

Reversibility of Asphaltene Aggregation As Revealed by Magnetic Resonance Imaging in Situ

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ABSTRACT: Aggregation of asphaltenes followed by precipitation presents severe problems for existing technologies in the production, recovery, and processing of heavy oils. Better understanding of asphaltene behavior behind the processes of their precipitation and dissolution is vital to address this issue. While investigating the inhomogeneity of different oil systems, the reversibility of the asphaltene aggregation process initiated by flocculant in either asphaltene solution in toluene or crude heavy oil was revealed and investigated using magnetic resonance imaging methods. It was found that the inhomogeneous distribution of the flocculant initiates local spatial-selective asphaltene aggregation registered in a thin layer around the flocculant/oil sample interface. The local excess of flocculant concentration over the threshold of asphaltene precipitation onset is a driving force of this process. As the flocculant diffuses into the volume of the sample, a decrease of the asphaltene flocculated area is observed until it disappears when the equilibrium composition throughout the whole volume of the system is achieved. Depending on the overall flocculant concentration, the asphaltene aggregation may not be reversible and could be followed by subsequent precipitation of the asphaltene aggregates. The similarity of the phenomena observed for the model asphaltene solutions and crude heavy oil samples was established. Partial mechanical stirring of the multicomponent system comprising flocculant and oil or asphaltene solution does not prevent the formation of the local zones with increased concentration of asphaltene aggregates; those sizes evolve depending on the flocculant concentration. The results obtained in this work are consistent with the generally accepted concept of asphaltene precipitation reversibility depending on the system composition and are compatible with the observations obtained by other methods. The approach presented can provide deeper insight into the asphaltene precipitation reversibility issue and can facilitate the understanding of asphaltene behavior in heavy oils.

1. INTRODUCTION

The current trend in the petroleum industry is an obvious shift of technologies toward processing of heavier crude oils and residues. These feedstocks are more difficult to process, in comparison with light crude oils, because of higher content of heavy constituents such as asphaltene and resin and greater quantities of nondistillable hydrocarbons having many heteroatoms and metals.¹ As a result, heavy oil production and processing becomes a more and more challenging task for the petroleum industry because of the expense caused by the necessity of refining pipelines, internal surface of reservoirs, and catalysts in reactors from deposits.

Among the thousands of components present in crude oil,^{2,3} asphaltenes are highlighted to be the most important group of compounds that undergo deposition during processing, refining, and transportation of heavy oil.⁴ They are typically defined as the nonvolatile fraction of crude oils that are insoluble in *n*-alkanes.^{5,6} This definition captures the heaviest fraction of oil, which is composed of a broad distribution of molecules which have a strong tendency for destabilization and phase separation. The detailed structure of asphaltene molecules has not been completely understood yet,^{7–9} but generally they are considered to be formed by a system of

polycondensed aromatic rings with aliphatic chains attached to them.^{10–12} Usually, asphaltenes also contain heteroatoms, such as oxygen, nitrogen, and sulfur, and some metals, such as nickel and vanadium, can also be observed.¹³ The theories regarding the asphaltene states in crude oil are also controversial;^{14,15} nevertheless, it is generally accepted that they exhibit colloidal behavior in crude oil, resulting in association and aggregation processes, followed by precipitation under certain external factors, such as temperature, pressure, and chemical composition changes.^{6,16–18}

Aggregation of asphaltenes followed by precipitation can present severe problems during the production and recovery of crude oils as well as for processing and catalytic refining of fossil hydrocarbon feedstocks. Consequently, much effort has been devoted to studying these processes from molecular to industrial scales.¹⁹ As a result, the structure of the aggregates, mechanisms of deposit formation, and the factors influencing the asphaltene phase behavior nowadays are generally elucidated. However, all these studies were primarily focused

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on irreversible asphaltene precipitation, i.e., investigations were carried out during the transition “asphaltene molecules—nanoaggregates—flocks—solid deposit”. This approach provides information about critical parameters such as concentration of flocculant, pressure, and temperature which initiate the precipitation process.²⁰ At the same time, numerous studies have shown that the asphaltene aggregation can be partially or completely reversible with changes in pressure, composition, and temperature.^{20–27} Therefore, there are two different models which contradict each other regarding the issue of asphaltene precipitation reversibility. According to the solubility model, asphaltene aggregation followed by precipitation is a thermodynamically reversible process,^{28,29} while in the colloidal model, precipitation of asphaltenes is considered to be irreversible.^{30–32} Both evidence in favor and arguments against the reversibility of asphaltene precipitation can be found in published papers.³³ Recently, the dramatic role of slow aggregation kinetics was demonstrated to contribute into systematic overestimation of asphaltenes stability, and a strong need to revisit previous works was declared.^{34,35}

Restabilization of asphaltenes after they precipitate out of heavy oil is of great practical significance for the petroleum industry, and better understanding of reversibility issues may provide correct modeling of asphaltene phase behavior. The majority of experimental studies on asphaltene precipitation reversibility were carried out with respect to changes in system composition:^{19–26} the precipitated asphaltenes were redissolved upon the removal of precipitant or upon addition of the aromatic solvents or fresh oil. In these experiments it is difficult to test reversibility without disturbing the system; for example, intensive stirring, centrifugation, in some cases sonication should be applied to the precipitant–heavy oil mixture while removing and/or reintroducing precipitates. This makes the system homogeneous, which ensures complete precipitation or dissolution of the asphaltenes. However, little knowledge is available in the open literature about restabilization of aggregated and precipitated asphaltenes that could have happened in the blends without any external impact. Another questionable point arises regarding a spatial distribution of aggregated asphaltenes in the inhomogeneous blends or mixtures when no stirring is applied. For example, partial blending of two incompatible oils, water–oil, and brine–oil emulsions are often formed in petroleum reservoirs, pipelines, and tanks; consequently, asphaltenes, which are surface active, may precipitate around the interfaces and significantly modulate their properties.^{36–39} To address these issues an experimental study should be performed where the disturbance of the studied blend is sufficiently diminished.

To study the asphaltene precipitation reversibility, a number of methods have been intensively employed: gravimetric analysis associated with centrifugation of the samples, optical microscopy, refractive index measurements, near-infrared transmittance (turbidimetry), pressure depletion in a flow-loop apparatus, etc.^{20–27} All these methods are considered to be sufficient to give an answer to whether precipitated asphaltenes are redissolved and to quantify this process. However, it is difficult to understand the nature and essence of this process using only the methods listed above. In situ methods are needed to elucidate and separate the factors that have influence on the stability of asphaltenes in crude oils and determine the mechanism and conditions providing the reversibility or irreversibility of asphaltene aggregation, deposit formation, and fouling.^{40–42} In this regard we believe that the

magnetic resonance imaging (MRI) is a very complementary method which is capable of providing deep insight into the problem of reversibility in situ. The main advantages of MRI stem from the fact that the NMR signal is very sensitive to small alternations of the chemical composition and/or physical structure of the systems under study. Thus, MRI is a well-known noninvasive visualization technique that has successfully been applied in many areas of research such as materials science,⁴³ chemical engineering,⁴⁴ petroleum science,^{45–48} etc. Recently, MRI proved to be a very informative tool for studying the phase behavior of heavy constituents in crude oils.^{49–51}

In this paper, we investigate the process of flocculant-induced asphaltene precipitation in strongly inhomogeneous mixtures and blends formed by flocculant (*n*-heptane) and heavy oil. Particularly, our attention is focused on the asphaltene phase behavior during the transition of inhomogeneous systems into an equilibrium compositional state. For better understanding of the processes which could occur in the crude oils, the model sample of the asphaltene solution in toluene was also studied. The role of interfaces in phase behavior is intended to be elucidated. The MRI approach in situ looks promising for visualization of the spatial-selective asphaltene aggregation and dissolution and related phenomena when neither stirring nor removing or reintroducing of materials is necessary.

2. EXPERIMENTAL SECTION

2.1. Asphaltenes and Crude Heavy Oil. Two types of samples were prepared for the study. The first type is the asphaltene solutions in toluene used as model samples. Asphaltenes were extracted from heavy crude oil following ASTM Standard D6560-00 [*Standard Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products*⁵²] substituting *n*-heptane and toluene as solvents for hexane and benzene, respectively, to facilitate distillation. All solvents used were reagent-grade or higher. The second type of samples is crude heavy oil. Chemical composition and physical properties of this oil are listed in Table 1. The concentration of

Table 1. Chemical Composition and Physical Properties of Heavy Oil

composition or property	value
saturates (wt %)	21.0
aromatics (wt %)	37.2
resins (wt %)	35.1
asphaltenes (wt %)	6.7
API gravity (deg)	16.4
kinematic viscosity (mm ² /s) (at 20 °C)	3868.7

asphaltenes in the model samples was adjusted to be 6 wt % in order to match the composition of heavy oil. For initiation of the precipitation processes in both types of the samples, *n*-heptane was used as a flocculant.

Liquid samples (either asphaltene solution in toluene or heavy oil) were poured in a flat-bottomed glass tube (6 mm inner diameter) followed by careful adding of heptane onto the surface of the sample. In the case of partial stirring of the sample, the mechanical shaking of the tube was performed for 1–2 min. The overall volume of the specimen loaded into the tube was approximately 1 mL. After that, the tube with the sample was inserted into the MRI probe, and the NMR image acquisition process was started immediately. A temperature of 25 ± 2 °C was maintained during the measurements.

2.2. Magnetic Resonance Imaging. The imaging experiments were carried out using an NMR imaging installation based on a Bruker Avance DPX 200 console and superconducting magnet with an 89 mm diameter vertical bore, water-cooled and self-shielded Bruker gradient set (maximum gradient strength up to 292 mT/m); probe PH MINI

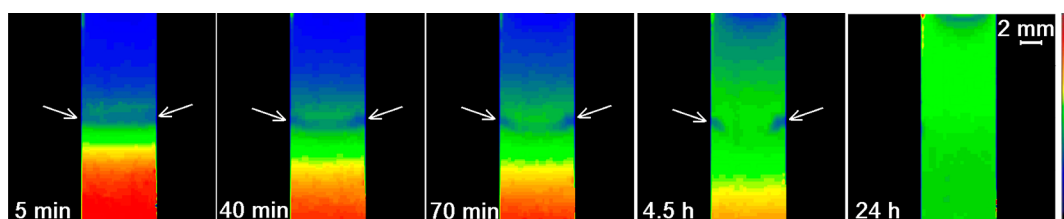


Figure 1. Series of NMR images (T_2 maps) obtained after adding the *n*-heptane from the top on the surface of asphaltene solution in toluene. The volume ratio of heptane to asphaltene solution is 1:1.5. For convenience, the thin layer with lower signal intensity/relaxation time appearing in mixing zone is pointed out by the white arrows. Scale and time elapsed since the beginning of experiment are indicated in the figure.

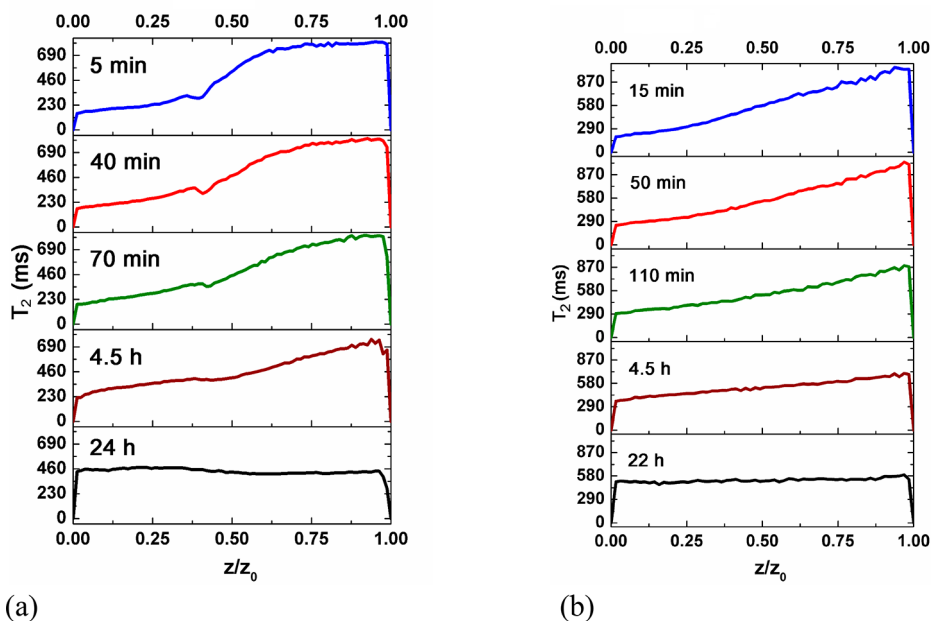


Figure 2. Series of vertical T_2 relaxation time profiles obtained after adding the heptane from the top on the surface of asphaltene solution in toluene (a) and on the surface of toluene without asphaltenes (b). The volume ratio of heptane to asphaltene solution (a) or neat toluene (b) is 1:1.5. Relative position z/z_0 starts from the top of the sample and comes to 1 at the bottom. Time elapsed since the beginning of the experiment is indicated in the figure.

0.75, 40 mm internal diameter birdcage coil tuned and matched to ^1H nuclear resonance frequency of 200.13 MHz; and a console operated with Paravision 4.0 software.

The principles of the NMR imaging technique are well-known and can be found elsewhere.^{43,44,53} Slice selective 2D NMR images were acquired using the spin-echo-based pulse sequence supplied by the imager software: T_2 -weighted and proton density (PD)-weighted images were acquired by the rapid acquisition with relaxation enhancement (RARE) technique; T_2 maps were plotted by the processing of the image sequences acquired by the multi-slice multi-echo (MSME) technique (using standard Image Sequence Analysis option supplied by software).

The difference between a parameter-weighted image and a T_2 -map is the following: in the map, every pixel corresponds to a certain value of T_2 , i.e., the map reflects the distribution of the T_2 value directly. In the parameter-weighted image, every pixel corresponds to a certain value of the NMR signal which combines the T_1 , T_2 , and proton density of the sample. Playing with the technical parameters of the imaging pulse sequence, one can adjust an appropriate contrast in the NMR image (this procedure is referred to as “weighting”) which will reflect the distribution of the signal influenced by the parameter of interest. Thus, the T_2 -weighted image represents the distribution of the NMR signal influenced by T_2 , diminishing the contributions of other parameters. As a result, T_2 -map and T_2 -weighted images could be similar but do not match exactly. However, for convenience, those regions in the images which demonstrate the significant effects were

defined and magnified, cutting off the rest of the image. Therefore, the highlighted regions of interest for different sets of images are presented apparently at similar levels although they are at different vertical positions.

The parameters of image acquisition were as follows: minimal slice thickness of 0.7 mm; field of view (FOV) of 40 mm; matrices of 128×128 (T_2 maps) or 256×256 and 512×512 pixels (T_2 -weighted images). The repetition time (TR) and echo time (TE) were adjusted over a wide range depending on the sample’s spin-lattice (T_1) and spin-spin (T_2) relaxation times to provide the best contrast. The time of image acquisition (TA) resulted from the TR and TE parameters, and the number of scans was maintained as short as possible; the echo train for the RARE technique consisted of 128 equally spaced echoes, and the number of echoes for the MSME technique was 28. Vertical T_2 profiles were evaluated by plotting T_2 versus the coordinate corresponding to the position of the pixel in the T_2 map.

Despite the common multiexponential nature of spin-spin relaxation in complex organic mixtures, NMR imaging works with an effective T_2 . This value comprises all contributions with their partial weights, and T_2 -weighted images are sensitive to changes of the relaxation time itself and weight of corresponding components.

It is worth noting that the NMR imaging technique itself in principle may slightly disturb the systems investigated because of acoustic noise and vibrations during the image acquisition. Careful analysis, however, revealed that different intensity of vibrations measured for various pulse sequence parameters TR and TE has no

influence on the image registered. This corroborates the results obtained before and indicates that the effect of vibration on the studied systems is negligible.^{49–51}

3. RESULTS AND DISCUSSION

3.1. Model *n*-Heptane/Asphaltene Solution in Toluene Systems. Because of the density difference between *n*-heptane and toluene, careful adding of the flocculant from the top on the surface of the asphaltene solution does not lead to immediate homogenization of the mixture. Instead, a slow process of counter diffusion of two miscible media occurs. Preliminary experiments revealed a big difference in relaxation times between the heptane and asphaltene solution in toluene: T_1 values observed for heptane and asphaltene solution were 2500 and 3200 ms, respectively, whereas T_2 values were 178 and 450 ms, respectively. Based on this difference, a deep contrast of the NMR images was expected for any operation scheme used.

As soon as 5 min after addition of the heptane onto the surface of the asphaltene solution, NMR images obtained clearly show the appropriate regions and mixing zone between them, Figure 1 (blue corresponds to flocculant area, and red corresponds to asphaltene solution; the mixing zone is mainly observed in green). As the counter diffusion process proceeds, a mixing zone becomes broader that is accompanied by partial homogenization of the sample. However, the mixing zone appears complicated: once the heptane contacts the surface of asphaltene solution in toluene, a thin layer (with thickness up to 1 mm, indicated by the white arrows in Figure 1) with lower signal intensity/relaxation time becomes visible in the images. This layer persists as long as the region nearby is strongly inhomogeneous (Figure 1, three images in a row from 5 to 70 min). For approximately 1 h after flocculant addition, the relaxation time of the central part of this layer increases, and the highlighted local zone eventually disappears (Figure 1, 4.5 h image). A continuous process of slow diffusion leads to the fact that after 1 day of experiment no signs of the former highlighted layer can be found in the blend. At this moment, the mixing process is complete and system appears homogeneous.

Appearance of the layer with lower relaxation time within the mixing zone, its evolution, and homogenization of the system are clearly seen also in the relaxation profiles plotted along the vertical axis of the tube, Figure 2a. According to the first profile (Figure 2a, 5 min), diffusion of the heptane into the asphaltene solution dramatically reduces the relaxation time in the mixing zone: the T_2 increase in the region of $0 < z/z_0 < 0.33$ is small as compared to T_2 decrease in the $0.33 < z/z_0 < 0.65$ region. Thus, the mixing zone visible in the images (Figure 1) is primarily formed by a T_2 drop near the asphaltene solution surface. In view of this observation, the thin layer revealed in the images most likely appears around the flocculant/solution interface and is seen as a gap in the relaxation profile. Furthermore, the position of the layer is slightly shifting downward as heptane and toluene are penetrating each other (Figure 2a, 5–70 min profiles). Close to the moment of system homogenization the gap disappears, which is in agreement with NMR images.

The gap on the relaxation profiles associated with the layer in NMR images is an essential effect of the system studied. A simple experiment with the same fluids (heptane and toluene in the same volume ratio) free of asphaltenes shows a normal fashion of the mixture homogenization (Figure 2b): the upper

part of the blend (heptane) slowly gains in T_2 value, whereas the T_2 value of the lower part of the blend (toluene) decreases during mutual diffusion of the fluids. As is seen, no signal gaps appeared in the reference profiles as heptane and toluene were penetrating each other.

Because of the nature of the model system comprising only mobile molecules of *n*-heptane and toluene (with long T_2) and relatively immobile molecules of asphaltenes (with short T_2), the thin layer with reduced T_2 value observed in either NMR images or relaxation profiles must be attributed to the asphaltenes-enriched region. The relaxation time of asphaltene molecules, however, is likely too short to contribute to the NMR signal directly; therefore, the apparent decreasing of T_2 in asphaltenes-enriched region is associated with a shortening of the relaxation times of the heptane and toluene molecules in asphaltene surrounding. Consequently, the increase of the local asphaltene concentration leads to a greater shortening of resulting T_2 for the particular region. However, there is another mechanism which can lead to shortening of the T_2 to a much higher extent than the simple concentration increase. This mechanism comes from the ability of flocculated asphaltenes to form clusters of aggregates with a porous structure. As was shown previously,^{49,50} flocculant-induced asphaltene precipitation gives raise to the deposits and sediments which reduce the apparent T_2 sufficiently because of increased specific surface area of the aggregated particles.

Taking into account these considerations, the nature of the phenomena observed is suggested as follows. Adding the heptane on the solution surface produces a strongly inhomogeneous distribution of the flocculant, making the interface region oversaturated by heptane. As a result, asphaltenes lose their stability and begin to aggregate. Eventually the aggregation process yields a deposit layer which was visualized in the mixing zone, Figures 1 and 2a. Active mutual penetrating of the heptane and toluene makes the system homogeneous with time, and local excess of heptane concentration disappears. Therefore, the aggregation is reversed and flocculated asphaltenes start to dissolve.

Based on the experimental data it is difficult to draw an unambiguous conclusion whether the asphaltenes are restabilized completely, i.e., do they form exactly the same state as they initially had or do we just observe homogeneous distribution of asphaltene flocks with the size smaller than the resolution of the method. However, there is some evidence in favor of complete reversibility. Neither images nor profiles demonstrate deposit or precipitated particles settled down on the bottom of the tube after homogenization of the system, i.e., the size of aggregates which could form is too small to provide a noticeable gravity-driven sedimentation. Yet the resulting T_2 value of the relaxed system seems to be relatively high as compared to those systems where the aggregation processes have occurred.⁵⁰

The heptane:asphaltene solution volume ratio in the present experiment was 1:1.5, which is well below the threshold value of the asphaltene precipitation onset in the case of the homogeneous mixture. For this reason, a spatial-selective asphaltene aggregation is reversible upon achieving the equilibrium state: the asphaltene precipitated layer is stable as long as local excess of flocculant concentration persists. If the overall concentration of flocculant appears higher than a threshold value of asphaltene precipitation onset, the asphaltene aggregation followed by precipitation should be expected in the whole volume upon achieving the thermody-

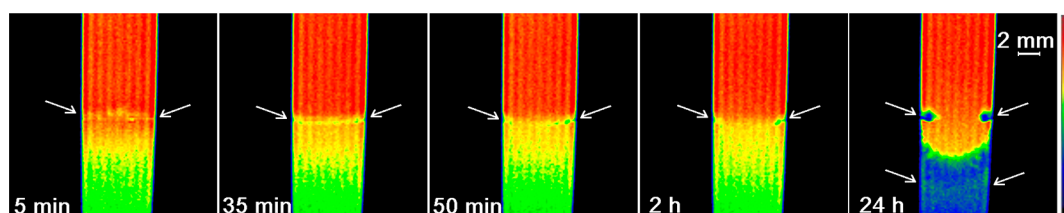


Figure 3. Series of PD-weighted NMR images obtained after adding the heptane from the top on the surface of asphaltene solution in toluene. The volume ratio of heptane to asphaltene solution is 2:1. Appearance of the thin layer within mixing zone and eventual deposit are indicated by the white arrows. Scale and time elapsed since the beginning of experiment are indicated in the figure.

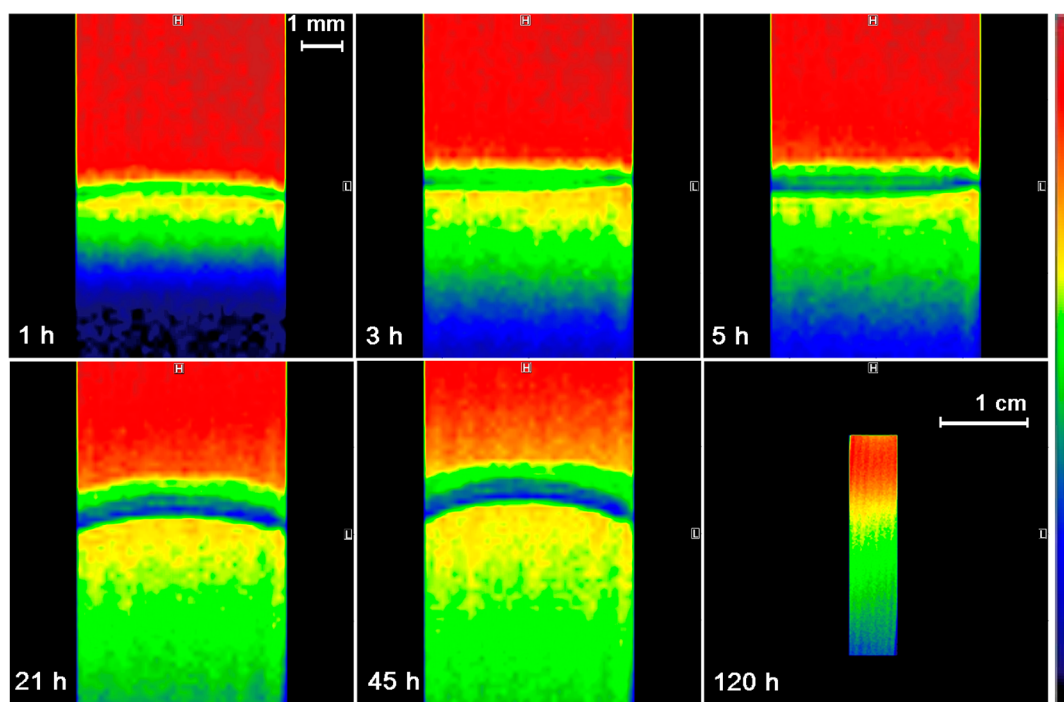


Figure 4. Series of T_2 -weighted NMR images obtained after adding the heptane from the top on the surface of heavy oil. The volume ratio of heptane to heavy oil is 1:1. Scale and time elapsed since the beginning of the experiment are indicated in the figure.

namically favorable homogeneous mixture. In this case, the flocculated asphaltenes may not completely dissolve. The experiment with the system having heptane:asphaltene solution volume ratio of 2:1 proved this suggestion: the asphaltene precipitated layer that appeared at the beginning of the experiment is dissolved partially until the concentration of heptane reaches the threshold for the precipitation onset, **Figure 3** (red corresponds to the heptane, green to the asphaltene solution, and yellow to the mixing zone). In contrast to **Figure 1**, the flocculant area demonstrates higher signal intensity due to prevalence of the PD-weighting: the heptane contains twice as many protons as toluene. Finally, dissolved asphaltenes turn into the deposit, whereas the remaining flocculated asphaltenes are still visible in the local zone around the former heptane/asphaltene solution interface (**Figure 3**, 24 h image).

The results obtained for the model asphaltene solution in toluene are difficult to compare with the previous data directly. Surprisingly, little knowledge is available in the literature about the reversibility of the flocculated/precipitated asphaltenes in models with respect to the changes of the system composition. Typically, the heavy oils and bitumen with high content of asphaltene are dissolved in toluene or polycyclic aromatic hydrocarbons to use as a model system for investigation.^{20,25,26}

The model asphaltene solution in methylnaphthalene was recently used³⁵ to isolate different factors influencing the asphaltene reversibility; however, a conventional invasive scheme of experiment was applied there, and the current issues were beyond the scope of that work.

Another reason for poor comparability of the experimental data obtained by different authors is the different methodologies used. Generally the reversibility tests have been performed either by evaporating of the flocculant (*n*-heptane, *n*-dodecane) or adding of the solvent (toluene, fresh oil); in this case, the mixtures and blends are essentially homogeneous because of the intensive stirring that is applied. Our experiments were primarily focused on asphaltene phase behavior in strongly inhomogeneous mixtures and blends; therefore, the flocculant was carefully added from the top on the sample's surface without any stirring. At the same time the noninvasive MRI technique in situ provides the data about transformations occurring within the system under negligible external impact. Nevertheless, our approach demonstrates the results which are consistent with the previous data, evidencing that the changes of system composition almost always lead to reversible asphaltene precipitation. It should be noted that the local reversibility of aggregated and flocculated asphaltenes that

occurs in a thin layer around interfaces is visualized for the first time.

3.2. Heptane/Heavy Oil Systems. Using the model samples composed of *n*-heptane and asphaltene solution in toluene, the basic regularities of local aggregation and flocculation of asphaltenes and its reversibility in spatially inhomogeneous system have been elucidated. However, the heavy oils consist of huge amounts of different chemical compounds that can lead to more complicated behavior of the system. For example, it is well-known that resins present in heavy oils are prone to stabilize the asphaltene molecules^{54,55} that may prevent or slow the precipitation process.

Density difference between the heptane and heavy oil accompanied by huge difference in their viscosities makes it easier to avoid mixing when adding the flocculant on the oil surface. The counter diffusion of the heptane and oil constituents is relatively slow, which assists capturing more detailed information during the experiment. Relaxation time measurements revealed an inversed difference between the heptane and heavy oil as compared to model samples: T_2 values of heptane are higher than those observed for heavy oil. This difference is big enough to provide deep contrast in the NMR images.

Similar to the model system, the addition of the heptane on the surface of heavy oil causes within the mixing zone the appearance of the thin layer (~ 0.4 mm thick) having low T_2 value/signal intensity that can be referred to the aggregated asphaltenes (Figure 4). Slow flocculant diffusion is the reason for slower dynamics of the processes taking place within the mixing zone and longer time required for the formation of this layer as compared to that observed in model samples. Long preservation of local excess of heptane near the interface region facilitates substantial growth of the layer thickness, which becomes approximately 0.8 mm thick after 2 days of experiment (Figure 4). The increase in the thickness of the layer is accompanied by simultaneous decrease in its signal intensity. Therefore, it is important to highlight that there is a kind of *aging phenomenon* of the layer with aggregated asphaltenes which was not observed in the model samples. Most likely the slow aggregation kinetics of asphaltenes in oil and its high viscosity are responsible for this effect; time elapsed from the beginning of experiment until complete dissolution of the asphaltene aggregates in model system is just a few hours, whereas it takes a few days in the case of heavy oil samples.

Slow mutual penetrating of the heptane and heavy oil results in eventual homogenization of the system. As soon as local excess of flocculant concentration disappears, the asphaltene precipitated layer starts to dissolve following the pattern observed in the model systems. For approximately 60 h after flocculant addition, the central part of the layer increases its signal intensity and eventually disappears. After 4 days, no signs of the former layer can be found in the sample. It is worth noting that dissolution of the asphaltene precipitated layer happens long before complete homogenization of the system.

The evolution of the system observed in the NMR images (Figure 4) is consistent with the relaxation profiles plotted along the vertical axis of the sample tube (Figure 5). As can be seen in Figure 5 (1 and 5 h profiles), the penetration of the heptane into heavy oil obviously prevails over the counter process: the T_2 increase under the heptane/oil interface ($z/z_0 = 0.5$) extends farther than the corresponding T_2 decrease above this interface. The gap in the relaxation profiles attributed to the asphaltene precipitated layer is located strictly at $z/z_0 = 0.5$

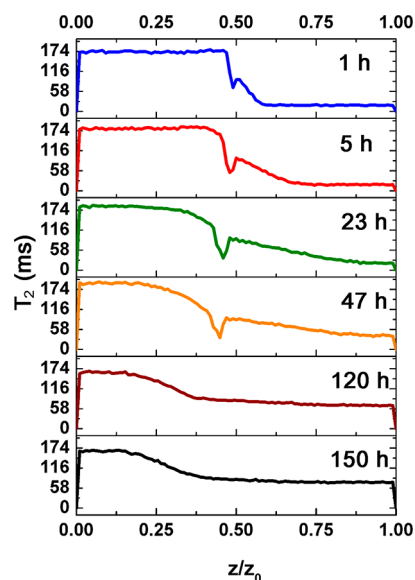


Figure 5. Series of vertical T_2 relaxation time profiles obtained after adding the heptane from the top on the surface of heavy oil. The volume ratio of heptane to oil is 1:1. Relative position z/z_0 starts from the top of the sample and comes to 1 at the bottom. Time elapsed since the beginning of the experiment is indicated in the figure.

level, i.e., the layer appears around the heptane/heavy oil interface. Furthermore, the position of the layer is slightly shifting upward as heptane and oil fractions penetrate each other, in contrast to the model system that demonstrated a downward shift of the layer. The counterintuitive upward shift and curving of the layer observed in the images (Figure 4) indicate osmotic pressure originating from intensive diffusion of heptane into “more concentrated” heavy oil. This means that the layer formed is sufficiently dense. The rather dense deposits can be formed in the crude oils as a consequence of aggregation of asphaltenes and numerous heavy constituents like maltenes, resins, and others. Despite the formation of a pronounced local zone having lower relaxation time, partial homogenization of the system initiates asphaltene aggregates dissolution that is in agreement with NMR images observed.

Interfacial reversibility of the asphaltene aggregated zone was observed in strongly inhomogeneous systems during their approach to the equilibrium state. In this case, the local excess of heptane concentration exceeding the threshold value for asphaltene precipitation onset around the interface is a driving force of this process. The homogenization of the system, for example by mechanical stirring, diminishes the driving force of the process and leads to the decrease of the size of the local zones where phase separation is observed. Surprisingly, a simple experiment with partial stirring of the heptane/heavy oil mixture shows persistence of the phenomenon of local asphaltene aggregation. Huge density and viscosity differences between heptane and heavy oil considerably decrease the rate of system homogenization and bring about the preservation of the local phase separation phenomenon and segregation of the aggregated asphaltenes despite 1–2 min stirring having been applied prior the experiment (Figure 6; the heptane area is presented by red, while the oil area is blue). As can be seen, stirring results in partial homogenization of the system and broadening of the mixing zone (Figure 6, 0 h image). Nevertheless, the driving force of the aggregation process is still preserved, and the relaxation profile demonstrates the

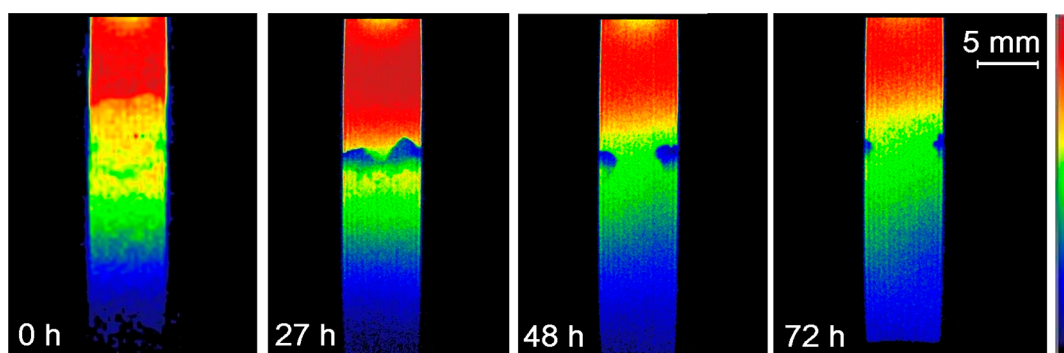


Figure 6. Series of T_2 -weighted NMR images obtained after short time stirring of heptane and heavy oil mixture. The volume ratio of heptane to heavy oil is 2:1. Scale and time elapsed since the beginning of the experiment are indicated in the figure.

formation of the gap 2 h after the experiment start (Figure 7, 2 h profile). In contrast to previous experiments, the asphaltene

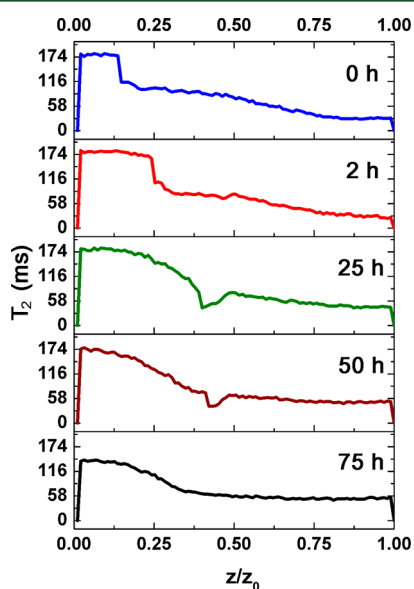


Figure 7. Series of vertical T_2 relaxation time profiles obtained after short time stirring of heptane and heavy oil mixture. The volume ratio of heptane to oil is 2:1. Relative position z/z_0 starts from the top of the sample and comes to 1 at the bottom. Time elapsed since the beginning of experiment is indicated in the figure.

precipitated layer is no longer thin and uniform, which is likely caused by local inhomogeneities in spatial distribution of heptane concentration after stirring (Figure 6, 27 h image). Once the local excess of flocculant concentration decreases, the dissolution of the aggregated layer is observed (Figure 6, 48 h image). This process continues until the system becomes homogeneous. In 3 days after the experiment start, only the tiny residual part of this layer is visible in the images (Figure 6, 72 h image). Again the dissolution of the asphaltene precipitated layer happens long before complete homogenization of the system, indicating the key role of local characteristics in the reversibility phenomenon observed.

The results of the experiment with partial stirring of heptane/heavy oil system demonstrates that the reversibility of asphaltene aggregated zones could occur inside the stock tanks or other oil production facilities when the light oil (with high content of light hydrocarbons) meets the heavy oil and forms a blend. Recently it was demonstrated that the

destabilization of asphaltenes occurs virtually immediately after a precipitant is added.⁵⁶ Thus, the aggregation process could start regardless of the overall flocculant–oil ratio. In this case, the interfaces in multiphase systems could modulate the rheological properties of the media within the pipelines, tanks, and other reservoirs.

Generally the results obtained for heavy oil are very similar to those observed in models. In particular, except the slow dynamic and aging processes, the asphaltene precipitated layer in heptane/heavy oil blend demonstrates the same reversibility patterns as those monitored in the heptane/asphaltene solution mixture. However, the reversibility phenomenon in a certain sense contradicts previous observations. Investigation of *iso*-octane/asphalt solution in toluene blends revealed the formation of the prominent interfacial deposit containing spherical globules.⁴⁵ This deposit layer was not prone to reversible dissolution, and normal asphaltene precipitation followed by sediment accumulation on the bottom was clearly observed simultaneously with the interface layer. Compositional analysis of that layer showed the prevalence of resin-like compounds which were the result of high-temperature oxidative aging of asphalt.⁴⁵ Consequently, the greater the degree of aging, the more prominent the observed deposit layer. The morphology of the layer, its dynamics, and composition indicate the phase separation process of aggregated compounds: aggregated and flocculated asphaltenes sink, whereas the aged constituents stay around the interface. In contrast, our results are purely the flocculant-induced spatial-selective asphaltene aggregation/flocculation, which is reversible upon blend homogenization.

4. CONCLUSIONS

In this paper, the reversibility of the asphaltene aggregation process in strongly inhomogeneous systems formed by flocculant and either asphaltene solution in toluene or heavy oil was investigated using magnetic resonance imaging techniques. MRI applied for *in situ* monitoring of the processes occurring in the blends demonstrates the feasibility of this technique for obtaining valuable information about the phenomenon of asphaltene aggregation reversibility. Adjusting the contrast in the NMR images and using the T_2 distribution maps enable proper visualization of the appropriate local regions of the blend and the quantitative measurement of their dynamics. It was determined that the local inhomogeneities of the flocculant concentration initiate spatial-selective asphaltenes aggregation detected as a thin deposit layer located around the interface between flocculant and asphaltene solution (heavy

oil). The local excess of flocculant concentration over the threshold of asphaltene precipitation onset is a driving force of this process. When the equilibrium state is achieved throughout the system volume, the asphaltene aggregated layer was found to disappear as the dissolution process occurs. Depending on the overall flocculant concentration (flocculant to sample volume ratio), the dissolution of the asphaltene aggregated layer may not be complete and even could be followed by subsequent precipitation over the whole volume of the sample.

The identity of the phenomena observed was demonstrated for the model asphaltene solutions and crude heavy oil sample. Some differences of local aggregated layer morphologies and dynamics are found, reflecting the complex nature of heavy oils composed of different constituents. Partial stirring of the mixed system, which often happens in petroleum industry, does not prevent the formation of local zones of aggregated asphaltenes as well as their dissolution upon achieving the equilibrium composition state. Consequently, formation of the local asphaltene aggregated zones and their dynamics in multiphase systems should be taken into account when modeling the fluid flow, rheological parameters, mass and heat transfer within the pipelines, catalytic reactors, and other petroleum facilities. The results obtained in this work are consistent with the generally accepted concept of asphaltene precipitation reversibility with respect to the changes in system composition and are compatible with observations carried out by other methods. The approach presented in this work can provide deeper insight into the asphaltene precipitation reversibility issue and facilitate better understanding of asphaltenes behavior in heavy oils.

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Notes

The authors declare no competing financial interest.

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