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How a range of metal ions influence the interfacial tension of n-decane/carboxylic acid/water systems: The impact of concentration, molecular- and electronic structure

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ABSTRACT

The data from more than 700 pendant droplet interfacial tension (IFT) measurements has been scrutinized to reveal the relation between salinity/surfactant structure and IFT in a brine – decane/carboxylic acid system. The large number of measurements enabled an experimental uncertainty of around 1% in the IFT range around 30 mN/m. Thus, small changes and trends in IFT as a function of salinity and surfactant structure become apparent. Five carboxylic acids are chosen to resemble natural naphthenic acids; individually, they only differ by a CH_2-group starting from cyclohexane carboxylic acid and ranging to 5-cyclohexyl pentanoic acid. The salt concentration was varied from 0.01 M to 1.0 M for a range of chlorides of monovalent and divalent metal cations: LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, and $ZnCl_2$. For Na^+, NaBr, NaI, were also investigated. The variation in IFT with salinity and carboxylic acid is subtle with divalent ions, not surprisingly, inducing larger IFT changes than monovalent ones when the concentration is varied. Zn^{2+} gives rise to a surprisingly large IFT reduction (up to 7.5 IFT units in the range from 0.01 M to 1.0 M) and clearly stands out as a special case. For the three smallest chain acids the IFT increases as a function of salinity whereas, for the system involving the two largest ones, 4-cyclohexyl butanoic acid and 5-cyclohexyl pentanoic acid, IFT decreases as a function of salinity. The distinct behavior of Zn^{2+} and the sudden crossover in the variation of IFT as a function of salinity when increasing the chain length of the carboxylic acid is taken to indicate that structure of both the (solvated) electrolyte and the carboxylic acid– particularly with regard to the orientation at the interface - are important factors in determining the magnitude and variation in IFT as a function of physical parameters.

1. Introduction

The properties and structure of the interface between two immiscible liquids containing electrolytes and surfactants is a topic that is associated with a great deal of interest and an equal proportion of uncertainty (Langevin, 1992). The complexity increases with the inclusion of dissolved species (Petersen and Saykally, 2006). The impact on the properties of the interfacial layer is undoubtedly most pronounced when the dissolved species are either charged or polarized allowing for a favorable interaction at the charged interface (Kudin and Car, 2008; Harkins and Humphery, 1916). A classic example of such a system is that of brine in contact with an organic phase that includes polarized organic molecules – commonly known as surfactants and, often, these surfactants are organic acids. One class of surfactants is naphthenic acids. These have a carboxylic acid functionality as head group and a saturated hydrocarbon backbone with one or more cyclic substructures (Wu et al., 2008; Speight, 2014). Interfaces in systems with organic liquids versus brines are relevant for a number of systems ranging from simple mayonnaise formulations to what dictates subsurface fluid flow in oil reservoirs (Wu et al., 2008; Chalbaud et al., 2009; Tiab and Donaldson, 2011). The interfacial property relevant to oil and gas contexts is (d)emulsification propensity, where both kinetic as well as thermodynamic considerations are critical. That is, not only the question of whether emulsions form and break, but how fast they form and how long they will persist (Subramanian et al., 2017; Czarnecki and Moran, 2005; Alyafei and Blunt, 2016). Although there is no simple correlation between the two, the phenomena of interfacial tension and formation of micellar structure, that are responsible for (d) emulsification processes, are intimately related (Shi et al., 2018; Subramanian et al., 2017; Tan el al., 2017). Also, IFT is an important factor in the sense that it enters the equation for capillary pressure and contact angle and, consequently, it is a key parameter in determining

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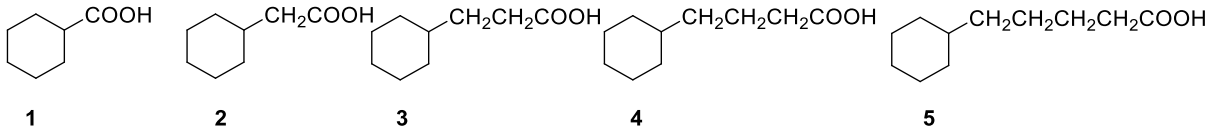
fluid flow in a system of connected capillaries, such as that in porous media (Ese and Kilpatrick, 2004). Since IFT is intimately related to fluid flow, it is of great interest to be able to control IFT with the focus of increasing the flow of oil from the subsurface (Schechter et al., 1994). One way of doing this is by modifying the composition of the brine that surrounds the oil. The nature of the electrolytes that are present in the water impact the ability of an oil droplet to accommodate the stress put forward by water repulsion (Harkins and Humphery, 1916; Wen et al., 2017). Water modification is by far the most cost-effective approach to enhanced oil recovery, but to target an approach beyond trial and error it is essential to fully understand the nature of the interfacial layer at the molecular level. That is, exactly how the structure of organic surfactants impacts their preferred orientation at the interface, and how does this impact their interaction with electrolytes. The changes are not expected to be large, so we devised a careful and systematic study that is accurate enough to tease out some of the interfacial secrets that ultimately are key drivers in enhanced oil recovery.

2. Experimental details

2.1. Chemicals

The five carboxylic acids (acids 1–5; cyclohexane carboxylic acid (**1**) (98%), cyclohexyl acetic acid (**2**) (98%), 3-cyclohexyl propanoic acid (**3**) (99%), 4-cyclohexyl butanoic acid (**4**) (99%) and 5-cyclohexyl pentanoic acid (**5**) (98%)) were purchased from Sigma-Aldrich and used without further purification. Their concentration was is all cases 1.66 mol%. Their structures are shown below:



Salts are standard stock chemicals from Aldrich as well and of a purity of >99%. Decane from Aldrich (HPLC grade) was purified by filtration through a silica column four times, and its IFT against milli-Q® deionized water was measured. The measured IFT was stable over 600 s, indicating no significant diffusion of impurities to the surface. The purified decane was kept in a dark place in a glass beaker resting upon a bed of silica powder in a closed container. The electrolyte solutions were stored in single-use plastic containers. The containers were systematically and thoroughly rinsed. First with a drop of soap then by brushing and flushing with tap water. Following this treatment, the containers were emptied and flushed several times again with Milli-Q® deionized water (Resistivity of 18.2 MΩcm). The adequacy of the cleaning process was checked by measuring the surface tension of Milli-Q® water that was stored in such a container overnight. Measured values were 72.87 mN/m, 73.06 mN/m, 72.99 mN/m where the reference value for the surface tension of water at 20 °C is 72.80 mN/m, 72 thus signifying, that after the cleaning, there were no significant impurities left in the container. Then 1.0 M solutions of salts were prepared using Milli-Q® deionized water, and from these, solutions of 0.01 M, 0.1 M, and 0.5 M were made by dilution, and all solutions transferred to their respective cleaned containers. Decane solutions of the five naphthenic acids were made by weighing out the liquid carboxylic acid into a clean container with a micropipette and adding purified decane up to the target concentration of 1.66 mol %. The solutions of the organic acids were stored in sealed glass containers in a dark place.

2.2. Interfacial tension measurements

Interfacial tension measurements were done on the Attension Theta Optical Tensiometer instrument from Biolin Scientific. The technique was pendant drop drop-shape-analysis. The interfacial tension can be calculated by analyzing the droplet shape in combination with the density difference between the two phases (Berry et al., 2015):

$$\gamma = \Delta\rho g r_o^2/\beta$$

Interfacial tension is γ and the difference in density of the phases is Δρ. g is the gravitational constant, while the drop's radius of curvature, measured at the apex, is r_o, and β is a shape parameter. For each drop shape, there exists a unique shape parameter. The instrument was calibrated with a calibration ball of diameter 4.000 mm ± 0.005 mm. Measurements were done with a gas-tight syringe with a J-shaped needle attached. The needle was immersed into Milli-Q deionized water contained in a quartz cell and from it, drops of either carboxylic acid solution or pure decane were generated. The drop shapes were captured and analysed with the OneAttension software. Each IFT value is an average over three measurements on three individual drops. After creation, the drop was imaged every fourth second to give a total of 46 measurement points after a period of 180 s. The IFT measurements do indeed depend on time and stopping after 180 s is based on an assumption that the dependencies are the same or at least very similar for the systems under study. The assumption is very unlikely to be completely fulfilled and deviations will obviously add to the uncertainty. The dynamical behavior of the IFT in pendent droplet measurements is due to factors such as diffusion and droplet size reduction and it will be the topic of a future independent study. The experimental data for each salt concentration arise from three replicate measurements, each consisting of 46 measured IFT values. The quartz cell and needle were cleaned before the quartz cell was filled with a new aqueous phase. Cleaning was done thorough flushing with Milli-Q® deionized water and acetone (interchangeably). For 3-cyclohexyl propanoic acid, the IFT value dropped by a unit before stabilizing after ten minutes, after which the measurements were done.

2.3. Data treatment

Each measurement contains 46 data points, and these were checked for outliers using the two-tailed Grubb's test (Grubbs and Beck, 1972) with a 95% confidence level. It was found that around every tenth measurement had one outlier, and it was very seldom for measurements to contain more than one outlier. It was found, using the Shapiro-Wilk test, that the vast majority of the data sets were normally distributed, and uncertainties of the average IFT value were expressed as 99.5% confidence intervals calculated from the measurements' standard deviation. To obtain an estimate of the uncertainty of the mean IFT value of the three replicate data sets for each system, the squared uncertainties of each replicate were summed, and the total uncertainty was expressed as the square root of that sum as per standard error propagation procedures. Using this procedure, each system containing three replicates had their average IFT and uncertainty calculated (the latter generally found to be between ±0.10 mN/m and ±0.30 mN/m).

2.4. Density measurements

To determine the interfacial tension, the densities of the employed solutions were recorded. Measurements were conducted on an Anton Paar DMA 4500 M density meter. For each solution, a small sample of 2–3 mL was injected into the instrument, and the density was measured at 22 °C – the average temperature of the laboratory in which the IFT measurements were conducted. Densities were measured with a precision of four decimal points and are provided in Table S1 of the supporting information.

3. Results and discussion

The present set of data represents a compilation of very carefully conducted and systematic experiments. The overlying idea is to reduce the uncertainty to a minimum to be able to observe even slight variations in the measured IFT when systematically varying the metal ion down along the first two main groups of the periodic table with the inclusion of zinc. The anion was chosen amongst the halides Cl^-, Br^-, I^-. Additionally, the carboxylic acids that we have chosen to shed light on the phenomena that take place at the interface were modified systematically to become longer chain and thus more hydrophobic. They are simply carboxylic acids where the COOH group and the lipophilic cyclohexyl group are separated by 0–4 methylene units.

3.1. Accuracy of the IFT values determined by the pendant drop method

The V_d/V_{max} ratio is the so-called Worthington number (where is V_d is the droplet volume and V_{max} is the volume at which the droplet dispatches from the needle); operating at Worthington numbers close to unity results in the most reliable measurements (Berry et al., 2015). Measurements were conducted with drop volumes corresponding to Worthington numbers in the range of 0.90–0.95. The spread of repeated interfacial tension values was lower when increasing the drop volume. The accuracy of the instrument and the quality of the calibration was tested by measuring pure decane against water yielding average IFT values of 51.51 mN/m, 52.04 mN/m, 51.43 mN/m, and 51.19 mN/m for four replicate measurements measured over 600s. With most literature values in the range of 51.1 mN/m to 53.2 mN/m, the agreement is excellent (Georgiadis et al., 2011; Goebel and Lunkenheimer, 1997; Sayed et al., 2019; Susnar et al., 1994; Zeppieri et al., 2001). Based on the statistical treatment, the precision of the individual measurements was found to be between ±0.10 mN/m and ±0.30 mN/m, and the repeatability of three replicates measured in succession of each other is therefore very high. The quartz cell and needle were removed for cleaning from one measurement to the next.

The variation of the overall method including the intermittent cleaning procedures was investigated using repeated measurements on the same system at three different days. The average measured IFT values from each set of three replicates were used to compute a mean and standard deviation. From this, the uncertainty owing to the variation of the method was expressed as a 99.5% confidence interval. This was done for acid 2–4, and the average uncertainty on the IFT values was ±0.23 mN/m. To express a total value for the uncertainty of the mean IFT value of each system, the uncertainty of ±0.23 mN/m was simply added to the uncertainty of the measurements as determined above. Note that a simple summation of uncertainties is not standard error propagation procedure. Standard propagation procedures would yield a total uncertainty that is smaller by a factor √2, however, to allow for a wider margin of error, total uncertainties on IFT results are a sum. From the repeated measurements described above, quality control charts of the type described by (Harris, 2016) were constructed (Fig. 1). These charts allow for an evaluation of the precision of the method over time, and serve as a reference check for the quality of the procedure. The mean (solid line) is calculated and lines of $\pm\ 2\sigma\sqrt{n}$ (warning line, narrow dashed) and $\pm\ 3\sigma\sqrt{n}$ (action line, wide dashed) are shown, where $n = 3$ is the number of replicate measurements, and σ is the standard deviation of the measurements. Because data are normally distributed 99.7% of data should be within the action lines.

t is essential to note that if one of the following six events are so unlikely that if one is witnessed, the experimental procedure should be re-evaluated and checked for flaws: A measurement outside the action lines. Two measurements in a series of three are between the action and warning lines. Seven back-to-back measurements above or below the mean. Six measurements in a row all increasing or decreasing. Fourteen measurements alternatingly increasing and decreasing. And lastly, any pattern that is obviously not random (Harris, 2016). According to these criteria, the present measurements are well behaved with total uncertainties on mean IFT values between ±0.30 mN/m and ±0.55 mN/m.

3.2. Impact of variation in structure of the carboxylic acids on the interfacial tension

The five acids that are employed in this study are not expected to differ much in terms of acidity or solubility in water.

All acids have a similar pK_a value which is slightly higher than that of acetic acid; in the case of cyclohexane carboxylic acid it is 4.9. Since the pK_a values are virtually identical, any observed IFT trend is not related to increased deprotonization but solely determined by the structure and orientation of the carboxylic group at the interface. It is exactly the detailed interfacially related phenomena, such as those related to structure and orientation, that we intend to address in this study. The results of the IFT measurements involving a pure water phase against a decane-acid phase are shown in Table 1.

There is a decreasing trend in the IFT when progressively adding one and two CH_2 groups to the base cyclohexane carboxylic acid. The trend stops at three CH_2 groups where the IFT suddenly increases only to go down again for the $(CH_2)_4$ species. The changes are subtle, but the trends are identifiable within the uncertainty. It is also noticed that the trend persists when electrolytes are added to the water in low

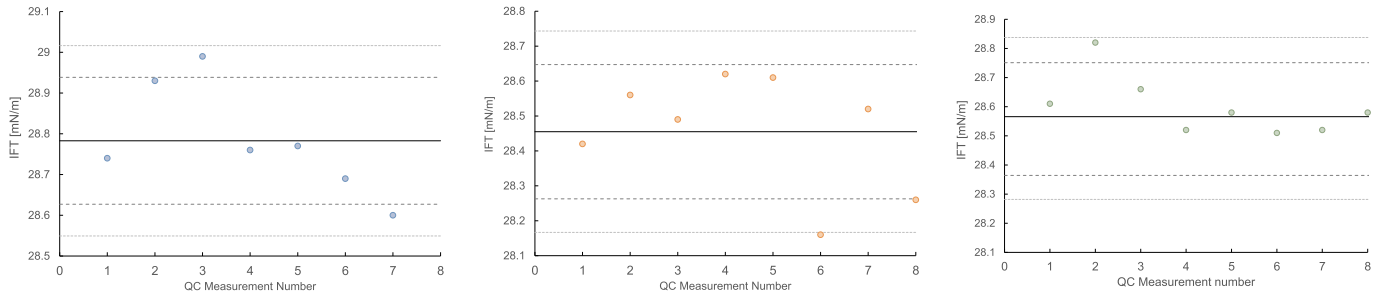


Fig. 1. Harris quality charts (Harris, 2016) to reveal the repeatability of the pendant drop IFT measurements. Solid line is the mean IFT value. Narrow dashed lines represent the mean IFT value $\pm\ 2\sigma\sqrt{n}$, while wide dashed line represents the mean value $\pm\ 3\sigma\sqrt{n}$ *for (left) acid 2, (middle) acid 3, and (right) acid 4.*

Table 1
IFT milli-Q water-decane/acid phases. The acid concentration was 1.66 mol%.

Conc. = 1.66 mol%	IFT (mN/m) Experimental
Cyclohexane carboxylic acid	30.39
Cyclohexyl acetic acid	28.79
3-Cyclohexyl propanoic acid	27.56
4-Cyclohexyl butyric acid	29.55
5-Cyclohexyl pentanoic acid	28.86

concentrations (up to 0.5 M); there is a decreasing trend from acid 1 to 3 but IFT goes back up for acid 4 and then down for acid 5. The only exception to this rule is found in the case of $CaCl_2$. This is evident from Tables 3 and 4 in the case of the mono- and divalent ions respectively.

3.3. Impact of electrolyte variation on the interfacial tension

Overall, there is little, if any, impact on IFT when the monovalent cation is varied down along the first main group from Li to K. If anything, potassium could be seen as reducing the IFT slightly more than the other alkali metal ions. This is illustrated by considering the 1.0 M concentrations in Table 2 to potentially observe the largest impact on IFT. It is noticed that the IFT decreases from acid 1–5, this stands in contrast to what is the case for the lower concentrations (e.g. 0.01 M) where there is a decrease from acid 1–3 and an increase when it comes to acid 4 and a drop for acid 5.

A similar range of experiments were conducted, without the presence of carboxylic acids, what is, simply to investigate the impact of the electrolytes on a pure decane phase. The results are shown in Table 4. It is evident that the uncertainty is significantly higher than in the presence of carboxylic acid; this is probably due to a higher instability of the droplet surface in the absence of surface-active molecules. This increased uncertainty makes it difficult to recognize individual subtle effects. In most cases, the IFT values are lower compared to the pure-water/decane system, the IFT is highest for high salinities and in some of the cases even higher than the pure-water/decane system – similar to what was found for acid 1–3 in combination with decane-where the IFT also increases with salinity. This is not surprising as an increased number of electrolytes will increase the hydrophilic-hydrophobic interaction at the interface. It has also been verified theoretically by the Gibbs excess absorption theory for air-aqueous NaCl systems that larger NaCl concentration leads to larger absorption particularly by chloride to result in an increased surface tension (D'Auria and Tobias, 2009; Levin, 2000). The data does seem to indicate that KCl regardless of concentration induces a slightly higher IFT reduction as is also the case when a carboxylic acid is present in the system.

The impact of changing the anion is a little more striking (Table 5). The results are pointing towards a reduction in IFT when varying the halides down the row Cl^-, Br^- and I^-. It was also noticed that the high salinity trend for NaI differs from all the other 1.0 M brines where the IFT decreases from acid 1 to acid 5. For NaI, the trend resembles that of the lower concentrations - decrease from acid 1–3, increase for acid 4 and decrease for acid 5. This finding, together with that of K^+, shows that the solvation of the electrolytes in play has a central role. Iodide is a large and easily polarizable species that does not have a high demand to be surrounded by solvent molecules (here water) and by the same token iodide is much more free in enter into a specific interaction at the interface to engage all available surfactant sites even at low concentrations. Thus, 1.0 M iodide will resemble the low-concentration/pure case much more. The same argument can be applied towards K^+ - the cation is freer to bind more tightly to the carbonyl lone pair to stabilize the interface and reduce the IFT.

The IFT is influenced to a slightly higher degree by the divalent species (Table 3) which to a certain extent is no surprise because the interfacial behavior is determined by the covalent and electrostatic interactions between the oil/carboxylic acid layer, the polarized and unperturbed water molecules, and ultimately directly by donor-acceptor interactions between electrolytes and the organic acids at the interface. The effect is not a large one though. It seems like the values start slightly higher, a big impact is only in place in the case of Zn^{2+}; here crystallites are observed to form on the actual droplet when acids 4 and 5 are in play; but only in those cases. This latter phenomenon made it difficult to calculate an accurate IFT owing to a poor fit of the drop profiles. The crystallites also act as a stabilizing interfacial shield between the brine and the decane as shown in Fig. 2. The fact that the crystallization only is pronounced for acid 4 and 5 is indicating that the interfacial structure is highly important, dependent on the bipolar molecules in the oil phase and, unfortunately, hitherto not properly understood.

3.4. Impact of electrolyte concentration on the interfacial tension

The relation between brine concentration and IFT is a story in its own right, and to a certain extent, the discussion has already been opened up above. The trends that are apparent from Tables 2–5 can be summarized in a few very general statements:

1. For the monovalent cations the IFT increases with concentration in the case of acid 1–3, for acid 4 and 5, IFT decreases with concentration. NaI is an exception. In this case, IFT decreases with concentration in all cases but for acid 1.
2. For the divalent cations, IFT is mostly increasing with concentration for acid 1–4 and decreasing in all cases for acid 5. $BaCl_2$ is an exception; here a decrease with concentration is observed in the case of acid 4 as well.

These observations point in the same directions as those for the investigation of the structural variation of the acid and the electronic

Table 2
IFT brine-decane phases as a function of the monovalent cation.

IFT	Acid 1	Error	Acid 2	Error	Acid 3	Error	Acid 4	Error	Acid 5	Error
LiCl 0.01 M	30.40	0.47	28.75	0.52	28.50	0.30	29.21	0.41	26.46	0.53
LiCl 0.1 M	30.68	0.41	28.95	0.44	28.08	0.39	29.01	0.41	25.60	0.48
LiCl 0.5 M	31.04	0.37	29.14	0.49	28.24	0.29	28.46	0.47	25.05	0.48
LiCl 1 M	31.29	0.38	29.38	0.33	28.31	0.36	27.88	0.48	24.16	0.29
NaCl 0.01 M	30.44	0.49	28.93	0.35	28.36	0.32	29.16	0.47	26.90	0.30
NaCl 0.1 M	30.55	0.43	29.10	0.32	28.53	0.34	29.00	0.38	26.45	0.13
NaCl 0.5 M	31.10	0.43	29.37	0.42	28.48	0.37	28.76	0.42	24.79	0.44
NaCl 1 M	31.24	0.48	29.65	0.38	28.64	0.40	28.45	0.46	24.01	0.38
KCl 0.01 M	30.39	0.40	28.99	0.31	28.44	0.35	29.19	0.45	27.29	0.25
KCl 0.1 M	30.42	0.35	28.93	0.43	28.01	0.39	28.83	0.57	24.43	0.25
KCl 0.5 M	30.61	0.47	29.30	0.57	28.08	0.42	28.42	0.44	25.26	0.33
KCl 1 M	31.30	0.43	29.25	0.34	28.48	0.40	28.11	0.41	23.29	0.36

Table 3
IFT water-decane phases as a function of the divalent cation.

	Acid 1	Error	Acid 2	Error	Acid 3	Error	Acid 4	Error	Acid 5	Error
$MgCl_2$ 0.01 M	30.70	0.48	28.67	0.31	27.98	0.45	28.80	0.42	24.16	0.49
$MgCl_2$ 0.1 M	30.59	0.30	28.75	0.36	27.84	0.47	28.36	0.48	23.46	0.32
$MgCl_2$ 0.5 M	31.41	0.44	29.54	0.37	28.68	0.48	28.82	0.43	22.78	0.48
$MgCl_2$ 1 M	32.63	0.35	30.78	0.36	29.43	0.45	29.43	0.42	21.42	0.40
$CaCl_2$ 0.01 M	30.52	0.36	28.73	0.38	27.86	0.40	26.57	0.66	26.95	0.36
$CaCl_2$ 0.1 M	30.75	0.43	28.85	0.44	27.80	0.49	26.22	0.63	24.89	0.26
$CaCl_2$ 0.5 M	31.36	0.44	29.48	0.35	28.22	0.52	25.84	0.59	22.29	0.50
$CaCl_2$ 1 M	32.39	0.35	30.40	0.35	28.51	0.49	25.22	0.61	20.47	0.37
$SrCl_2$ 0.01 M	30.58	0.29	28.61	0.31	27.70	0.52	28.97	0.50	26.64	1.17
$SrCl_2$ 0.1 M	30.55	0.31	28.83	0.35	28.21	0.51	28.22	0.39	25.23	0.36
$SrCl_2$ 0.5 M	31.30	0.43	29.19	0.35	28.34	0.42	28.52	0.48	23.26	0.39
$SrCl_2$ 1 M	32.05	0.38	30.28	0.32	28.93	0.43	28.90	0.41	21.97	0.30
$BaCl_2$ 0.01 M	30.48	0.38	28.39	0.30	27.94	0.54	28.85	0.49	25.78	0.23
$BaCl_2$ 0.1 M	30.59	0.46	28.30	0.36	27.79	0.46	28.20	0.40	23.52	0.32
$BaCl_2$ 0.5 M	31.22	0.34	28.94	0.33	27.64	0.42	28.05	0.36	22.75	0.24
$BaCl_2$ 1 M	32.12	0.33	29.82	0.30	27.76	0.39	27.79	0.42	21.57	0.18
$ZnCl_2$ 0.01 M	30.50	0.39	28.43	0.33	27.98	0.50	28.15	0.45	23.80	0.41
$ZnCl_2$ 0.1 M	30.58	0.32	28.19	0.35	27.40	0.50	25.21	0.37	20.20	0.22
$ZnCl_2$ 0.5 M	30.57	0.37	27.02	0.34	20.79	0.39	19.85	0.40	18.76	0.38
$ZnCl_2$ 1 M	29.50	0.33	22.26	0.31	N/A	N/A	20.81	0.32	18.70	0.34

Table 4
IFT milli-Q water-decane phases as a function of the mono- and divalent valent cation and halide anion.

	0.01 M	Error	0.1 M	Error	0.5 M	Error	1 M	Error
LiCl	49.58	1.14	50.58	0.76	50.85	0.74	51.65	1.02
NaCl	49.73	0.93	50.29	0.63	50.63	0.85	51.46	0.96
KCl	46.93	1.31	47.56	0.90	47.35	1.23	47.35	1.23
NaBr	49.99	0.78	50.25	0.78	50.72	0.83	50.91	0.98
NaI	50.85	0.79	50.41	0.89	50.21	1.00	49.83	1.22
$MgCl_2$	49.62	1.07	48.73	1.63	49.66	1.65	50.37	1.70
$CaCl_2$	50.59	0.85	50.83	0.74	50.95	0.88	51.45	0.85
$SrCl_2$	46.77	1.16	47.65	1.17	46.58	1.33	45.51	1.51
$BaCl_2$	50.16	1.17	49.49	1.16	48.23	1.04	48.19	1.22
$ZnCl_2$	50.33	0.86	50.68	0.72	50.97	0.97	51.32	1.11

nature of the electrolyte. Because of the distinct change-overs from one ion to another and from one carboxylic acid to another, the results indicate that there are several factors in play to influence the IFT when the electrolyte concentration is varied. The most obvious being the electronic structure of the involved ions and the molecular structure of the involved carboxylic acid.

4. Key factors in determining the interfacial tension: unifying picture

There is not one unifying trend, but rather a sudden shift in concentration and electrolyte dependence when the length of the alkyl chain that separates the ring structure from the polar end is extended. The changing nature of the IFT interplay between acid structure, electrolyte concentration and electrolyte identity is testament to a delicate structure at the water-decane interface that is influenced by the surrounding environment. The fact that divalent ions give rise to a stronger impact than monovalent ions is indicating that electrostatic interactions at the interface rather than specific interactions are in play. The fact that IFT increases as a function of concentration for the smaller acids is also an indication of an electrostatic rather than a specific interaction being in play. The size of acid 1 forces it to orient itself more specifically than the rest of the acids to ensure that the (hydrophobic) ring is fully submerged in the decane phase. This leaves little room for the electrolytes to stabilize the interface as the hydrophilic ends will be able to pack quite closely; thus, additional electrolytes will not stabilize the system but rather destabilize it through coulombic repulsion the electrolytes in between. In the case of the longer chain acids, the position of the acid at the interface is more forgiving. This leaves room for more acids to interact at the interface. This idea is illustrated with the schematic in Fig. 3 showing that structural parameters such as packing at the surface are important because the carboxylic acid has to be directed very specifically when small compared to the larger system that leaves some flexibility to the orientation of the carboxylic acid at the interface.

The fact that acids 4 and 5 results in crystallization at the interface is in line with this argument. The ability of the acids to adopt a variety of configurations allow for re-orientation in response to electrolytes. Apparently, it would seem that large concentrations of zinc induce a structure in the interface that can lead to the seed of a crystallization process.

Table 5
IFT water-decane/acid phases as a function of anion. The acid concentration was 1.66 mol%.

	Acid 1	Error	Acid 2	Error	Acid 3	Error	Acid 4	Error	Acid 5	Error
NaCl 0.01 M	30.44	0.49	28.93	0.35	28.36	0.32	29.16	0.47	26.90	0.30
NaCl 0.1 M	30.55	0.43	29.10	0.32	28.53	0.34	29.00	0.38	26.45	0.13
NaCl 0.5 M	31.10	0.43	29.37	0.42	28.48	0.37	28.76	0.42	24.79	0.44
NaCl 1 M	31.24	0.48	29.65	0.38	28.64	0.40	28.45	0.46	24.01	0.38
NaBr 0.01 M	30.63	0.43	29.04	0.43	28.51	0.53	29.13	0.50	27.66	0.53
NaBr 0.1 M	30.61	0.38	28.84	0.35	28.06	0.41	28.93	0.44	26.88	0.40
NaBr 0.5 M	30.89	0.53	29.24	0.37	28.42	0.55	28.71	0.42	25.07	0.38
NaBr 1 M	31.20	0.42	29.49	0.39	28.29	0.45	28.30	0.37	24.55	0.27
NaI 0.01 M	30.64	0.39	29.08	0.34	28.21	0.44	29.09	0.45	26.30	0.94
NaI 0.1 M	30.48	0.35	28.72	0.43	27.77	0.50	28.70	0.48	25.21	0.15
NaI 0.5 M	30.54	0.38	28.81	0.38	27.58	0.41	28.15	0.40	23.72	0.36
NaI 1 M	30.73	0.36	28.66	0.31	26.97	0.46	27.64	0.40	21.78	0.38

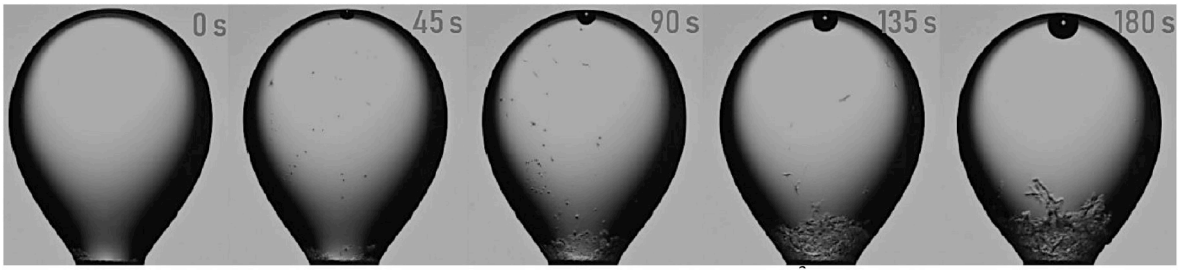


Fig. 2. The growth of Zn containing crystals as a function of time in a Zn^{2+}(aq)-decane system.

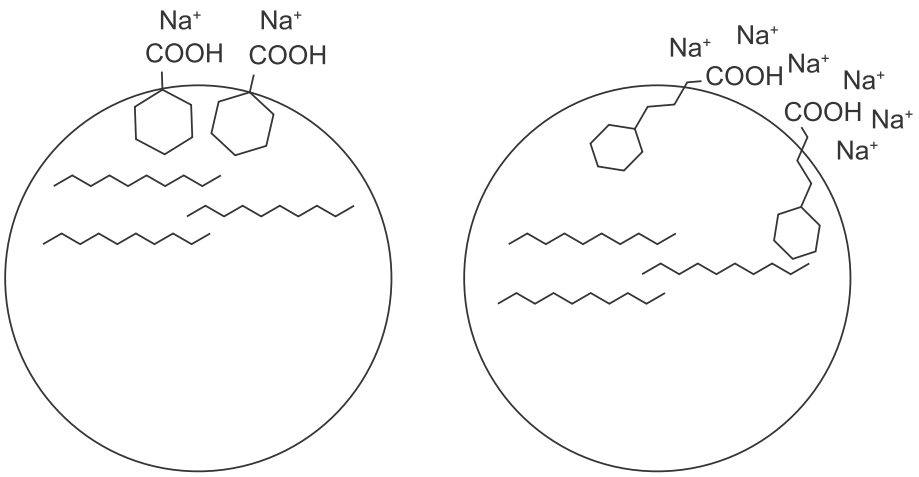


Fig. 3. Schematic drawing to illustrate the interpretation of the interplay between structure and electrolyte concentration. The cartoon exemplifies the situation for cyclohexane carboxylic acid (acid 1, left) and 4-cyclohexyl-butanoicacid (acid 3, right). When the larger acid (right, acid 3) leaves more room for interaction with the electrolytes at the surface the IFT goes down as the concentration goes up.

The behavior of the halide ions Cl^-, Br^- and I- and that of K^+ vs. Na^+ is clearly indicating that the solvation of the electrolytes by water also plays an important role. This is most evident for anions because of their ability to form strong hydrogen bonds. The need for solvation decreases from Cl^- to I^-. Thus, I^- will be less solvated in the bulk water phase and more active in impacting IFT. This latter observation could also be taken to indicate the involvement of specific interactions at the interface, such as the hydrogen bonding suggested here, plays a key role.

5. Conclusion

The variation in IFT is generally quite small and often almost not discernible from the experimental error. Therefore, it is only with great experimental care that it is possible to observe any overarching trends. The addition of carboxylic acids to the oil causes an average IFT reduction of roughly 20 mN/m. The IFT-drop from milli-Q deionized water to brine is 4 mN/m at the max for comparison. The impact of increasing the tail length of the carboxylic acid from acid 1–5 is around 10 mN/m for all electrolytes albeit the most pronounced changes seem to occur in the divalent cases. This is not surprising given the fact that it is all about stabilizing charges that build around the interface and to this end divalent ions are better. The effect of changing the concentration is therefore also most pronounced for the divalent ions with the largest change being observed for $CaCl_2$ in combination with acid 5 where the reduction is 6.5 mN/m. The relatively small changes could be taken to indicate that the low salinity brine is not able to reduce the IFT between oil and an aqueous phase, but that higher salinities seem to drive the system towards lower IFT. Whether this means a larger propensity for (micro)emulsification is a different matter that requires further investigation. The results presented here show that interfacial phenomena are playing a very delicate role when it comes to phase behavior; sudden reversal of IFT trends in for example the concentration dependence when adding a single $–CH_2–$ group to the carboxylic acid. A subtle balance is in play at the interface; an actual determination of the structure at the surface should be the objective of future studies ideally from an experimental angle, but a theoretical approach via molecular dynamics may prove to give important insight too.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petrol.2019.106307.

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