Enhanced Sedimentation and Coalescence by New Generation of Yellow Chemicals of Petroleum Crude Oil Emulsions

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ABSTRACT

The purpose of this study was to compare the efficiency of new chemistry yellow demulsifiers with already commercially available yellow demulsifiers in destabilizing two types of systems: petroleum crude oil emulsions and model densely packed layers (DPL). Oil-water separation was measured by low field NMR, which allows monitoring the water content in emulsion as function of the sample height and the time. Separation profiles measured by NMR depicted an increase of the free water release kinetic as the concentration of demulsifier increased, as well as the sedimentation velocity. There was no observation of DPL formation in the crude oil emulsions. 4 different demulsifiers were tested on a model DPL and compared with normal crude oil emulsions. One chemical showed a higher efficiency in DPL than in crude oil emulsion. To gain more understanding on the destabilization mechanism, the interfacial rheology properties of the systems were determined. The interfacial experiments showed an increase on the elastic modulus (E'), therefore a stronger interface, as the concentration of demulsifier increased. The viscous modulus (E'') tend to reach a minimum value at low concentrations. There are differences on the experimental procedure for both techniques but the increment of the elastic modulus is not totally understood. The most important parameters were represented by Principal Component Analysis (PCA). PCA analysis did not contribute in a better characterization of the chemicals. The new generation of yellow demulsifiers has not reproduced the efficiency of commercially yellow available demulsifiers

1. INTRODUCTION

Crude oils are complex mixtures of hydrocarbons of various molecular weights and functionalities, and particles. In the crude oil industry, w/o emulsions of variable stability are created during the extraction and transportation procedures. As the oil and water need to be separated, destabilizing these emulsions is a common challenge within this industry. The emulsion stability in crude oil emulsions is enhanced by asphaltenes and resins. They create strong and elastic films at the water – oil interface,[1-3] which prevents coalescence of the dispersed water droplets.[4] These films may become a continuous rigid membrane, avoiding the aqueous and oil phases to be in contact.[5]

These stable w/o emulsions are totally undesirable for the oil industry. They cause serious problems of corrosion, an increase the costs of transportation and other problems. During the upgrading and refining of crude oil more problems are caused due to the presence of these emulsions.[6] Thus, they have to be treated in order to avoid all the problems mentioned and reduce the costs.

Many methods have been used to break down these water-in-crude oil emulsions. The most commonly used are the demulsification by gravity separation, addition of chemicals, electro-coalescence and heating.[7] Probably, the most convenient treatment is the addition of chemical demulsifiers, which is effective and not expensive.[8] At this point, should distinguish between emulsion inhibitors and demulsifiers. Meanwhile inhibitors are added before the emulsion is created, demulsifiers are injected into the emulsions once these are formed. It should be taken into account that a good emulsion inhibitor might not be equally effective in destabilizing an emulsion.[9] Demulsifiers contain interfacial active agents and they are capable to affect the film properties, reducing the interfacial elasticity and the interfacial viscosity.[8, 10, 11] There are also other important properties to take into account, such the ability to flocculate droplets[6] and changing of the wettability of the solid particles at the interface.[12] The demulsifiers used in the industry are mixtures of different chemicals, which each one has its own role in the process of destabilizing the emulsion. An important factor to consider is the aging of the film created in the interface by crude oil indigenous compounds like asphaltenes, an aged film can be more resistant to destabilization.[13] The complexity of the crude oil, and the differences that their origins cause,

makes difficult to determine the correct dosage and chemical for a specific oil-field without testing them in a macroscopic level.

The bottle test is the most used method to study the efficiency of demulsifiers. It is a very easy technique to implement and it is easy to analyze the results. From the bottle test method only can be extracted the water resolved and the sedimentation front in the emulsion if this one is transparent enough, which is problematic in the case of crude oil emulsions. [14, 15] Karl Fisher method gives us an extending of the information obtained. Another method for studying demulsifiers efficiency is the low-field NMR. This technique brings a lot of advantages. First, it is a non-invasive technique, second, it can monitor the water content in the whole sample allowing to follow the free water formation and the sedimentation front.[16] This allows comparing in a very easy way the efficiency of different demulsifiers: sedimentation rates, final oil quality or thickness of stable emulsion layers.[17]

The goal of this study is to compare the new generation of yellow demulsifiers with the already commercially available yellow demulsifiers and try to link the sedimentation and coalescence rates with the film properties in presence of a demulsifier.

2. MATERIALS AND METHODS

2.1.Chemicals

Nine different demulsifiers were tested in this study. The different demulsifiers were codenamed as chemical 1, chemical 2, etc. According to the procedure settled with the suppliers, the chemicals were dissolved in xylene. The chemicals from 1 to 6 are classified as yellow according to the actual norwegian legislation[18] meanwhile 7, 8 and 9 are already available yellow commercial demulsifiers. They differ in their chemistry. The new generation of yellow chemicals are poly(alkylene oxide)-polyglycol esters and the chemicals 7 and 8 (commercially available yellow chemical) are oxyalkylated resins. No information regarding to the chemistry was provided for chemical 9.The aqueous phase (synthetic brine) was 3.5 weight % NaCl. The initial pH of the synthetic brine was 6.5. The brine fraction used for all the emulsions was 40 % in volume. **Table 1** gives the key crude oil parameters.

2.2. Methods

2.2.1. Emulsion preparation

Emulsions were prepared by stirring synthetic brine and oil using an Ultra-Turrax T 25 (Ika®-Werke Co., Germany) for 3 minutes at 24.000 rpm at a temperature of 33°C. The total volume was 100 mL. Right after preparation, 0.2 ml of demulsifier solution was added into the mixture and it was shaken by hand gently 50 times.

The model dense packed layers (DPLs) were prepared by mixing 25 mL of synthetic brine and 25 mL of oil, 8 g/L asphaltenes (extracted from crude oil by precipitation in n-hexane) in xylene (VWR Chemicals). The emulsification process was done by using an Ultra-Turrax T 25 for 3 minutes at 24.000 rpm. The asphaltenes stabilized emulsions were left overnight at room temperature and subsequently, the free water and the free oil phases were removed. The remaining emulsion phase was centrifuged at 5.000 rpm for 15 minutes (Eppendorf centrifuge 5810), and once again, the free phases formed were extracted to obtain the DPLs. The demulsifier was added then into the DPL and the mixture was shaken by hand gently for 20 seconds.

2.2.2. Asphaltene preparation

Asphaltenes were extracted by diluting 25 g of crude oil in 1 L of n-hexane. The dilution was stirred overnight and filtered using a 0.45 μm HVLP (millipore) membrane filter. The filtered asphaltenes were rinsed with n-hexane in order to remove completely other crude oil components. Afterwards, the asphaltenes were dried overnight in a nitrogen atmosphere protected from light to avoid oxidation.[19]

2.2.3. Analysis by low field NMR

A MARAN low field NMR with resonance frequency of 23 MHz (400G/cm) from Oxford Instrument (England) was used to measure both the brine separation profiles and the Droplet Sizes Distribution, according to sequences developed previously.[17] The NMR magnet was tempered at 33 °C. The brine separation profiles were obtained by measuring the position

dependent signal of the sample at short and long observation times.[16, 20] By measuring the distribution of the transversal relaxation time (T$_2$), the droplet sizes can be obtained.[21]

2.2.4. Interfacial Rheology

A Sinterface PAT-1M (Germany) was used to measure the interfacial tension and the interfacial rheology of crude oil interfaces. One oil droplet attached to a syringe is created into an aqueous phase. A camera monitors the shape of this droplet. The shape is related to the interfacial tension between the oil and water. The interfacial tension and interfacial rheology measurements were performed by immersing an oil droplet (20 mm^3) created in a 0.7 mm diameter u-bent needle. The rheological properties were studied at frequencies of 0.010, 0.012, 0.017, 0.025 and 0.050 Hz (which correspond to periods of 100, 80, 60, 40 and 20 s respectively) with a total of 10 periods. The oscillations were started after 200 min. The drop volume oscillated with and amplitude of 3 mm^3. Synthetic brine was used as the aqueous phase. The syringe has a piston connected to a computer, thus the droplet volume can be changed and also monitored. Appling a volume sinusoidal oscillation in the droplet, the interfacial response can be studied. The complex interfacial dilational modulus, E, is defined as the change in interfacial tension, γ, and in interfacial area, A.

$$E = \frac{d\gamma}{d \ln A}$$
(1)

The interfacial dilational modulus is complex function of the angular frequency, ω.

$$E = E_d + i\omega\eta_d = E' + iE''$$
(2)

Where the real part, E_d, reflects the elastic response and the imaginary part, $i\omega\eta_d$, reflects the viscous response of the interfacial layer. Therefor E' is the storage modulus and E'' the loss modulus of the interface.[22-24]

2.2.5. Principal Component Analysis (PCA)

Principal component analysis (PCA) is a projection method that helps to visualize and to extract the most important information from a data set. PCA finds combinations of variables that describe trends in the data set.[25] PCA bases its math in an eigenvector decomposition of the covariance matrix of the variables in a data set. Given a data matrix X with m rows of samples and n columns of variables, the covariance matrix of X is defined as

$$cov\,(X) = \frac{X^T X}{m-1} \tag{3}$$

The result of the PCA procedure is a decomposition of the data matrix X into a principal components (k) called score and loading vectors.

$$X_{n\times m} = t_1 p_1^T + t_2 p_2^T + t_i p_i^T + \cdots + t_k p_k^T + E_{n\times m} \tag{4}$$

Where t_i is the score vector, p_i is the loading vector, and E is the residual matrix. These two vectors, vector and score vectors, relate how samples and variables are related to each other. The direction of the first principal component, (t_1, p_1) or PC1, is the line in the variable space that best describes the variation in the data matrix X. The second principal component (PC2) is the second coordinate, and so on. The score plot is defined by the graph where one score vector is represented against another score vector. The most common score plot is the one that represents the principal component (PC1) versus the second principal component (PC2), since these two are used to have the major variance in the data.[26] The data set was composed of 9 samples which represented brine in crude oil emulsions prepared with 9 different chemicals at one concentration (100 ppm). As normal variables sedimentation rate, coalescence rate, initial droplet size, free water observation time and residual content of water in the oil phase after 2 hours were considered. Quality of the separated water after experiments was defined as a category variable with three levels (clear, hazy and turbid, corresponding to the water quality).

3. RESULTS AND DISCUSION

3.1. Emulsion stability from low field NMR

Low field NMR has been showed as a very trustful method to monitor the water profile in oil continuous samples.[16] The emulsion stability of water in crude oil emulsions in presence of the 9 chemicals provided by the supplier was studied at a demulsifier concentration of 30 ppm and at a temperature of 33°C. An Example of a separation profile is given in **Figure 1**. The contour plot depicts the water content as a function of time and position, showing the areas rich in oil as red with a 0 – 20 % water content, yellow areas with 20 – 40 %, green areas with 40 – 60 %. The blue areas correspond to high water content, showing a light blue color for water contents of 60 – 80 % and dark blue for 80 – 100 %. The first tests at a concentration of 30 ppm did not show efficient performances. All the chemicals but not chemical 8 and 9, which are yellow commercial available demulsifiers, showed low performances at those conditions. As can be seen from **Table 1**, the crude oil used in the present study can be classified as heavy and viscous oil, therefore it makes water recovery to be difficult as it can be observed in **Figure 1a**.[27] The fastest time in observing a breakthrough of free water was at 10 minutes, and it was observed for chemical 8. Chemical 9 also had a fast free water formation, it could be observed at 20 minutes. The other yellow commercial available chemical (chemical 7) did not show a good performance, having a very similar performance as chemical 1 (**Figure 1b**). Sedimentation velocity for chemical 8 has shown to be faster than chemical 9. Regarding to chemical 1, it can be appreciated a slow sedimentation of the droplets but not breakthrough of free water. At a concentration of 30 ppm and a temperature of 33 °C, commercial demulsifiers have showed a higher performance in free water recovery and higher sedimentation velocities. However, chemical 8 has proved to be the more efficient demulsifier, causing a faster coalescence than chemical 9.

The chemicals were compared at higher both concentration and temperature. **Figure 2** shows a comparison between chemicals 1,2, 8 and 9 at a temperature of 60 °C and at a concentration of 100 ppm. An increase in the performance can be noticed in this figure. Chemicals 8 and 9 had a very similar efficiency, having a very good destabilization effect in the emulsion. In the other hand, even though the new generation demulsifiers (**Figure 2a** and **Figure 2b**) had increased their efficiency, was not as good as the commercial available demulsifiers (**Figure 2c** and **Figure**

2d). **Figure 3** depicts both the sedimentation and free water formation fronts for the chemical 1, 30 ppm at 33 °C, 100 ppm and 200 ppm at 60 °C. The sedimentation front was obtained by considering the iso-volumetric curve of 30 % of water content, and the free water front was established by considering the 90 % of water content. An improvement of the performance is observed when the concentration is increased to 100 ppm at a temperature of 60 °C. The observed sedimentation velocity is increased from 0.020 mm/min (30 ppm) to 0.048 and 0.052 mm/min for 100 ppm and 200 ppm respectively. The sedimentation velocity values were estimated by considering as the initial linear slope in the sedimentation front. It is observed that increasing the concentration from 100 to 200 ppm there is a slightly improvement in the sedimentation rate as well as the free water formation rate.

Figure 4 shows the iso-volumetric curves of 30 % and 90 % water for 4 different chemicals under different concentrations and temperatures. It can be seen how there is no difference between 100 ppm and 200 ppm for the chemical 9. Chemical 3 has a slightly better performance increasing the concentration from 100 to 200 ppm. The sedimentation rate is similar for both concentrations but free water front is faster for 200 ppm. That means a slower coalescence rate for 100 ppm. Chemical 2 and chemical 4 showed a notorious improvement by increasing the concentration, even from 100 to 200 ppm. For instance, chemical 9 (**Figure 4d**) has a sedimentation velocity of 0.088 mm/min when the concentration is 30 ppm and 1.968 mm/min for concentrations of 100 and 200 ppm at 60 °C. When the emulsion is treated with the chemical 4, the sedimentation velocity is 0.014 mm/min for 30 ppm, 0.092 mm/min for 100 ppm at 60 °C and 1.818 mm/min for 200 ppm at 60 °C as well. In this case we still see an improvement in the efficiency by increasing the concentration. That gives information about the optimal efficient concentration. For instance for the chemical 9, to increase the concentration from 100 to 200 ppm can be considered as overdosing the emulsion, for chemical 4 that clearly not the case.

Table 2 summarizes all the observed sedimentation velocities at 100 ppm and 60 °C. They are compared to the Stokes' sedimentation velocity,[28] which is given in **Equation 5**.

$$v = \frac{2a^2 g \Delta \rho}{9\mu}$$

(5)

Where a is the droplet radius, g the gravity constant, $\Delta\rho$ the density difference between the internal and external phase and μ the viscosity of the external phase. Comparing both sedimentation velocities, observed and Stokes', can be observed that they do not match. Observed sedimentation velocities are always higher than the theoretical ones in all the cases. This can be explained because theoretical model considers a monodispersed droplet size. Moreover, the NMR allos to measure a volume-average size depending more on "big" droplets. The droplet size is 3 µm for the emulsion with no chemical addition, then than can be considered as the initial droplet size, therefore as a baseline. The kinetics of sedimentation studied by the low field NMR has shown there is no substantial improvement for some demulsifiers when the concentration is increased from 100 to 200 ppm (i.e. **Figure 4b**). Studying the quality of separated water after the breakthrough of the emulsion will bring information about overdosing the emulsion with demulsifier. **Table 3** shows how by increasing the dosage up to 200 ppm reduces the quality of the separated water. Having water turbidity after separation indicates there was a solubilization effect, so part of the demulsifier passed into the aqueous phase, therefore meaning an overdose of the system. That can be observed for all the chemicals, excluding chemical 8, which had separated clear water even at 200 ppm.

Since at 200 ppm the water quality of the separated aqueous phase was decreased, we took 100 ppm as a good concentration to continue the experiments. **Table 4** shows the sedimentation velocities and coalescence velocities for all the chemicals. In order to estimate the coalescence velocity, the iso-volumetric curve of 90% water content was considered by adjusting an initial linear slope in the free water formation front. Sedimentation velocities are higher than coalescing velocities. The representation of the coalescence velocity in front of the sedimentation velocity is plotted in the **Figure 5**. Moreover, it can be easily seen that there is a linear relationship between the coalescence rate and the sedimentation rate. The slope of the curve is 0.44 close to 40 % v/v, the initial water cut of the emulsion. That means that as soon as the droplets have reached the freewater boundary, they coalesce. Consequently there is no possibility for the droplets to accumulate in a dense packed layer in the investigated system. From this curve it can be difficult to classify the different chemicals as flocculent or coalescing agents as it can be seen. Excluding the chemical 3, all the other chemicals fit in the regression line showed in the figure and cannot be classified as flocculent or coalescent agents. Only chemical 3 has a clear flocculent effect as it can be seen from the **Figure 5** and the **Table 4**.

3.2. Effect in the Densely Packed Layer (DPL)

An Emulsion under the effect of sedimentation, the droplets move downwards. After a given time, in the lower part of the emulsion the concentration of droplets has increased. This high droplet content region of the emulsion is the so-called Densely Packed Layer (DPL). In case of water separation, the DPL would be found above the interface between the oil and the brine. It is very interesting to study the efficiency of the chemicals in that region, where the higher concentration of water droplets is found. Also, formation of DPLs in our systems with presence of demulsifiers was not observed, except in a few cases. It can be observed from **Figure 1c** after 100 min, there is free water region in the bottom of the sample, a lower water content w/o emulsion in the upper part and a small region at the 0.25 height (right above the interface) where the DPL is found. It is interesting to study the stability of these layers and how efficient the demulsifiers are in it.

Obtaining a DPL from the studied crude oil was impossible due to the high viscosity of the crude oil, therefore a model system had to be found. The system used to create this model DPL was an asphaltenes stabilized water in xylene emulsion, the procedure is explained in detail in section 2.2.1. The determination of brine separation profile by low field NMR was not possible in this case due to the low viscosity of the oil phase.[16] Consequently bottle testing was used to study their stability.

Chemical 1, 2, 3 and 4, because of their condition of yellow new generation of demulsifiers, were tested in the DPL with a concentration of 100 ppm. **Figure 6** depicts the comparison of efficiency between DPL and crude oil emulsions studied by bottle test. Chemical 1 is not showed in the figure. It had no effect on the DPL and in the bottle test any separation was observed. Chemicals 2 and 3 did not show any effect, any free water formation was observed after 2 hours. In the other hand, their efficiency in crude oil emulsion was notorious. On the contrary, chemical 4 showed a better performance in DPL than in crude oil emulsion. The free water formation was much faster and the total water separated was higher than the ones observed in the emulsion.

3.3. Interfacial Rheology

Interfacial properties were studied for chemical 2, which is a new yellow generation demulsifier and has a good performance, at different concentrations to observe how it affects at the oil water interfaces. By studying the interfacial rheology by the oscillating drop technique, it should be mentioned that this method assumes that the only forces acting on the droplet shape are gravity and interfacial tension. As it has been reported before, for certain viscous liquids, viscous and inertial forces do perturb the oscillating pendant drop measurements.[17, 29, 30] This perturbation and its limits can be quantified by the capillary number, given in **Equation 6**.

$$Ca = \frac{\Delta\mu \ \omega\Delta V}{\gamma_0 a^2}$$

(6)

Where $\Delta\mu$ is the viscosity differences between both phases, ω is the volume drop oscillation frequency, ΔV the volume oscillation amplitude, μ_0 the interfacial tension once reached the equilibrium and a the radius of the capillary tube. By studying the crude oil without diluting it, exists the possibility of measuring an apparent interfacial tension influenced by the high viscosity of the oil phase. In order to avoid this problem there are two possible solutions. One would be extracting the interfacial active compounds from the crude oil (resins and asphaltenes) and dissolve them into a model oil with a lower viscosity. This would affect the diffusion and intermolecular properties of the surfactants. The second method would be diluting the crude oil with some diluent such as pentane, toluene or others. By using this method the properties of the resins and asphaltenes would change and their activity would be affected depending in the nature of the diluent. Based on a previous work,[17] a dilution of crude oil with Heptol at 30 wt.% (a mixture of 1:1 weight ratio of toluene and heptane) was taken as the oil phase to avoid perturbations. **Figure 7** depicts the interfacial tension at different concentrations for chemical 2. It can be observed from the figure that the interfacial tension decreases when the concentration is increased. For the concentration of 100 ppm the droplet got released from the syringe at a time of 125 minutes approximately. The same problem was observed at a time of 40 minutes for a concentration of 200 ppm.

Figure 8 shows the elastic (E') and viscous (E'') response of the interface for different concentrations of chemical 2 at different oscillation frequencies after the interfacial tension had reached the equilibrium. It can be seen from the figure that the elastic modulus increases with the concentration of chemical and then, tends to stabilize when the concentration has a value of 100 ppm. On the contrary, the viscous modulus has a minimum value when the concentration has reached a value of 50 ppm. That is in disagreement with the separation profiles showed in **Figure 3**, where the separation was improved by an increment of concentration. According to the interfacial experiments the elastic modulus increases with demulsifiers concentration which means that the film properties become more resistant, therefore the emulsion becomes more stable. There are differences regarding to the experimental procedure between both methods. In the emulsion destabilization measurements performed by NMR the chemicals were added after creating the emulsion, thus the interface was already created. On the contrary, during the interfacial experiments the chemicals were added in the oil phase before the interface was created, so the chemicals had to compete against the indigenous surfactants contained in the crude oil to obtain their position at the interface. The dilution of the crude oil also has to be taken into account. As mentioned before, the crude oil was diluted with 30 wt. % 1:1 Heptol, this could change the diffusion properties of the chemicals and the indigenous surfactants of the crude oil. The possibility of having asphaltenes aggregates, leading into a creation of organic particles is also plausible. In a previous work, it was reported that this minimum anomaly found in the viscous modulus could be related to the high concentration of demulsifier per interfacial area, thus in the interfacial tension experiments the interface would be overpopulated by surfactants, having a higher surfactant concentration per interfacial area in the interfacial tension experiments than in the stability measurements by NMR.[17] That does not explain why the elastic modulus has an increasing trend as the concentration is raised. This is not understood so we cannot have any conclusion for the results showed.

3.4. Principal Component Analysis (PCA)

Since the experimental test matrix was large and complex, multivariate analysis can be a useful tool to study and understand the effect of different chemicals on water in crude oil emulsions. As described in the section 2.2.4, the data set was composed of 9 samples which represented brine in crude oil emulsions prepared with 9 different chemicals at one concentration

(100 ppm). As normal variables sedimentation rate, coalescence rate, initial droplet size, free water observation time and residual content of water in the oil phase after 2 hours were considered. The samples in the matrix were named from S1 to S9 for referring to the chemical and the number in parenthesis shows the concentration of the chemical. Results for PCA analysis are shown in **Figure 9**. Two principal components explain 90 % of the variation in the data set (PC1 explained the 75 % of variance and the PC2 explained the 15 %). PC1 seems to be directly related to sedimentation and coalescence rate as it is illustrated in the loading plot (**Figure 9b**). In addition, PC2 seems to be related to the resolved emulsion or residual oil dryness.

Figure 9a shows the score plot of the PCA analysis. This analysis reveals similarities between the yellow commercial available demulsifiers which are grouped in the left side of the plot. In blue color are grouped the new generation of yellow demulsifiers, which are localized in the right side of the plot, they showed lower sedimentation and coalescent rates. Chemicals 7 and 8 have a very similar behavior, the same for chemicals 4, 5 and 6. Also it can be noticed that sample 3 is the most efficient among the new generation of yellow demulsifiers, and chemical 1(found in the right upper part of the figure) can be identified with a different behavior from the rest of the chemicals with the same chemistry.

4. CONCLUSIONS

Destabilization of brine in crude oil emulsions by using different demulsifiers, comparing new and commercial yellow demulsidiers, was studied by bottle test and low field NMR. The results showed that at low concentrations, 30 ppm, the chemicals has a low efficiency. By increasing the concentration until 100 ppm the performance was improved considerably, but at dosages of 200 ppm the concentration the efficiency did not improve their efficiency evidently for most of the chemicals. The new generation of yellow demulsifiers was difficult to characterize, there was a linear relationship between the coalescence rate and the sedimentation rate, which means that as long as the droplets reached the free water boundary they coalesced. Only the chemical 3 could be classified as a coalescent agent. The water quality test showed that once the 100 ppm concentration was exceeded the aqueous separated phase became turbid. That could be explained as an overdosing of demulsifiers in the emulsion. Among the new generation of yellow demulsifiers, the chemical 4 showed a very good performance under the DPL conditions. The

interfacial experiments showed the elastic modulus (E') had a tendency to stabilize when the concentration is 100 ppm whereas the viscous modulus (E'') had a minimum value when the concentration was 50 ppm. This contrast between interfacial tension measurements and the stability measurements by NMR is attributed to the difference in surfactant concentration per unit of interfacial area. According this results and a previous study,[17] in order to select the right chemical dosage the dispersed interfacial area is a determining parameter to consider. Yellow commercial available demulsifiers had a better performance than the new generation of yellow demulsifiers at low concentrations, even if at 100 ppm chemical 3 had showed a good performance in the stability measurements.

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Notes

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TABLES

Table 1. Summary of the Key Crude Oil Properties.

Parameter	Crude Oil
SARA fractionation	
Saturates (wt.%)	37.4 ± 0.5
Aromatics (wt.%)	44.1 ± 0.5
Resins (wt.%)	16.1 ± 0.6
Asphaltenes (asphaltenes precipitated) (wt.%)	2.54 ± 0.03
Density (33°C) [g/cm^3]	0.927 ± 0.001
Viscosity (33°C) [mPa·s]	156
Total Acidic Number, TAN [mg KOH/g]	2.15 ± 0.02

Table 2. Sedimentation velocities, average droplet sizes and average droplet growth of the emulsions at 100 ppm and 60°C.

Chemical	Stokes' Sedimentation velocity [mm/min]	Experimental Sedimentation velocity [mm/min]	Average intial droplet radius [µm]
No	-	-	3
1	0,014	0.048	26.42
2	0.007	0.252	18.72
3	0.010	1.322	22.73
4	0.005	0.092	15.76
5	0.004	0.066	13.78
6	0.007	0.078	18.99
7	0.019	2.940	30.51
8	0.025	1.626	35.26
9	0.012	1.968	24.52

Table 3. Water Quality of the separated water after 2 h of applying the demulsifiers in the emulsions at 60 °C.

| Chemical | Water quality after 2 h | |
	100 ppm	200 ppm
1	Clear	Turbid
2	Clear	Turbid
3	Clear	Turbid
4	Clear	Hazy
5	Clear	Turbid
6	Clear	Turbid
7	Clear	Hazy
8	Clear	Clear
9	Hazy	Turbid

Table 4. Sedimentation and coalescence velocities at a concentration of 100 ppm at 60 °C.

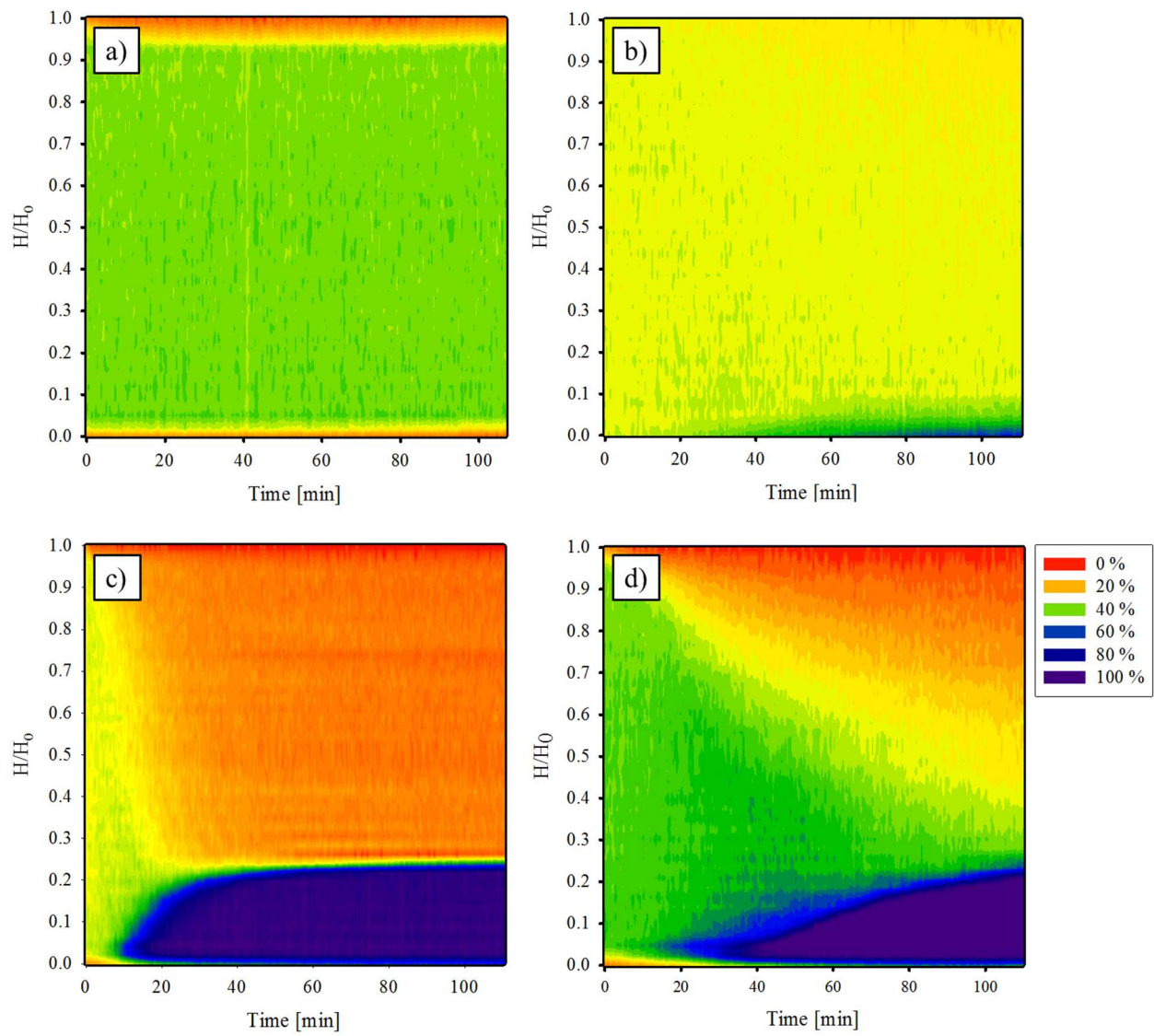| Chemical	Sedimentation velocity [mm/min]	Coalescence velocity [mm/min]
1	0.048	0.014
2	0.252	0.086
3	1.322	0.150
4	0.092	0.036
5	0.066	0.028
6	0.078	0.048
7	2.940	1.388
8	1.626	0.742
9	1.968	0.850

FIGURE CAPTIONS

Figure 1. Contour plots for crude oil emulsions at 33 °C. (a) No chemicals added; (b) 30 ppm of chemical 1; (c) 30 ppm of chemical 8; (d) 30 ppm of chemical 9.
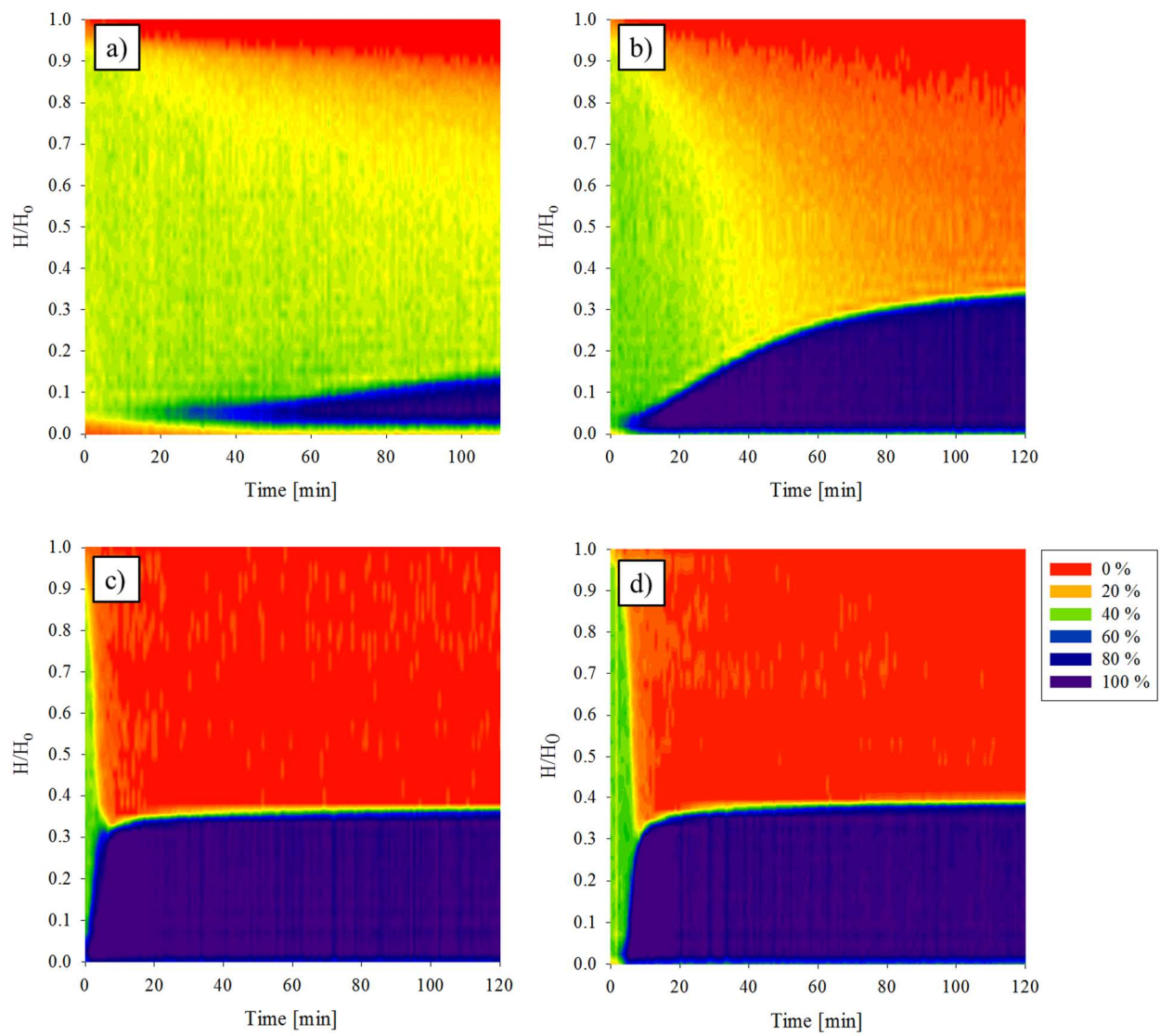
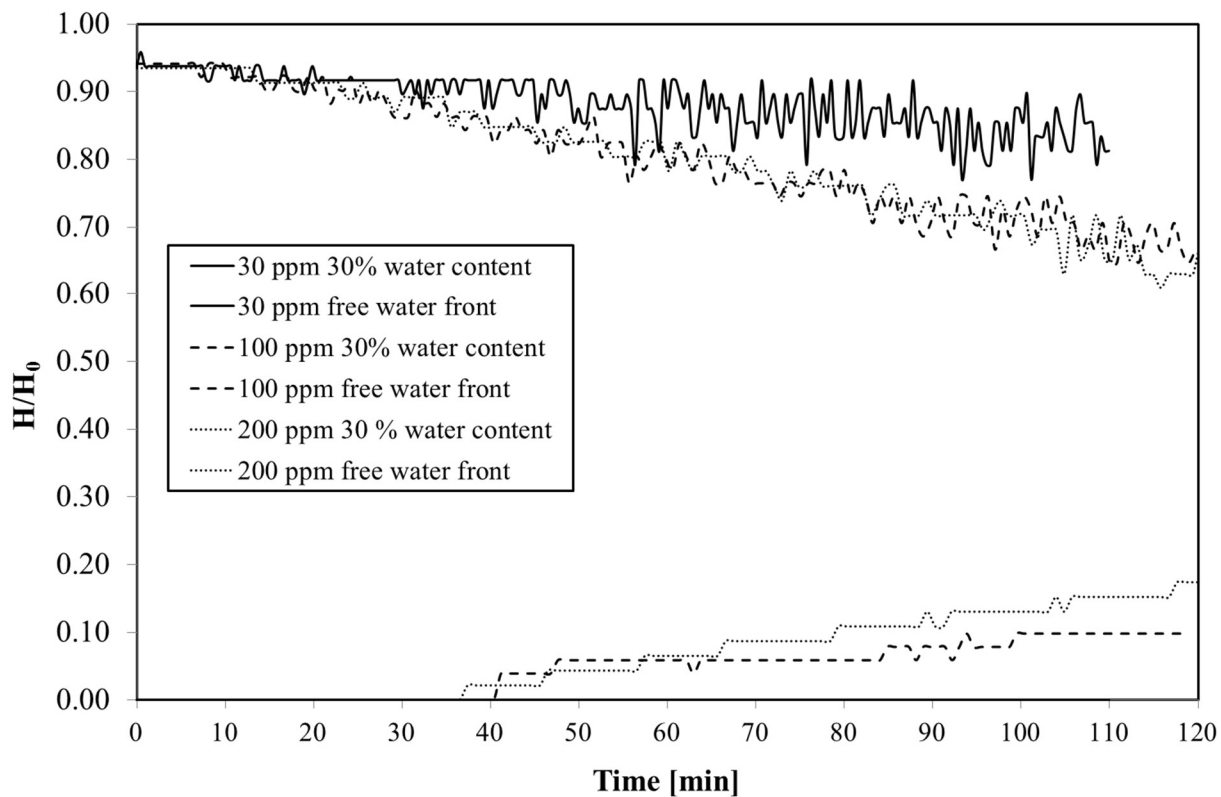**Figure 2.** Contour graph at a concentration of 100 ppm and 60 °C.

Figure 3. Comparison of sedimentation and free water formation of chemical 1 at different concentrations and temperatures (30 ppm at 33 °C, 100 and 200 ppm at 60 °C). The sedimentation fronts are the 30 % iso-volumetric curves and the free water formation fronts are the 90 % iso-volumetric curves from contour plots.
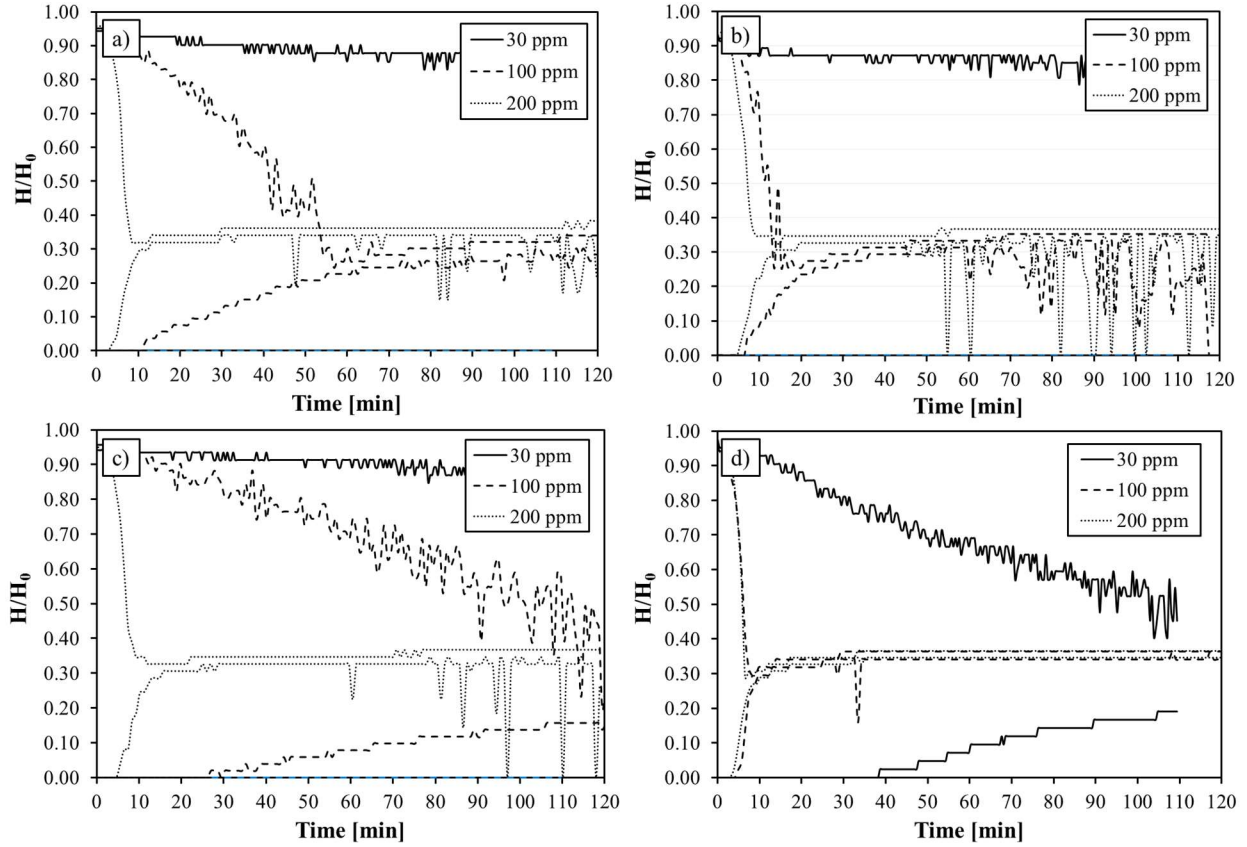
Figure 4. Comparison of sedimentation and free water formation fronts for: (a) chemical 2; (b) chemical 3; (c) chemical 4; (d) chemical 9.
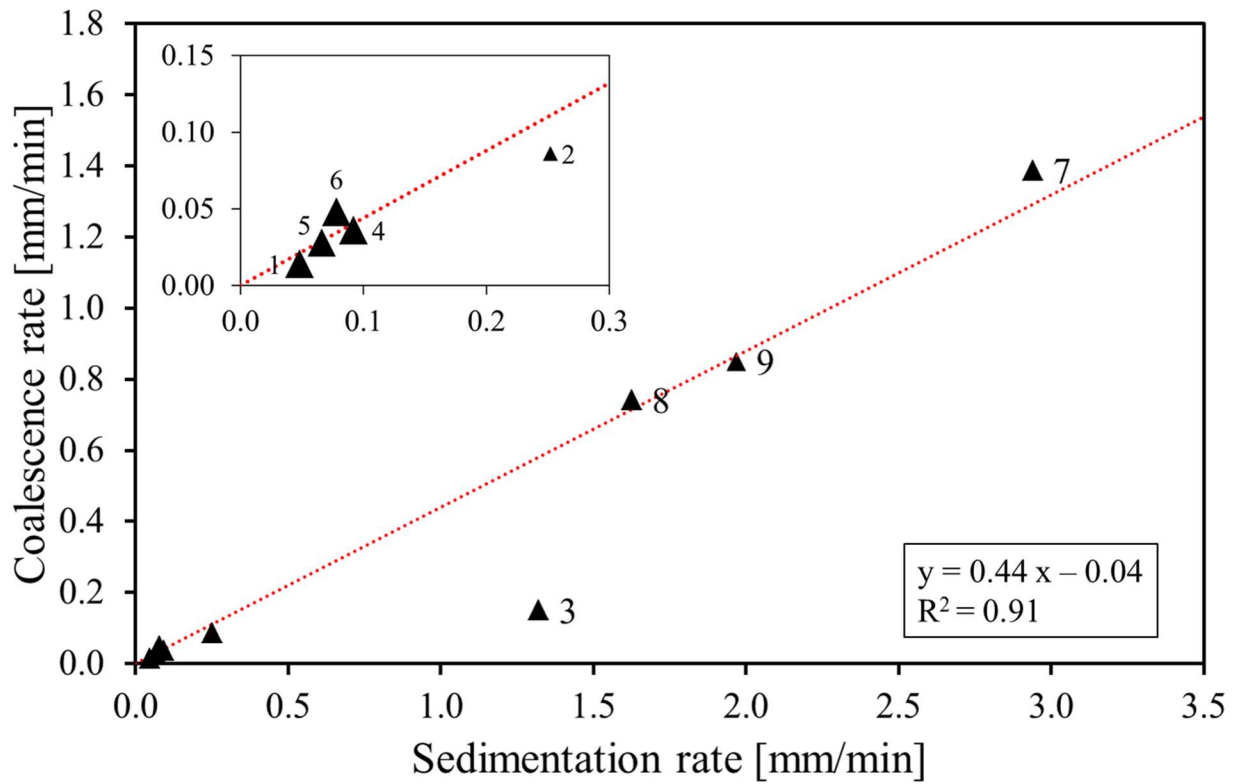
Figure 5. Coalescence velocity represented in front of sedimentation velocity at a concentratrion of 100 ppm.

Figure 6. Comparison of water separation profiles of chemical 2, 3 and 4 in crude oil emulsions and in Densely Packed Layers (DPL).

Figure 7. Dynamic interfacial tension with the crude oil diluted with 30 wt. % of 1:1 Heptol at different concentrations of chemical 2.

Figure 8. (a) Elastic Modulus and (b) Viscous modulus as function of the chemical concentration for chemical 2.

Figure 9. Score a) and loading b) plots of PC1 versus PC2.

FIGURES

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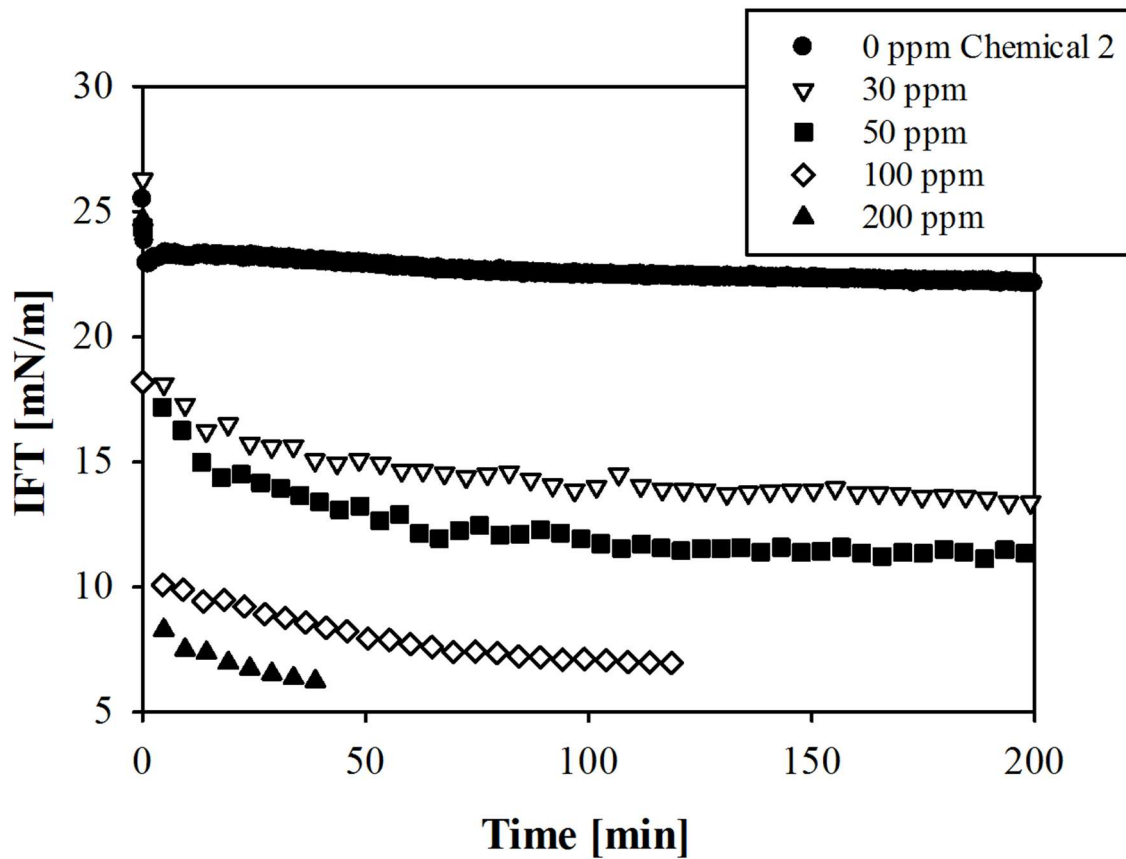
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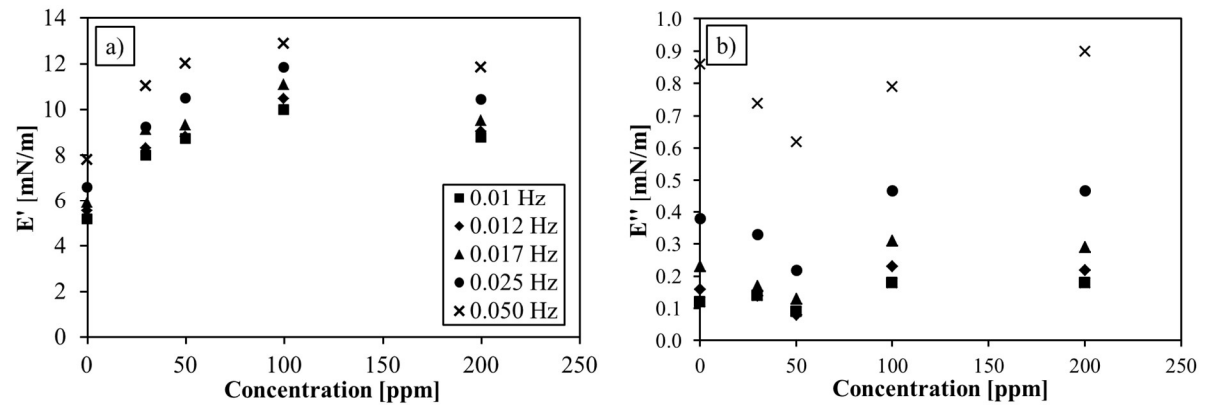
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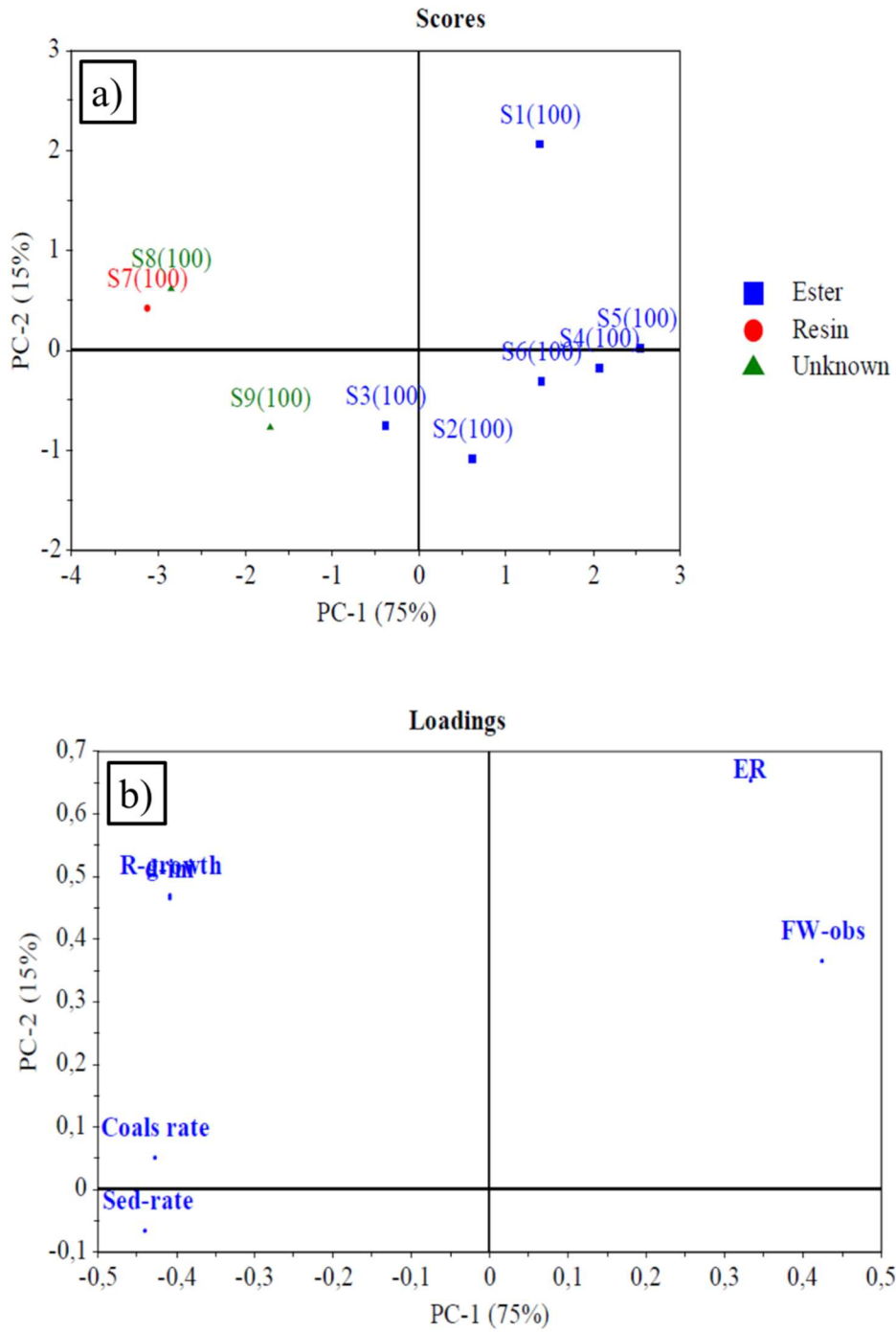
Figure 9. Score a) and loading b) plots of PC1 versus PC2.