Influence of Asphaltenes on Gelation of Tetrameric Acid with Calcium Ion at the Oil/Water Interface under Flow Condition

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Abstract

The first step in calcium naphthenate deposition is supposed to be the formation of an interfacial gel by crosslinking between ARN tetrameric acid and Ca^{2+}. Several aspects of the inhibition of the interfacial gel formation by asphaltenes are studied by sessile drop tensiometry fitted with a special device allowing to continuously exchange the droplet subphase to simulate the dynamic conditions due to the flow of oil in crude oil processing facilities.

First experiments were performed by exchanging simultaneously ARN and asphaltenes. Interfacial tensions and interfacial dilational moduli have shown that asphaltenes prevent the formation of interfacial ARN gel. The interface is composed mostly of asphaltenes with a small proportion of non-crosslinked ARN. Influence of different parameters (pH, asphaltene concentration, exchange time, asphaltene solvency) were tested and they do not significantly alter the conclusions. The inhibition of interfacial gel formation is most likely due to bulk interactions between ARN and asphaltenes and not to interfacial competition since ARN is more surface active than asphaltenes. The interfacial concentration of ARN is critical for the crosslinking with Ca^{2+}.

Furthermore, asphaltenes were exchanged in droplet bulk subphase after formation of ARN/Ca^{2+} interfacial gel. A significant part of the interfacial gel seems to be desorbed or dispersed by asphaltenes, especially during the initial moments of the exchange.

In conclusion, this study shows how important asphaltenes are in the calcium naphthenate deposition mechanism.

Keywords:
Tetrameric acids, ARN, calcium naphthenate deposits, interfacial dilational rheology, coaxial capillary system

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1 Introduction

ARN tetrameric acid is a complex compound present in petroleum crude oils at the part-per-million level[1]. Even at this concentration, ARN is responsible for the formation of calcium naphthenate deposits that can result in oil production issues even leading to production shutdown in the worst cases[2-4]. These deposits are found in several geographical areas (North Sea, Western Africa, Brazil, China[5-7]) and contain 20-40 wt. % of ARN[8].

Due to the economic consequences, ARN and the deposition phenomenon have been the object of several studies since its discovery in 2004[9-11]. Different aspects have been considered: Exacted ARN structures have been determined by modern NMR instrumentation by Lutnaes et al. in 2006[12-14]. Different methods have been developed to detect and determine the concentration of ARN in crude oils and deposits[8, 15-17]. The ARN self-association properties have been studied in bulk both in aqueous and in oil phases[18, 19]. Models to calculate the solubility of ARN as a function of pH have been proposed[20-22]. Its adsorption and reaction with calcium at oil-water interface have been particularly studied[5, 11, 23-25]. Interactions between ARN and other crude oil components such as asphaltenes and naphthenic acids have been assessed both in bulk and at the interface[26, 27]. Finally, different methods have been developed to study the inhibition by chemicals of calcium naphthenate deposition[28, 29].

Recently, Simon et al.[30] have extended and completed the mechanism of calcium naphthenate deposition proposed by Vindstad et al.[2]. First, the depressurization and release of CO_2 during the production induces an increase in the produced water pH[2]. When the pH is high enough, ARN initially present in the oil phase is ionized[31] and adsorb at the oil-produced water interface[11]. Here, it reacts with Ca^{2+} ions to create cross-linking point between adsorbed ARN molecules. This creates a 2D structure that has rheological properties of a gel[5, 23, 25, 32]. The gelation then propagates with time and with coalescence of water droplets. The flow of oil also allows to continuously bring more ARN that accumulates at the interface. This gel can also, at a later stage, entrap particles and other crude oil components which ultimately leads to the formation of solid deposits blocking oil production facilities.

The first steps in this mechanism have been tested using a co-axial capillary device fitted to a profile analysis tensiometer. The apparatus allows to continuously exchange the ARN solution inside the oil drop formed in an aqueous phase. The exchange mimics the continuous flow of oil in petroleum production facility. If the pH of the aqueous phase is high enough (and in presence of calcium), a gel is formed at the interface. This gel grows as more oil ARN solution is exchanged into the droplet and if the area is reduced by contracting the droplet (mimicking coalescence). These results are in line with the proposed deposition mechanism.

However, more works are currently required to be able to develop tools for the prediction of the formation of calcium naphthenate deposits in new production units[4]. For instance, the proposed mechanism does not take into account the composition of the oil phase. The composition seems to be an important parameter since static experiments, i.e. performed without oil phase flow, have shown that crude oil components such as asphaltenes and other naphthenic acids can prevent the formation of interfacial gels[5, 23]. Another study by Brocart et al.[33] have reported the presence of ARN in a larger number of crude oils. However, most of the tested oils do not present any deposition issue in operation.

This article is continuation of a previous work by Simon et al.[30]. It involves the same equipment i.e. a co-axial capillary device fitted to a profile analysis tensiometer to study the formation of an interfacial gel under oil flowing conditions. This new work aims to determine the effect of asphaltenes on the formation of ARN-Ca^{2+} interfacial gels. Different possibilities have been considered: Either asphaltenes have been injected along with ARN i.e. before and during the gel formation process or after the interfacial gel have been formed.

2 Experimental Section

2.1 Chemicals

ARN samples have been extracted from a calcium naphthenate deposit using the acid-IER method previously described[34]. The obtained sample purity has been characterized by ^{1}H NMR[8].

Asphaltenes were extracted from a North Sea crude oil. 160 mL of n-hexane was added to 4 grams of crude oil sample and stirred overnight. The next day, the asphaltene fraction is recovered by filtration using a 0.45μm HVLP (milipore) membrane filter. The filtrate is washed up by warm n-hexane and finally dried under N_2 atmosphere. Asphaltenes obtained from the same crude oil (but different batches) have already been characterized (in Simon et al.[35], asphaltenes from crude 3).

All the other chemicals are commercially available and were used without further purification. Sodium tetraborate decahydrate – borax (≥99.5 %) was obtained from Sigma-Aldrich), sodium chloride (for analysis) was from Merck, calcium chloride dihydrate (≥99 %) was from Sigma, and xylene (mixture of isomers, ≥98.5 %) and n-hexane (for HPLC quality analysis) were both obtained from VWR. Water was from a Milli-Q system (Millipore).

2.2 Solution Preparations

Aqueous solutions containing 20mM NaCl (1.17 g/L), 10 mM borax (3.81 g/L) and 10 mM $CaCl_2$ (1.11 g/L) were prepared and their pH adjusted to 8 by adding 1 M HCl.

Solid ARN was dissolved in xylene at a 500 µM concentration and shaken overnight. Then, after filtration (0.2µM PTFE filter), the 500 µM ARN solution was diluted to the required concentration.

Asphaltene solutions were prepared at a concentration of 1 g/L by dissolving solid asphaltenes with xylene, then the mixture is sonicated for 30 min, and then shaken at 200 rpm overnight. The day after, the solution is sonicated for 10 min before or after dilution with xylene to the desired concentration,

Solutions containing asphaltenes and xylenes were prepared by independently preparing the 500 µM ARN solution and the 1 g/L asphaltene solution as described above. The final solution solutions were prepared by mixing the ARN solution, asphaltene solution, pure xylene, and (potentially) hexane and sonicated for 10 minutes.

2.3 Interfacial Tension Measurements and Interfacial Dilational Rheology

Experiments were performed with a sessile/pendant drop tensiometer (PAT 1m) from SINTERFACE Technologies (Berlin, Germany) fitted with a co-axial capillary device (i.e. composed of an inner and an outer capillary) shaped as a hook. Every capillary is linked to a 100 µL syringe pump piloted by the SINTERFACE software. The principle of this technique is the following: An oil drop is created at the tip of the hook in a cuvette filled with an aqueous phase. The Sinterface apparatus continuously determine the interfacial tension at the interface between the oil and the aqueous phase from the shape of the drop and the densities of the two phases by using the Young-Laplace equation[36].

Interfacial dilational rheology moduli E' and E''can be determined with the same apparatus: the area (A) of a droplet is oscillated at an angular frequency ω from an initial area (A_0) with an amplitude A_α according to the following equation:

$$\Delta A = A - A_0 = A_a \sin(\omega t) \qquad (1)$$

Concomitantly, interfacial tension varies in a sinusoidal way but with a phase shift

The complex dynamic apparent dilatational modulus (E*) is defined as the Fourier transform ($\mathcal{F}$) of the change in interfacial tension (γ) relative to the change in interfacial area via equation (3):

$$E^*(\omega) = \frac{\mathcal{F}\{\Delta\gamma(t)\}}{\mathcal{F}\{\Delta \ln (A(t))\}} = E'(\omega) + iE''(\omega) \qquad (2)$$

Two experimental procedures were performed in this study:

-In section 3.1: A 15 µL oil droplet was created at the tip of the hook inside a 20 mL aqueous solution. Immediately after formation, the droplet subphase was exchanged, for 720 s, by injection of the same oil solution from the inner capillary by step of 1 µL every 7 s. This is equivalent to a flow rate of 0.143 µL/s. The droplet volume was kept constant by simultaneously withdrawing oil from the outer capillary thanks to a feedback system. After 720 s, 2700 s, or 5400 s the exchange was stopped. Interfacial rheology measurements started after the end of the exchange. The principle of measurement is further described in Simon et al.[30].

-In section 3.2: A 15 µL oil droplet was created at the tip of the hook by pumping oil from the outer capillary containing a first solution. The volume was kept constant for 3600 s. Then, the droplet subphase was exchanged for 720, 2700, or 5400 s, by injection of a second oil solution from the inner capillary by step of 1 µL every 7 s. The exchange was then stopped, and the oscillations started respectively 4800, 6780, or 9480 s after the beginning of the experiment.

Interfacial rheology measurements were performed to determine E' and E'' moduli. The procedure consisted in applying five cycles of five different periods (100, 80, 60, 40, and 20 seconds) at a volume amplitude of 3.5% and an average volume of 15 µL except stated otherwise. Only the results obtained at a period of 20 s were reported

Two parallels were at least performed for every system studied. The error bars represent the range of obtained experimental values.

3 Results

3.1 Competitive Adsorption of ARN and Asphaltenes

3.1.1 Influence of pH

Previous studies have shown that the interfacial reaction between ARN and Ca^{2+} ions only happens when the pH is higher than a critical value i.e. when ARN is ionized. This pH is comprised between 7 and 8 in the conditions considered in this article and in absence of asphaltenes or other naphthenic acids than ARN[30]. An interfacial gel characterized by a high dilational elasticity modulus E' is formed as a consequence of this reaction.

In order to study the effect of asphaltenes on the ARN/Ca^{2+} interfacial reaction, three systems were characterized at different pH: ARN alone, asphaltenes alone, and mixture of ARN and asphaltenes. All these systems were studied by continuously exchanging the oil phase in the droplet subphase for 720 s to try to mimic the flow of oil in an oil-water separator and the accumulation of ARN. Figure 1 presents the variations of IFT with time for all these systems for pH varying from 6 to 10 ([NaCl]=20 mM). The variations of IFT measured after 720 s of exchange as well as interfacial moduli E' and E'' subsequently measured are presented in figure 2. The same experiments were also performed at 600 mM (not shown), and similar results were obtained.

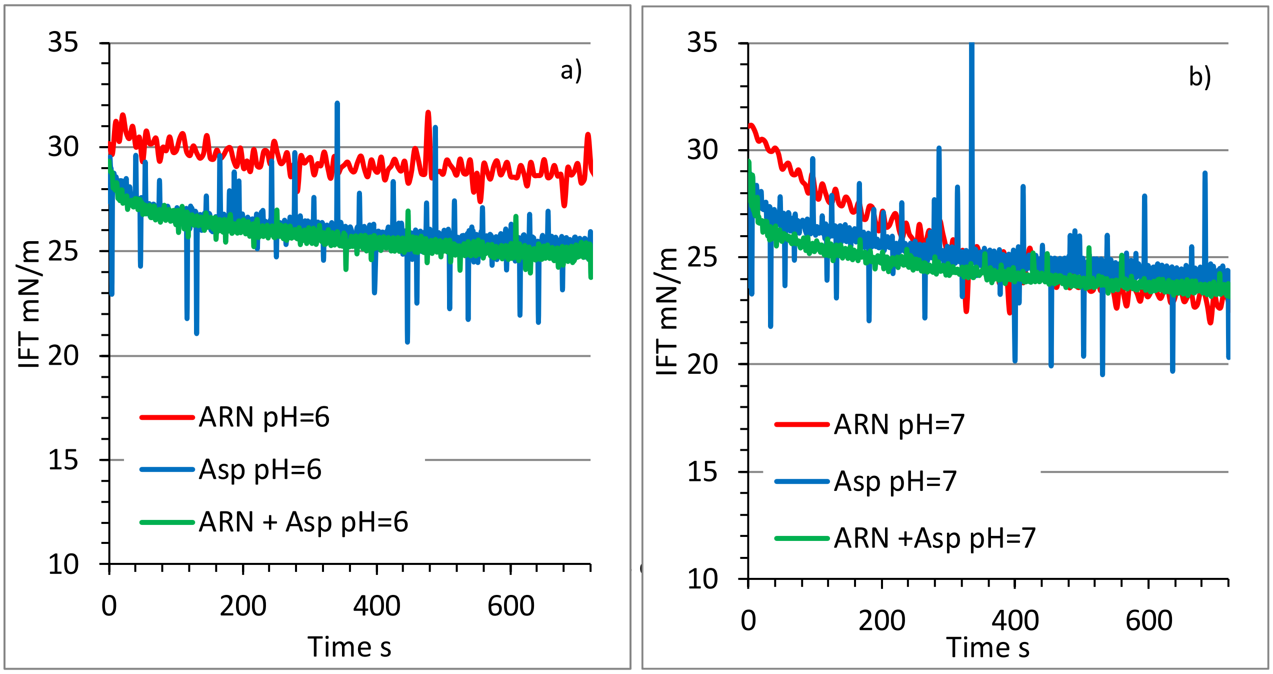
Before comparing the systems at these pHs, it must be noticed that IFT of asphaltenes and ARN decreases when pH increases. This increase in surface activity has previously been reported several times and is linked to the ionization of the COOH functions of ARN and asphaltenes[11, 31, 37].

At pH=6, the low E' for the system containing only ARN indicates that no gel is formed at the interface and consequently, there is no reaction between ARN and Ca^{2+}. The similarity between the interfacial tension values for the systems containing only asphaltenes and a mixture of ARN and asphaltenes indicate that the interface is fully covered by asphaltenes when ARN and asphaltenes are present at the concentrations tested.

The situation seems to be similar at pH=7. Indeed, here also there is no reaction between ARN and asphaltenes at the interface (no gel). The similarity of IFT (after 720 s) and E' values between the three systems does not allow to deduce the composition at the interface when ARN and asphaltenes is present in the bulk even if the resemblance of IFT variations between the two systems containing asphaltenes gives rise to a speculation that asphaltenes are predominant at the interface.

In absence of asphaltenes, pH= 8 shows the onset of the reaction between ARN and Ca^{2+} ions at interface as proven by the increase of E' to ≈ 39 mN/m compared with lower values measured at pH=6 and 7. If ARN is the only component in the oil phase, there is formation of gel at interface. This has also been previously checked at higher ARN concentrations (7.5 µM), than used in figure 1 (2.5 µM), where the transition if even more pronounced (E' reaches ca. 116 mN/m)[30]. In presence of asphaltenes, the situation is very different. Indeed, the variations of IFT with time as well as the E' values are similar to the system containing only asphaltenes at short times. This shows that the interface is mostly composed of asphaltenes. At longer times, the difference between pure asphaltenes and asphaltenes + ARN becomes more important meaning there are incorporation of more and more ARN in the asphaltene layer with time. The low E' modulus indicate that no gel is formed at interface. In conclusion, asphaltenes predominantly adsorb at interface, especially at short times, and prevent the reaction between ARN and Ca^{2+}. Similar conclusion were found from interfacial shear[23] and dilational[5] (with no exchange prior to the oscillation) rheology.

The results obtained at pH=9 and 10 are similar to the ones obtained at pH=8 and the same conclusion could be drawn i.e. asphaltenes dominate the interface, especially at short times. The only difference is the IFT decreases when pH increases which indicates that the ionisation rate of asphaltenes present at interface is higher. This also indicates the presence of acidic asphaltenes (in carboxylate form) at interface[37].



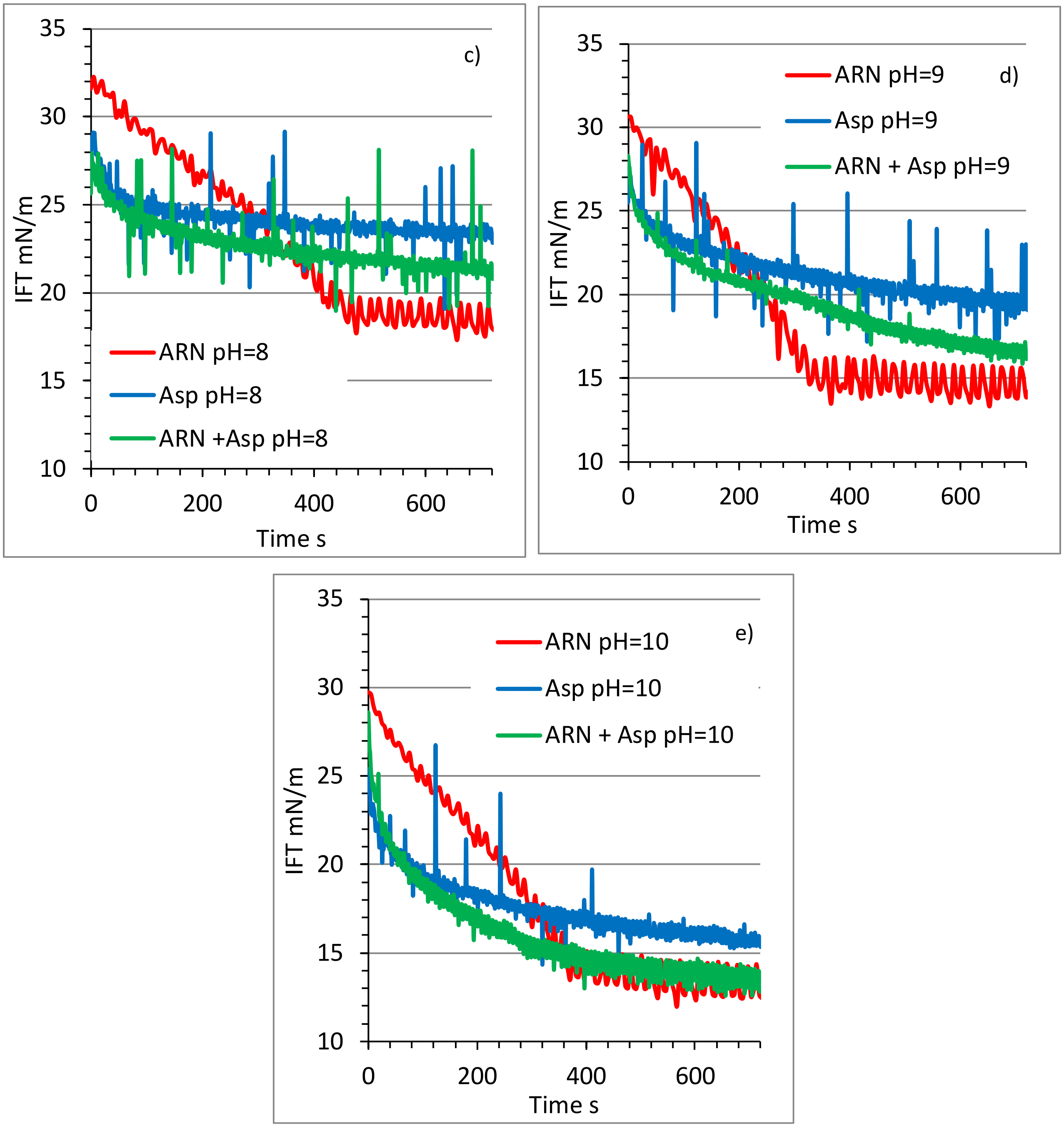


Figure 1: Variations of interfacial tension with time for ARN alone, asphaltenes alone, and mixture of ARN and asphaltenes during exchange period. Conditions: [NaCl] = 20 mM, [Asp]=0.4 g/L, [ARN]= 2.5µM, oil phase=xylene, exchange for 720 s, a) pH=6, b) pH=7, c) pH=8, d) pH=9, and

e) pH=10. The data for the ARN alone systems were taken from Simon et al30. Reproduced with permission

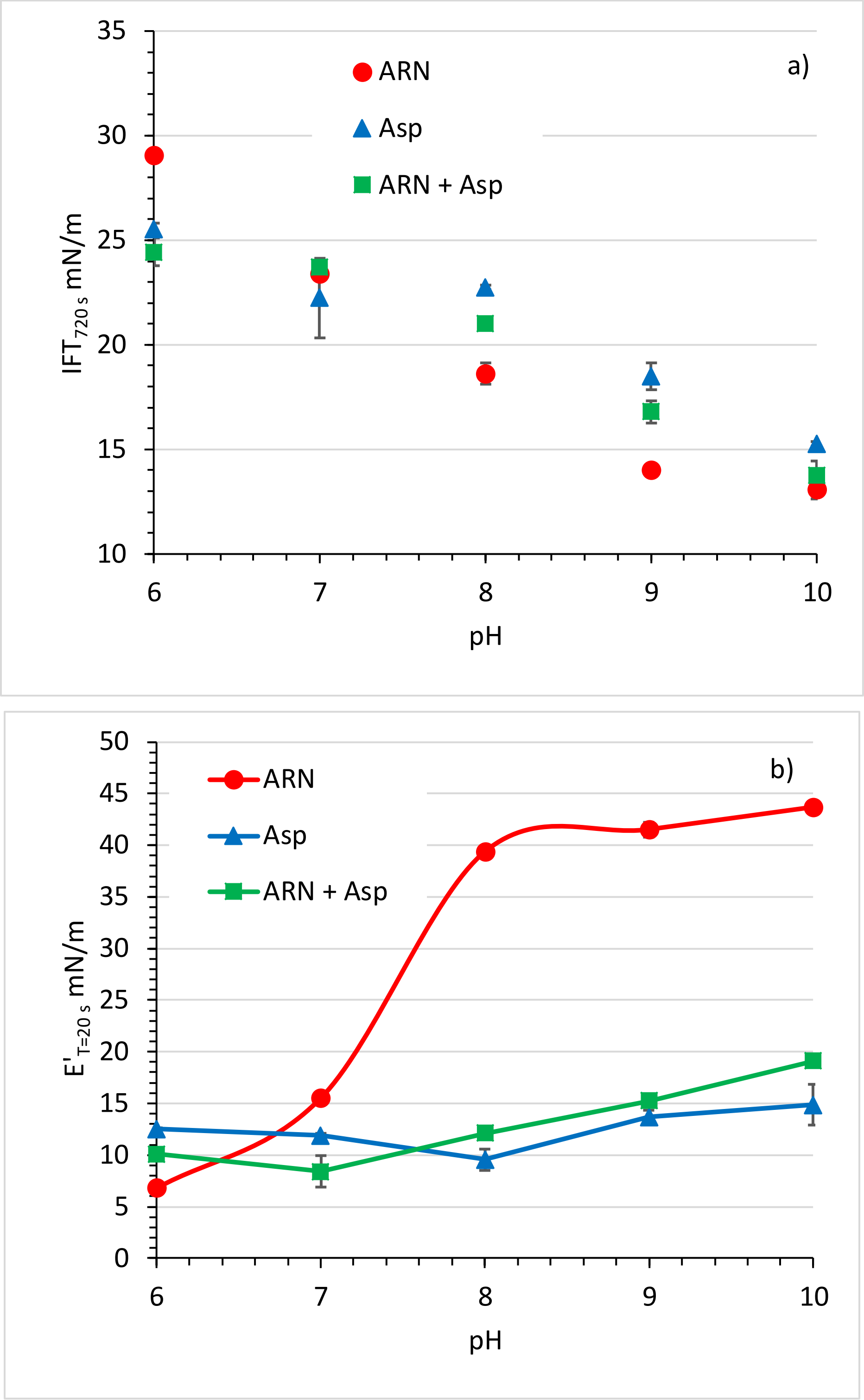


Figure 2: a): Variations of interfacial tension (after 720 s of exchange) with aqueous phase pH for ARN alone, asphaltenes alone, and mixture of ARN and asphaltenes. b) E' measured at a period of 20 seconds as a function of aqueous phase pH for ARN alone, asphaltenes alone, and mixture of ARN and asphaltenes. Conditions: [NaCl]=20 mM, [Asp]=0.4 g/L, [ARN]= 2.5µM, oil phase=xylene. The data for the ARN alone systems were taken from Simon et al.[30]. Reproduced with permission. Lines are guides for eyes.

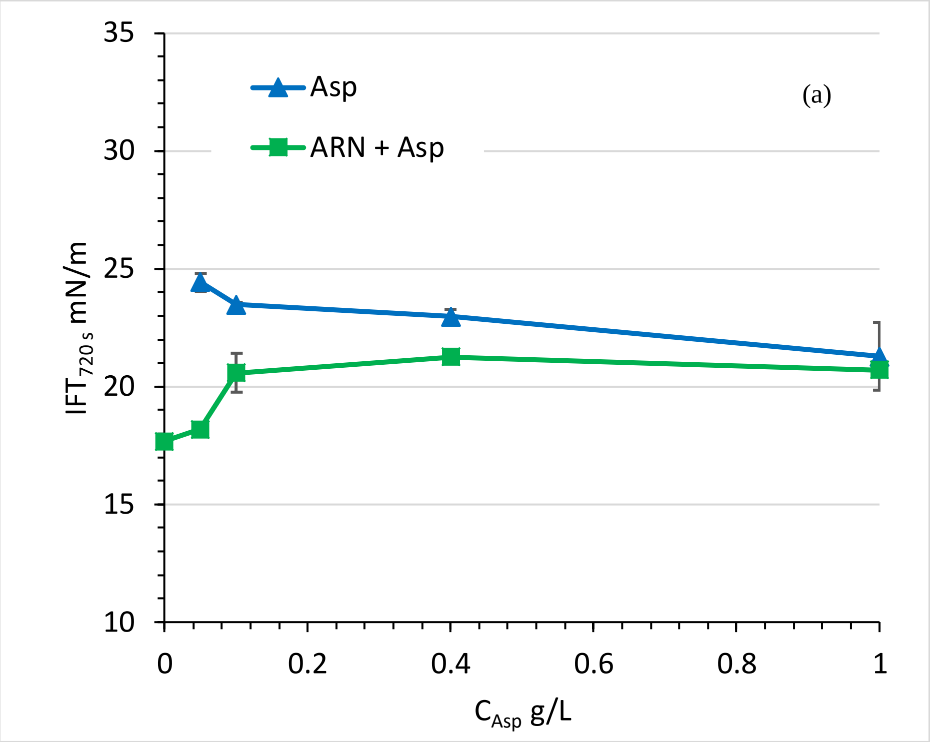
3.1.2 Influence of Asphaltene Concentration

After studying pH, the second investigated parameter is the asphaltene concentration. Figures 3 a) and b) present the variations in the interfacial tension (after 720 s of exchange) and E' modulus with asphaltene concentration for systems containing only asphaltenes and a mixture of asphaltenes and ARN, respectively. The pH was buffered to 8 to keep the pH constant and allow the formation of interfacial gels in absence of asphaltenes.

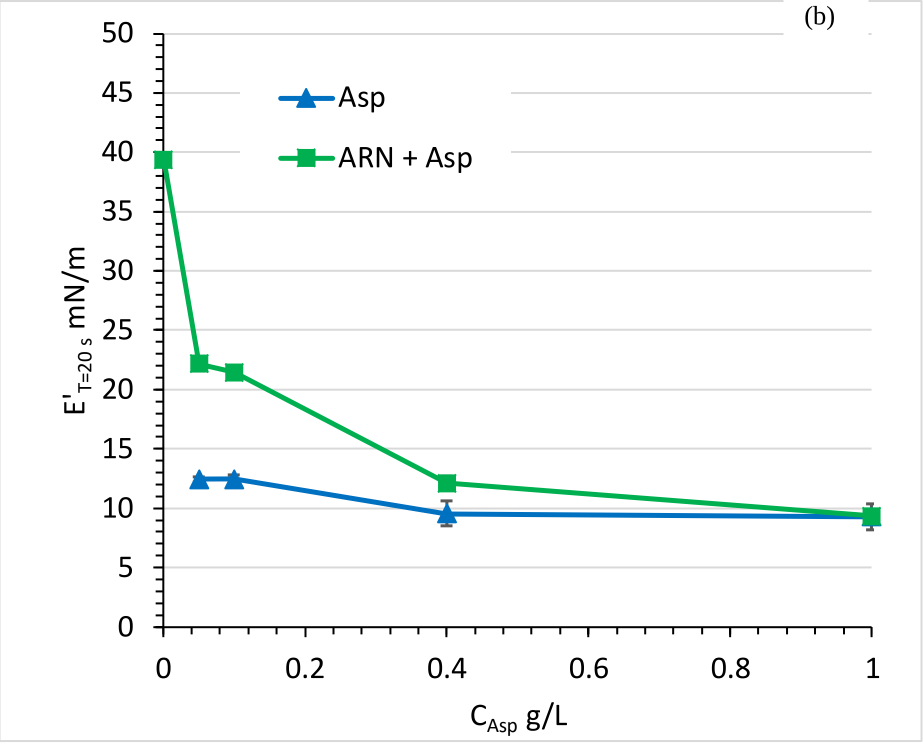
For asphaltenes, the interfacial tension classically decreases when the concentration increases (higher adsorption) while E' slightly decreases. Obtained values agree with values reported in the literature[38-41].

The situation is different when asphaltenes and ARN are mixed. At constant ARN concentration, the interfacial tension increases with asphaltene concentration before reaching the values for pure asphaltene at the highest concentration tested (1 g/L). E' modulus is high in absence of asphaltenes (39 mN/m at T=20 s) and decreases with increasing asphaltene concentration until reaching the value of pure asphaltenes. These data show that asphaltenes inhibit the formation of ARN/Ca^{2+} interfacial gel and are more and more dominant at the interface until fully blocking ARN adsorption at the highest tested concentration (1 g/L). The IFT data also allows to illustrate the inhibition mechanism. The IFT is higher for the ARN and asphaltene mixtures compared with ARN alone. This is also true for ARN is absence of Ca^{2+} in the aqueous phase[5]. That means, that the interfacial energy is higher in presence of asphaltenes. Another phenomenon must exist to compensate for this increase. Most likely, ARN and asphaltenes interact in bulk. That would explain why asphaltenes, which are less surface active than ARN, manage to be the predominant specie at interface.

Bulk interactions (solvent=xylene) between asphaltenes and ARN have already been studied by Isothermal Titration Calorimetry (ITC)[26]. It was found that ARN have strong exothermic interactions with only a part of the asphaltenes, corresponding to 2 % of asphaltene molecules in the sample studied by Wei et al.[26]. These interactions are not specific to ARN since they can be found in the system stearic acid /asphaltenes. It was therefore concluded by Wei et al. that ARN interact in bulk with a part of asphaltene molecules or nanoaggregates (probably acidic asphaltenes) due to the formation of hydrogen bonds. Interactions between ARN and basic asphaltenes could perhaps also exist but this hypothesis has not been tested experimentally yet.



(a)
Asp
ARN + Asp
$IFT_{720\,s}$ mN/m
35
30
25
20
15
10
0
0.2
0.4
0.6
0.8
1
C_{Asp} g/L



(b)
Asp
ARN + Asp
$E'_{T=20\,s}$ mN/m
50
45
40
35
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
C_{Asp} g/L

Figure 3: Variations of interfacial tension measured after 720 s of exchange a), and E’ b) as a function of asphaltene concentration with or in absence of ARN. Conditions: [NaCl] = 20 mM, pH=8, [ARN]=2.5µM, oil phase=xylene. For information, the molar ratio between asphaltenes and ARN for an asphaltene concentration of 1 g/L, and by assuming a molar mass for asphaltenes of 750 g/mol[42, 43], is 533.

3.1.3 Influence of Exchange Time

In this section, the influence of the exchange time is studied. Three exchange times are studied: 720 s (like in previous sections), 2700, and 5400 s. These times were arbitrarily chosen and used in a previous work[30]. Figure 4 presents the variations of IFT with exchange time for ARN alone, asphaltenes alone, and ARN+Asphaltenes. First, it must be noticed that the IFT data obtained up to 720 s are consistent with the figure 1.c). The peculiar variations of IFT for ARN alone have already been presented in Simon et al. and were attributed to either reorganization/conformational changes of ARN/Ca^{2+} at the interface or to multilayer formation. Variations for asphaltenes alone, and ARN+Asphaltenes are smoother and similar. No plateau and therefore no equilibrium state were reached for the two systems even after 5400 s of exchange.

The E’ and E’’ moduli for the three investigated systems as a function of the exchange time are reported in figure 5. The E’ modulus for ARN alone strongly increases with exchange times and even reached extremely high value of 234 mN/m after 5400 s of exchange time. This indicates a strengthening of the crosslinking between ARN and Ca^{2+} with time. The values obtained for the two other systems are much lower (12-14 mN/m for asphaltenes alone and 16-19 mN/m for ARN + asphaltenes) and hardly increase with exchange time. As the E’ moduli of ARN+asphaltene and Asphaltenes alone are similar and interfacial tension of the former is comprised between the values for asphaltenes alone and ARN alone, it can therefore be concluded that the exchange time has a minor effect on the composition of the interface when asphaltenes and ARN are simultaneously present. No, or very limited, crosslinking between ARN and Ca^{2+} exist in presence of asphaltenes even for long contact times.

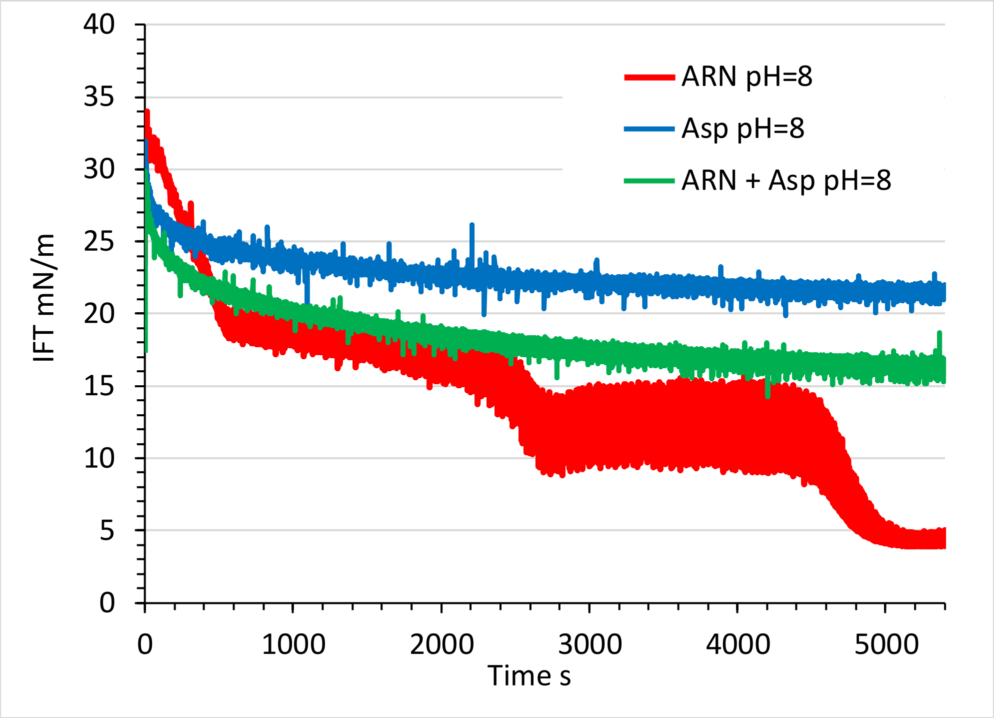


Figure 4: Variations of interfacial tension with time during the continuous exchange of ARN alone, asphaltenes alone, and mixture of ARN and asphaltenes solutions inside the droplet (total exchange time=5400 s). Conditions: [NaCl] = 20 mM, pH=8, [Asp]=0.4 g/L, [ARN]= 2.5µM, oil phase=xylene. The data for the ARN alone systems were taken from Simon et al[30]. Reproduced with permission

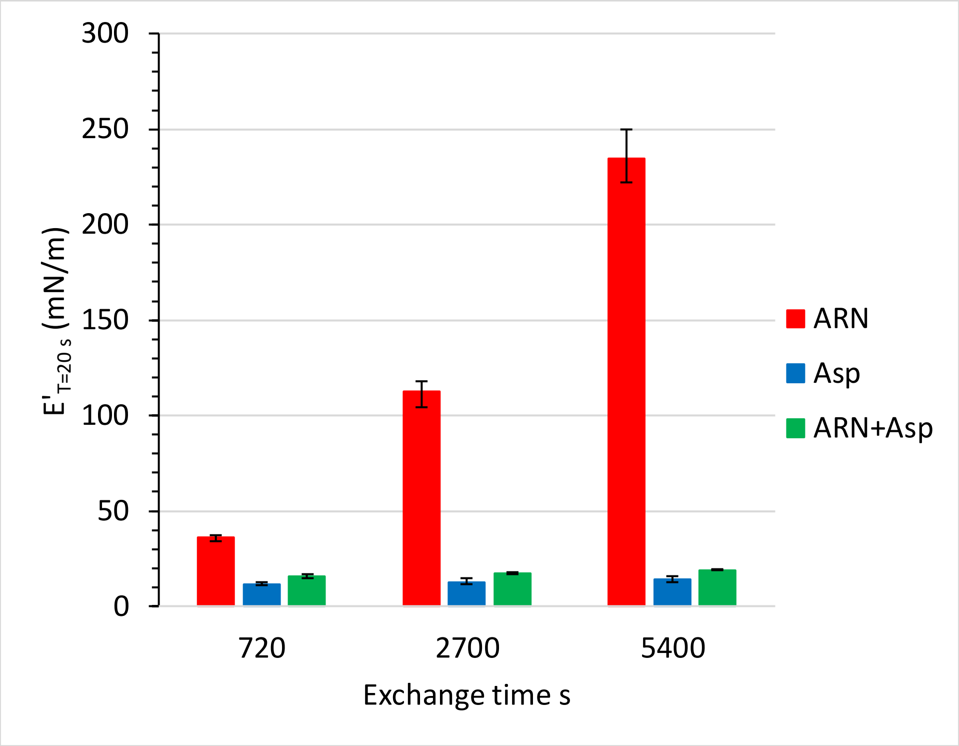


Figure 5: Variations of E', measured at a period of 20 seconds, after 720, 45, and 90 seconds of exchange of ARN alone, asphaltenes alone, and mixture of ARN and asphaltenes solutions inside the droplet. Conditions: [NaCl]=20 mM, [Asp]=0.4 g/L, [ARN]= 2.5µM, oil phase=xylene. Oscillations after 90 minutes for ARN alone were performed at an amplitude of 3 %. The data for ARN alone were taken from Simon et al[30]. Reproduced with permission.

3.1.4 Influence of Asphaltene Solvency Conditions

Surface and interfacial properties of asphaltenes are very dependant of the solvent composition. For instance, asphaltenes are at their optimum to stabilize emulsions at their point of incipient precipitation[44, 45]. Their interfacial shear moduli increases with the heptane content in toluene-heptane mixture[46]. Considering this important aspect, the competitive adsorption between ARN and asphaltenes was studied in an oil phase composed of 55 % hexane /45 % v/v xylene and compared with results obtained in pure xylene. In this hexane/xylene mixture, asphaltenes are still under nanoaggregate form (no floc was detected by microscopy).

The measurements performed with ARN alone at low pHs (6 and 7), asphaltene alone and asphaltenes + ARN at all the pHs were reproducible. It was not the case for the ARN alone systems at high pHs (8 to 10) as shown for the data obtained at pH=9 (figure 6). This was the worst case obtained and it can be noticed that the initial slope of the variations of the interfacial tension with time are all different from the 8 tests performed in this system. However, it appears that all the data converges to the same value at 1200 s, that means, when the oscillations start. We do not have any explanation for this reproducibility issue which has necessitated to multiply the number of parallels per conditions for pHs=8, 9, and 10 (between 5 and 8 per pH) to secure the conclusion. The immediate consequence is the interfacial tensions measured for the three systems between pH=6 and 10 were compared after 1200 s of exchange, adsorption and reaction with Ca^{2+} i.e. after 720 s of exchange and 480 s of "rest" (constant volume) for reproducibility reasons (figure 7). E' moduli are also presented in the figure.

The results obtained in 55 % hexane /45 % v/v xylene are similar to trends observed in pure xylene (figure 2): Interfacial tensions decrease when the pH increases due to the ionization of carboxylic acid functions. E' moduli are high in the case of ARN alone for pH higher or equal to 8 (more than 40 mN/m) but are much lower in the ARN + asphaltene systems (between 15 and 23 mN/m) and just slightly higher than for asphaltene's. The conclusions are therefore similar as in pure xylene: Asphaltenes prevent cross-linking between ARN and Ca^{2+} at all solvation conditions (below the flocculation point).

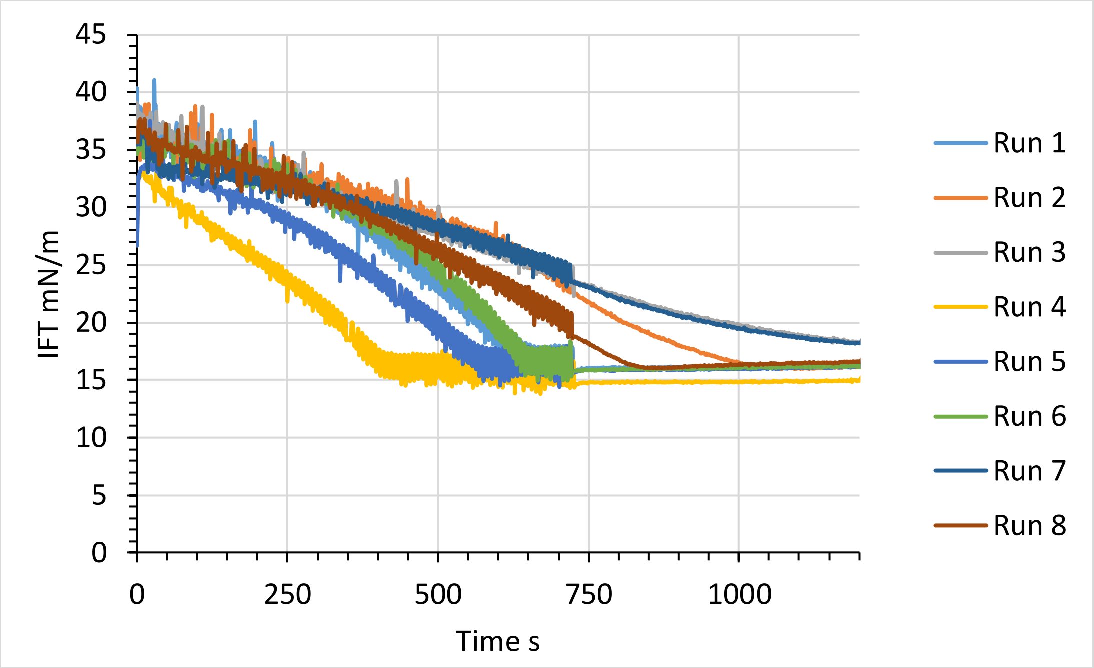
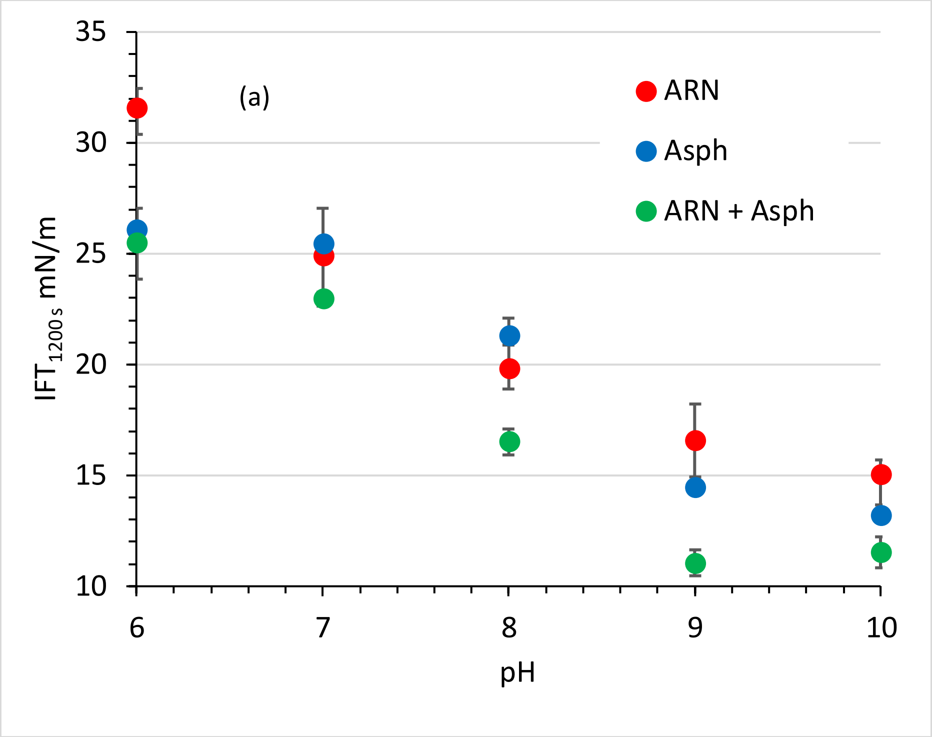


Figure 6: Example of reproducibility issue for the system containing only ARN. 8 different parallels were performed. Conditions: [NaCl] = 20 mM, [ARN]= 2.5µM, oil phase= 55 % v/v hexane /45 % xylene.



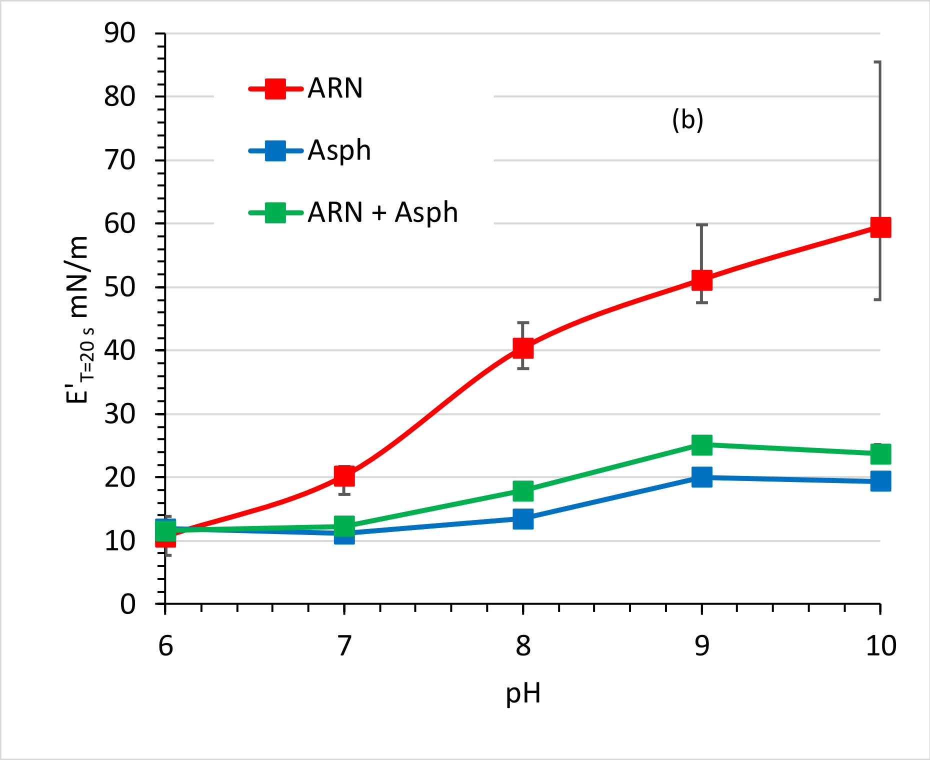


Figure 7: a): Variations of interfacial tension (after 1200 s of exchange, adsorption, and reaction with Ca^{2+}) with aqueous phase pH for ARN alone, asphaltenes alone, and mixture of ARN and asphaltenes. b) Variations of E' measured at a period of 20 seconds as a function of aqueous phase pH for ARN alone, asphaltenes alone, and mixture of ARN and asphaltenes. Conditions: [NaCl] = 20 mM, [Asp]=0.4 g/L, [ARN]= 2.5µM, oil phase= 55 % v/v hexane /45 % xylene.

3.2 Stability of ARN/Ca^{2+} Pre-Formed Gel

All the results obtained so far were obtained under conditions where ARN and asphaltenes were simultaneously present since the beginning of the measurements, and have allowed to determine the effect of asphaltenes on the build-up of the ARN/Ca^{2+} interfacial gel. Here, the asphaltenes are injected in a system where ARN/Ca^{2+} interfacial gel is already present. It therefore allows to determine the interactions between asphaltenes and the interfacial gel.

The procedure is presented in the experimental section and can be divided into 3 parts:

-First ARN adsorbs and reacts with Ca^{2+} at the water-xylene interface for 1 hour. There is no exchange.

-Then droplet subphase was exchanged by an asphaltene solution in xylene for 720, 2700, or 5400 s.

-Finally, the exchange is stopped, and oscillations are performed to determine the dilational rheology properties of the interface.

Results obtained with this system, codenamed ARN-Asp, are compared with two reference systems. In the first ARN adsorbs and are then exchanged by pure solvent (ARN-Xyl), and, in the second, a drop of pure xylene is let for 1 hour and then exchanged by an asphaltene solution (Xyl-Asp).

The cleaning and droplet formation procedure appears to be critical to obtain meaningful results. Indeed, the first performed tests showed that ARN-Asp and ARN-Xyl had different interfacial tension during the first hour of adsorption, even if the droplet composition should be the same. The interfacial tension for the former was higher and did not present a minimum of IFT as in the ARN-Xyl (also seen by Subramanian et al.[5]). This difference was attributed to a pollution of the ARN drop by asphaltenes from the inner capillary in the ARN-Asp system. Consequently, a cleaning and droplet formation procedure was developed that seems to prevent the pollution: After cleaning the system by passing excess amount of ARN solution (or pure xylene) through the outer capillary then asphaltene solution (or pure xylene) through the inner capillary, an asphaltene solution drop is created from the inner capillary and discarded. Then 4 ARN solution drops from the outer capillary are created and discarded before a last ARN solution drop is created and retained for the experiment.

The interfacial tension variations with time for the three systems for an exchange time of 2700 are presented in figure 8. The oscillations are not presented.

The IFT variations with time are similar for the ARN-Xyl and ARN-Asp during the first hour of adsorption of ARN and its reaction with Ca^{2+} indicating the cleaning procedure is effective. Then the IFT increases for both systems during the exchange period; the increase is more marked when asphaltene solution is exchanged than pure xylene and with increasing exchange times (figure 9). This increase indicates that there is an evolution of the composition of the interfacial layer, most likely involving desorption or dispersion of ARN from the interface. Concerning the xylene/asphaltene system, the IFT is close to the value corresponding to a naked xylene/brine interface during the first hour (even if there is a slight downward trend indicating minor pollution of the tubings), then decreases when exchange starts due to the adsorption of asphaltenes. The IFT reached at the end of the exchange period is higher than for the ARN/asphaltene system showing that the interface is not only composed of asphaltenes for the latter.

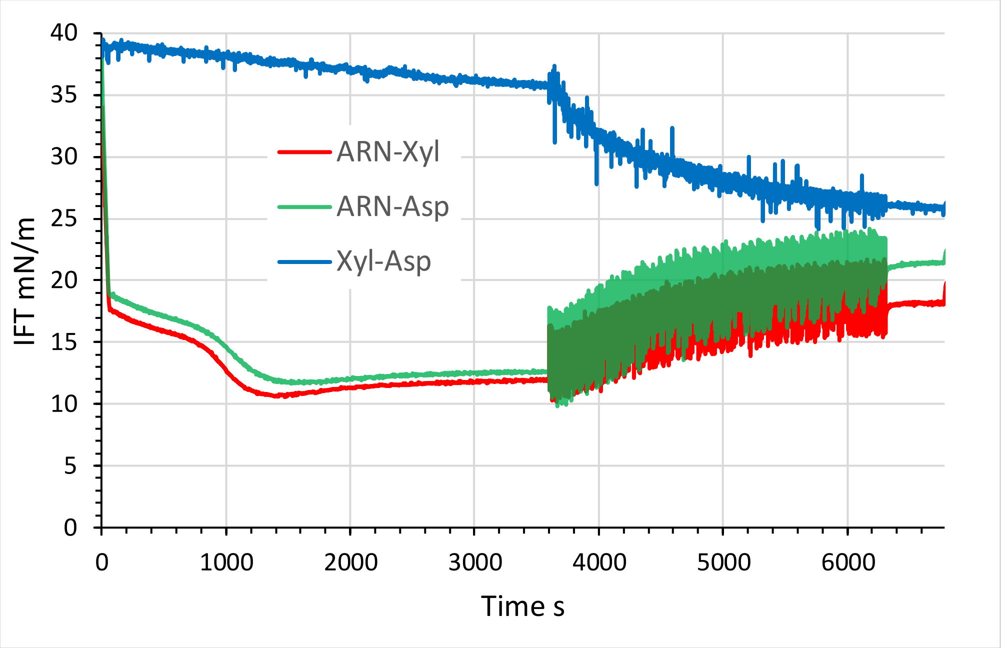


Figure 8: Adsorption of an ARN solution (or pure xylene as a blank) for 1 hour then exchange with an asphaltene solution or pure xylene for 2700 s. After a 480 s rest period, oscillations are performed (not shown). Conditions: [NaCl]=20 mM, pH=8, [Asp]=0.4 g/L, [ARN]= 8.8 µM, oil phase=xylene.

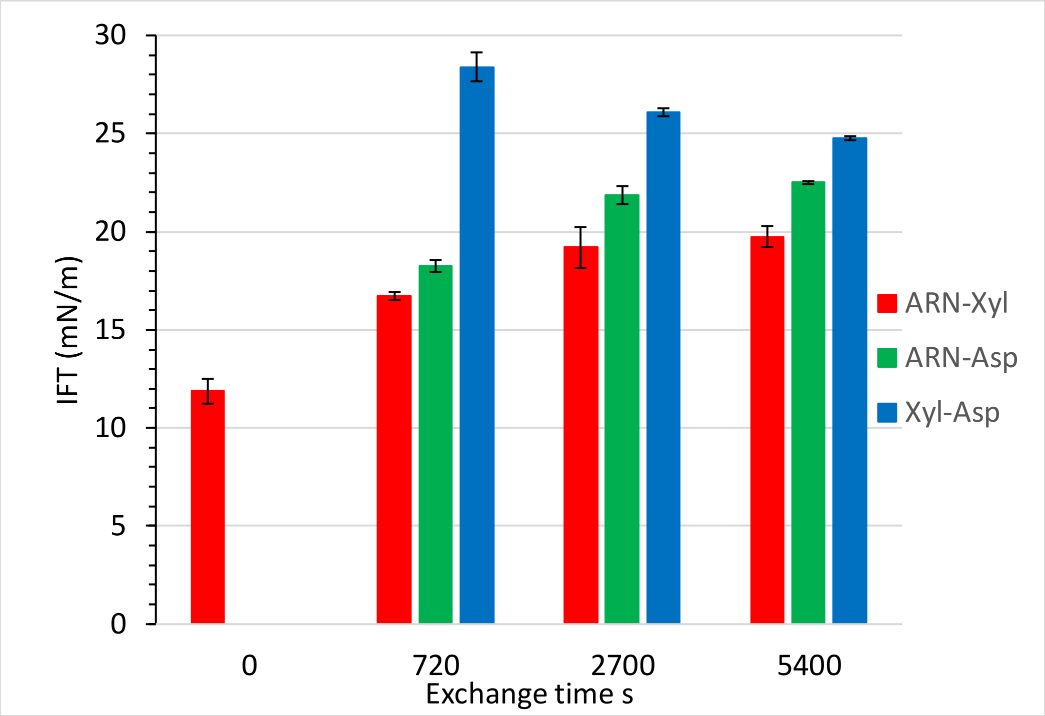


Figure 9: Interfacial tension measured at the onset of the oscillation period. Conditions: [NaCl]=20 mM, pH=8, [Asp]=0.4 g/L, [ARN]= 8.8 µM, oil phase=xylene.

More information can be obtained by plotting the variations of E'. Figure 10 presents the variation of the E' and E'' moduli for the system ARN-Xyl for different xylene exchange time. E' moduli are high (between 89 and 132 mN/m) and systematically higher than E'' which is consistent with the formation of an interfacial gel[5]. The E' moduli decreases when the exchange time increases which is consistent with the interfacial tension variations during the exchange period observed in figure 8. This confirms the assumption that ARN/Ca^{2+} interfacial material is partly desorbed or dispersed from the interface by the flow of pure xylene. The lowered but still high values of E' after exchange indicates still a presence of ARN crosslinked with Ca^{2+} at interface since, in absence of Ca^{2+}, pure non-crosslinked ARN has a E' less than 10 mN/m[5].

The values of E' and E'' for the systems ARN-Xyl, ARN-Asp, and Xyl-Asp for the three tested exchange times are presented in figures 11. Several observations can be done:

-E' moduli for the Xyl-Asp systems (≈15 mN/m) are typical of values reported for asphaltenes (no exchange)[38-40]. They do not depend on the exchange time. Even if E' values for only asphaltenes are relatively low, asphaltenes form an elastic film at interface, as shown by Jerribi et al.[47] by suddenly contracting asphaltene-covered droplets.

-E’ moduli for the ARN-Asp systems are much lower than for the ARN-Xyl ones and strongly decrease when the exchange time increases to very low values (28 mN/m after 5400 s of exchange). As this value is still superior to Xyl-Asp system’s, it can be deduced that the interface for the system ARN-Xyl seems to be composed of a mixture of asphaltenes and ARN. Consequently, asphaltenes are able to desorb or disperse ARN/Ca^{2+} interfacial material formed beforehand. The extent of the crosslinking between ARN and Ca^{2+}, if there is any, would probably be very limited. Most of the desorption seems to take place in the initial stage of the exchange process since, after only 720 s of exchange, E’ modulus is strongly reduced (58 mN/m of difference between ARN-Xyl and ARN-Asp systems). The slope of this reduction decreases for longer exchange times.

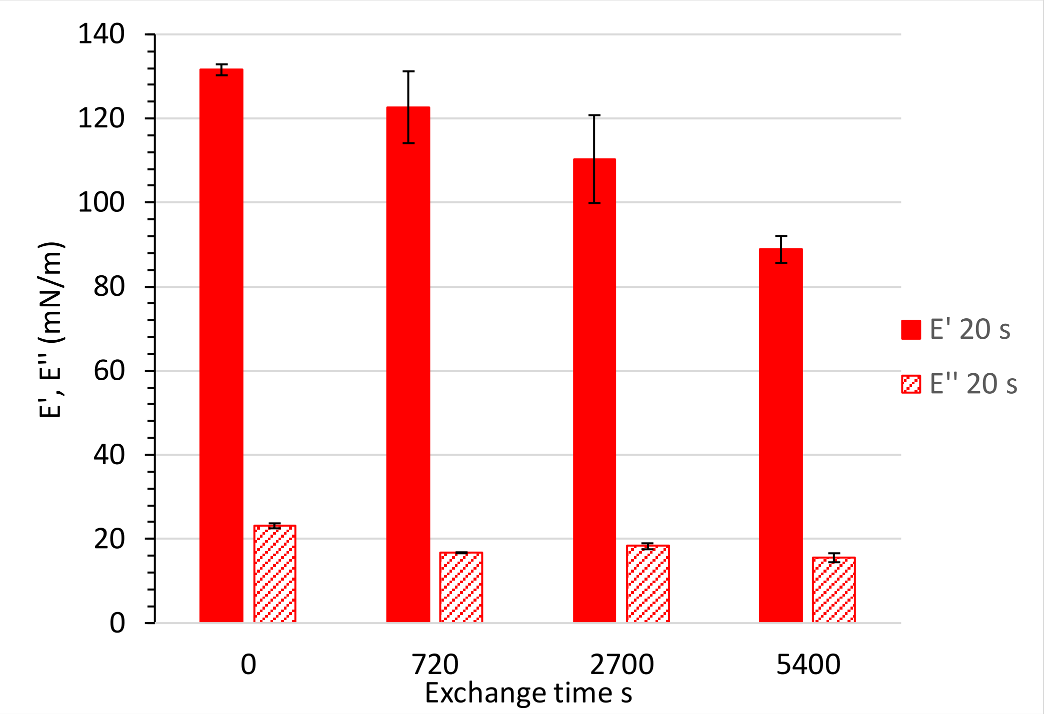
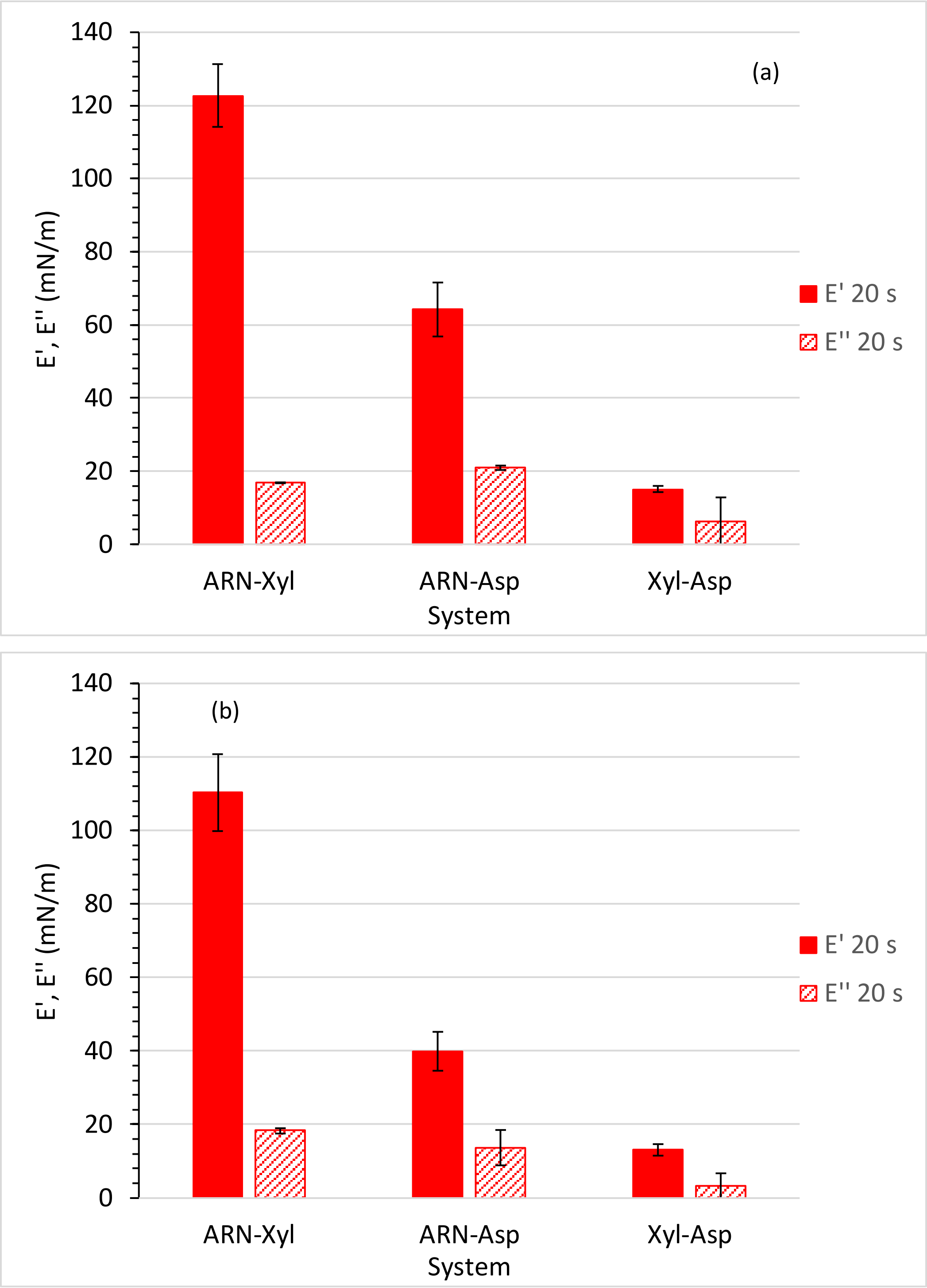


Figure 10: E’ (measured at a period of 20 seconds) measured after adsorption of an ARN solution for 1 hour, then exchanged with pure xylene for various times. The oscillations started 480 s after the end of the exchange period. Conditions: [NaCl]=20 mM, pH=8, [ARN]= 8.8 µM, oil phase=xylene.


(a)
E', E'' (mN/m)
140
120
100
80
60
40
20
0
ARN-Xyl
ARN-Asp
Xyl-Asp
System
E' 20 s
E'' 20 s
(b)
E', E'' (mN/m)
140
120
100
80
60
40
20
0
ARN-Xyl
ARN-Asp
Xyl-Asp
System
E' 20 s
E'' 20 s

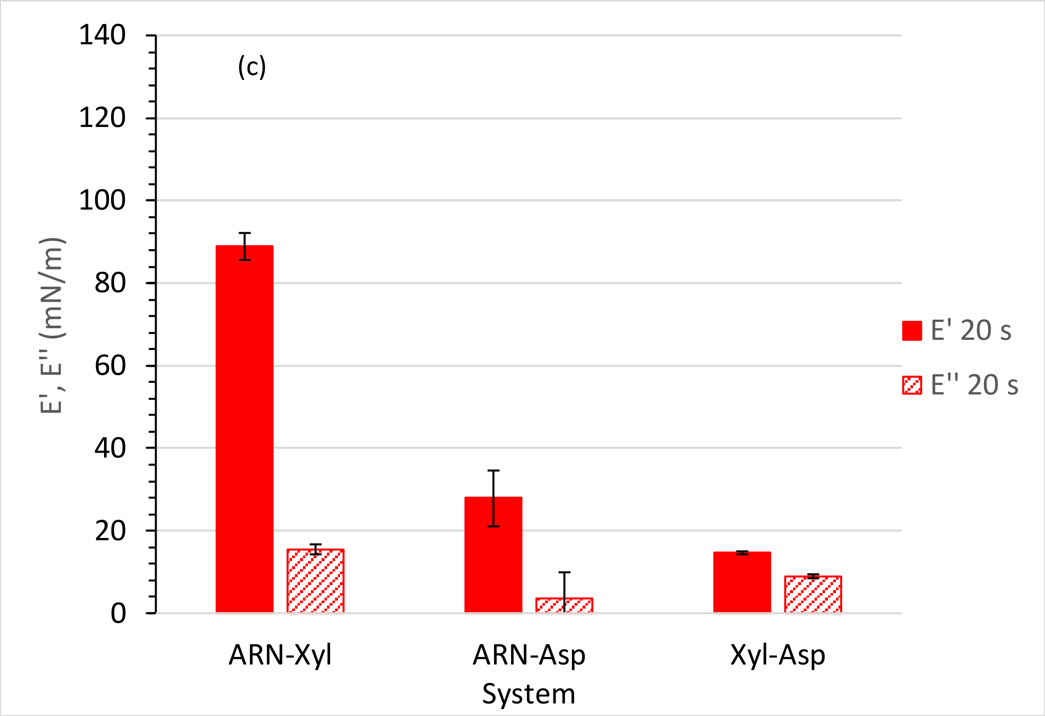


Figure 11: E’ (measured at a period of 20 seconds) measured after adsorption of an ARN solution (or pure xylene as a blank) for 1 hour, then exchanged with an asphaltene solution or pure xylene for various times: a) 720 s, b) 2700 s, c) 5400 s. Conditions: [NaCl]=20 mM, pH=8, [Asp]=0.4 g/L, [ARN]= 8.8 µM, oil phase=xylene. Oscillations for the Xyl-Asp system were performed at an amplitude of 7 %.

4 Conclusion

The results clearly demonstrate the active role of asphaltenes in the initial step of the calcium naphthenate deposition mechanism. Asphaltenes either inhibit the formation of ARN/Ca^{2+} interfacial gel or desorb or disperse if already formed. This inhibition takes place in all the conditions tested (various pHs, asphaltene concentrations, exchange times, and asphaltene solvency conditions) and therefore appears to be general. The inhibition seems to result from bulk interactions between ARN and asphaltenes in the oil phase and not from interfacial competition between these two components since asphaltenes is less surface active than ARN (even in absence of Ca^{2+}). The propensity of asphaltenes to desorb or disperse interfacial gel could also be the result of the same interactions.

Even if the molecular origin of the interactions have not be studied in the present work, published calorimetry data by Wei et al.[26] seems to indicate that ARN interacts with only a part of the asphaltenes via the formation of hydrogen bonds in bulk.

In conclusion, asphaltenes should be always considered in the studies dealing with the deposition of calcium naphthenate.

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