both drainage and imbibition processes, as the drive mechanism behind the water flood transitions from capillary forces to gravitational forces.

Thus, it is worth examining the parameters influencing the magnitude of interfacial tension of a system. The interest of this study are specific ion effects on interfacial tension, particularly the effects of different cations in the aqueous phase, and, also, how the interfacial tension varies with homologues of a series of naphthenic acids.

In the literature there are several significant results as to salt and specific ion effects on interfacial tension. Early research by Harkins and Humphery (1916) showed that the addition of salt to the two-phase benzene-water system increases the interfacial tension. Recent molecular dynamics simulations and interfacial tension measurements on the n-decane-water system have suggested that this phenomenon is due to an increase in the order of the water structure at the interface, since the number of hydrogen bonds near the interface increases with salt addition because of an enhanced need for solvation of the ionic species (Wen et al., 2017). However, for the ionic surfactant mediated interface, salt addition has very different effects, and these appear to be largely dependent of the type of aqueous ions in the system. A study involving 4-heptyl benzoic acid as surfactant showed that increasing the NaCl concentration – at a pH where a significant amount of the acid

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was dissociated – decreased the interfacial tension of the system (Spildo and Hoiland, 1999). Arguing that the interfacial region must be electroneutral, the presence of cations at the interface must mean that hydronium ions migrate into the bulk water phase, thus shifting the acid dissociation equilibrium locally. Dissociated species are better solvated and increases in pH significantly reduce the interfacial tension for ionic surfactants (Danielli, 1937; Peters, 1931). Similarly, it has been shown that acid fractions extracted from crude oil, and dissolved in toluene, facilitate significant drops in interfacial tension against water when the pH is increased (Hoeiland et al., 2001). Another suggested mechanism by which cations decrease interfacial tension is via intercalation into the interfacial surfactant layer to stabilize the otherwise repulsive interaction between the anionic dissociated acids and/or the undissociated polar heads (Li et al., 2005). This enables more surfactant molecules at the interface, giving a more hydrophilic interface and a lower interfacial tension. This mobilization of surface active components to the interface has been used by a study to explain the decrease in interfacial tension of crude-oil/brine systems when NaCl was added (Farooq et al., 2013). Additionally, the same study argued that CaCl<sub>2</sub> seemed to operate via a different mechanism, allegedly due to the ability of calcium ions to form highly solvated complexes with deprotonated acidic species. This mechanism has also been suggested by others (Brandal et al., 2004; Spildo and Hoiland, 1999). Furthermore, for salt effects, the anion of the salt also affects changes in interfacial tension of surfactant mediated interfaces. Specifically, it has been shown that MgCl<sub>2</sub> is more effective in reducing interfacial tension than MgSO<sub>4</sub>, and both are more effective than the corresponding calcium salts (Lashkarbolooki et al., 2014). However, at higher concentrations, salts again increase interfacial tension due to salting-out of the interfacially active compounds (Al-Sahhaf et al., 2005; Aveyard et al., 1985).

A molecular dynamics study on the relationship between molecular architecture of the surfactant and the hydrocarbon phase, and the effects on interfacial tension has been conducted by Jang et al. (2004). They found that for four different structural isomers of hexadecane benzene sulfonate, (the benzene sulfonate being attached to either the 2nd, 4th, 6th, or 8th carbon) the isomer yielding the lowest interfacial tension in a n-decane-water system was 4-C16 benzene sulfonate arguing that the effective chain length of the surfactant's longest alkyl chain was similar to that of n-decane. Additionally, this surfactant has the smallest interfacial area, thus indicating that both the area of the surfactant at the interface and its miscibility with the oil phase are important parameters for the size of interfacial tension. Likewise, it has been shown that, for one specific surfactant, variation of the average number of alkane carbons in the hydrocarbon phase yields a single minimum in interfacial tension signifying that for each surfactant there is an optimal hydrocarbon phase for producing ultra-low interfacial tension (Cash et al., 1977). Variation of surfactant also yielded one specific minimum in interfacial tension as a function of average alkane carbon number – different minima for each surfactant (Doe et al., 1977). Further research in emulsion formulations have confirmed the importance of the molecular architecture of surfactant molecule as a parameter for the magnitude of interfacial tension (Davis, 1994; Shinoda et al., 1981). The surfactant-oil miscibility is an important and often neglected factor it is, however, very important how well the surfactant is “hidden” in the oil phase and it was been shown that when the surfactant has a high affinity for the oil the IFT is not influenced by the surfactant structure to a great extent (Andersson et al., 2014).

To the best of our knowledge, however, there seems not to be research attempting to evaluate specific ion effects on a series of homologues of surfactants. This study hopes to elucidate the different responses of homologues of model naphthenic acids towards specific ions in brines, thus serving as a reference for interfacial tension studies. While it would be ideal to conduct IFT investigations under reservoir conditions this is not an option with the pendant droplet technique that we have decided to focus on here. We wish to maintain that

understanding the fundamental aspects at ambient conditions still has relevance for upstream processes. Additionally, there are downstream processes that takes place at ambient conditions, such as separation, which clearly depends on interface related phenomena and pendant droplet based workflows are therefore highly relevant in oil and gas contexts.

## 2. Experimental details

### 2.1. Equipment

All experiments were carried out using ramé-hart goniometer model 500, which uses an upgraded digital camera (750 fps) and a fiber optic illuminator for backlighting. The whole setup was covered with a wooden box, to eliminate noises from other lighting sources in the lab. Water/brines were the drops phase while the decane – organic acid mixtures were the surrounding phase. The decane mixtures were contained in a transparent cell, made of Infrasil<sup>®</sup> quartz that was affixed in a removable base on the stage of the goniometer.

After proper calibration of the setup using the manufacturer's standard calibration device (4 mm calibration ball), the accuracy of the system was tested using ramé-hart's “fixed pendant drop calibration tool”. This tool had images of several pendant drops of different liquid-liquid systems printed on a transparent sheet. The integrity of the calibration was tested by comparing the software computed interfacial tensions of these drops with the real certified values obtained from the manufacturer. The setup was adjusted and re-calibrated until the error between the computed and certified values were within 1%.

The pendant drops were created with an automated dispensing system. The drops created had an average volume of around 12 μm<sup>3</sup>. Readings were taken while an automated system kept the volume of the drop fixed by injecting into or sucking from the drop when necessary. When this automated volume control system was not activated (manually injecting the drop phase from a syringe), the drop volume tended to slightly increase with time. Even though the volume of the drop should not affect the reading based on the method used, it was noticed that the variations in the interfacial tension values with time was smaller when the automated volume control system is activated.

The mixing of the n-decane with the organic acids, and the deionized water with salts was performed using a magnetic stirrer for at least 10 min. All fluids with n-decane were contained in glass bottles to avoid reaction with plastics.

The quartz cell was cleaned after every new n-decane – organic acid mixture. This was done first with deionized water then with acetone (by Sigma-Aldrich, > 99%). The tube of the automated dispensing system was cleaned after every run with deionized water, and drops with lower salinities were tested first.

### 2.2. Chemicals

The brines were prepared using Milli-Q<sup>®</sup> water (resistivity = 18.2 M Ω cm) and reagent grade salts purchased from Sigma-Aldrich. The concentration was prepared in mole percent (rather than weight percent) to keep the number of charges species under control so that the effect of the changing the cations and the anions constitutes the central point of the study. The various brine compositions are summarized in Table 1.

The n-decane used as the base for all the mixtures shown in Table 2 (the concentration in mole percent yielded identical results so for consistency with the previous work of Wu et al. (2008) we kept the concentration in wt.%), it was supplied from Sigma-Aldrich and had a mole purity of 99%. It was purified further to remove potentially oxidized alkane by passing the n-decane through a column of activated alumina (by LabSorbents) several times until the value of the interfacial tension between n-decane and water was stable with time. It was found that the readings became constant after four purification runs. The

**Table 1**

Salt concentrations of the water/brines used in this study.

Label	NaCl [wt. %]	NaCl [mol %]	KCl [wt. %]	KCl [mol %]	CaCl <sub>2</sub> [wt. %]	CaCl <sub>2</sub> [mol %]	Na <sub>2</sub> CO <sub>3</sub> [wt. %]	Na <sub>2</sub> CO <sub>3</sub> [mol %]	Salinity [ppm]
D1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
B1	<b>4.60</b>	<b>1.50</b>	0.00	0.00	0.00	0.00	0.00	0.00	45,540
B2	0.00	0.00	<b>5.80</b>	<b>1.50</b>	0.00	0.00	0.00	0.00	57,420
B3	0.00	0.00	0.00	0.00	<b>8.20</b>	<b>1.50</b>	0.00	0.00	79,540
B4	0.00	0.00	0.00	0.00	0.00	0.00	<b>8.05</b>	<b>1.50</b>	79,695
B5	<b>5.00</b>	<b>1.63</b>	<b>1.00</b>	<b>0.26</b>	0.00	0.00	0.00	0.00	20,400
B6	<b>5.00</b>	<b>1.63</b>	0.00	0.00	0.00	0.00	0.00	0.00	10,400
B7	<b>2.00</b>	<b>0.65</b>	0.00	0.00	0.00	0.00	0.00	0.00	4160

The bold values highlight the non-zero salt concentrations of the brines.

**Table 2**

The compositions of the n-decane – organic acid mixtures used in this study.

Fluid	Label
98.5 wt. % n-decane and 1.5 wt. % Cyclohexanecarboxylic Acid	OA
98.5 wt. % n-decane and 1.5 wt. % Cyclohexanepropionic Acid	OB
98.5 wt. % n-decane and 1.5 wt. % Cyclohexanebutyric Acid	OC
98.5 wt. % n-decane and 1.5 wt. % Cyclohexanepentanoic Acid	OD
Pure n-decane	O

cyclohexanecarboxylic acid, cyclohexanepropionic acid, cyclohexanebutyric acid and cyclohexanepentanoic acid were supplied from Sigma-Aldrich and had a purity of 98%, 99%, 99% and 98% respectively.

### 2.3. Procedure

Computer controlled drop shape analysis was conducted to find the interfacial tension between the n-decane/organic acid mixtures and brines with different composition and concentrations. All readings were taken at atmospheric pressure and 22 °C. For every n-decane/water system the drop was monitored for 600 s and the experiment was repeated for at least three times. It was noticed that the readings are most stable after 200 s, therefore the interfacial tension reported in this paper was taken as the average of values between 200 and 600 s. The decane concentration has been attempted to be kept constant throughout the series to avoid artefacts induced by differences in partition of surfactants between the phases.

The interfacial tension was computed with ramé-hart's DROPImage Advanced Software, which was set to take a reading every five seconds. The software computes the interfacial tension by fitting the droplets to theoretical profiles by the numerical integration of Young-Laplace equation. The following equations are derived simultaneously:

$$\frac{d\theta}{dS} = \frac{2}{R_0} + \frac{\Delta\rho g}{\gamma} y - \frac{\sin\theta}{x} \quad (1)$$

$$\frac{dx}{dS} = \cos\theta \quad (2)$$

$$\frac{dy}{dS} = \sin\theta \quad (3)$$

Where  $\gamma$  is the interfacial tension,  $\Delta\rho$  is the difference in the densities of the two liquids (the drop and surrounding phases),  $g$  is the gravitational acceleration. As show in Fig. 1  $y$  is the position in the vertical axis,  $x$  is the position in the horizontal axis,  $S$  is the arc length from the bottom point,  $\theta$  is the angle,  $R_0$  is the radius of curvature.

Solving the above equations, an expression for the interfacial tension is derived (eq. (4)). The software computes the radius of curvature ( $R_0$ ) and the shape factor ( $\beta$ ), which is computed using the ratio between  $D_s$  and maximum diameter  $D_E$  shown in Fig. 1.

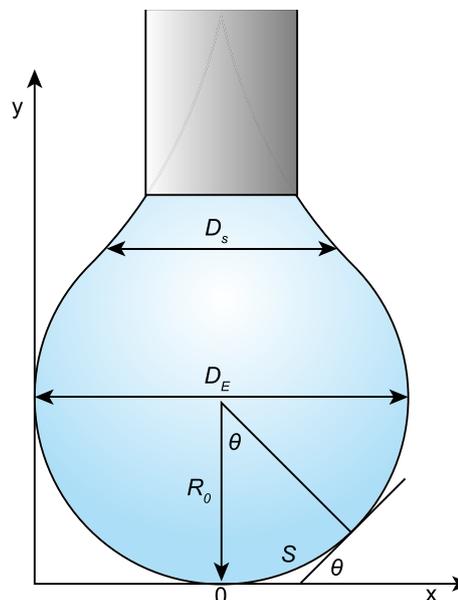


Fig. 1. Geometric representation of a pendent drop.

$$\gamma = \frac{\Delta\rho g R_0^2}{\beta} \quad (4)$$

### 2.4. Supporting measurements

The densities of the water and brines were measured by Chase's high precision hydrometer, the electric resistivity was measured with an analog resistivity meter by OFI Testing Equipment (Table 3). The densities of the n-decane – organic acids mixtures were determined three times using a density meter (Anton Paar DMA 5000 M) and the averages are presented in Table 4.

The measured densities of the brines and n-decane – organic acids mixtures, were inputted in the DROPImage Advanced Software to be

**Table 3**

Density and resistivity values of the water/brines used.

Label	Density	Electric Resistivity
	[kg/m <sup>3</sup> ]	[Ω.cm]
B1	1032	18
B2	1038	14
B3	1070	13
B4	1092	16
B5	1044	10
B6	1035	12
B7	1014	28
D1	995	a

a = 18.2 MΩ cm from the deionized water source.

**Table 4**

The densities and the calculated (assuming complete dissociation of the acids) total acid numbers of the n-decane – organic acid mixtures used.

Label	Density	TAN
	[kg/m <sup>3</sup> ]	[mg KOH/g oil]
OA	733.1 ± 0.05	6.57
OB	731.9 ± 0.03	5.39
OC	731.7 ± 0.06	4.94
OD	731.5 ± 0.02	4.57
OO	728.8 ± 0.02	–

used for the interfacial tension computations.

### 3. Results and discussion

The impact on the interfacial tension of having different cations in different concentrations has been addressed systematically in the present study. Moreover, we have included the carbonate ion for two reasons: Firstly, it is a central component of the formation water in any carbonate reservoir and secondly, to study the effect on IFT when (partial) deprotonation of the carboxylic acids takes place.

#### 3.1. The effects of surfactants and electrolytes on decane-water interfacial tension

The interfacial tension for deionized water and pure n-decane was found to be 51.1 mN/m, which is almost identical to the values reported by Jennings (1967) and Wiegand and Franck (1994). Table 5 shows previously published values for the same system.

The effect of salinity on IFT between saline water and pure decane is illustrated by the measured values in Table 6. It can be seen that salinity does not modify the IFT significantly. This suggests that the change in wettability at different brines concentration for water/oil/rock systems is in fact induced by fluids-rock interactions rather than fluid-fluid interactions. The same conclusion was reached by Yousef et al. (2011) who studied the effect of salinity on the interfacial tension between live oil and different diluted versions of sea water.

As much as we would like to claim a high degree of repeatability and reproducibility, we made a few observations that did trigger some concern. Firstly, the measured IFT value does slide as a function of time. The reason for this being impurities in the systems regardless of stringent attempts to keep solvents and surfaces clean. Because of diffusion even tiny amounts of impurities will eventually make to the surface and act as surfactants to reduce IFT. The result of a measurement conducted over 30 h is shown in Fig. 2 and a drop of roughly 10% is observed.

Additionally, measurements on different days did result in IFT values that differ by up to 10% - so we will have to take this to be the most conservative margin of error. With this in mind our results indicate that the IFT between the aqueous phases and decane is independent of salinity. The particular outliers are the OC-B2 and OB-DI experiments.

**Table 5**

Literature values for the Interfacial tension of water – pure n-decane systems.

Study	Interfacial tension [mN/m]
Michaels and Hauser (1951)	46.5
Aveyard and Haydon (1965)	52.3
Jennings (1967)	51.2
Susnar et al. (1994)	51.59
Wiegand and Franck (1994)	51.1
Cai et al. (1996)	51.55
Goebel and Lunkenheimer (1997)	53.2
Zeppieri et al. (2001)	52.3
Georgiadis et al. (2011)	51.96
This work	51.08

**Table 6**

The measured IFTs for the decane-water and decane-brine systems.

Aqueous Phase	Interfacial tension [mN/m]
DI	51.1
B1	49.0
B2	49.5
B3	52.7
B4	52.5
B5	52.3
B6	51.7

Disregarding these two, the margin of error drops to 1.5% but further systematic work is required to narrow the experimental uncertainty to this value.

The scenario is somewhat different when it comes to decane mixtures that have been modified by addition of carboxylic acids as they act as surfactants that will inevitably reduce the surface tension between decane and water. Table 7 does indeed reveal a reduction of 22–26 mN/m compared to the pure water and brine cases. There is no immediate trend in the data and the IFT reduction seems to be independent of the acid in play. The OB mixture could be representing an outlier, but it is close to being within the nominated conservative 10% margin of error.

#### 3.2. Variation of the cation

The first three brines B1-B3 represents a variation of the cation from Na<sup>+</sup> (B1) to K<sup>+</sup> (B2) and finally to Ca<sup>2+</sup> (B3) with the anion being kept unchanged as Cl<sup>-</sup>. The results are shown in Table 8 for all the artificial oils.

There are no immediate trends in between the IFT values in Table 8. The numbers weave around an average value of roughly 28. The only potential outlier is the B3, OC system where the IFT is somewhat lower and the OC mixtures in the other brine cases also result in a lower IFT, albeit not distinguishable beyond the experimental uncertainty. If the mechanism for IFT reduction had been involving for example intercalation of electrolytes in the micellar network that constitutes the molecular interface between oil and water one might have anticipated an impact from the nature of the cation. The three cations possess different solvent coordination spheres and will interact differently with the carboxylic acids in play. The fact that the cation does not impact IFT to a significant extent is taken to indicate that it is too heavily solvated by water and that no specific surfactant-cation interactions are therefore in play.

#### 3.3. Variation of the cation concentrations

The brines B5-B7 constitute a variation of electrolyte concentration and composition. The measured IFT values are presented in Table 9.

Again, the values are the same within the experimental margin of error and a comparison with the values in Table 8 doesn't reveal any differences either. So, with the salinity window that we have investigated, there is no impact of the electrolyte concentration. It seems possible to deduce a similar trend from the data reported previously by (Cai et al., 1996). Admittedly, it is a rather narrow window of salinities that have been investigated, and since it is known that particularly the formation of Winsor type-III emulsions happens at very low concentrations (Salager, Morgan, Schechter, Wade, Vasquez, 1979) there is room for an additional survey which will be the scope for a future investigation.

#### 3.4. Variation of anion

We incorporated CO<sub>3</sub><sup>2-</sup> in the study because it is a central component of a carbonate reservoir. The change from chloride to carbonate

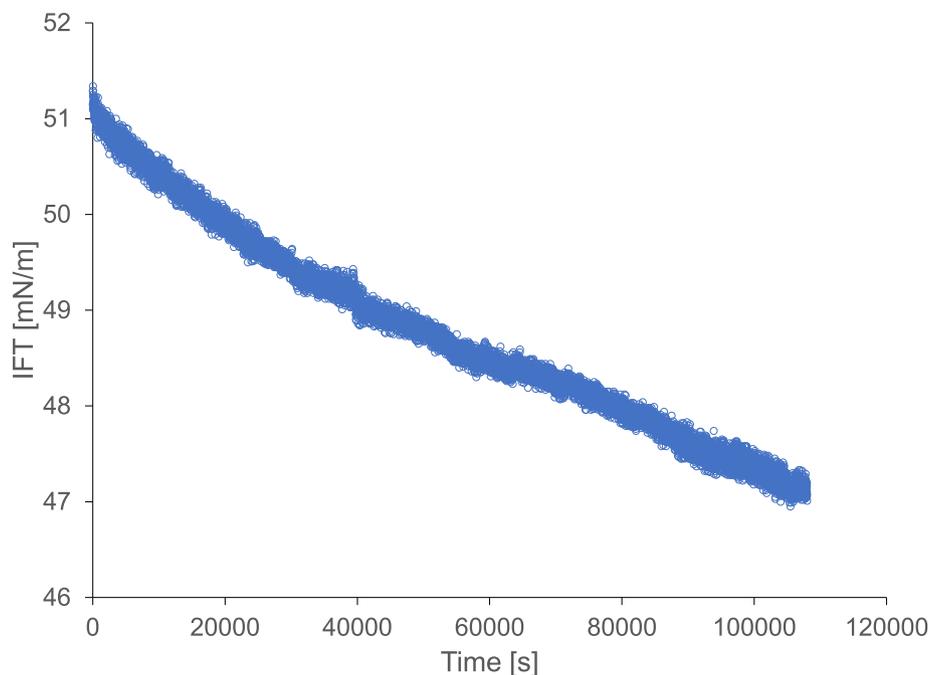


Fig. 2. Interfacial tension of deionized water and pure n-decane over a period of 30 h.

Table 7

The measured IFTs for the decane/acid mixture-water systems.

Aqueous Phase	Interfacial tension [mN/m]
OA	29.1
OB	25.4
OC	27.8
OD	28.2

Table 8

Average interfacial tension values for the brine/artificial oil.

Brine	n-decane – organic acid mixture	Interfacial Tension Average (from 200 s to 600 s)
B1	OA	30.5
	OB	26.0
	OC	26.1
	OD	30.0
B2	OA	30.1
	OB	26.9
	OC	25.7
	OD	29.4
B3	OA	33.6
	OB	28.7
	OC	24.0
	OD	28.1

adds a significant pH change to the picture and results in deprotonation of the carboxylic acids to result in a more dipolar surfactant with an anion carboxylate end and a non-polar tail. This, not surprisingly, results in IFTs that are by far the lowest to the extent that it was not possible to maintain a droplet to measure the interfacial tension for some of the systems. It was only possible to measure the IFT in the case of OB and OD where the result was 12.8 and 11.0 mN/m, respectively. Also, in this case there does not seem to be a significant impact of the brine concentration, and the fact that OA and OC compositions did not result in stable drops could be due to variations in the experimental conditions that are beyond our control or it could simply be due to the fact the acids are now deprotonated and therefore resides in the water-phase too. As has been pointed out by previously (Andersson et al.,

Table 9

Average interfacial tension values for the brine/artificial oil.

Brine	n-decane – organic acid mixture	Interfacial Tension Average (from 200 s to 600 s)
B5	OA	30.0
	OB	29.4
	OC	27.3
	OD	26.2
B6	OA	29.7
	OB	29.5
	OC	27.5
	OD	26.3
B7	OA	29.3
	OB	29.7
	OC	28.8
	OD	27.3

2014) the IFT is more sensitive to surfactant structure when the surfactant resides in the aqueous phase rather than being imbedded in the oil phase.

#### 4. Conclusion

It seems evident that the salinity and cation character do not have a significant impact on the interfacial tension. Subtle changes may be hidden in the experimental uncertainty of the IFT as determined by the pendant droplet method. A very conservative estimate of the reproducibility is here estimated to be up to a 10%. This is, however, based on one outlier and all other experiments indicate a number in the percent range. To address the matter further a large series of electrolytes will be addressed in a future study with a large range of concentrations. Additionally, it is known that IFT is a temperature dependent quantity something which also is beyond the scope of the present contribution but is to be included in the future study. Quite possibly supported by theory to clarify the key interactions at the molecular level. The aim will be to determine the salinity range, where IFT is in fact impacted to generate low IFT emulsions that are highly relevant in EOR contexts. This study also shows that the impact of the carbon chain length is small, which again calls for a test in a large set of acids. All in

all, water and decane are probably in too large excess for subtle structural influences to reveal themselves.

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