Influence of fatty-alkylamine amphiphile on the asphaltene adsorption/deposition at the solid-liquid interface under precipitating conditions

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ABSTRACT

The ability of a fatty-alkylamine amphiphile to inhibit asphaltene adsorption/deposition as well as its ability to disperse the asphaltene layers on stainless steel was studied using quartz crystal microbalance with dissipation (QCM-D). The experiments were performed at both good solvent conditions and above asphaltene precipitation onset. The adsorption/deposition of asphaltenes from model oil solution in xylene/n-hexane was found to strongly increase up to the asphaltene precipitation onset (i.e., ~60 – 65 vol% n-hexane), with a 7-8 times increase of the adsorbed amount compared with adsorption from xylene. Beyond the precipitation onset, the amount of asphaltene adsorbed/deposited decreases.

Under both good solvent and precipitating conditions, the amphiphile was unable to form a protective layer on stainless steel to prevent asphaltene adsorption/deposition. However, the amphiphile exhibited an excellent ability to reduce asphaltene adsorption/deposition by 80 – 95 wt% when injected along with asphaltene solution. It is found that the interactions between asphaltenes and inhibitor that are responsible for the adsorption/deposition inhibitory action are not of acid-base nature. Maximum inhibitory action in minimizing the asphaltene adsorption/deposition was observed corresponding to a mole ratio (amphiphile/asphaltenes) ~ 0.10, despite this mole ratio not being sufficient to prevent asphaltene precipitation. Similarly, the amphiphile also displayed an ability to remove 90 – 95 wt% of asphaltenes already adsorbed/deposited on stainless steel under precipitating conditions, thereby showing its effectiveness as both asphaltene inhibitor (AI) and dispersant (AD) under good solvent conditions as well as precipitating conditions.

KEYWORDS

Asphaltene adsorption/deposition, QCM-D, Asphaltene inhibitor/dispersant

1. INTRODUCTION

The flow assurance challenges due to precipitation and adsorption/deposition of asphaltenes during hydrocarbon production is well documented.[1-3] Asphaltenes are by definition a solubility class: soluble in aromatic solvents (toluene, xylene) but insoluble in n-alkanes (n-pentane, n-heptane). They represent the most polar fractions of crude oil, and consist of polyaromatic core with alkyl side chains at their periphery.[4] Asphaltenes have a tendency to aggregate, and the formation of nanoaggregates in toluene even at a concentrations of 100 mg/L has been reported.[5] The destabilization of nanoaggregates induced by changes in pressure, composition and/or temperature leads to asphaltene precipitation.[6] The precipitation of asphaltenes is considered to be a necessary but not sufficient condition for deposition.[7] In addition, not all the precipitated asphaltenes form deposits.[8] The initially formed asphaltenes micro-aggregates can either continue to flocculate thereby forming larger particles, or can diffuse to the surface of the tubing or wall.[9]

Field operations under conditions where asphaltenes do not phase separate eliminates the precipitation and deposition problems.[8] This option is however not always feasible, and hence mechanical (pigging) and chemical means (use of oil soluble amphiphiles known as inhibitors/dispersants) are employed to prevent the problem. The asphaltene inhibitors/dispersants are believed to function similar to resins, by stabilizing the asphaltenes in crude oil.[10] The performance of an inhibitor is generally tested based on its ability to delay the onset of asphaltene precipitation using light scattering[11, 12] or ultraviolet-visible (UV-vis) spectroscopy[13, 14] techniques. In the UV-vis technique, the asphaltenes and inhibitors are generally mixed and allowed to age for a few hours. The solution is then centrifuged, and the absorbance of supernatant solution measured. A high absorbance reading indicates that the inhibitor is effective in keeping the asphaltenes in solution.[13]

Inhibition of asphaltene adsorption and deposition is generally explained by the establishment of a protective steric layer due to the adsorption of inhibitor on the asphaltene aggregate surface. It has been reported that the acid-base interaction between the inhibitor and asphaltenes seem to play an important role in the inhibition mechanism[15, 16], since the inhibitor efficiency is related to the amount of inhibitor that is adsorbed on the asphaltene surface[17]. The inhibitor efficiency is also influenced by the length of amphiphile alkyl chain[15], because the alkyl chain helps in formation of a steric-stabilized layer around the asphaltenes[18]. The use of low inhibitor concentrations can cause earlier asphaltene precipitation as observed with anionic surfactant DBSA (dodecyl benzene sulfonic acid), which interacts to form a salt of lower solubility than asphalenes.[12] On the other hand, addition of higher concentrations of inhibitor can also lead to a reduced efficiency due to self-association of inhibitor molecules induced by the solvent medium.[19] Hence, the inhibitors are effective only over a limited range of concentrations. The efficiency of inhibitor is dependent on both the inhibitor and asphaltene chemistries. Cationic surfactant DDAB (didodecyl dimethyl ammonium bromide)[20] and cationic gemini surfactant N2,N3-didodacyl-N2,N2,N3,N3-tetramethylbutane diaminium bromide[21] have also shown asphaltene inhibitory abilities. DDAB was in fact found to be more effective inhibitor than DBSA for unstable Hassi-Messaoud oil (Algeria).[20] Non-ionic polymeric surfactants have also been recently tested for their inhibition ability.[22, 23] The non-ionic polymeric inhibitor’s performances have been correlated with its molecular weight, with higher molecular weight inhibitors showing greater efficiency due to longer hydrophobic chain length.[22]

While several studies focus on inhibitor’s efficiency to shift asphaltene precipitation onset, studies showing the influence of inhibitors/dispersants on the asphaltene adsorption/deposition on metallic surfaces is limited[24]. Similarly, only a few authors[25] have studied the ability of amphiphiles to dissolve the preformed asphaltene deposits. The asphaltene dissolution ability of DBSA is well-known, and is attributed to protonation of asphaltene heteroatoms via acid-base interaction and the ability of DBSA’s long tail to form a solvation shell around the asphaltenes.[25] Similarly, alkyleneamine-fatty acid condensation reaction product has been reported to exhibit ability to dissolve asphaltene deposits.[26]

Asphaltene deposition on metallic surfaces is generally studied using Taylor-Couette device[27-29], capillary tube[6, 30-33] or quartz crystal microbalance with dissipation (QCM-D)[34, 35]. Experiments by Nabzer et al.[30] indicated that the asphaltene deposition is diffusion limited at low shear rates, while no deposition occurred at high shear rates. Eskin and co-workers[24, 29] studied asphaltene deposition in a Couette device, and modelled the phenomena by assuming that large particles do not contribute to deposition process. They introduced the concept of a critical asphaltene size (typically below ~100 nm), above which particles do not deposit. In oils from Gulf of Mexico, the asphaltene deposition induced by pressure reduction was found to reduce by 50 – 67% in presence of 150 – 200 ppm of inhibitors. However, the use of higher amounts of inhibitor (500 ppm) did not improve the removal efficiency.[24]

Tavakkoli and co-workers[34, 35] investigated the asphaltene deposition tendency of both model oils and crude oils using QCM-D. The model oil system containing 100 ppm asphaltenes in toluene formed viscoelastic layers on gold surface. The adsorbed asphaltene mass increased with temperature due to increased diffusion of particles to surface, and the n-pentane precipitated asphaltenes showed a significantly higher adsorption (by almost 5 – 8 times) than n-heptane asphaltenes. In presence of precipitant (n-heptane), the adsorption/deposition of asphaltenes increased up to the precipitation onset. Beyond the onset, a reduction in mass of asphaltene deposited was observed, thereby supporting the assumption of large particles not participating in deposition process.[34] Similar tendencies were observed when the authors extended the study to a crude oil system.[35]

In the present work, the ability a commercial fatty alkylamine inhibitor to influence the asphaltene adsorption/deposition phenomena on a stainless steel surface is studied using QCM-D. The results obtained based on experiments performed under both good solvent conditions and in presence of a precipitant (n-hexane) are reported. It is found that the amphiphile does not form a protective layer on stainless steel but, instead, are able to reduce asphaltene adsorption/deposition when injected along with asphaltenes. The interactions between asphaltenes and inhibitor, responsible for the adsorption/deposition inhibitory action, are not of acid/base nature, as it could be expected, but of other nature as shown in experiments performed with esterified asphaltenes. This work is a continuation of our earlier work[36], which studied the interaction between asphaltenes and fatty-alkylamine inhibitor in bulk solution.

2. EXPERIMENTAL SECTION

2.1. Chemicals

2.1.1. Asphaltenes

Asphaltenes were precipitated from a chemical free crude oil from the Norwegian Continental Shelf. The dilution ratio used for asphaltene precipitation was 40 vol of n-hexane/g of crude oil. A 0.45µm HVLP filter from Millipore was used for filtration, and the asphaltenes were washed with n-hexane till the filtrate was colorless. The asphaltenes obtained was called *whole* asphaltenes. The characteristics of the crude oil and *whole* asphaltenes can be found in our earlier publication.[37]

The whole asphaltenes were esterified using methanol and sulfuric acid (as catalyst). The procedure used for esterification can be found elsewhere.[38, 39] The asphaltenes obtained were called *ester* asphaltenes, and were characterized by Fourier Transform Infrared (FTIR) spectroscopy and interfacial tension (IFT) measurement at pH=10 to assess the efficiency of the esterification procedure as described in Simon et al.[38].

2.1.2. Other chemicals

A fatty alkyl-amine inhibitor (molecular weight ~1000 g/mol) was obtained from AkzoNobel AB. The solvents used for the QCM-D experiments were xylene (VWR, >98.5%) and n-hexane (VWR, >97%). The stainless steel coated quartz crystals were obtained from Biolin Scientific (Sweden). Hellmanex III (Helma Analytics), ethanol (VWR, 96%) and milli-Q water were used for cleaning the crystals before use.

2.2. Experimental Technique

2.2.1. Quartz crystal microbalance with dissipation (QCM-D)

QCM-D operates based on the property of piezoelectricity. The peizoelectric quartz crystal is placed between the two metal electrodes. When an AC voltage is applied across the electrodes, the quartz crystal oscillates. The frequency of oscillation of crystal is related to the mass adsorbed on its surface. Sauerbrey[40] established the relationship between the change in frequency (*Δf*) due to mass adsorbed (*Δm*) as:

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Where *ρq* (=2648 kg/m3) and 𝑡𝑞 (=0.3 mm) are the mass density and thickness of the crystal, 𝑓0 (=5 MHz) is the fundamental frequency crystal and 𝑛 is the overtone number. The constant C (=0.177 mg/Hz.m2) is known as the sensitivity factor of the quartz crystal. The Sauerbrey’s relation is valid only when there is an even and rigid distribution of adsorbed mass on the surface, and the adsorbed mass is much smaller than the mass of the crystal.[40] If these assumptions are not valid, other relationships are available to determine the adsorbed amount. In this manuscript, the Sauerbrey’s relation has been used to calculate the adsorbed amount except otherwise stated.

In many cases, the mass adsorbed on the surface is not rigid. Instead, a viscoeleastic film is formed, which dampens the oscillation. The softness of the film formed is described based on dissipation factor (*D*):

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*Edissipated* refers to the dissipation of energy during one period of oscillation and *Estored* the energy stored during the oscillation. When QCM measurements are performed in a liquid medium, the major contribution to the dissipation is from the viscous losses. The change in dissipation factor (Δ*D*) in a liquid medium is given by:

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Where, *ρl* and ηl refer to the density and viscosity of the liquid.[41]

The crystals were cleaned prior to use based on the following protocol: the crystal was immersed in 1% hellmanex III solution in water for at least 1 hour, followed by washing with purified water, sonication in ethanol for 10 min, drying with N2 and finally treatment in UV-O3 chamber for 15 min.

2.2.1.1. Experiments in good solvent conditions:

To determine the adsorption isotherm of the inhibitor, a 10 g/L stock solution of inhibitor in xylene was prepared and sonicated for 30 min before aging overnight. Inhibitor solutions at different concentrations in the range 0.5 – 5 g/L were prepared the next day by diluting the stock inhibitor solution with xylene. In the case of *whole* and *ester* asphaltenes, 4 g/L stock solutions of asphaltenes in xylene were prepared and sonicated for 30 min before aging overnight. The stock solution was diluted with xylene to obtain different asphaltene solutions in the concentration range 0.2 – 2 g/L. For experiments with mixture of asphaltene and inhibitor, the stock asphaltene solution was diluted with xylene and stock inhibitor solution to the required concentrations. The prepared mixture solutions was then sonicated for 30 min and aged overnight before performing experiments.

2.2.1.2. Experiments under precipitating conditions

On the first day, the *whole* asphaltene and inhibitor solutions in xylene were separately prepared, sonicated and aged overnight. The next day, the asphaltene solution was diluted with xylene and/or inhibitor solution and aged overnight. The addition of n-hexane to asphaltene or asphaltene + inhibitor solution was done on the day of experiment, either 2 (for experiments in 25/75 and 15/85 % v/v xylene/n-hexane solutions) or 60 min (for experiments at or below precipitation onset ) before their injection into QCM-D. In addition, solutions of xylene + n-hexane for baseline and washing were prepared only on the day of experiment.

All the experiments in QCM-D were performed at 20°C using a single sensor microbalance system Q-sense E1 from Biolin Scientific (Sweden). A schematic of the QCM apparatus is presented in figure 1. First, the pure solvent (xylene) or xylene/n-hexane mixture was injected, and the initial baseline was considered to be stable when the change in frequency (Δ*f*) was ± 1 Hz over 15 min. A constant solution addition rate (0.5 mL/min) was maintained for all experiments. The solution addition time was either 10 minutes in the case of addition of asphaltenes, inhibitors or mixtures of them, or 30 minutes for washing with solvent or inhibitor solutions. The waiting time after solution addition varied up to 4 hours. At least two parallels were done for all experiments to ensure reproducibility.

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Figure 1: Schematic of the QCM-D set-up.

2.3. Viscosity measurements

The dynamic viscosity (η) of xylene/n-hexane mixtures were determined experimentally using an Anton Paar MCR 301 rheometer with CC-27 geometry. Each measurement was repeated at least twice. 18 mL of xylene/n-hexane mixture was introduced in the cell and the temperature was equilibrated at 20°C. The viscosity measurement was done in two steps: in the first step, the shear rate was varied between 1s-1 and 100s-1 over 5 minutes, while the second step consists of repeating the previous step to ensure that no evaporation loss of solvent occurred during the measurement.

3. RESULTS and DISCUSSION

3.1. Experiments in good solvent conditions

This part presents the results obtained in pure xylene. Asphaltenes form nanoaggregates in xylene and, therefore only the adsorption is measured by QCM.

3.1.1. Adsorption isotherms

Two different asphaltene samples were studied in this article. First, the asphaltenes extracted from crude oil (named *whole* asphaltenes) and, second, *ester* asphaltenes. The ester asphaltenes are obtained by esterification of carboxylic acid functionalities in whole asphaltenes, and therefore the ester asphaltenes are not able to create acid-base interactions with basic molecules. As fatty-alkylamine is basic, comparing the results obtained with *whole* asphaltenes and *ester* asphaltenes will allow us to get information about the nature of asphaltene - fatty-alkylamine interactions. A similar strategy was employed to study interactions in bulk[36].

The adsorption isotherms of *whole* asphaltenes, *ester* asphaltenes and fatty-alkylamine inhibitor in xylene is shown in figure 2. All the curves present similar aspects with an increase of the adsorbed amount at low concentrations, followed by a plateau. The *ester* asphaltenes (4.2 ± 0.1 mg/m2) show a slightly higher adsorption capability on stainless steel than the *whole* asphaltenes (3.2 ± 0.2 mg/m2). This observation relatively agrees with an earlier study[39] even if the difference between *ester* and *whole* asphaltenes was lower. However, the earlier adsorption study was carried out in a different solvent (toluene).

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Figure 2: Adsorption isotherm of asphaltenes and inhibitor in xylene before xylene washing. Adsorbed amounts are calculated based on 5th overtone using Sauerbery relationship (equation (1)). Error bars represent the reproducibility of two independent experiments.

The adsorbed asphaltene (*whole* and *ester*) amounts show only a slight variation in concentration range of 0.5 – 2 g/L, thereby indicating a saturation of surface with asphaltenes. Similarly, washing with xylene at the end of experiment resulted in removal of only 20 – 25 wt% of asphaltenes adsorbed on stainless steel for both *whole* and *ester* asphaltene systems. These values are consistent with other reports[37, 39]. The fatty alkylamine amphiphile however has a low adsorption capability (~1 mg/m2) on stainless steel even at concentrations as high as 5 g/L (amphiphile adsorption data between 2 – 5 g/L not shown in figure 2). After washing with pure xylene, the remaining adsorbed amount of inhibitor varied between 0 and 0.3 mg/m2, thereby indicating that the amphiphile is not strongly adsorbed on to the stainless steel surface.

3.1.2. Ability of amphiphile to form a protective layer on stainless steel

Next, the ability of fatty-alkylamine amphiphile to form a protective layer on the stainless steel thereby preventing asphaltene adsorption was tested as shown in figure 3. Initially, the amphiphile (inhibitor) solution was injected. Figure 3(a) shows the asphaltene adsorption when the asphaltene solution was injected directly after the inhibitor injection. The adsorbed amount was 2.4 ± 0.1 mg/m2. In figure 3 (b), the initially adsorbed inhibitor was washed using xylene before injecting the asphaltene solution. The total mass adsorbed was 2.6 ± 0.2 mg/m2, which is very similar to the earlier value.

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Figure 3: Ability of inhibitor to form protective coating on stainless steel in xylene (a) without xylene wash before asphaltene addition (b) with xylene wash before asphaltene addition. Two independent experiments are presented in each figure based on 5th overtone. The adsorbed amounts (right y-axis) are calculated using Sauerbery relationship from the change in frequency.

QCM-D allows us to only calculate the total mass adsorbed onto the crystal, i.e. asphaltenes + inhibitor. When a mixture is present, information on the composition of the adsorbed layer can be obtained by comparison with data concerning the adsorption of single component in similar conditions. A comparison of the adsorbed values reported in figures 3(a) and 3(b) (~2.4 and ~2.6 mg/m2) with 2 g/L asphaltene adsorption in absence of inhibitor (3.2 ± 0.2 mg/m2 in figure 2) indicates that prior injection of inhibitor results in only a marginal reduction (~ 20 – 25 wt%) in amount of asphaltene adsorbed. However, this reduction is very small if the experimental uncertainties are taken into account, and hence there is no conclusive evidence of the fatty-alkylamine amphiphile forming a protective coating on the stainless steel surface: the adsorbed layer after adsorption of asphaltenes is, most likely - composed of asphaltenes. Figure 3 also shows that an inhibitor washing followed by xylene wash at the end results in ~ 80 – 85 wt% removal of asphaltenes from the stainless steel surface .This high value is not due to multiple injections of solvents but to interaction between the inhibitor and asphaltenes. Indeed, Subramanian et al.[37], using asphaltenes from the same origin as in this work, have shown that the amount of desorbed asphaltene increases only marginally if pure solvent is injected more than one time. Thus, the fatty-alkylamine amphiphile is able to disperse the adsorbed asphaltene layers.

3.1.3. Inhibition ability of fatty-alkylamine amphiphile

Figure 4 shows the typical experiments carried out in good solvent conditions to determine the ability of the fatty- alkylamine amphiphile to reduce the amount of adsorbed asphaltenes. The asphaltene concentration in xylene was maintained constant at 2 g/L for all the experiments, while the inhibitor was tested at 0.5 g/L and 2 g/L concentrations. From figure 4, it can be observed that in presence of 0.5 g/L inhibitor, the mixed inhibitor + asphaltene adsorption (*Γasp/inh*) reduced to 1.0 ± 0.1 mg/m2 for both *whole* and *ester* asphaltenes. The first xylene wash effectively removes 50 – 60% of the adsorbed mass. The 0.5 g/L inhibitor solution wash most likely helps to remove the adsorbed asphaltenes, and the adsorbed amounts after inhibitor wash is close to the value obtained when only inhibitor is adsorbed (Γ ~ 0.5 mg/m2). It can therefore be deduced that the layer is mostly composed of inhibitor. By the end of the second xylene wash, almost all the adsorbed species were removed from the stainless steel surface.

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Figure 4: Example of adsorption of mixed asphaltene + inhibitor solutions in xylene on stainless steel based on 5th overtone. The adsorbed amounts (right y-axis) are calculated using Sauerbery relationship from the change in frequency.

Figure 5 gives a comparison of adsorbed asphaltene or asphaltene/inhibitor mixture amounts on stainless steel. In the absence of inhibitor, the asphaltene adsorbed amounts are 3.2 ± 0.2 mg/m2 for *whole* asphaltenes and 4.2 ± 0.2 mg/m2 for *ester* asphaltenes respectively. The use of 2 g/L fatty-alkylamine amphiphile resulted in only a marginal change in adsorbed mass (*Γasp+inh*) than compared to 0.5 g/L amphiphile usage. Thus, the ability to minimize asphaltene adsorption as well as to disperse asphaltene layers formed on the stainless is clearly demonstrated by the fatty-alkylamine amphiphile.

In order to gain insight behind the mechanism of asphaltene adsorption/deposition, asphaltenes were esterified. The effect of the fatty-alkylamine inhibitor on the *ester* asphaltene adsorption/deposition was then compared with *whole* asphaltenes (figure 5). This comparison shows that the inhibitor has the same effect on both the asphaltenes, thereby indicating a similar asphaltene-inhibitor interaction. Consequently, as reported in our earlier work[36], the acid-base interaction between asphaltenes and the inhibitor is not the main interaction responsible for the inhibitor’s ability to reduce asphaltene adsorption. This conclusion, in disagreement with other studies presented in the introduction section, could be explained by the nature of the inhibitor used in this - study. Alkylamine inhibitor is a base, contrary to more acidic molecules like DBSA used in other studies[15].

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Figure 5: Effect of fatty-alkylamine inhibitor on asphaltene + inhibitor adsorption on stainless steel in pure xylene. The values represent the Γ*asp+inh* marked in figure 4, and is based on 5th overtone.

3.2. Experiments under precipitating conditions

3.2.1. Asphaltene adsorption/deposition at different xylene/n-hexane (v/v) ratios

The properties of asphaltenes in solution vary in presence of a precipitant like n-hexane:

below the precipitation onset, i.e. for amount of precipitant lower than the one required to induce asphaltene precipitation, the asphaltenes are soluble and the size of the asphaltene aggregate increases with the precipitant content, while still remaining in the nanometer range nevertheless.[42] Above the precipitation onset, the asphaltene aggregates flocculate to form micrometer-sized flocs.

It should however be noted that the value of the precipitation onset depends on the time since it is influenced by slow asphaltene precipitation kinetics.[43] The precipitation onset (determined by near infrared spectroscopy) of the *whole* asphaltenes used was earlier found to be ~ 60 – 65 vol% n-hexane after 1 day for 2 g/L asphaltenes in toluene/n-hexane.[36] Since toluene and xylene have similar solubility parameters, the asphaltene precipitation onset is expected to show minimal variation with use of either solvent.

Figure 6 shows the adsorption of whole asphaltenes from a 50/50 (v/v) xylene/n-hexane solution onto stainless steel. As the n-hexane content is lower than the precipitation onset, it is expected that the asphaltenes form nanoaggregates in solution as described above and therefore only adsorption is expected. The 2 g/L asphaltene solution was injected for 10 min, and the system was allowed to stabilize/equilibrate. It must be noticed that a similar study was undertaken by Tavakkoli et al. [34] but at a much lower asphaltene concentration (100 ppm) than in the present study. It can be observed that the frequency curve does not reach any plateau even after 4h, thereby indicating that asphaltene adsorption on stainless steel has not reached equilibrium yet. This could possibly be attributed to the kinetic effects associated with asphaltene aggregation. In addition, the asphaltene adsorption is characterized by the spreading of frequency overtones and dissipation values higher than 1 x 10-6, and hence the adsorbed layer is considered to be viscoelastic[34]. The observed adsorption behavior is different from asphaltene adsorption in pure xylene. In good solvent conditions, the asphaltene adsorption is faster, a constant value (plateau) is reached, and negligible spreading of with overtones is observed.[37] Moreover, the adsorbed asphaltene amounts from 50/50 (v/v) xylene/hexane systems (Γ = 12.9 ± 0.5 mg/m2) is significantly higher than in pure xylene (Γ = 3.2 ± 0.2 mg/m2 based on 5th overtone). This means that there is a significant evolution of asphaltene layer conformation in presence of n-hexane.

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Figure 6: Adsorption of 2 g/L whole asphaltene solution in 50/50 (v/v) xylene/n-hexane solution. The symbol ‘n’ refers to the overtone number.

The change in frequency and dissipation based on 5th overtone during adsorption/deposition of asphaltene from solutions containing different ratios of xylene/n-hexane is given in figure 7. The xylene/n-hexane content varies from 50/50 to 15/85 (v/v), therefore including the precipitation onset composition. Conseqeunetly, the conditions span systems composed of nanoaggregates (below the precipitation onset) and mixture of nanoaggregates and micrometer flocs (above the flocculation onset). For the former, only adsorption is expected, while a mixture of adsorption and deposition process is expected for the latter. Liquid loading effects were minimized by maintaining the same xylene/n-hexane (v/v) ratio throughout the experiment (i.e., for baseline, asphaltene adsorption/deposition stage and desorption/solvent washing) corresponding to each run. The spreading of frequency overtones (n = 3, 5, 7- results not shown for all the solvent compositions) and a large dissipation change was a common feature observed for all the asphaltene adsorption experiments up to the precipitation onset (60 – 65 vol% n-hexane). Similarly, the frequency curve does not reach a plateau value in the 4h of experimental time, thereby indicating that asphaltenes continued to adsorb on to the stainless steel surface. Also, the effect of waiting time before asphaltene solution injection (2 min and 60 min) below precipitation onset was tested for system in 45/55 (v/v) xylene/n-hexane, and found to be negligible at the end of 4h experimental time.

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Figure 7: *Whole* asphaltene adsorption/desorption from solution at different xylene/n-hexane ratios based on 5th overtone (a) frequency change (b) dissipation change.

Due to the viscoelastic nature of layer formed, the adsorbed asphaltene mass was estimated based on Voigt model[44] using the Qtools analysis software provided by the instrument supplier (Biolin scientific, Sweden). The software requires the following input parameters: (i) the frequency and dissipation at different overtones (ii) density of the adsorbed asphaltene layer, and (iii) The bulk density and viscosity of the xylene/n-hexane mixture. The density of the adsorbed asphaltene layer was assumed to be 1200 kg/m3, similar to other studies[45], while the density of xylene/n-hexane mixture (*ρmix*) was calculated based on:

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Where, the subscripts *xyl* and *hex* refer to xylene and n-hexane respectively, while *x* and *ρ* refer to the mass fraction and density. The viscosities of xylene/n-hexane mixture were determined experimentally using rheometer as described in section 2.3, and the values obtained are reported in table 2. The asphaltene adsorbed/deposited mass obtained before xylene/n-hexane mixture wash is shown in figure 8.

In comparison, for experiments performed with asphaltenes in 25/75 (v/v) and 15/85 (v/v) xylene/n-hexane, the spreading of frequency curves corresponding to different overtones (n = 3, 5, 7) was negligible. Similarly, the dissipation changes for these two cases were small, as seen in figure 7(b). Thus, above the precipitation onset, the asphaltenes form more compact or rigid layers. Another interesting observation is that only a limited desorption (~20 – 25 wt%) of adsorbed/deposited asphaltenes after 4h was achieved by washing with xylene/n-hexane solvent mixture (as seen desorption stage in figure 7(a)).

The amount of asphaltene adsorbed at all xylene/n-hexane ratios tested in figure 8 are significantly higher than the asphaltene adsorption from only xylene (3.2 ± 0.1 mg/m2), thereby confirming the role of precipitant n-hexane to destabilize the asphaltenes in solution and promote increased asphaltene adsorption. Initially, the amount of asphaltenes adsorbed increases as the amount of n-hexane content in the solution is increased. The maximum asphaltene adsorption/deposition was observed near the precipitation onset conditions, with the adsorbed mass from 40/60 (v/v) solution (Γ40/60) = 24.5 ± 1.4 mg/m2, and from 35/65 (v/v) solution (Γ35/65) = 25.2 ± 1.3 mg/m2 respectively after 4h of adsorption/deposition. This observation could be explained as follows: increasing the n-hexane content in solution leads to greater destabilization of asphaltenes. The maximum amount of destabilized asphaltenes is present near the precipitation onset, and hence the asphaltene adsorption/deposition on to the stainless steel surfaces also increases up to the precipitation onset. At these solvency conditions, asphaltenes would continue adsorbing onto the solid surface thereby forming a viscoelastic and multi-asphaltene layers.

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Figure 8: Amounts of whole asphaltenes (concentration: 2 g/L) adsorbed/deposited at different xylene/n-hexane (v/v) ratios up to 4h. Mass values calculated from the Voigt model from data presented in figure 7.

Above precipitation onset, a mixture of asphaltene adsorption + deposition occurs, and the change in frequency curve is less after the initial adsorption/deposition. In 25/75 (v/v) xylene/n-hexane solution, the adsorption/deposition reduces to Γ25/75 = 18.9 ± 0.7 mg/m2 at the end of 4h, while for 15/85 (v/v) solution, the reduction is even further with Γ15/85 = 10.9 ± 0.1 mg/m2. A similar decrease in asphaltene adsorption/deposition above precipitation onset has been reported by Tavakkoli et al.[34], and the reason attributed to this observation was the likelihood of precipitated asphaltenes not participating in the deposition process.

The masses measured in 25/75 and 15/85 (v/v) xylene/n-hexane solutions encompass both adsorption and deposition, and, therefore, it would be interesting to determine the relative contribution of the two phenomena. However, this determination is not easy. It could be thought that the deposition could be linked to the fraction of weakly bonded asphaltenes i.e. the one removed by pure solvent. However, a significant part of adsorbed asphaltenes is washed away by pure xylene even in the case of systems exhibiting pure adsorption (results presented in Subramanian et al. [37]). Therefore, this is not a viable method. Another method was therefore implemented.

In order to differentiate the adsorption/deposition capability of asphaltenes dissolved in solution and the precipitated asphaltenes, it was decided to allow the 2 g/L *whole* asphaltenes solutions containing 75 and 85 vol% n-hexane respectively to precipitate over 24 hours. The solution was then centrifuged for 30 min at 4000 rpm, and the supernatant filtered using a 0.45µm HVLP filter to remove any asphaltene flocs. The adsorption capability of the supernatant solution on stainless steel was then measured, and the results obtained are summarized in table 1. As it is assumed that only asphaltenes in the form of monomers and nano-aggregates remain in the supernatant, contrary to micrometer-sized flocs, this procedure would provide the information about the amount of asphaltenes adsorbed from the initial *whole* asphaltene solution.

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| Asphaltenes in xylene/n-hexane (v/v) solution | Total asphaltenes adsorption + deposition (mg/m2)\* | Asphaltenes precipitated in bulk (wt%)[36] | Supernatant solution adsorption (mg/m2)\* |
| 25/75 | 18.9 ± 0.7 | ~ 25 % | 10.6 ± 0.2 |
| 15/85 | 10.9 ± 0.1 | ~ 62 % | 5.9 ± 0.4 |

Table 1: Amounts of asphaltene adsorption/deposition above precipitation onset. The initial *whole* asphaltene concentration in solution was 2 g/L. \*values after 4 h

The quantification of asphaltene precipitation in bulk presented in table 1 was based on toluene/n-hexane mixtures, and the procedure and the data are presented in an earlier article[36]. A similar quantification was not done for xylene/n-hexane mixture due to the difficulty in complete evaporation of xylene. It can however be reasonably assumed that the precipitated asphaltene amounts will not vary much due to similarities between the solvents toluene and xylene, and the observation that the *whole* asphaltene precipitation onset lies between 60 – 65 vol% n-hexane for both toluene/n-hexane and xylene n-hexane systems.

From table 1, it can be seen that the 15/85 (v/v) solution contains much higher amounts of precipitated asphaltenes (~62 wt%) than compared to 25/75 (v/v) solution (~25 wt%). This could explain the lower adsorption/deposition of asphaltenes from 15/85 (v/v) solution, since not all the precipitated asphaltenes are expected to contribute to the deposition phenomena. When asphaltene supernatant solutions were tested, a lower adsorption capability was observed for both 25/75 (v/v) supernatant and 15/85 (v/v) supernatant solutions, with the corresponding adsorbed amounts of 10.6 ± 0.2 mg/m2 and 5.9 ± 0.4 mg/m2 respectively. The supernatant solution adsorption values are significantly lower than the values obtained for the original 2 g/L whole asphaltene in 25/75 (v/v) and 15/85 (v/v) xylene/n-hexane solutions. This can be attributed to the decrease in concentration of the dissolved asphaltenes in solution, and would represent the adsorption of asphaltene molecules or nanoaggregates that are stable, i.e. not flocculating, from solution in 25/75 or 15/85 (v/v) xylene/n-hexane mixtures.

The difference in asphaltene adsorption/deposition observed above precipitation onset could thus be explained as follows: the first layer formed on the stainless steel surface is most likely due to adsorption of asphaltenes, while the precipitated asphaltenes interact with the adsorbed layers and form subsequent layers. The number of interaction sites available in precipitated asphaltenes could be much lower, which results in them contributing less to the growth of multilayers (deposits) than compared to the destabilized asphaltenes.

3.2.2. Kinetics of asphaltene adsorption

The kinetics of adsorption at the surface can be determined based on the Ward and Tordai equation[46] if the adsorption is controlled by the diffusion of the solute from the bulk to the surface. At short interval times, the following equation is valid:

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Where, Γ refers to the adsorbed asphaltene mass (kg/m2), *C* the concentration of asphaltenes in bulk phase (kg/m3), *D* the diffusivity (m2/s) and *t* the time after solution injection (s). Thus, the slope of plot between Γ and t1/2 can be used to determine the diffusivity of asphaltene adsorbing species.

Figure 9 shows the comparison of asphaltene adsorbed/deposited mass (Γ) at short time (t ~ up to 10 s) after injection of 2 g/L asphaltene solution at different xylene/n-hexane ratios. A relatively linear plot is obtained between Γ and t1/2 for all the asphaltene solutions in different xylene/n-hexane, except for the 35/65 (v/v) xylene/n-hexane solution. A linear Γ and t1/2 relationship is considered to be a characteristic of diffusion controlled adsorption/deposition.[45] In addition, the simplified Ward-Tordai relationship (equation 5) is based on the assumption of irreversible asphaltene adsorption on surface. The linear plots in figure 9 are characterized by non-zero intercepts, thereby indicating that not all the asphaltenes are irreversibly adsorbed on stainless steel surface. The reasoning is also supported by observation of 20 – 25 wt% asphaltene desorption from surface by a simple xylene/n-hexane wash in figure 7.

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Figure 9: Γ vs t1/2 plot showing the comparison of asphaltene adsorption + deposition at different xylene/n-hexane (v/v) ratios at short times.

The estimated diffusivity of asphaltenes from the slope of Γ and t1/2 plots is given in table 2. Based on the estimated diffusivity values, the size of adsorbing/depositing asphaltene species (assuming a spherical geometry) was determined using the Stokes-Einstein relationship[47]:

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Where, the terms *d* refers to diameter of particle (m), *Kb* the Boltzmann constant (1.38 x 10-23 m2kg/s2K), *T* the temperature (293 K), *ηs* the dynamic viscosity (Pa·s).

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| --- | --- | --- | --- |
| Asphaltenes in solution of  xylene/n-hexane (v/v) | Average asphaltene diffusivity (m2/s) | Bulk solution viscosity# (Pa·s) | Average asphaltene diameter (m) |
| 50/50 | 5.5 x 10-13 | 4.34 x 10-4 | 1.80 x 10-6 |
| 45/55 | 7.6 x 10-13 | 4.22 x 10-4 | 1.33 x 10-6 |
| 40/60 | 28.7 x 10-13 | 4.12 x 10-4 | 0.37 x 10-6 |
| 35/65 | 8.5 x 10-13 | 4.00 x 10-4 | 1.40 x 10-6 |
| 25/75 | 12.9 x 10-13 | 3.76 x 10-4 | 0.89 x 10-6 |
| 15/85 | 4.5 x 10-13 | 3.53 x 10-4 | 2.71 x 10-6 |

Table 2: Estimated asphaltene diffusion coefficients and diameter (size). #Experimentally determined values of different xylene/n-hexane (v/v) solutions using rheometer.

The diffusivity values obtained in table 2 are lower than those obtained using QCM technique by other authors.[34, 45] Vilas Bôas Fávero et al. [48] have determined the diffusion coefficient, and therefore the hydrodynamic size of depositing asphaltenes from the asphaltene deposition rate in various crude oil/heptane mixtures, at concentrations of heptane above the precipitation onset. They found diffusion coefficient varying from 0.67 to 7.1×10-12 m2/s, i.e., significantly higher than coefficients reported in table 2.

The low diffusivity values reported in table 2 translated into high average asphaltene diameters (in micrometer size), i.e., a size range indicative of the dominance of sedimentary mechanism over Brownian motion. Thus, the most likely reason for unreliable/inconsistent asphaltene diffusivity (and size) values obtained is that the adsorption/deposition of asphaltenes from 2 g/L solutions in xylene/n-hexane mixtures is not diffusion controlled, but more a reaction controlled phenomena.

3.2.3. Effect of fatty-alkylamine amphiphile under precipitating conditions

3.2.3.1 Adsorption of fatty-alkylamine amphiphile under precipitating conditions

The solvent ratio of 25/75 (v/v) xylene/n-hexane was chosen for inhibitor testing based on figure 8, since this solvent ratio is above the asphaltene precipitation onset (60 – 65 vol% n-hexane) and the observed asphaltene precipitation/deposition from 25/75 (v/v) solutions is significant. To begin with, the adsorption of the 2 g/L pure fatty-alkylamine amphiphile in solution of 25/75 (v/v) xylene/n-hexane was determined. Unlike the whole asphaltenes, the fatty-alkylamine amphiphile exhibited limited adsorption capability, with the adsorbed amount, Γ*inh* = 0.6 ± 0.1 mg/m2 within the tested range 0.5 – 5 g/L inhibitor concentration under precipitating conditions. A simple wash with 25/75 (v/v) xylene/n-hexane removed all the amphiphile from the stainless steel surface similar to the observation in pure xylene system, thereby indicating the absence of strong interaction between the amphiphile and the stainless steel surface.

3.2.3.2 Dispersive capability of fatty alkylamine amphiphile

Figure 10 shows the ability of the fatty-alkylamine inhibitor to act as a dispersant/desorbant after the formation of adsorbed/deposited asphaltene layer on the stainless steel surface. Washing of the adsorbed/deposited asphaltene layer after 240 min (4 h) results with a 25/75 (v/v) xylene/n-hexane solution in removal of only ~ 25 wt% of asphaltenes (i.e., from ~18.9 mg/m2 to ~14.6 mg/m2). Further washing of the asphaltene layer with 2 g/L fatty alkylamine solution significantly reduces the adsorbed amounts to ~1.5 mg/m2. The washing is characterized by an increase in dissipation values at the start of amphiphile injection, followed by a gradual tapering off. The amphiphile probably interacts with the asphaltenes, and disperses the asphaltenes into the bulk solution. The 25/75 (v/v) xylene/n-hexane solution wash then results in further reduction of adsorbed amount to ~1 mg/m2. Thus, the fatty-alkylamine amphiphile demonstrates its ability to remove/disperse asphaltene layers/deposits from the stainless steel surfaces.

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Figure 10: Effect of fatty-alkylamine amphiphile on asphaltenes adsorbed/deposited above precipitation onset in solutions of 25/75 (v/v) xylene/n-hexane based on the 5th overtone. 2 independent experiments are presented

3.2.3.3. Inhibitory action of fatty-alkylamine inhibitor under precipitating conditions

In order to test the ability of the fatty-alkylamine amphiphile to act as a inhibitor under precipitating conditions, mixed solutions of 2 g/L asphaltenes and varying amounts of amphiphile were prepared in 25/75 (v/v) xylene/n-hexane. The protocol followed was similar to that shown in figure 4, with the exception that 25/75 (v/v) xylene/n-hexane solution was used for precipitating conditions instead of pure xylene (for good solvent conditions). Figure 11 shows the effect of fatty-alkylamine amphiphile on asphaltene adsorption/deposition from 2 g/L asphaltene solutions. The values corresponding up to 0.2 g/L inhibitor refers to conditions where the shift in asphaltene precipitation onset is minimal[36], and therefore the effects seen at these two inhibitor concentrations is entirely due to the dispersing ability of the inhibitor and not due to an increase in the solubility of asphaltenes. At 2 g/L inhibitor concentration, the asphaltene precipitation onset shifts from 60 – 65 vol% n-hexane to 70 – 75 vol% n-hexane.[36] Hence, the results obtained at the highest tested inhibitor concentration of 2 g/L could be influenced by the shift in precipitation onset. As seen in figure 11, the amphiphile displays an ability to reduce the asphaltene adsorption/deposition from 18.9 ± 0.7 mg/m2 (in absence of inhibitor) to 5.6 ± 0.2 mg/m2 on addition of 0.05 g/L of fatty-alkylamine amphiphile. This concentration is typical of the dosage of inhibitor injected in oil field, and therefore proves that the fatty-alkylamine inhibitor is worthy of further investigation.

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Figure 11: Effect of fatty-alkylamine amphiphile on asphaltene adsorption/deposition under precipitating conditions. Adsorbed values based on the 5th overtone.

When the amphiphile concentration is 0.2 g/L, the adsorbed/deposited amounts are further reduced to 1.2 ± 0.4 mg/m2. Thus, the use of 0.2 g/L amphiphile results in reduction of ~90 – 95 wt% asphaltene adsorption/deposition on stainless steel i.e., a ratio of 1 to 10 between the inhibitor and asphaltene concentrations. This result appears to be in agreement with our earlier observation carried out with isothermal titration calorimetry (ITC) that only ~6 mole% of the *whole* asphaltenes interacts strongly with the fatty-alkylamine amphiphile in the bulk.[36] The dominance of bulk interaction between the asphaltenes and the amphiphile is therefore visible. The optimum usage of this fatty-alkyl amine amphiphile corresponds to a mole ratio (inhibitor/*whole* asphaltenes) ~0.10.

4. CONCLUSIONS

In this article, the ability of a fatty-alkylamine amphiphile to prevent asphaltene adsorption/deposition was studied along with its ability to act as a dispersant of preformed layers/deposits using QCM-D. The amphiphile showed only a limited ability (~1 mg/m2) to adsorb onto stainless steel, which could easily be removed by solvent washing. The amphiphile also did not exhibit an ability to form a protective layer on stainless steel to prevent asphaltene adsorption. The amphiphile however reduced the *whole* asphaltenes adsorption on stainless steel from 3.2 ± 0.2 mg/m2 to 0.7 ± 0.1 mg/m2 in good solvent conditions.

In presence of a precipitant (n-hexane), the asphaltene adsorption/deposition on stainless steel from 2 g/L asphaltene solution was found to increase up to the precipitation onset (i.e., ~60 – 65 vol% n-hexane), with maximum amount of ~ 25 mg/m2. The asphaltene adsorption/deposition decreases beyond the precipitant onset, which could most probably be due to non-participation of all the precipitated asphaltenes in the deposition process. In addition, the asphaltene adsorption process under non-precipitating and precipitating condition was found to be reaction limited phenomena.

Above the precipitation onset, the fatty-alkylamine amphiphile reduced asphaltene adsorption/deposition from 18.9 ± 0.7 mg/m2 (no inibitor) to 1.2 ± 0.4 mg/m2 in 25/75 (v/v) xylene/n-hexane solutions The maximum inhibitory action with the amphiphile was achieved corresponding to an inhibitor/*whole* asphaltene mole ratio of ~0.10, despite this mole ratio not being sufficient to prevent asphaltene precipitation. The amphiphile also exhibited an ability to disperse the adsorbed/deposited asphaltene layers, with estimated removal efficiency in the range of 85 – 90%. Our studies thus indicate that the fatty-alkylamine amphiphile functions effectively both as an asphaltene inhibitor (AI) and dispersant (AD) under good solvent conditions as well as under precipitating conditions.

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