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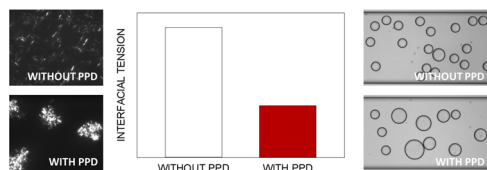
Characterization and assessment of wax and wax inhibitors systems in microfluidic oil-in-water coalescence experiments

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GRAPHICAL ABSTRACT



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ABSTRACT

During produced water treatment, one of the key underlying phenomena affecting separation performance is coalescence between oil droplets. These processes can be affected by several factors, including chemical composition of fluids, process conditions, droplet characteristics, but also presence of different production chemicals. In this paper, we study the effect of wax and wax inhibitors on the stability of oil droplets in brine with a microfluidic coalescence method. Three wax inhibitors with known chemistries were added to crude oil and solutions of macrocrystalline wax in dodecane. All the systems were characterized with regards to their physicochemical, rheological and interfacial properties, while the microfluidic coalescence measurements were performed below and above the wax appearance temperature. In most cases, higher concentration of the inhibitors lowered the coalescence frequency between the droplets, however the presence of wax often reduced the stabilizing effect of the additives. The most stable emulsions, often by 1–2 orders of magnitude, were obtained for the polycarboxylate wax inhibitor with the lowest molecular weight and exhibiting highest interfacial activity. Styrene block copolymer was also found to prevent coalescence, most likely by changing the mechanical properties of the interface, however this was strongly affected by the concentration of wax in the solution. Higher temperature mostly affected the inhibitor-paraffin or inhibitor-solvent interactions, which resulted in increase or reduction of emulsion stability, depending on the inhibitor. Crude oil systems, more stable than model solutions to begin with, were found to be only slightly affected by the presence of additives. This was mostly attributed to the abundance presence of crude oil indigenous surface-active components. Still, in all cases when an additive was present, the stability of droplets increased. Overall, this study underlines the importance of non-separation related production chemicals within the wider frame of separation processes in upstream petroleum processing.

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1. Introduction

Oil and water separation during processing of crude oil often rely on the efficient coalescence between droplets [1]. While the poor treatment of the oil-continuous stream will affect the quality of the export product, the ineffective separation of crude oil from produced water (PW) is much more urgent from the environmental and process safety point of view, whether PW is discharged [2,3] or re-injected [4]. Crude oils contain a wide variety of indigenous components, such as asphaltenes, resins or naphthenic acids, that exhibit surface activity and can inhibit merging between drops. Additionally, during the course of upstream petroleum production, a number of chemicals are injected into the production stream. These chemicals are often added in order to mitigate or remediate specific problems occurring during the production. Depending on the solubility of the additives, they can follow the oil or water streams through their respective treatment processes, where their presence could potentially cause undesirable separation problems. For example, various chemicals are used to improve oil recovery [5] or can be injected to avoid issues arising from gas hydrates [6], asphaltene precipitation and deposition [7] or wax crystallization [8].

Wax crystallization and deposition is one of the major flow assurance issues, which pose significant challenges to the petroleum industry. Upon leaving the reservoir, the produced fluids are usually at a high temperature. Cooling of the petroleum, for example by cold subsea environments or at the processing facility, can lead to wax crystallization once the wax appearance temperature (WAT) is reached. Problems associated with wax crystallization include wax deposition, increased fluid viscosity, waxy gelling during production stop, and the formation of Pickering emulsions [9–11]. All of these scenarios can impart significant costs or even force a production stop [12,13], which highlights the importance of understanding and addressing wax crystallization and related phenomena.

The process of wax crystallization can be summarized as a three-step process [14]: (i) Nucleation and incipient crystal formation, (ii) wax crystal growth, and (iii) agglomeration. Various crystal geometries can be the result of the second step, for example plates, needles, and mal-crystalline masses [15]. In a plate-like crystal, the n-alkanes tend to be aligned in parallel [16]. Co-crystallizing species may greatly affect the wax crystal growth, as these can contort the alignment of alkanes that crystallize subsequently. The resulting crystals can be distorted, exhibiting more compact or condensed structures with a reduced hydrodynamic radius and lesser propensity to interlock. This effect is greatly exploited by pour point depressants (PPD) [17,18]. The pour point is defined as the temperature, at which an oil loses its ability to flow freely [19]. Wax inhibitors hence need to function as PPD to ensure sufficient oil flow-ability. The mechanism of PPDs is commonly ascribed to a combination of co-crystallization, crystal distortion, and affecting wax solubility and nucleation [20–22].

Industrial wax inhibitors are mostly based on co-polymers or comb-type polymers [17], which can comprise various polar, non-polar, and branched sections [13]. The non-polar sections are deemed responsible for interacting with the wax, as these can co-crystallize on the wax crystal lattice [16,23]. The branched or polar sections may subsequently induce crystal distortion. Co-polymer type inhibitors often exhibit a straight-chain backbone that resembles polyethylene, while containing randomly distributed side groups, as for example in polyethylene-vinyl-acetate copolymer (EVA) or poly(ethylene-butene) (PEB) [17,18]. Comb-type polymers typically have pendant alkyl chains with a length of 8–22 carbon atoms or more [18]. Reports state that the wax inhibition efficiency is best, if the carbon number of the side chains is similar to the molecular weight of the crystallizing wax [23]. Industrial wax inhibitors may furthermore contain surfactants or dispersants [9,24], which are designed to prevent adhesion of wax crystals to each other and to the pipeline wall.

Production chemicals are in general known to affect the separation processes downstream their injection, and influence the oil and

produced water quality. However, very little is known about the effect of wax inhibitors. As mentioned above, most of the wax inhibitors are primarily nonpolar oil-soluble substances, however some additives in the formulation can exhibit surface-active properties. Considering quite wide range of dosage concentration (100–2000 ppm [13]), they could potentially affect the separation processes in the produced water treatment stream. Literature review revealed very few examples of systematic studies on the effect of any non-treatment-related chemicals on the separation efficiency. The most comprehensive study with several additives, including corrosion and scale inhibitors, was conducted by Yang et al. in 1996 [25]. Corrosion inhibitors seemed to affect the emulsion stability to the highest extent. Other examples are related to the treatment processes after enhanced oil recovery (EOR) with polymers or surfactants. For instance, Luo et al. investigated the effect of alkali-surfactant-polymer floods on the coalescence of oil droplets [26]. AlSofi et al. showed, amongst other things, the possible effect of EOR chemicals on the separation and water quality [27]. Dalmazzone et al. studied the separation processes, such as gravity separation and electrocoalescence, for diluted heavy oil emulsions with and without the presence of surfactants and polymers [28]. Some work has also been published on the effect of crystallized wax on the emulsion stability, but mostly concerning systems where the paraffin containing oils were the continuous phase [10,29,30]. In one paper, Zhang et al. studied water-continuous systems, but found little effect of wax on the separation process [31]. Overall, to the best of our knowledge, no reports were found on the effect of wax inhibitors on separation-related issues.

In this report, we systematically investigate the coalescence of model oil (doped with macrocrystalline wax) and crude oil droplets in the presence of model inhibitor. Previously reported microfluidic method was used to generate monodispersed droplets and record their merging after flowing through a coalescence chamber [32]. Measurements were performed both below and above the wax appearance temperature. To better understand and explain the measured emulsion stability, extensive interfacial, rheological and thermoanalytical characterization was performed on all systems. This holistic approach allowed to identify correlations between the chemical composition of the fluids, their properties and resulting coalescence stability.

2. Material and methods

2.1. Materials

Model dispersed phase solutions were prepared with dodecane, macrocrystalline wax 5405 Sasolwax (0%, 5% and 10% wt.) and wax inhibitors α , τ and Ω (0, 500 and 1000 ppm, for more details please see Table 1). Prior to usage, the additive α was purified, as the original product was supplied as a blend with petroleum distillate. Toluene was repeatedly added and removed from the sample in a rotary evaporator

Table 1

Characteristics of the wax inhibitors used in this study [35,36]. The number average molecular weight (MW) and the polydispersity index (PDI) are an polystyrene (PS) equivalent, measured at 1000 ppm PPD in tetrahydrofuran. The hydrodynamic radius (Rh) corresponds to 1000 ppm wax inhibitor in toluene. The precipitation temperature was measured at 1000 ppm PPD in dodecane using DSC at a cooling rate of 5 K/min.

Wax inhibitor	Chemistry based on	Number av. MW [kDa]	PDI	Rh [Å]	Precipitation temperature [°C]
Alpha (α)	Polycarboxylate	17.7	3.7	20.4	5.4
Tau (τ)	PS-block-poly (ethylene-ran-butylene)-block-PS	142.7	1.1	88.0	10.0
Omega (Ω)	Ethylene-vinyl acetate (25% vinyl acetate)	72.0	15.2	61.9	12.7

up to 90 °C and 200 mbar, after which the remaining substance was dried in an oven at 60 °C and ambient pressure for 24 h. The qualitative precipitation profile of PPDs was furthermore plotted in Fig. S1. This figure used n-octane as solvent to avoid the solvent crystallization peak that pure dodecane exhibits at - 10 °C.

After preparation, all the solutions were heated at 60 °C for at least 4 h and then ultrasonicated for 15 min at the same temperature to ensure full dissolution of the wax and inhibitors. Light crude oil, produced at the Norwegian Continental Shelf, with 200 ppm of an oil-soluble surfactant (to avoid adsorption of crude oil components on glass walls of the chip [32]) and 0, 500 and 1000 ppm of wax inhibitors underwent similar preparation procedure. To be consistent with our previous reports, we use the same abbreviation for that oil (crude oil G) [33,34]. All the solutions were later heated and distributed into smaller glass vials, which were subsequently used only once during experiments. This ensured the same composition of the oil phase, as repeated heating of the samples could cause solvent evaporation and change the concentrations of wax or inhibitors. The continuous phase in all experiments was 3.5% wt. NaCl solution, prepared with deionized water. Prior to all experiments, the oil phases were heated to min. 60 °C for at least 1 h.

2.2. Methods

2.2.1. Differential Scanning Calorimetry (DSC)

DSC experiments were run on a Q2000 (TA Instruments). A sample mass of 10 – 30 mg was filled into Tzero Hermetic Pans and sealed hermetically. Each measurement consisted of heating to 100 °C for 3 min (samples containing dodecane as solvent) or heating to 70 °C for 15 min (samples containing crude oil), after which a constant cooling rate was applied and the data recording commenced. Quick cooling to around 60 – 70 °C could be done for samples containing dodecane to shorten the total experiment duration. Thermal cycling was done with each sample, where the cooling rates 10 K/min, 8 K/min, 5 K/min, 3 K/min, and 1 K/min were measured first in descending and then in ascending order. A total of at least four measurements per cooling rate were done. Samples were weighed before and after the experiment, to verify that no loss of solvent had taken place. The WAT was determined via a previously published procedure [37], in which the heat flow before wax crystallization onset is approximated by a straight line. The WAT is then defined as the highest temperature, for which three consecutive points are outside the confidence interval. This confidence interval was calculated as 3.291 times the standard deviation of data around the straight-line approximation. In addition, extrapolation to the WAT₀ at zero cooling-rate was done, as this approximates the thermodynamic WAT more closely. Extrapolation was done similar as in previous publications [37,38], i.e. by linear regression of experimental data at low cooling rates, that is, 1–5 K/min in this case.

2.2.2. Rheometry

Gelation point measurements were conducted on a MCR Physica 301 (Anton Paar). Experiments were conducted using sandblasted cone and plate geometry, which had a 2 ° cone inclination and 4 cm cone diameter. A standard gap size of 0.17 mm was used. For each run, the hot waxy sample was loaded into the geometry preheated at 60 °C. Cooling at a rate of 10 K/min was done down to 40 °C, after which cooling at a rate of 1 K/min was applied and the measurement started by imposing an oscillation shear stress of 0.01 Pa at a frequency of 1 Hz. The gelation point temperature was linearly interpolated at the intersection of storage (G') and loss modulus (G'').

2.2.3. Cross Polarized Microscopy (CPM)

Microscope images of wax crystals were shot with a Nikon Eclipse ME600 microscope fitted with CoolSNAP Pro camera (Media Cybernetics) and cross polarization filters. The sample temperature was controlled via a PE 94 and LTS-120E Peltier system (Linkham). Prior to the experiment, samples were filled into glass capillaries with a cross-

section of $0.3 \times 0.03 \text{ mm}^2$, which was sealed on both ends using Loc-tite ethyl-2-cyanoacrylate glue. An air bubble was left in between sample and glue on both ends to prevent sample contamination. The temperature program consisted of heating to 70 °C for 15 min, quick cooling to 40 °C at a cooling rate of 10 K/min, and then slow cooling at a rate of 0.1 K/min to the target temperature of 22 °C or 4 °C, respectively, which was held isothermally. Images were made between 30 min and 1 h after reaching the target temperature.

2.2.4. Interfacial tension (IFT) measurements

A spinning drop tensiometer (SVT20N, DataPhysics Instruments) was used to measure the interfacial tension between oil and water phases. A glass capillary was filled with the continuous phase, after which a small 2–3 mm drop of the oil phase was injected through a syringe with a needle. To limit temperature gradients and possible wax precipitation, all used items were preheated to 60 °C. The instrument was equipped with a water bath to control the temperature of the experiments (22 or 45 °C). Rotation speed was adjusted accordingly, typically between 6,000 and 10,000 rpm to obtain appropriate width to length ratio of the droplet. Measurements were performed until steady state was reached, which typically took between 2 and 4 h, depending on the system.

2.2.5. Microfluidic coalescence measurements

Microfluidic setup and methods were conducted in a similar fashion as in the previous reports [32,33]. In short, custom-made microfluidics chips (Micronit Microtechnologies) made of borosilicate glass with a uniform channel depth of 45 μm were used for all coalescence measurements. The chips were placed in a Fluidic Connect PRO chip holder (Micronit Microtechnologies) and connected to syringe pumps (neMESYS mid-pressure module V3, Cetoni) with FFKM ferrules and PEEK tubing. For measurements at increased temperature, a custom-designed temperature-controlled chip holder was used (the detailed description of the design can be found elsewhere [39]). The flow rates of the continuous and dispersed phases were always set to 160 and 8 $\mu\text{l}/\text{min}$, respectively. The inlets for both water and oil phases were 100 μm wide and led to a T-junction, in which the monodisperse oil droplets (ca. 55–60 μm in diameter) were generated. After passing a 15 mm aging channel, the droplets entered a 33 mm long coalescence chamber with the width of 500 μm . In there, they could undergo collisions and coalescence events (Fig. 1). Following the measurements, the microfluidic chips were ultrasonicated in 3:1 v/v toluene-acetone mixture, 2% Decon90 solution, isopropanol, and deionized water for 20 min in each solution or solvent, respectively. Sonication was performed at elevated temperature to ensure no precipitated wax remained in the channels. Finally, the chips were baked in a muffle furnace at 450 °C for 6 h.

The events in the microfluidic chip were recorded with a high-speed camera (AX100, Photron), connected to an inverted microscope (Ti-U Eclipse, Nikon) equipped with a LED light source (pE-100, CoolLED). The framerate of the recordings was always set to 8 500 frames per second, with the shutter speed set to 1/60 000. The sets of recordings (10 000 frames per each) were taken at the inlet and outlet of the coalescence chamber, however in some cases due to extensive coalescence, the measurements were taken at a middle point of the chamber.

The recorded images were then processed with ImageJ software. After converting to binary, the size and position of the detected droplets were extracted with the Analyze Particle feature. The datasets were imported into a custom-written Matlab script, which estimated the average velocity that was later used to calculate the average residence time in the coalescence chamber. In these calculations, the location of the previously mentioned recording point was also taken into consideration. As the droplet area was proportional to the number of coalescence events, it was possible to sort the droplets into size classes and create a size distribution. Finally, based on the number of droplets in each size class and residence time in the channel, the coalescence frequency was computed and used as a parameter to compare between

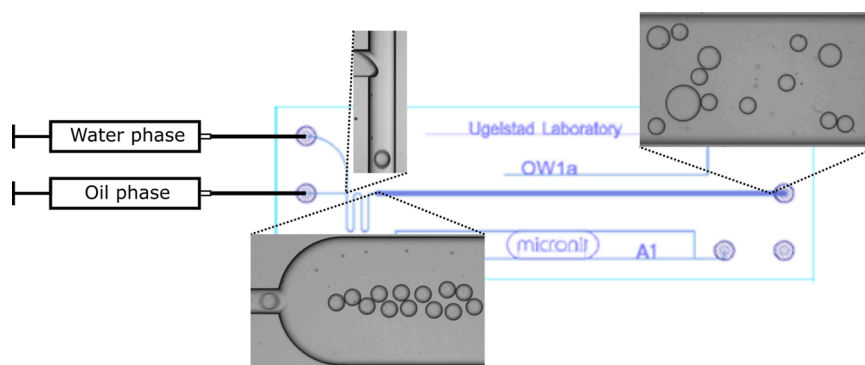


Fig. 1. Experimental overview of the microfluidic setup for coalescence measurements used in this study.

different systems.

3. Results & discussion

3.1. Characterization of wax inhibitors

The effect of wax inhibitors on wax crystallization was studied by thermal, rheological, and optical methods. This was done to lay the fundament and enable comparison with subsequent microfluidic experiments. A better inhibition efficiency is attributed with a higher reduction of WAT and wax gelation temperature (gelation point), which is frequently accompanied by morphological changes of the wax crystals.

Wax crystallization will occur as the waxy oil is cooled, which shows as an increase in heat flow (endothermic peak) during DSC experiments. The WAT was determined as early as this increase was calculated to be statistically significant. As shown in Fig. 2 (left), the observed WAT was higher at lower cooling rates, which is due to a decreasing nucleation lag [40]. However, measuring the thermodynamic WAT, i.e. by exclusion of nucleation and other effects, is experimentally challenging, since a certain fraction of wax must precipitate in order to be detected [41]. The WAT_0 was hence used to compare the effect of different PPDs on the wax crystallization onset. As described in a previous publication [37], this linear extrapolation to zero cooling rate has the advantages of approximating the thermodynamic WAT more closely, while taking into account kinetic effects and a larger data set. As can be seen in Fig. 2 (right), the effect of PPD Alpha was greatest for 5 wt% and 10 wt% wax in dodecane, while PPD Omega reduced the WAT_0 of the crude oil the most. The effect of PPD Tau and Omega was positive but less

pronounced for the model waxy oils with dodecane. A reduction of WAT can be explained by improving the thermodynamic wax solubility, e.g. by the formation of solute complexes [42]. On the other hand, PPD Alpha and Tau increased the WAT_0 of crude oil. Such an increase may be due to unfavorable effects on wax solubility, or by providing nucleation sites as has been reported e.g. for asphaltenes [43].

The gelation temperature describes the point, at which the waxy oil behaves more like an elastic body than a viscous fluid [44]. Such circumstance is comparable to the no-flow condition satisfied at the pour point temperature, and the gelation point results will hence be treated in analogy to pour point measurements in this article. As can be seen in Fig. 3, the effect of PPD Alpha was again most pronounced for the two synthetic oils, 5 wt% and 10 wt% wax in dodecane. In previous studies, this polycarboxylate-based polymer has also shown efficient wax inhibition of non-polar solutions of macrocrystalline wax [20,35]. In addition, 1000 ppm Tau with 5 wt% wax in dodecane decreased the gelation point by 2 °C. However, the addition of PPD Tau or Omega to wax in dodecane would otherwise not affect the gelation point in a positive manner. Both PPD Alpha and Omega reduced the gelation point of crude oil below -20 °C, while PPD Tau led to an increase of about 15 °C with respect to the blank case.

Examples of cross polarized microscopy (CPM) images are shown in Fig. 4, while the remaining data is shown in SI (Figs. S7–10). These mirror to some extent the quantitative results of WAT and gelation point measurements. For instance, no wax crystals could be detected at 22 °C with PPD Alpha, which was also the PPD to invoke the greatest reduction of WAT_0 . At 4 °C, the macrocrystalline wax crystallized to the typical plate and needle shape. Such morphologies have indeed been observed for similar model oils in the past [22,45]. In comparison, the

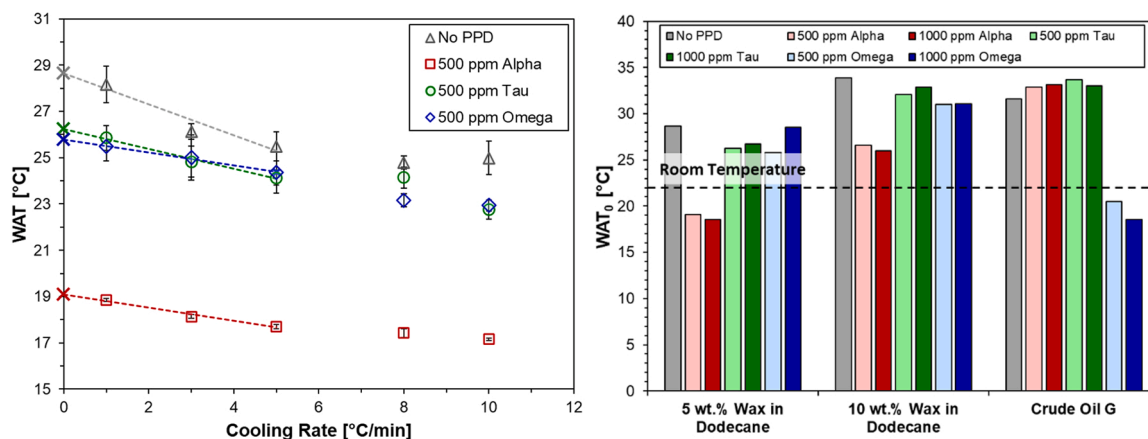


Fig. 2. Exemplary progression of WAT in 5 wt% wax in dodecane with cooling rate and extrapolation to WAT_0 at zero cooling rate during DSC experiments (left). Error bars mark the standard deviation around the mean. All other plots are shown in Figs. S2–6 in SI. Effect of PPD and dosage on the calculated WAT_0 in waxy oils (right).

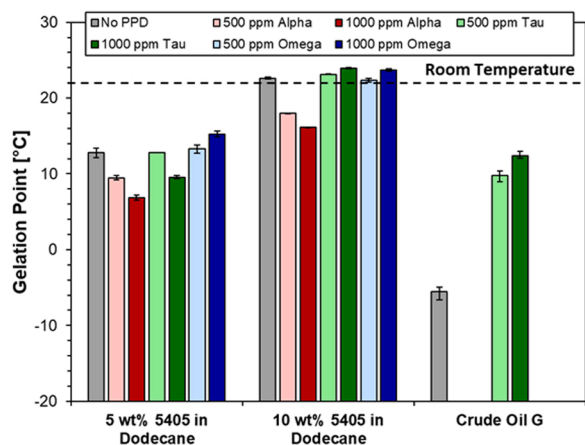


Fig. 3. Gelation point temperatures of waxy oils determined by oscillatory rheometry at 1 K/min cooling rate. Bars that are now shown indicate that the sample did not exhibit gelled at $-20\text{ }^{\circ}\text{C}$ and above.

addition of PPD Alpha led to fewer and more compact wax crystal. Despite the larger size of individual crystal-aggregates, these morphology-changes appear to have impaired waxy gelling, as the

gelation temperature was reduced by a few degrees. The WAT and gelation temperature were less depreciated by adding PPD Tau or Omega. Addition of PPD Tau yielded larger crystals with the same morphology as the blank case, whereas PPD Omega resulted in a finely dispersed but dense network of wax crystals.

3.2. Interfacial properties of wax inhibitors

The chemical composition of the wax inhibitor will affect its surface-active properties. Fig. 5 (left) shows the interfacial tension (IFT) reported for dodecane without and with the addition of wax, as well as the crude oil, for the three wax inhibitors tested in this study.

As explained in the experimental section, the IFT results were obtained with a spinning drop technique. While it is a popular and widely accepted type of measurement for many applications, it tends to work more accurately at lower ranges of interfacial tensions. At higher values, i.e. above 35–40 mN/m, one could expect some deviations from table values or results from other techniques. In this case, values for pure dodecane are few units lower than obtained with a ring tensiometer for a different study [39]. However, since many of the tested oil phases had a WAT below the room temperature, spinning drop technique was the only viable method to measure IFTs with, as both the pendant drop measurements and ring tensiometer would be heavily affected by the gelation of the oil phase during the measurement. In the former, the wax

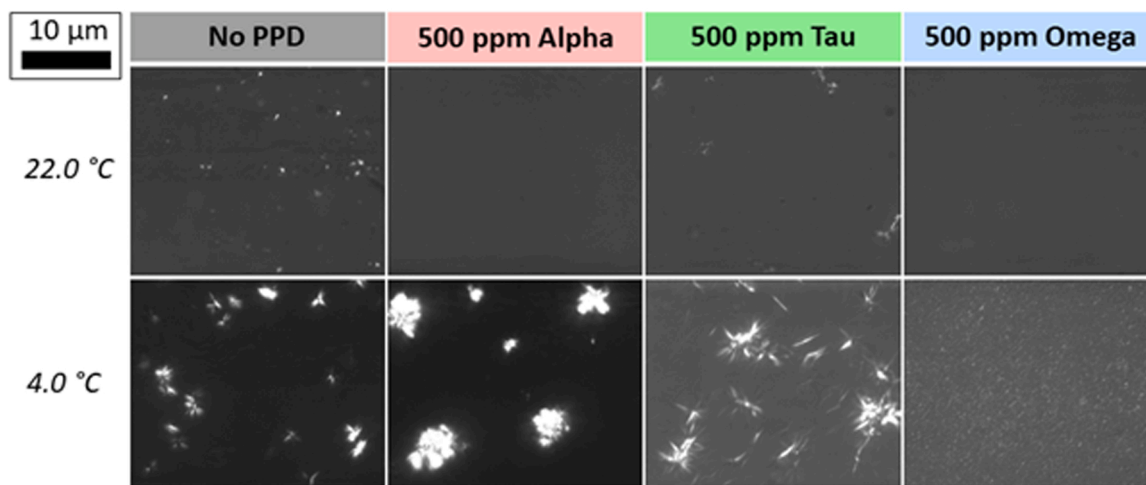


Fig. 4. CPM images of 5 wt% wax in dodecane with and without 500 ppm PPD. All other systems are shown in Figs. S7–10 in SI.

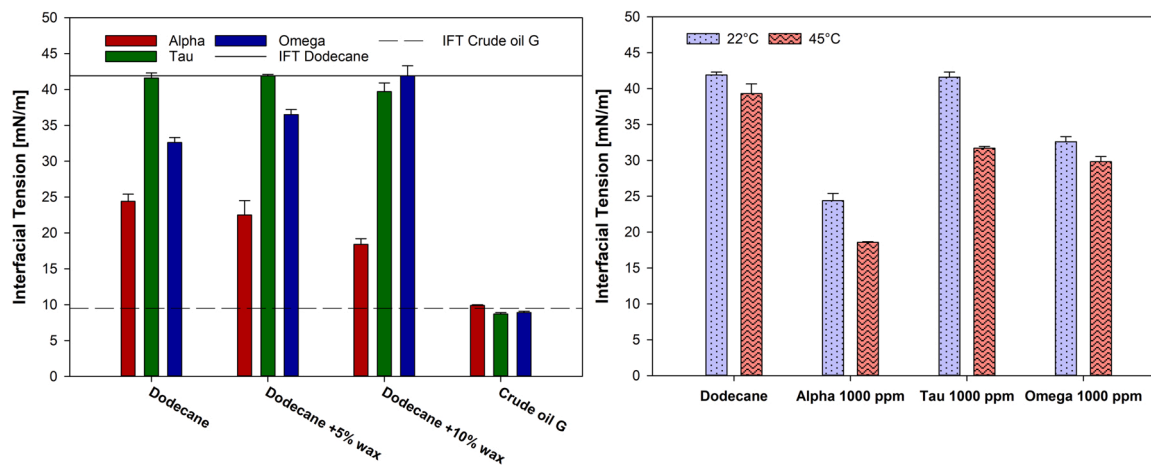


Fig. 5. Interfacial tension values of model systems and crude oil: (left) systems including 1000 ppm of selected wax inhibitors, with and without the addition of wax, where horizontal lines refer to pure systems: dodecane (solid) and crude oil G (dashed); (right) dodecane solutions without and with the addition of 1000 ppm of wax inhibitors at 22 °C and 45 °C.

can crystallize in the tubing and/or hook, disallowing the volume of drop to be kept constant, while in the latter the crystallization and gelation of the oil phase would seriously affect the force measurement of the ring pulling against the interface. In the spinning drop method, the droplet could be injected at the temperature above WAT. During the measurement, the drop is a discrete volume, suspended in the continuous phase. Wax crystallization might still affect its ability to deform, as explained later, but this method was deemed to be the best option for the systems at hand.

The interfacial tension of pure dodecane is annotated with the solid line in the graph. The values for dodecane with 5% and 10% of wax were also very similar, therefore the solid line can serve as a reference for all dodecane solutions without wax inhibitors. Addition of the wax inhibitor α to all the dodecane solutions decreased the IFT significantly, with the lowest values obtained for the highest concentration of wax. The effect was also stronger for higher concentrations of that wax inhibitor (Fig. S11 in SI). The interfacial tension of dodecane solutions with wax inhibitor τ did not change from the original value for pure dodecane, with an exception for the highest inhibitor concentration at 10% wax, where a small decrease was observed. However, as noted later during microfluidic coalescence experiments, after several minutes of measurements, the droplets were not prone to deformation and seemed quite unresponsive to changes in the rotation speed. This could mean that the steady-state IFT presented here might not fully correspond to the actual values of that system in equilibrium. However, even in the initial stages of the measurements with τ , when the droplet was still deformable, we observed little changes in the interfacial tension. It could be concluded that even if this wax inhibitor exhibits some surface-activity, its adsorption kinetics are quite slow. For the solutions of dodecane with the wax inhibitor Ω , the decrease of interfacial tension was less marked compared to inhibitor α , however it was clearly affecting the interfacial properties of the dodecane droplets. Interestingly, an increase of the IFT was observed when more wax was present in the solution. The changes in the interfacial tension were less notable for the crude oil. The dashed line shows the value of the crude oil without added wax inhibitors. It can be seen that all the values oscillate around the line for that oil, however one could observe a minor decrease for the inhibitors τ and Ω . This, however, does not exclude their potential effects on the coalescence behaviour, as observed later. In fact, in previous work [46], where several flocculants (chemicals designed to improve separation during produced water treatment) were tested, we have also observed a relatively limited effect of the chemicals on the interfacial tension, while the effect on the separation was quite significant.

Fig. 5 (right) compares the IFT results at lower (22 °C) and higher (45 °C) temperature for pure dodecane solutions with and without the addition of 1000 ppm of inhibitors. As it can be seen, the temperature had a small decreasing effect on the pure dodecane and the system with the inhibitor Ω , while the interfacial tension dropped significantly for α and τ .

Wax inhibitor α is based on polycarboxylate chemistry, which could be expected to be surface-active due to the presence of both hydrophobic and hydrophilic group in the structure. In addition, it has the lowest molecular weight, with some degree of polydispersity. It should also be noted that it is the only commercial inhibitor in this study, which could suggest the presence of other components that are typically present in these products, such as small additions of other solvents, polymers with different chemistries or surfactants [13]. This could additionally explain the lower IFT at higher temperatures. While the interfacial tension in pure dodecane does not really change for the lower and higher concentration of the additive, suggesting that the oil-water interface is already filled at 500 ppm, the IFT seems to be lower for the 1000 ppm concentration with more wax present in the system. This could indicate interactions between PPD α and wax crystals, leading to its adsorption on the wax crystals, destabilization or even precipitation. As a consequence, its interfacial stability could increase [47,48], resulting in even lower IFT values observed here.

The interfacial tension of systems with wax inhibitor τ did not change much, independent of the oil phase composition, and only at higher temperatures it dropped significantly. Inhibitor τ has little polarity in its molecular structure (methylene and phenyl groups), and therefore it was anticipated to have a very limited affinity to the oil-water interface. This additive, however, seemed to affect the mechanical properties of the interface. It was observed that several minutes after starting the measurement, the droplets inside the spinning capillary became quite rigid and resistant against deformation. Similar observations about “rigidness” of droplets were also made during the microfluidic coalescence measurements, as explained later. Higher temperature could have reduced the degree of self-association of the polymer, as has been observed for example in case of polystyrene [49]. Being less coiled up, the aromatic moieties of PPD τ would become more exposed, which could increase the interfacial-activity and hence explain the drop of IFT.

The surface-activity of the last additive, Ω , was in between the other two. The ester group probably provided some polarity to its structure and improved the affinity to the oil-water interface, as seen in the pure dodecane system (Fig. S11 in SI). Roe showed that the surface tension of ethylene-vinyl acetate (EVA) was in the range of 32 mN/m (at 60 °C), while the interfacial tensions between polymer blends were always lowest with EVA present in the blend [50], which confirms its (limited) surface-active properties. The interfacial tensions of solutions with Ω were found to increase with the increasing content of wax in the solution. It suggested that the inhibitor reacted with the crystallized wax, hence being removed from the interface. In another study with isothermal calorimeter [51], this additive (PPD4 in that paper) was shown to have the highest absolute interaction heat in wax solutions, even though its performance as wax inhibitor is considered quite poor (as also seen in Figs. 2 and 3). Still, it shows that Ω interacts with wax molecules, and the more wax is present, the less inhibitor will be available to adsorb at the oil-water interface. As a consequence, the interfacial tension will increase.

3.3. Effect of wax inhibitors on coalescence

This section deals with the effect of the wax inhibitors on the coalescence of oil droplets in the continuous water phase, generated on a microfluidic chip. These oil-in-water systems are emulating processes occurring during produced water treatment, where coalescence is one of the most important fundamental phenomena, affecting the outcome of separation. Two sets of measurements are presented: at room temperature (22 °C, for most systems below WAT) and at elevated temperature (45 °C, always above WAT).

3.3.1. Coalescence in model systems below WAT

Coalescence frequencies of dodecane without and with wax, as well as pure dodecane solutions of both concentrations of wax inhibitors are shown in Fig. 6.

Droplets of pure dodecane, with and without added wax, coalesced extensively. There seemed to be a slight increasing trend when there was more wax in the oil phase, however the standard deviation for these measurements had also increased. Coalescence in dodecane – Alpha/Tau systems was significantly lower, especially at higher concentrations of any of the additives. In the case of Omega, stability increased only slightly, even at the 1000 ppm concentration.

With slight increase in viscosity and the presence of solid wax in dodecane, one would expect a more stable system, i.e., less coalescence, however here we have observed the opposite. Our previous tests with fluids of different viscosities (heptane/dodecane) showed, that this parameter has in fact an effect on the coalescence time [39] and will probably contribute to increased stability. In this case, we suspect that the presence of wax crystals might have affected the interactions between drops, as the wax appearance temperature for both systems, according to the DSC data (Fig. 2), was significantly above the temperature

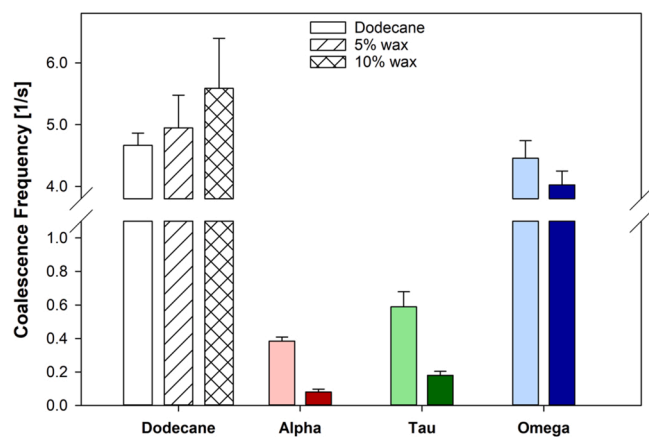


Fig. 6. Coalescence frequencies for dodecane without and with the addition of wax, as well as pure dodecane with the addition of various PPDs at 500 and 1000 ppm concentrations (brighter and darker colours, respectively). Measurements performed at 22 °C.

of measurements. Crystallized wax was found to have a dual effect on emulsion stability [52]. On one hand, when allowed to form a structured network, it can stabilize the droplets against coalescing. On the other hand, less homogenous crystal network, with more dispersed wax crystals could be responsible for lower stability. It is anticipated that the relatively fast flow and recirculation within the droplets inhibited network crystallization and therefore led to less stable systems. Prileszky et al. observed a change in orientation of wax crystals, encapsulated within microfluidic droplets, with the increase in wax (petrolatum) concentration [53]. They, however, used significantly higher concentrations, 60% by mass or more, which leads us to believe that our relatively low concentration of wax, together with fast flow of droplets, was most likely the reason for the unstructured crystals, trapped within droplets. Furthermore, wax crystals present at the interface could have also improved the attraction between droplets, which led to the slight increase in coalescence. This effect can also be seen later in systems with wax and the additive Tau.

It should be noted that the gelation temperature for the higher concentration of wax was slightly lower than the room temperature. This meant that, given enough time, the solution would eventually become gel-like. Still, the pre-heating of the solutions and the constant movement of the syringe probably provided enough shear to keep the solution in a liquid state. It has indeed been established that high-shear conditions will delay and weaken the observed gelation temperature and strength, respectively [54,55]. Some of the precipitated wax could have possibly stayed in the syringe or in the tubing. However, as we have observed here and also during other measurements with the higher

amount of added wax, we have observed very clear differences between 5% and 10% wax solutions, and therefore we expect to the droplets in the dispersed phase to contain corresponding concentrations of wax. In fact, in several systems wax crystals could have been observed flowing inside the droplets.

The stability of the dodecane drops improved visibly, when the additive α was dissolved in dodecane. The coalescence was also lower at the higher concentration. Since the wax inhibitor Alpha was the most surface-active of the chemicals used in the present study, it was not surprising to find that it would also inhibit coalescence between the droplets. As it can also be seen in Fig. 7 (left), it worked similarly in the presence of wax. Interestingly, the coalescence slightly increased when more wax was present in the system. This could have been an indicator that instead of adsorbing at the oil-water interface, the components of the Alpha inhibitor interacted with the paraffin molecules. Still, especially at the higher concentration of the inhibitor, the change in emulsion stability was relatively insignificant.

Concerning wax inhibitor τ , its effect on the coalescence was much more dependent on the composition of the oil phase. In pure dodecane, coalescence was similar to the inhibitor α and also decreased with the increasing concentration. With the wax present, there was a slight decrease in emulsion stability for the 5% wax and 500 ppm of inhibitor, and a considerable increase for 10% wax at both tested concentrations, Fig. 7 (right). As mentioned before, the droplets with the inhibitor τ seemed to be much more rigid, which could have also affected the coalescence between them. The coalescence between drops highly depends on the film drainage process. Upon collision, a thin film, made up of the continuous phase, is formed and has to be drained prior to the merging event. In the case of the additive Alpha, its surface-active components acted opposingly to the drainage through the Marangoni effect, creating a reverse flux of the water film in the proximity of the interface that prolonged the coalescence time. With Tau, however, a viscoelastic film was observed in the spinning drop tensiometer. It has long been established that viscoelastic interface layers can impede droplet coalescence [56]. This is likely the stabilization effect of PPD Tau, since its effect on the interfacial tension was the lowest of all three PPDs. At higher concentrations of wax, most of the Tau inhibitor in the oil phase has likely interacted with the paraffin molecules, for example by adsorption and co-crystallization. Depletion of PPD Tau would consequently lower its effect on the interface, increasing droplet coalescence. Surprisingly, the droplet coalescence with PPD Tau was even higher than the PPD-free case at 10 wt% wax in dodecane. These changes could be explained e.g. by the interfacial phenomena or by Tau's effect on the wax crystal morphology (Fig. 4). As it can be seen, the crystals grew in size compared to the blank case with a mostly needle- and dendrite-like structure. It has recently been suggested that the ability of the inhibitors to co-crystallize with the wax can affect the water-oil interface and hence droplet coalescence [57]. It appears that in

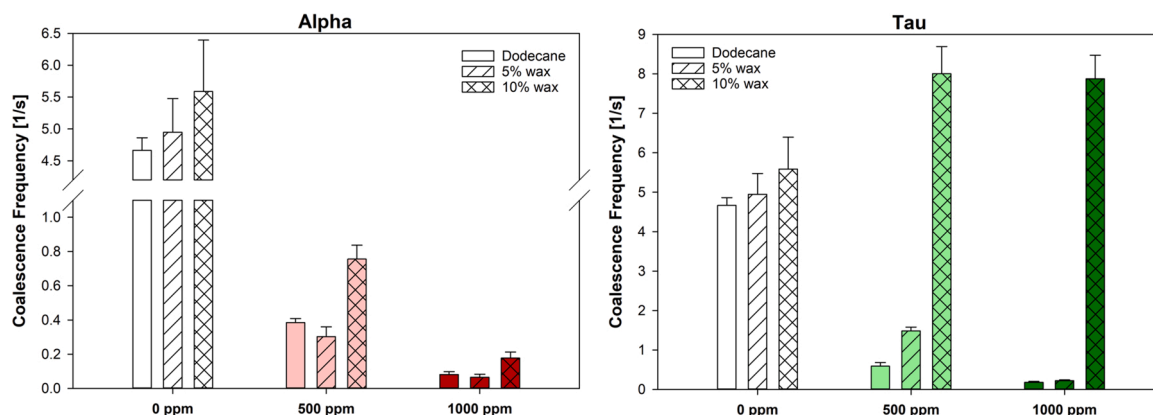


Fig. 7. Coalescence frequencies for dodecane systems without and with the addition of wax inhibitor α and τ . Measurements performed at 22 °C.

this case, co-crystallization of Tau caused droplet destabilization at the elevated wax content.

The last wax inhibitor, Ω , had a limited effect on the coalescence in pure dodecane system. We could, however, observe a small improvement in the emulsion stability as the concentration of the additive was higher. This is in agreement with the corresponding decrease in the interfacial tension. In the systems with wax present, the measurements were unfortunately not possible to be performed. The mixture of the inhibitor and paraffins seemed to cause the droplets to stick to the glass walls of the microfluidic channel, creating large ganglia as the droplets continuously collided and coalesced with the large deposition of the oil phase. Several attempts, including more rigorous cleaning of the chips and preparing new solutions, were tried, however with no successful result. We speculate that this inhibitor, in the presence of wax, could have potentially precipitated and adsorbed on the walls of the device.

3.3.2. Coalescence in model systems above WAT

All previous measurements were performed at room temperature, which for most systems was also below the wax appearance temperature. To nullify the effect of the crystallized wax, the following coalescence experiments were conducted at 45 °C, which for all systems is at ca. 15 °C above WAT.

The results for the coalescence of dodecane with and without wax, as well as pure dodecane with the addition of 1000 ppm of wax inhibitors, are presented in Fig. 8. In the former case, similarly to the measurements at lower temperature, the merging between drops increased with the amount of wax. Likewise, the results are somewhat unexpected, as one would anticipate slightly higher viscosity of the dispersed phase with paraffins, that should prolong the coalescence time between drops [58], and therefore lower coalescence frequency. One possible explanation is the increased hydrophobic attraction between the drops arising from larger amounts of longer hydrocarbons, which in the almost complete absence of electrostatic repulsion in brine solutions, could be the main long-ranged interaction governing the film drainage process. Nevertheless, the decreased stability of the wax-containing droplets at higher temperatures was also observed in the work of Caggioni et al., where local heating of multiple endoskeleton drop structures led to their coalescence [59].

The change in coalescence between the lower and higher temperature in dodecane – inhibitor systems depended on the type of the additive, Fig. 8 (right). In the case of Alpha, the stability decreased quite significantly, although still well below the values for pure dodecane system. In general, this trend is to be expected, as in higher temperatures the drainage time, and the stability of emulsions, tends to be lower. It should be remembered that this inhibitor is in fact a commercial mixture of products, and its exact composition is proprietary. Wax inhibitor τ experienced hardly any change in coalescence. In accordance with Fig. S1, this inhibitor crystallizes at very low temperature, meaning one

should not expect a large difference in its behaviour at 22 or 45 °C. We could not, however, justify why Tau also experienced quite a significant drop in the interfacial tension when the temperature increased. Possibly, it could have been some contaminants that had higher solubility at 45 °C and could have affected the IFT. Conversely, inhibitor Omega had the highest crystallization temperature, largely overlapping with the lower temperature measurements. Increasing it to 45 °C could possibly increase the stabilizing effect of this component (as well as slightly decreasing interfacial tension), as observed in the coalescence frequency data.

For the wax inhibitor α with wax present, the coalescence frequency values were consistently higher at 45 °C, Fig. 9 (left). The least stable system was observed at 0% and 10% wax concentration, with a slightly more stable emulsion for 5% wax. Since there was no crystallized wax present for the inhibitor components to interact with, it would be reasonable to assume that these values should be quite similar to each other, and the main factor influencing coalescence could then be wax content. However, it seemed to have a little effect on the merging in this system. By contrast, the experiments at higher temperature with inhibitor τ showed a gradual increase of merging, together with the increase of the wax content, Fig. 9 (right). In addition, the values were quite similar between the lower and higher temperatures. The coalescence with the highest wax concentration was also in the same order of magnitude as for the other concentrations, as opposed to the same measurement in the room temperature conditions. This again might point to the explanation that changing the temperature for this inhibitor will not really affect its behaviour due to very low crystallization temperature. Furthermore, it could also confirm that at room temperature, droplet coalescence is primarily governed by the crystallized wax.

As in other cases, the measurements with the inhibitor Ω and wax were difficult to conduct. At higher temperature, some of them were successful, however it was also observed that the velocity of the droplets decreased by ca. 30% compared to other systems, suggesting possible deposition of the polymer and hence interactions between the droplet and the channel walls. Since drop velocity is a major parameter affecting coalescence frequency [60], it was decided not to include those results in this section.

3.3.3. Coalescence in crude oil system

To bring the studied system closer to the actual produced water treatment facility, a crude oil without and with the addition of wax inhibitors was chosen for further studies. Crude oils contain a variety of surface-active components that affect droplet stability, for example asphaltenes, resins or naphthenic acids. As shown in many studies, their composition is important to consider for an efficient separation [61,62]. Equally important, however, is the type and concentration of added chemicals [25]. This particular crude oil was also used in a few other publications, concerning both microfluidic coalescence [33] and wax

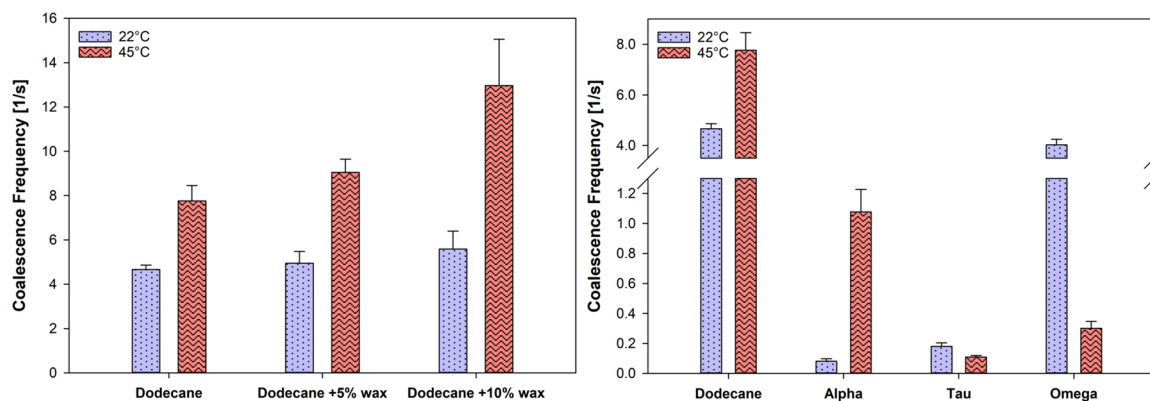


Fig. 8. Coalescence frequencies for solutions of dodecane without and with wax (left) and dodecane solutions without and with the addition of 1000 ppm of wax inhibitors (right). Data for measurements conducted at 22 °C and 45 °C.

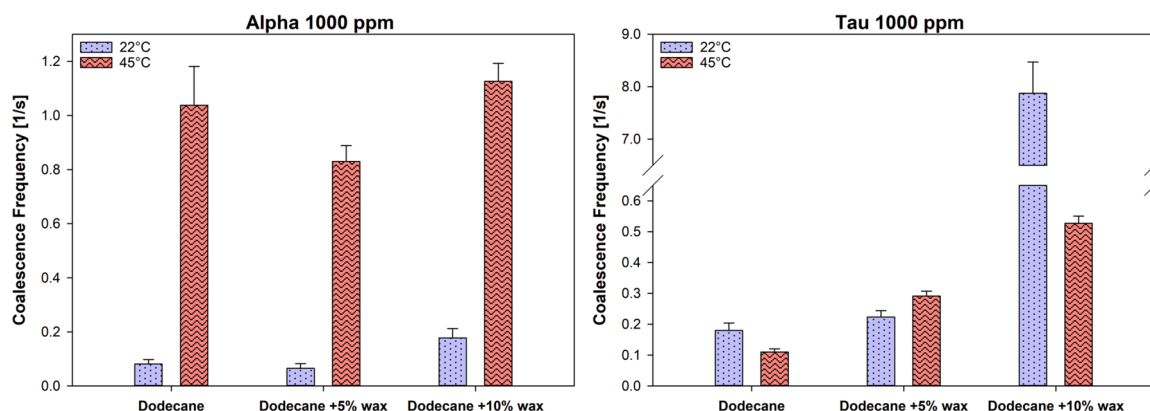


Fig. 9. Coalescence frequencies for solutions of dodecane without and with wax, and with and without the addition of Alpha (left) and Tau (right) wax inhibitors. Data for measurements conducted at 22 °C and 45 °C.

precipitation studies [35]. DSC analysis estimated a WAT of 8.5 °C and a wax content of 1.4 wt% for the crude oil.

Fig. 10 shows the coalescence frequencies of crude oil G. The solid and dashed line show the value and standard deviation for the system without any inhibitor, respectively. In general, the stability of emulsions was found to be higher upon addition of any additive, but most stable systems were probably obtained with the inhibitor α . It is also worth noting that in all cases, the coalescence frequency was higher, or at least equal, at the larger concentration of the additive. Compared to tests with model oils, the connection between the chemistry of the additive and the coalescence tendency is not that clear. It seemed that the most surface-active of the inhibitors (α) had also the largest effect on the coalescence of crude oil droplets, however Ω had also visibly inhibited merging between the drops. Both additives showed moderate interfacial activity (Fig. 5) in model systems, but the change of IFT when added to crude oil was relatively insignificant. It is also worth mentioning that while τ was very efficient at increasing the stability of drops in dodecane, it did not have the same effect when dissolved in crude oil. This could have been due to a much different and more complex composition of the oil, that would dissolve the block-copolymer much more efficiently than pure dodecane.

At room temperature, some wax in crude oil G could precipitate (Fig. 2) and adsorb on the oil-water interface, increasing the rigidity to the interfacial film [52]. In addition, interactions between wax and surfactants could have also enhanced emulsion stability. It was proposed that wax may co-crystallize with certain surfactants that are adsorbed at

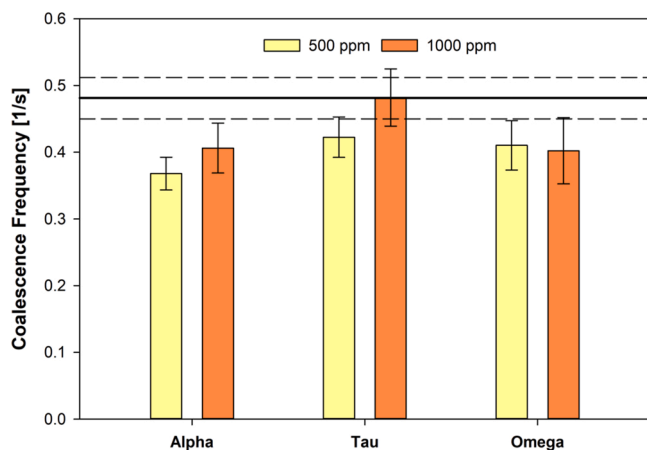


Fig. 10. Coalescence frequencies for crude oil without and with the addition of all wax inhibitors. Measurements performed at 22 °C. Solid line and dashed line show the mean and standard deviation of the measurement without any additives, respectively.

the interface, building a solid layer that can prevent droplet coalescence [10]. A similar effect has been described for asphaltenes [63], which may interact with the wax e.g. by providing nucleation sites and by co-crystallization [43,64,65]. The effect of pure wax on emulsion stability is reportedly weaker than that of pure asphaltenes or resins [31]. However, synergies between waxes and other components within the crude oil may arise, as adsorption of asphaltenes onto wax crystals can hence change their surface properties [66].

For further tests at higher temperature, wax inhibitor α was selected, as it seemed to have the largest effect on the coalescence. At higher temperature, the coalescence frequency of crude oil G has also increased (Fig. 11). This is in general agreement with other studies, where the increase in temperature was connected to more efficient separation of oil from water [32,67,68]. Furthermore, at higher temperature, the merging seemed to decrease with the increase in concentration of the additive. This suggests, that overdosing wax inhibitors could potentially aggravate separation problems during produced water treatment process.

4. Conclusions

Wax inhibitors are an important additive during the production and processing of petroleum, especially from the flow assurance point of view. They can, however, affect the separation processes in an unexpected way. This report focused on a previously unexplored area of their influence on the phenomena occurring during produced water treatment, specifically coalescence between oil droplets. Measurements were

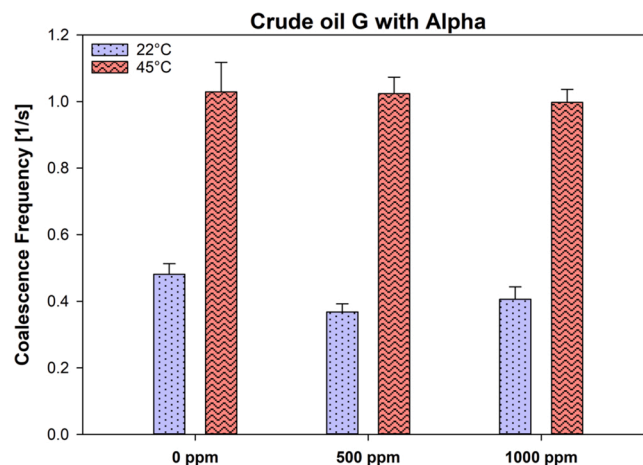


Fig. 11. Coalescence frequencies for crude oil without and with the addition of the wax inhibitor Alpha. Measurements performed at 22 °C and 45 °C.

performed on well-defined and characterized systems, allowing to better understand the underlying cause of emulsion stability. It was shown that the coalescence between droplets is not only affected by the presence of inhibitors, but also concentration of wax in the oil phase. In the wax-free systems, most results obtained with the wax inhibitors were explained by their physicochemical and interfacial properties. Upon addition of wax, however, an increase in coalescence was often observed, which could signify the interactions between crystallized wax and inhibitors, but also the general tendency of improving coalescence with the increase in wax concentration. To some extent, similar observations were made for systems both below and above wax appearance temperature. On the other hand, systems with crude oil showed slight decrease in coalescence upon addition of all tested wax inhibitors. Overall, our results underlined the need for a more comprehensive and holistic understanding of the effect that various additives have on upstream processing of crude oil.

CRedit authorship contribution statement

Marcin Dudek: Conceptualization, Methodology, Investigation, Formal Analysis, Writing – Original Draft, Visualization. **Jost Ruwoldt:** Conceptualization, Methodology, Investigation, Writing – Original Draft, Visualization. **Gisle Øye:** Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2021.128186](https://doi.org/10.1016/j.colsurfa.2021.128186).

References

- [1] M. Dudek, et al., Colloid chemistry and experimental techniques for understanding fundamental behaviour of produced water in oil and gas production, *Adv. Colloid Interface Sci.* 276 (2020), 102105.
- [2] J. Beyer, et al., Environmental effects of offshore produced water discharges: A review focused on the Norwegian continental shelf, *Mar. Environ. Res.* 162 (2020), 105155.
- [3] Y. Liu, et al., A review of treatment technologies for produced water in offshore oil and gas fields, *Sci. Total Environ.* 775 (2021), 145485.
- [4] I. Azizov, M. Dudek, G. Øye, Emulsions in porous media from the perspective of produced water re-injection – A review, *J. Pet. Sci. Eng.* (2021), 109057.
- [5] S.-J. Chen, et al., Factors influencing the aggregation behavior of residual associative polymer in produced oily fluids, *Pet. Sci.* 14 (1) (2017) 195–202.
- [6] M.A. Kelland, History of the development of low dosage hydrate inhibitors, *Energy Fuels* 20 (3) (2006) 825–847.
- [7] M. Barcenás, et al., Study of medium effect on asphaltene agglomeration inhibitor efficiency, *Energy Fuels* 22 (3) (2008) 1917–1922.
- [8] H.P. Soni, Kiranbala, D.P. Bharambe, Performance-based designing of wax crystal growth inhibitors, *Energy Fuels* 22 (6) (2008) 3930–3938.
- [9] A. Aiyejina, et al., Wax formation in oil pipelines: a critical review, *Int. J. Multiph. Flow.* 37 (7) (2011) 671–694.
- [10] X. Chen, et al., Two effects of wax crystals on stabilizing water-in-oil emulsions, *Colloids Surf. A: Physicochem. Eng. Asp.* 625 (2021), 126884.
- [11] Z. Wang, et al., Investigation on gelation nucleation kinetics of waxy crude oil emulsions by their thermal behavior, *J. Pet. Sci. Eng.* 181 (2019), 106230.
- [12] A.M. Elsharkawy, T.A. Al-Sahhaf, M.A. Fahim, Wax deposition from Middle East crudes, *Fuel* 79 (9) (2000) 1047–1055.

- [13] M.A. Kelland. Production chemicals for the oil and gas industry, Second ed., CRC press, Boca Raton, 2014.
- [14] A.Ld.C. Machado, E.F. Lucas, Poly(Ethylene-co-Vinyl Acetate) (EVA) Copolymers as Modifiers of Oil Wax Crystallization. *Pet. Sci. Technol.* 17 (9–10) (1999) 1029–1041.
- [15] E.W. Clarke, Crystal types of pure hydrocarbons in the paraffin wax range, *Ind. Eng. Chem.* 43 (11) (1951) 2526–2535.
- [16] C. Wu, et al., Molecular dynamics simulation guiding the improvement of EVA-type pour point depressant, *Fuel* 84 (16) (2005) 2039–2047.
- [17] F. Yang, et al., Polymeric wax inhibitors and pour point depressants for waxy crude oils: a critical review, *J. Dispers. Sci. Technol.* 36 (2) (2015) 213–225.
- [18] B. Wei, Recent advances on mitigating wax problem using polymeric wax crystal modifier, *J. Pet. Explor. Prod. Technol.* 5 (4) (2015) 391–401.
- [19] Standard Test Method for Pour Point of Crude Oils, ASTM International, 2016, p. D5853.
- [20] J. Ruwoldt, et al., Inhibitor-wax interactions and PPD effect on wax crystallization: New approaches for GC/MS and NMR, and comparison with DSC, CPM, and rheometry, *J. Pet. Sci. Eng.* 177 (2019) 53–68.
- [21] J. Zhang, et al., Theoretical study of the prohibited mechanism for ethylene/vinyl acetate co-polymers to the wax crystal growth, *J. Phys. Chem. B* 112 (1) (2008) 36–43.
- [22] K.G. Paso, et al., PPD architecture development via polymer–crystal interaction assessment, *J. Pet. Sci. Eng.* 115 (2014) 38–49.
- [23] Z. Chen, et al., A study on the interaction of crude oil waxes with polyacrylate pour point depressants by monte carlo simulation, *Pet. Sci. Technol.* 32 (17) (2014) 2151–2157.
- [24] L.Z. Hao, H.S. Al-Salim, N. Ridzuan, A review of the mechanism and role of wax inhibitors in the wax deposition and precipitation, *Pertanika J. Sci. Technol.* 27 (2019) 1.
- [25] Yang, M., A.C. Stewart, and G.A. Davies. Interactions Between Chemical Additives and Their Effects on Emulsion Separation. in SPE Annual Technical Conference and Exhibition. 1996.
- [26] X. Luo, et al., An experimental study on the coalescence behavior of oil droplet in ASP solution, *Sep. Purif. Technol.* 203 (2018) 152–158.
- [27] A.M. AlSofi, et al., Assessment of enhanced-oil-recovery-chemicals production and its potential effect on upstream facilities, *SPE J.* 24 (03) (2019) 1037–1056.
- [28] C. Dalmazzone, C. Noik, J.-F. Argillier, Impact of chemical enhanced oil recovery on the separation of diluted heavy oil emulsions, *Energy Fuels* 26 (6) (2012) 3462–3469.
- [29] B.P. Binks, A. Rocher, Effects of temperature on water-in-oil emulsions stabilised solely by wax microparticles, *J. Colloid Interface Sci.* 335 (1) (2009) 94–104.
- [30] G.B. Freitas, et al., Influence of wax chemical structure on W/O emulsion rheology and stability, *Colloids Surf. A: Physicochem. Eng. Asp.* 558 (2018) 45–56.
- [31] J. Zhang, et al., Effect of resins, waxes and asphaltenes on water-oil interfacial properties and emulsion stability, *Colloids Surf. A: Physicochem. Eng. Asp.* 507 (2016) 1–6.
- [32] M. Dudek, et al., Microfluidic tools for studying coalescence of crude oil droplets in produced water, *Chem. Eng. Sci.* 191 (2018) 448–458.
- [33] M. Dudek, J. Chicault, G. Øye, Microfluidic investigation of crude oil droplet coalescence: effect of oil/water composition and droplet aging, *Energy Fuels* 34 (5) (2020) 5110–5120.
- [34] M. Dudek, et al., Microfluidic testing of flocculants for produced water treatment: comparison with other methodologies, *Submitt. Water Res. X* (2020).
- [35] J. Ruwoldt, et al., Influence of wax inhibitor molecular weight: Fractionation and effect on crystallization of polydisperse waxes, *J. Dispers. Sci. Technol.* 41 (8) (2020) 1201–1216.
- [36] M. Kurniawan, et al., Influence of wax inhibitor molecular weight on solution crystallization and rheology of monodisperse waxes, *Energy Fuels* 35 (9) (2021) 7666–7680.
- [37] J. Ruwoldt, M. Kurniawan, H.-J. Oschmann, Non-linear dependency of wax appearance temperature on cooling rate, *J. Pet. Sci. Eng.* 165 (2018) 114–126.
- [38] J. Ruwoldt, et al., Asphaltene fractionation based on adsorption onto calcium carbonate: Part 3. Effect of asphaltenes on wax crystallization, *Colloids Surf. A Physicochem. Eng. Asp.* 554 (2018) 129–141.
- [39] M. Dudek, et al., Microfluidic method for determining drop-drop coalescence and contact times in flow, *Colloids Surf. A Physicochem. Eng. Asp.* 586 (2020), 124265.
- [40] K. Paso, et al., Paraffin polydispersity facilitates mechanical gelation, *Ind. Eng. Chem. Res.* 44 (18) (2005) 7242–7254.
- [41] H.P. Roenningsen, et al., Wax precipitation from North Sea crude oils: 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties, *Energy Fuels* 5 (6) (1991) 895–908.
- [42] P. Claudy, et al., Interactions between n-alkanes and cloud point-cold filter plugging point depressants in a diesel fuel. A thermodynamic study, *Fuel* 72 (6) (1993) 821–827.
- [43] Md.C. García, Crude oil wax crystallization. The effect of heavy n-paraffins and flocculated asphaltenes, *Energy Fuels* 14 (5) (2000) 1043–1048.
- [44] Venkatesan, R., P. Singh, and H.S. Fogler, Delineating the Pour Point and Gelation Temperature of Waxy Crude Oils. 2004.
- [45] M. Kurniawan, et al., Influence of Microcrystalline Wax on the Properties of Model Wax-Oil Gels, *Energy Fuels* 32 (5) (2018) 5857–5867.
- [46] M. Dudek, et al., Microfluidic testing of flocculants for produced water treatment: Comparison with other methodologies, *Water Res. X* 9 (2020), 100073.
- [47] L.E. Nielsen, R. Wall, G. Adams, Coalescence of liquid drops at oil-water interfaces, *J. Colloid Sci.* 13 (5) (1958) 441–458.

- [48] J. Ruwoldt, S. Simon, G. Øye, Viscoelastic properties of interfacial lignosulfonate films and the effect of added electrolytes, *Colloids Surf. A Physicochem. Eng. Asp.* 606 (2020), 125478.
- [49] M. Pritchard, D. Caroline, Hydrodynamic Radius of Polystyrene around the θ Temperature, *Macromolecules* 13 (4) (1980) 957–959.
- [50] R.-J. Roe, Interfacial tension between polymer liquids, *J. Colloid Interface Sci.* 31 (2) (1969) 228–235.
- [51] J. Ruwoldt, et al., Wax-Inhibitor Interactions Studied by Isothermal Titration Calorimetry and Effect of Wax Inhibitor on Wax Crystallization, *Energy Fuels* 31 (7) (2017) 6838–6847.
- [52] S.M. Hodge, D. Rousseau, Flocculation and coalescence in water-in-oil emulsions stabilized by paraffin wax crystals, *Food Res. Int.* 36 (7) (2003) 695–702.
- [53] T.A. Prileszky, E.M. Furst, Crystallization kinetics of partially crystalline emulsion droplets in a microfluidic device, *Langmuir* 32 (20) (2016) 5141–5146.
- [54] Y. Zhao, et al., Controlled shear stress and controlled shear rate nonoscillatory rheological methodologies for gelation point determination, *Energy Fuels* 27 (4) (2013) 2025–2032.
- [55] R. Venkatesan, et al., The strength of paraffin gels formed under static and flow conditions, *Chem. Eng. Sci.* 60 (13) (2005) 3587–3598.
- [56] B. Biswas, D. Haydon, The coalescence of droplets stabilised by viscoelastic adsorbed films, *Kolloid-Z. und Z. für Polym.* 185 (1) (1962) 31–38.
- [57] X. Chen, et al., Two effects of wax crystals on stabilizing water-in-oil emulsions, *Colloids Surf. A: Physicochem. Eng. Asp.* (2021), 126884.
- [58] T. Krebs, C.G.P.H. Schroën, R.M. Boom, Coalescence kinetics of oil-in-water emulsions studied with microfluidics, *Fuel* 106 (2013) 327–334.
- [59] M. Caggioni, et al., Microfluidic production of endoskeleton droplets with controlled size and shape, *Powder Technol.* 329 (2018) 129–136.
- [60] T. Krebs, K. Schroën, R. Boom, Coalescence dynamics of surfactant-stabilized emulsions studied with microfluidics, *Soft Matter* 8 (41) (2012) 10650–10657.
- [61] A. Hannisdal, et al., Stability of water/crude oil systems correlated to the physicochemical properties of the oil phase, *J. Dispers. Sci. Technol.* 28 (4) (2007) 639–652.
- [62] A. Silset, et al., A multivariate analysis on the influence of indigenous crude oil components on the quality of produced water. Comparison between bench and rig scale experiments, *J. Dispers. Sci. Technol.* 31 (3) (2010) 392–408.
- [63] N. Zaki, P.-C. Schoriing, I. Rahimian, Effect of asphaltene and resins on the stability of water-in-waxy oil emulsions, *Pet. Sci. Technol.* 18 (7–8) (2000) 945–963.
- [64] E. Ariza-León, D.-R. Molina-Velasco, A. Chaves-Guerrero, Review of studies on asphaltene - wax interaction and the effect thereof on crystallization, *CTF - Cienc., Tecnol. Y. Futuro* 5 (2014) 39–53.
- [65] L.A. Alcazar-Vara, J.A. Garcia-Martinez, E. Buenrostro-Gonzalez, Effect of asphaltenes on equilibrium and rheological properties of waxy model systems, *Fuel* 93 (2012) 200–212.
- [66] T.A. Al-Sahhaf, M.A. Fahim, A.M. Elsharkawy, Effect of inorganic solids, wax to asphaltene ratio, and water cut on the stability of water-in-crude oil emulsions, *J. Dispers. Sci. Technol.* 30 (5) (2009) 597–604.
- [67] H.S. Almarouf, et al., Demulsification of stable emulsions from produced water using a phase separator with inclined parallel arc coalescing plates, *J. Pet. Sci. Eng.* 135 (2015) 16–21.
- [68] V.K. Rajak, et al., Optimization of separation of oil from oil-in-water emulsion by demulsification using different demulsifiers, *Pet. Sci. Technol.* 34 (11–12) (2016) 1026–1032.