Asphaltene Deposition and Removal in Flowlines and Mitigation by Effective Functional Molecules

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Summary

Efficient removal of deposited asphaltenes on the surface of metallic flowlines by functional molecules is investigated by nonionic and ionic surfactants at low concentrations. Deposition removal by aromatic solvent toluene is measured as a reference. Water is often coproduced with crude oil and may affect deposition of asphaltenes and removal. In this study, we investigate the effect of water in both asphaltene deposition and removal by functional molecules. Two different crudes from different fields that give rise to serious asphaltene deposition are extensively investigated. For these two crudes, we find one ionic and one nonionic surfactant to be effective in deposition removal at 1 wt% concentration in the crude. This concentration is much lower than that of the commonly studied acidic dodecylbenzene sulfonic acid (DBSA) surfactant. Toluene concentration in the crude varies from 40 to 60 wt% for asphaltene deposition removal. Water delays deposition significantly. However, water does not have an appreciable effect on performance of functional molecules on removal of deposited asphaltenes.

Introduction

Asphaltenes are the most polar components of crude oil known to be soluble in aromatic solvents but insoluble in paraffinic liquids (Goual and Firoozabadi 2002; Speight 2014). They consist of polycondensed aromatic sheets, aliphatic side chains, heteroatoms of nitrogen, sulfur, and oxygen, and metal impurities like vanadium and nickel (Firoozabadi 1999; Akbarzadeh et al. 2007). The aromatic rings often stack in the crude oil, giving rise to colloidal aggregation and sedimentation (Andreatta et al. 2005). Asphaltenes in crudes may precipitate and then deposit on solid surfaces from changes in temperature, pressure, and crude oil composition as the oil flows from the reservoir to wellbore, wellhead, transport pipelines, and ultimately into downstream treatment facilities. Asphaltenes form an unstable oil mixture, go through molecular and colloidal-scale aggregation, sedimentation, and eventual deposition and adsorption on surfaces, causing operational complications. There are two chemical methods in asphaltene mitigation. One is the removal of deposited asphaltenes by aromatics like toluene at high concentration or through effective functional molecules at low concentration, which is the subject of this paper. The other approach is through stabilization of asphaltene particles in the crude by a very small concentration of functional molecules (Hashmi et al. 2010; Aslan and Firoozabadi 2014; Paridar et al. 2018). The first method is a batch process. It is implemented once deposition has built up after a few weeks to months. The second process is continuous.

Generally, some light crude oils with low asphaltene content give rise to asphaltene deposition (Ting et al. 2007). The process has been linked to higher instability and lower solubility of higher molecular weight asphaltenes in light oils (Zendehboudi et al. 2014). Crude oils with high saturates (including naphthenes) and low aromatics have lower stability of asphaltenes than crude oils with similar asphaltene content but higher aromatic content (Gabrienko et al. 2014). Gas mole fraction in the crude oil composition also plays a role in asphaltene precipitation. Higher gas mole fraction increases both asphaltene onset pressure and maximum weight percent of precipitation (Ngheim et al. 1998). Formations with high gas-to-oil ratio are known to suffer from precipitation problems (Al-Taq et al. 2016).

As mentioned above, asphaltene mitigation can be achieved by two types of functional molecules. In one approach, asphaltenes are allowed to separate from the crude but they are stabilized as small particles by very low concentration of functional molecule. This category of functional molecules is referred to as dispersants (Hashmi et al. 2015; Rashid et al. 2018). In vials, the stabilized asphaltene particles sediment slowly. The second category of functional molecules are polymers that can dissolve deposited asphaltenes on the surfaces in the crude (Hashmi and Firoozabadi 2016). The concentration required for dissolution is higher than the dispersants but much lower than aromatic solvents such as toluene.

Asphaltene dispersants are effective due to their strong polar hydrophilic heads and lipophilic tail structures (Chang and Fogler 1994). The selection of functional molecules largely depends on the polarity of asphaltenes in the oil. The asphaltene dissolution can be a result of acid/base interactions, hydrogen bonding, and Π-Π associations of the aromatic rings (Hashmi et al. 2015; Madhi et al. 2017). The concentration of inhibitors is equally important. DBSA is an amphiphilic molecule that has been studied extensively for asphaltene mitigation due to its strong ionic properties (Rogel et al. 2001; Al-Sahhaf et al. 2002). Goual and Firoozabadi (2004) conducted systematic tests to study the effect of resins with different dipole moment and concentrations (2.4–3.2 D, 7–23 wt%) and DBSA at different concentrations (0.3–5 wt%) on asphaltene precipitation in three different petroleum fluids. The amount of precipitated asphaltenes was found to increase with the addition of resins; however, resins with high dipole moment resulted in only a slight increase in precipitation. There was an increase in precipitation up to a DBSA concentration of 1 wt%. However, increasing DBSA concentration from 1 to 5 wt% reduced the precipitation as well as delayed onset point. DBSA is believed to dissolve deposited asphaltenes. Some of the functional molecules may operate as dispersants as well as molecules that can dissolve deposited asphaltenes (Hashmi and Firoozabadi 2016). In the early work, these two features were not recognized (Hashmi and Firoozabadi 2013).

Hashmi et al. (2010) studied the delay of asphaltene precipitation and sedimentation in a vial from a Mexican crude oil containing 3.5 wt% asphaltenes by the addition of two proprietary dispersants and an anionic surfactant at concentrations ranging from 0.5 to 200,000 ppm. Anionic surfactant, even at 20 wt% concentration, was not found to be effective in delaying sedimentation. Hashmi and Firoozabadi (2010) reported the effect of the changing amount of n-heptane dilution and dispersant addition (as low as 2 ppm with respect to n-heptane) on asphaltene deposition and sedimentation. In dissolution, Hashmi and Firoozabadi (2013) highlighted the dependence of effective DBSA concentration in asphaltene colloidal stabilization on various factors—oil type, resins, heteroatomic and

metal content of asphaltenes. The primary mechanism of asphaltene dissolution by DBSA is the protonation of the heteroatoms in the asphaltene molecule by the strong acid.

Water may affect the asphaltene stability and dissolution in vials. Subramanian and Firoozabadi (2015) studied the effect of water and brine on the action of a nonionic surfactant and ionic DBSA surfactant on asphaltene precipitation in two crude oils. They conducted vial sedimentation by adding paraffin n-heptane, and measured aggregate size and electrophoretic mobility of asphaltene particles. Addition of up to 8 wt% of water or brine to crude oil did not affect the amount of precipitation, same was the case in the presence of 50 ppm of nonionic surfactant mixed with crude oil. However, for 5 wt% DBSA in crude oil, increase in water content increased the amount of precipitation in vials.

Asphaltene stability and dissolution in bulk in glass vials have been the predominant approach in the literature in asphaltene mitigation research. Deposition on metallic surfaces and rocks with and without flow has been investigated to a lesser degree. Asphaltene deposition and surfactant effectiveness can be greatly influenced by the surface properties. The surface type of both the porous media as well as the production flowlines can affect the rate and amount of asphaltene deposition and the performance of surfactant to mitigate the deposition. Behbahani et al. (2015), in addition to mathematical modeling of asphaltene deposition, have also performed deposition measurements in coreflooding in carbonate, sandstone, and dolomite rocks using live crude oils. They showed that asphaltene deposition in carbonates is more pronounced than in sandstone. They also performed experiments in dead oil and observed a similar trend.

A recent study by Sultan et al. (2018) included bulk asphaltene precipitation, and deposition using asphaltenes extracted from Athabasca bitumen on two types of surfaces—stainless-steel and glass—in the presence of varying concentrations of DBSA surfactant. The deposition tests were conducted in a glass column consisting of stainless-steel or glass beads. In both surfaces, increase in n-heptane concentration increased asphaltene deposition. For stainless-steel surface, addition of DBSA at 10,000 ppm and higher concentrations increased the asphaltene deposition, while for glass surface, DBSA at 10,000 and 25,000 ppm concentrations reduced deposition. They also examined the effectiveness of DBSA to remove already deposited asphaltenes by varying concentrations from 0 to 50,000 ppm. In glass surface, addition of DBSA at 30,000 ppm partially removed deposition, with complete removal achieved at 50,000 ppm. Conversely, in steel surface, even 50,000 ppm DBSA could not remove the deposited asphaltenes. They argued DBSA surfactant molecules to have an affinity to the stainless-steel surface, thereby promoting the adsorption of the surfactant-asphaltene aggregate onto the surface.

Vial tests may provide qualitative information regarding inhibitor effect on asphaltene precipitation. Flow and deposition and removal in metallic tubing provide more relevance to asphaltene mitigation in conduits. Surface effects may be a key element of the investigation. The effectiveness of functional molecules in delaying asphaltene deposition does not necessarily relate to efficiency in deposition removal. The effect of water on deposition by functional molecules may be also integrated in asphaltene deposition and removal by surfactants. Water, often coproduced with oil, is polar, and can associate with asphaltenes, as well as with the surfactants. It can also be adsorbed by the metal surfaces altering the wettability. Water may also associate with heteroatoms in asphaltene molecules or their aromatic rings (Anderson et al. 2001). Asphaltene deposition in flowlines has been studied in the past (Boek et al. 2008; Nabzar and Aguiléra 2008; Hoepfner et al. 2013; Hashmi et al. 2015) without consideration of the effect of water. All of these studies are based on creating asphaltene deposition using solvent-n-heptane. Aslan and Firoozabadi (2014) conducted flow tests to observe the effect of water in delaying asphaltene deposition in flowlines. They used n-heptane to induce asphaltene deposition in the flowline. They found that 1 vol% of deionized water, when coinjected into the flowline along with crude oil and n-heptane, affected asphaltene deposition, delaying the process. Contact angle measurements showed that the stainless-steel surface was oil-wetting. They measured the size of asphaltene aggregates in the presence of water, and differential interference contrast imaging as well as dynamic light scattering indicated that there is no noticeable change in average aggregate size with and without water. However, viscosity measurements showed that below 2,000 ppm water concentration, there was a decrease in viscosity, but above 2,000 ppm of water concentration, there was an increase in viscosity of crude oil and n-heptane mixture for the three crude oils investigated. They attributed the delay in asphaltene deposition in the presence of water to be due to hydrogen bonding between water molecules and the heteroatoms in the asphaltene molecules and change of wetting.

The flowline measurements above was focused on asphaltene deposition. In regard to effect of functional molecules on reducing deposition on the surface, Kuang et al. (2019a) investigated three commercial dispersants and three alkylphenols on their effectiveness to reduce asphaltene deposition in a crude oil and n-heptane mixture in a polytetrafluoroethylene multisection packed bed column having three sections, each packed with carbon steel spheres (3/32″ D), at 25°C and 1 atm. Crude oil (without and with dispersants) and n-heptane were injected from separate syringe pumps at constant volumetric flow rate, mixed together and injected from the bottom of the column to the top. Three different flow rates were used—9, 12, and 15 cm³/h, but the experiment duration was adjusted so as to inject a total of 54 cm³ of fluid volume in each run. Asphaltene deposition on the spheres in the column sections was then measured in milligrams by weighing the sections individually. The dispersive performance efficiency of the chemicals was first measured via vial tests, and then these chemicals were mixed in the crude oil at varying concentrations of 60, 70, and 200 ppm to test their deposition reduction efficiency in the flow tests. It was found that dispersants with high dispersive efficiency did not necessarily reduce the amount of deposition. Interestingly, some of the chemicals even increased the amount of asphaltene deposition compared to the base case of no chemical in the crude oil.

Conventional aromatic solvents such as toluene and xylene are often applied in the field to remove asphaltene deposition (Al-Taq et al. 2016; Budd et al. 2018; Kuang et al. 2019b). The process requires stopping the production and keeping the surfaces soaked by the aromatics for considerable periods of time. Kuang et al. (2019b) investigated the optimum solvent wash strategy for remediation of asphaltene deposition in a high temperature, high pressure packed bed column at 80°C and 100 psi backpressure. N-heptane and crude oil were first injected to induce asphaltene deposition in the column, the deposited asphaltenes were then aged at 120°C, and subjected to solvent soaking at 120°C. They measured the amount of asphaltenes removed after 24 hours of soaking by 1 pore volume (PV) of solvent and compared it with the solubility power of solvents. Aromatic naphtha, having the highest solubility parameter, resulted in lowest asphaltene redissolution (34.7 wt% of original deposition) compared to p-xylene (55%) and toluene (46.3%). It was reported that a solvent having high solubility power might not necessarily have high asphaltene deposition removal efficiency.

The functional molecules are generally more expensive than aromatic solvents; however, due to considerable difference in the quantities required, the former can be more economical overall. Moreover, exposure to aromatic solvents such as toluene for long time period can have a deteriorating impact on the central nervous system. Toluene is a neurotoxin, which has been studied to cause neurobehavioral dysfunction (Filley et al. 2004). Efficient removal of deposited asphaltenes by functional molecules has rarely been investigated. Schantz and Stephenson (1991) reported field case studies in, which polymeric dispersants were first selected by performing asphaltene dispersancy vial tests in the laboratory by mixing various concentrations of dispersants in crude oil consisting of 5–15 wt% asphaltenes and inducing precipitation through n-hexane. Then the best dispersants were directly applied to fields experiencing production slow down or shut down due to clogging of wellbores and pipelines. They, however, did not perform laboratory testing in flowlines to observe asphaltene deposition removal.

Hashmi and Firoozabadi (2016) conducted flow testing in flowlines to study effectiveness of organic acid surfactant DBSA compared to the aromatic solvent toluene to remove deposited asphaltenes. They found 5 wt% DBSA to dissolve deposited asphaltenes at ten times lower concentrations than toluene (50 wt%).

The broad literature review above shows limited work on asphaltene removal deposition. One difficulty in pipe flow systems is that very large duration is required. Although live crude oils and stock tank crude oils may be different, an attempt can be made first to deposit asphaltenes, explore the efficiency of their removal, and then follow-up by high-pressure live oil conditions. This study focuses on a search for effective surfactant molecules to remove asphaltene deposition in metallic flowlines. Two light crude oils from the Middle East are investigated. There is no deposition in the wellbore from one of the two crudes. There is mainly deposition on the well tubing. In the other crude, there is deposition in the wellbore. A group of six nonionic and ionic surfactants and aromatic solvent toluene are examined in deposition removal from stainless-steel flowlines. Simple bottle tests and microscopic imaging are also performed. It should be noted that the vial tests serve as a preliminary examination, the conclusions are drawn only after performing the dynamic flow tests in stainless-steel flowline. The effect of water on asphaltene deposition and removal is studied by adding known concentrations of water to the crude oil in deposition, as well as to the crude oil and surfactant in removal of deposition. To the best of our knowledge, no dynamic flow tests have previously been conducted to study the effect of low concentration of surfactants, in the presence of water, on deposition removal in metal capillary tubes. pH measurements are performed on the water equilibrated with the base oil, and oil mixed with the nonionic and ionic surfactants, to assess the corrosive tendencies of the chemicals in field-scale projects.

Materials and Methods

Two crude oils are used in this study—MN-132 from Kuwait and BAB from UAE. **Table 1** lists the properties. Viscosity (at 25°C) and asphaltene content are higher in BAB oil compared to MN-132. A group of six nonionic and ionic surfactants, provided by Lubrizol Corporation, are investigated in the mitigation of asphaltene precipitation in static tests and removal of asphaltene deposition in flow tests. The relevant data are listed in **Table 2**. Toluene, *n*-heptane, and deionized water are also used in the study.

Sample	Density (g/cm^3)	Viscosity at 25°C (cp)	Asphaltene Content (wt%)
BAB	0.8570	8.8	4.85
MN–132	0.8346	5.1	0.60

Table 1—Crude oil sample properties.

Name	Type	Description
N1	Weakly ionic	Alkylphenol polymer/quaternary amine polymer
N2	Nonionic	Alkylphenol polymer resin
N3	Nonionic	Alkylphenol polymer resin
BA	Nonionic	Polyolefin ester
DBSA	Ionic	Dodecylbenzene sulfonic acid
A35	Ionic	Polyolefin diester/disalt

Table 2—List of surfactants.

Vial Tests. Vial tests and microscopic imaging by a Leica DM 2700M microscope (Leica Microsystems Inc., Buffalo Grove, Illinois, USA) are performed to observe the precipitation of asphaltenes from the two crude oils. The goal is to assess the chemical efficiency in mitigation of asphaltene precipitation. Oil and *n*-heptane are mixed in proportion of 0.125 g and 2.5 cm^3 (1 g: 20 cm^3 ratio). The surfactants are then added at concentrations of 1 and 5 wt% with respect to crude oil. The vials are sonicated and allowed to stand. Asphaltene precipitation is monitored over a period of 7 days. Additionally, the effect of water on surfactant performance is monitored by mixing 50 wt% water with respect to crude oil in the vials.

Dynamic Flow Tests. Effect of surfactants, the aromatic solvent toluene, and water is investigated on removal of asphaltene deposition. We also investigate the effect of water in asphaltene deposition by mixing water (at 1 wt% in the crude oil) with the crude oil and the precipitating *n*-heptane, from the start of the experiment. In all the flow tests, the asphaltene deposition and removal are interpreted via pressure drop data using a pressure transducer. Omega pressure transducers are used in this study with the following specifications— model number: PX409-050GUSBH, pressure range: 0–50 psig (Omega Engineering, Inc., Norwalk, Connecticut, USA). Effectiveness of various functional molecules and toluene in deposition removal is quantitatively measured by the PV of the fluid flow in the flowline. Throughout the text, 1 PV refers to the volume of the flowline.

Fig. 1 presents the schematic of the experimental setup in flow testing. The figure includes an additional pump for water injection. In tests without water injection, the water pump is excluded from the setup. In the first step, crude oil and *n*-heptane are injected from two separate syringe pumps (KD Scientific Inc., Holliston, Massachusetts, USA) at 0.35 and 1.05 cm^3/h, respectively (1:3 volumetric ratio). In the second step, after the pressure drop across the pipe exceeds 15 psig due to asphaltene deposition, the *n*-heptane injection is stopped and crude oil alone is injected. The purpose of this step is to observe whether shearing due to oil flow is sufficient to remove the deposition. This step is omitted in subsequent runs because it is observed that deposition is not removed. The last step is to inject crude oil mixed with surfactant at specific concentrations to examine the effect of surfactant on the removal of deposited asphaltenes. In some flow tests we examined the removal of deposited asphaltenes by high concentration toluene dissolved in the crude oil. Two important parameters are noted while determining surfactant effectiveness—the buildup/decline in pressure caused by the asphaltene deposition/removal, and PV required to remove the asphaltene deposition in the flowline via surfactant or surfactant and water. After every test, the pipeline was repeatedly washed by flowing toluene through it, dissolving the remaining asphaltene deposits. The toluene washing was continued until the solvent flowing out of the pipeline was colorless, indicating complete removal of the deposition. The syringes, fittings, and connectors were all cleaned using the same method as the tubing. Next, all the components of the setup were placed in the oven at 55°C overnight to dry completely.
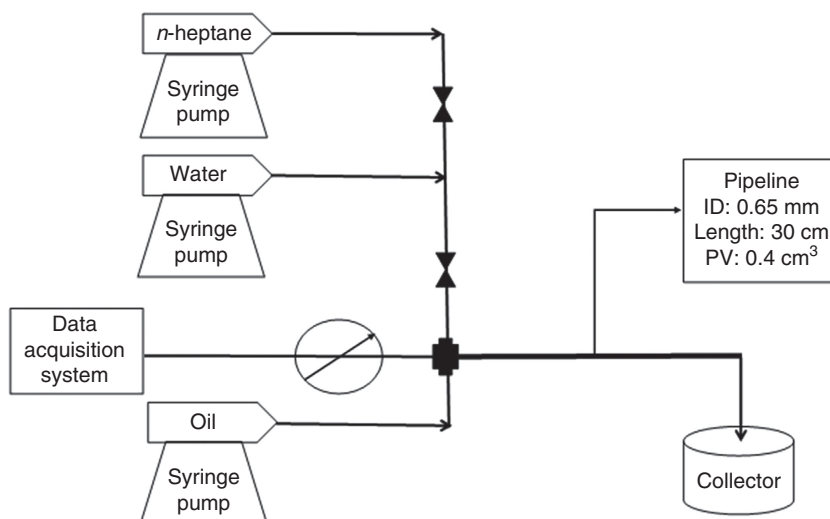
Fig. 1—Schematic of experimental setup for flow test experiments. Pipeline (shown in bold) length = 30 cm, internal diameter = 0.65 mm, PV = 0.4 cm³.

pH Measurements. Equal volumes of deionized water and crude oil (without and with the concentrations of nonionic and ionic surfactants mixed in the oil, as used in the flow tests) are mixed. The water is then allowed to separate and the pH is measured by an Apera Instruments pH20 pH tester (accuracy ± 0.1; Apera Instruments, Columbus, Ohio, USA) to assess whether the chemical might lead to side effect corrosion.

Results and Discussion

Vial Tests. Structural arrangement of asphaltene aggregates are viewed and compared in the two crude oils. The asphaltene layer is monitored over a period of 7 days. The amount of precipitated asphaltenes is observed to be higher for BAB oil than MN-132 oil. Microscopic imaging shows structural differences in aggregation of precipitated asphaltene molecules. The images are captured after 7 days for the top supernatant and bottom asphaltene layers. The vial and microscopic images are shown in **Figs. 2 and 3,** respectively. It is observed that the aggregation of asphaltene molecules is more significant in BAB oil compared to MN-132 (Fig. 3b).
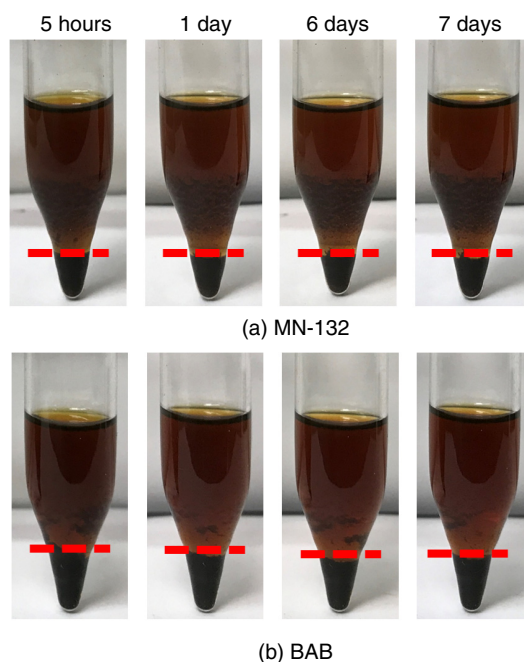
Fig. 2—Vial images showing asphaltene precipitation with time: MN-132 and BAB oils.

Vial tests may serve as a screening process to analyze the effectiveness of surfactants in asphaltene precipitation. The first set of vial tests are shown in **Fig. 4** for MN-132 oil and in **Fig. 5** for BAB oil. Two surfactant concentrations—10,000 and 50,000 ppm, corresponding to 1 and 5 wt%—are used for analyses. We allow the samples to stand in glass vials for 7 days and then examine the black layer of asphaltene precipitation observed at the bottom of the vials. This layer is shown by a red dashed line in the figures. Smaller volume of precipitated asphaltenes, and darker color of the supernatant indicate effectiveness of functional molecules in keeping the asphaltenes dissolved in solution.
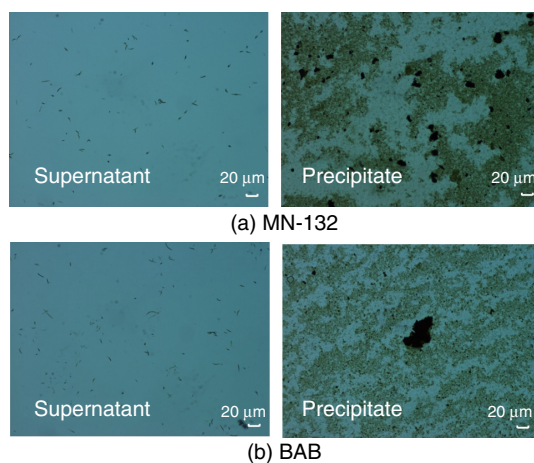
Fig. 3—Microscopic images of supernatant and precipitant in vials after 7 days: (a) MN-132 and (b) BAB oils.
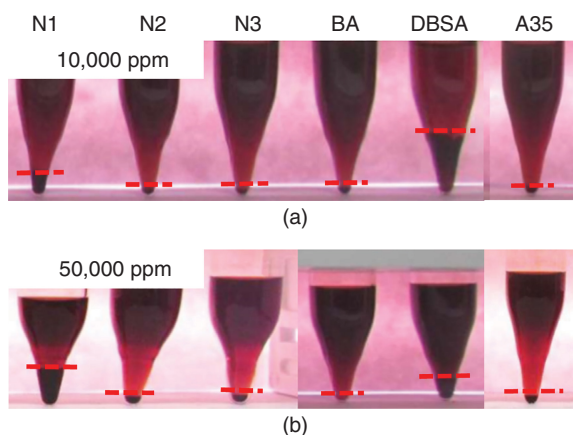

Fig. 4—Precipitated asphaltene in chemicals mixed with crude and heptane at concentrations of 10,000 and 50,000 ppm: MN-132 oil; time = 7 days.
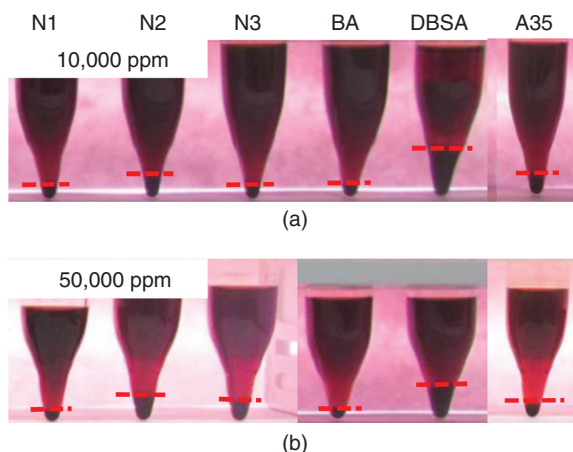

Fig. 5—Precipitated asphaltenes in chemicals mixed with the crude and heptane systems at concentrations of 10,000 and 50,000 ppm: BAB oil, time = 7 days.

For MN-132 oil, at 10,000 ppm, N2, N3, BA, and A35 chemicals are particularly effective. DBSA induces higher asphaltene precipitation compared to the other chemicals (Fig. 4a); it is the least effective. At 50,000 ppm, N1 and DBSA are found to cause considerable asphaltene precipitation, with N1 being the least effective (Fig. 4b).

In BAB oil, as shown in Fig. 5, apart from DBSA, all surfactants show comparable results. However, asphaltene precipitation is significantly higher from DBSA, similar to what is observed in MN-132 oil.

Water is known to interact with asphaltenes in crude and may form water-in-oil emulsions. The stability of water-in-oil emulsions is governed by a rigid asphaltene film of high interfacial elasticity, surrounding the water droplets and preventing their coalescence (Fan et al. 2010; Pradilla et al. 2015). The interfacial elasticity is an indication of the strength of asphaltene aggregation. We study the effect of water on surfactant performance by adding 50 wt% water (with respect to crude oil) to the vial mixtures. The vial images after 7 days are presented in **Figs. 6 and 7,** for MN-132 and BAB oils, respectively.
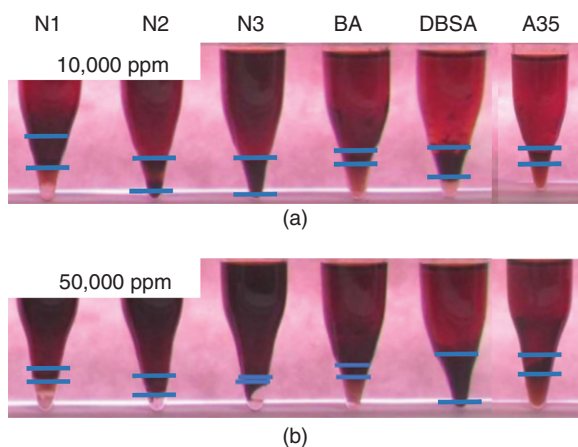
Fig. 6—Precipitated asphaltene and separated water in the crude/heptane/water system mixed with chemicals at concentrations of 10,000 and 50,000 ppm in MN-132 oil, all samples with 50 wt% water: time = 7 days.
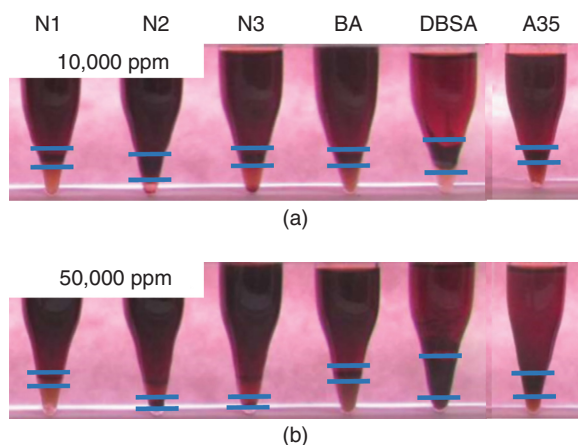

Fig. 7—Precipitated asphaltene and separated water in the crude/heptane/water system mixed with chemicals at concentrations of 10,000 and 50,000 ppm in BAB oil, all samples with 50 wt% water: time = 7 days.

No significant improvement is observed visually in the chemical performance by water addition. The water layer settles at the bottom due to higher density. The asphaltene layer settles at the top of the water layer, enclosed by two blue lines as shown in Figs. 6 and 7. The amount of asphaltene precipitation appears to be about the same as without water. The asphaltene layer may contain water-in-oil emulsions. In both MN-132 and BAB oils, the highest amount of asphaltene separation is observed in DBSA (50,000 ppm). This is consistent with the observations when there is no water.

In the flow testing section, we will show that water has a significant effect on deposition, consistent with the previous work (Aslan and Firoozabadi 2014), but does not affect the removal of asphaltene deposition by the surfactants.

Flow Tests. In the flow experiments we compare effectiveness of various functional molecules in asphaltene deposition removal with the aromatic solvent toluene. We also investigate the effect of water on the performance of the functional molecules. As part of the investigation, we analyze the delay in deposition of asphaltenes in flowlines due to water. Intermittent fluctuations in pressure drop in the flowline can arise from rearrangement of asphaltene aggregates deposited on the pipe surface (Hashmi et al. 2015).

Flow Tests: Effect of Surfactants on Removal of Asphaltene Deposition. The effectiveness of surfactants is observed to be higher for MN-132 than BAB oil. This is in line with the more severe asphaltene aggregation and networking observed for BAB oil (Fig. 3b). In general, a number of surfactants at 10,000 ppm (1 wt%) are found to be effective for removal of deposition in MN-132. Because these chemicals are intended to be injected in batch treatments in field-scale, 1 wt% concentration is set as the desired concentration in the crude. One major goal is to find effective functional molecules at 1 wt% for both crudes.

For MN-132 oil, most of the surfactants can remove the deposition at low PV flow at 1 wt% concentration. However, relatively higher volume (25 PV) of DBSA is needed to completely dissolve deposited asphaltenes. In BAB oil, only A35 and N2 are effective. Only surfactant A35 can remove deposition at 1 wt%. N1 requires 40 PV at 50,000 ppm to remove deposition. **Table 3** summarizes the results of all flow tests. We have repeated some of the flow experiments to examine reproducibility. N2, A35, and DBSA results of pressure drop with respect to PV flow in both oils are presented in **Fig. 8**. All the other flow test results and repeat runs for MN-132 and BAB oils with varying concentrations of the six surfactants are presented in **Figs. 9 through 12**.

In all the plots, the start of flow of surfactant mixed with oil is represented by the first dashed red line (from left). This indicates the pressure drop exceeds 15 psi from deposition of asphaltenes. The reduction in pressure drop to a value close to the initial low pressure drop is an indication of removal of asphaltene deposition. The PV required to remove deposition is shown in the plots. The region of removal is enclosed by the red dashed lines. The flow rate in terms of PV/D for each stage of the runs is represented at the top of the graphs.

Oil Sample	Functional Molecule	Chemical Conc. (ppm)	PV to Remove Deposition
MN–132	N1	10,000	6
	N2	10,000	10
	N3	10,000	12 ± 3
	BA	10,000	9 ± 1.9
	DBSA	50,000	24.8 ± 0.3
	A35	10,000	10
BAB	N1	50,000	40
	N2	50,000	6.5 ± 0.5
	N3	50,000	X
	BA	50,000	X
	DBSA	50,000	X
	A35	50,000	3
	A35	10,000	14

X denotes that the chemical is not effective.

Table 3—Summary of flow test results.

Fig. 8 shows the pressure drop vs. PV flow for A35, N2, and DBSA. For MN-132 oil and BAB oil, 1 wt% A35 functional molecule dissolved in the two crudes is effective in the removal of deposited asphaltenes. This is the most effective molecule in both crudes. The functional molecule N2 is effective in deposition removal in MN-132 at 1 wt%; however, for DBSA, 5 wt% concentration is required. Note that DBSA (Fig. 8a), which has been presented as an effective molecule in the literature (Wang et al. 2004; Salimi et al. 2016), is much less effective than A35 and N2 molecules for MN-132 oil. Fig. 8b shows that DBSA is not effective in asphaltene deposition removal in BAB oil even at 5 wt%.

Flow Tests: Effect of Aromatic Solvent Toluene on Removal of Asphaltene Deposition. Toluene is known to be a very effective aromatic solvent for washing of asphaltene deposition in flowlines. However, large volumes of this aromatic solvent are required for this purpose. We compare the efficiency of toluene to the ionic and nonionic surfactants A35 and N2, which are effective at 1 wt% (A35) and 1 wt% (N2 in MN-132) and 5 wt% (N2 in BAB). We investigate effectiveness of toluene at 10, 40, 60, and 70 wt% concentrations in deposition removal. At least ten times higher concentration of toluene is required to remove deposition compared to surfactants in MN-132 oil **(Fig. 13)**. These findings are in line with Hashmi and Firoozabadi (2016), where the difference in action of organic acid DBSA, via acid/base interaction (Hashmi and Firoozabadi 2013), and that of toluene, via bulk thermodynamic solvation, is investigated. For BAB crude oil, 70 wt% toluene concentration is effective in deposition removal **(Fig. 14).** The results at 40 and 60 wt% toluene in BAB oil are included in **Fig. 15.**

Flow Tests: Effect of Water on Performance of Surfactants in Removal of Deposition. Two surfactants, nonionic N2 and ionic DBSA are selected to investigate the likely effect of water on performance of functional molecules in deposition removal. After the buildup of asphaltene deposition in the flowline, deionized water is coinjected along with the surfactant-oil mixture from a separate pump at 1:2 water:oil volumetric ratio. We find that water does not appreciably affect the performance of either chemical as shown in panels 16a through 16d for MN-132 and 16e and 16f for BAB oil of **Fig. 16.** PV of flow stays about the same in deposition removal with and without water. Similar trend is observed when comparing panels 16e and 16f of Fig. 16 to panels 8d and 8f of Fig. 8 for BAB oil.

Additional tests are performed on the effect of water on surfactant performance in deposition removal. The results are included in **(Fig. 17).** These additional flow tests reconfirm that water does not have an appreciable effect on the performance of the surfactants.

Flow Tests: Effect of Water on Asphaltene Deposition. In the past in dynamic flow tests it has been shown that water considerably delays asphaltene deposition in two different crude oils (Aslan and Firoozabadi 2014). Water molecules form hydrogen bonds with heteroatoms in asphaltene aggregates, thereby forming bridges and delaying further aggregation of asphaltene molecules. In this work, we perform similar tests as in Aslan and Firoozabadi (2014) to examine the effect of 1 wt% water in both MN-132 and BAB oils. In line with the past work, we observe significant difference in pressure drop with time from the effect of water. These results are shown in **Fig. 18.**

In MN-132 oil, asphaltene deposition is delayed by water injection until 1,400 PV, while for BAB oil, deposition initially begins to develop. However, it is removed subsequently and the eventual pressure drop increases at 600 PV due to deposition (Fig. 18b).

pH Measurements. All six nonionic and ionic surfactants, which are effective in MN-132 oil, and the three surfactants effective in BAB oil are first mixed in equal volumetric oil/water proportions. The equilibrated water is then separated from the oil and its pH is measured. The purpose is to determine if there are any corrosion tendencies due to using chemicals.

On the basis of the results in **Table 4,** the nonionic surfactants do not change the pH of water, as expected. However, the acidic surfactant DBSA brings down the pH to the range of 2, making the water significantly acidic, in both crude oils. The ionic surfactant, A35, slightly reduces pH, however, the effect is negligible. The pH measurements indicate the harmful side effect of the acidic surfactant DBSA.
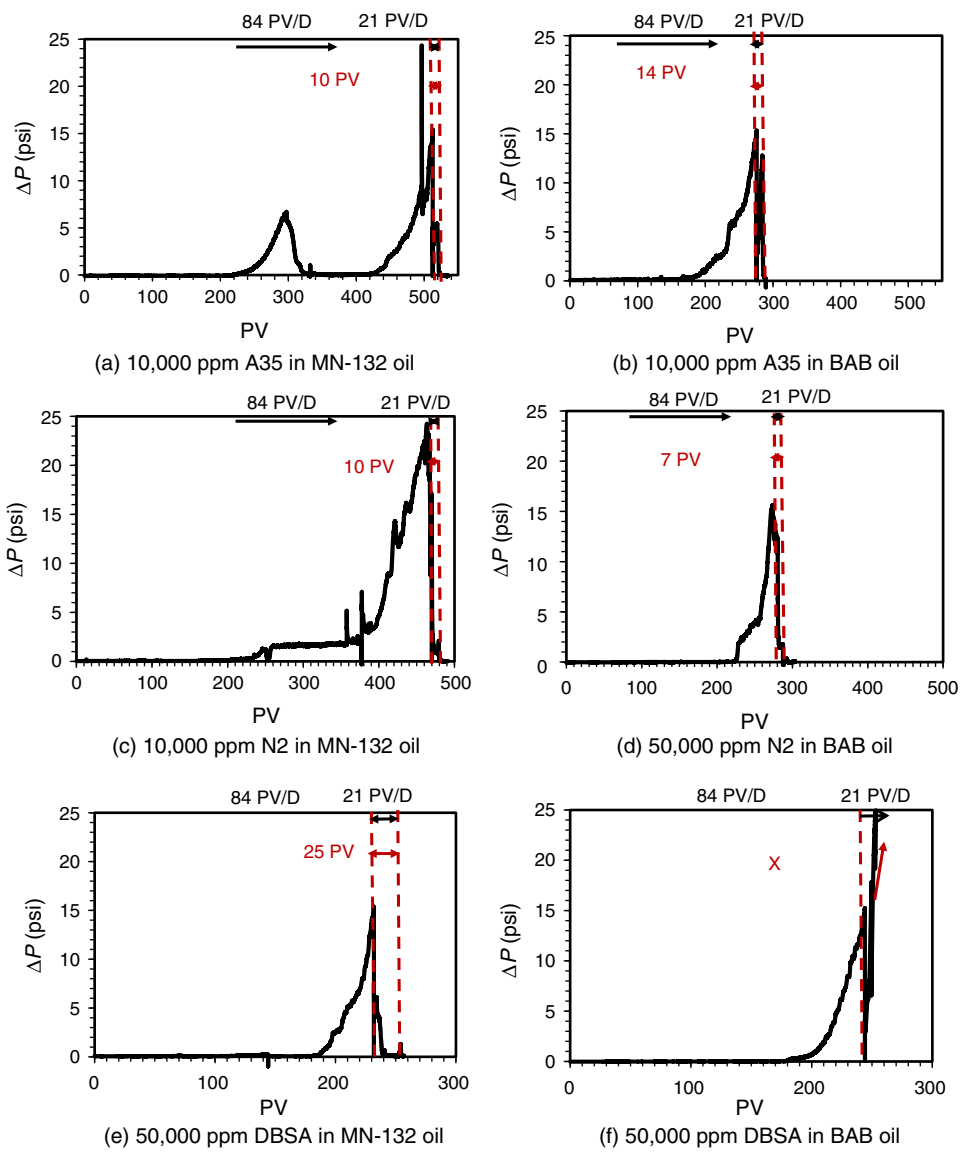
Fig. 8—Pressure drop vs. PV flow of A35 at 10,000 ppm: (a) MN-132, and (b) BAB oil, (c) 10,000 ppm N2 in MN-132 oil, (d) 50,000 ppm N2 in BAB oil, 50,000 ppm DBSA in (e) MN-132, and (f) BAB oil. Removal period is shown in red. X denotes that the chemical is not effective.
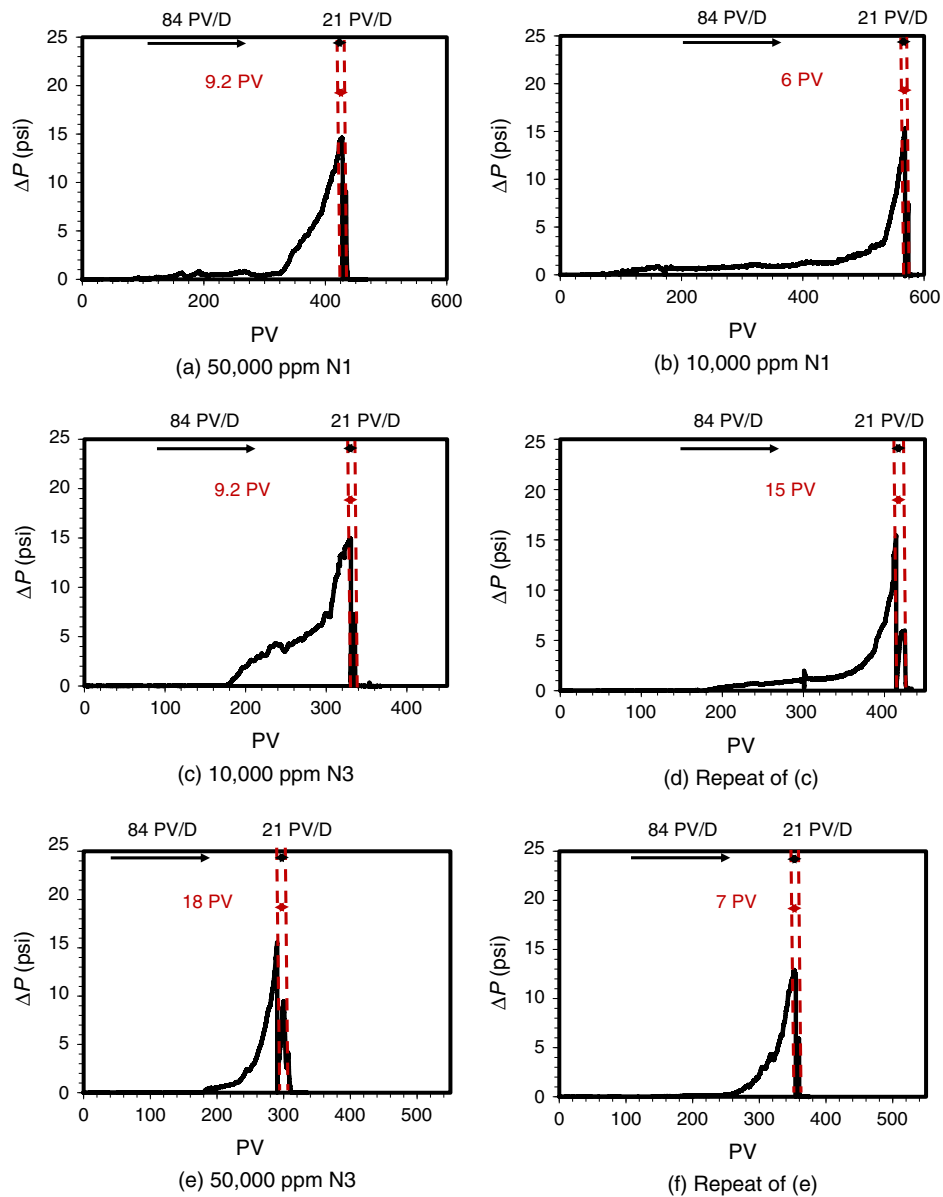
Fig. 9—Pressure drop vs. PV flow in MN-132 oil: (a) 50,000 ppm N1, (b) 10,000 ppm N1, (c) 10,000 ppm N3, (d) repeat of (c) run, (e) 50,000 ppm N3, and (f) repeat of (e) run.
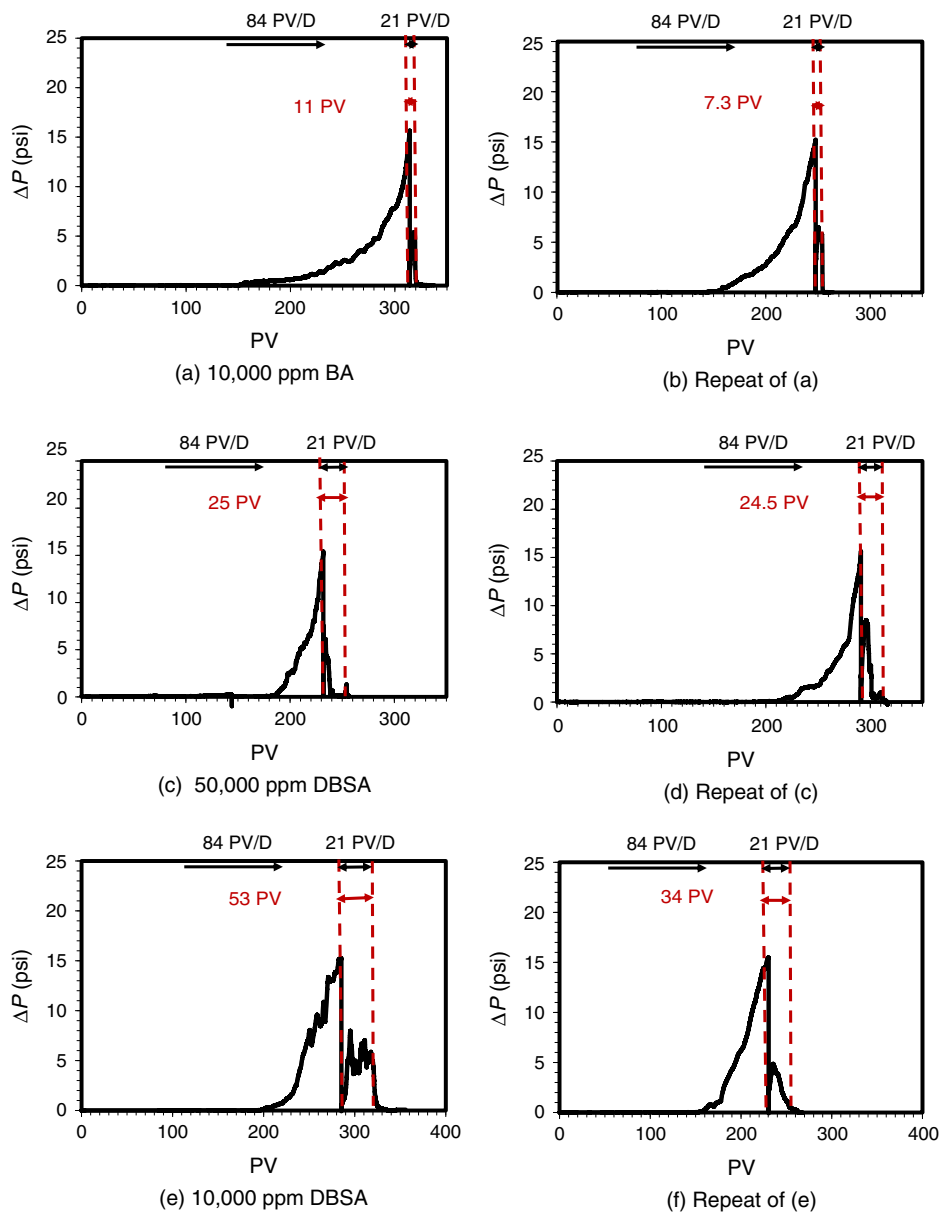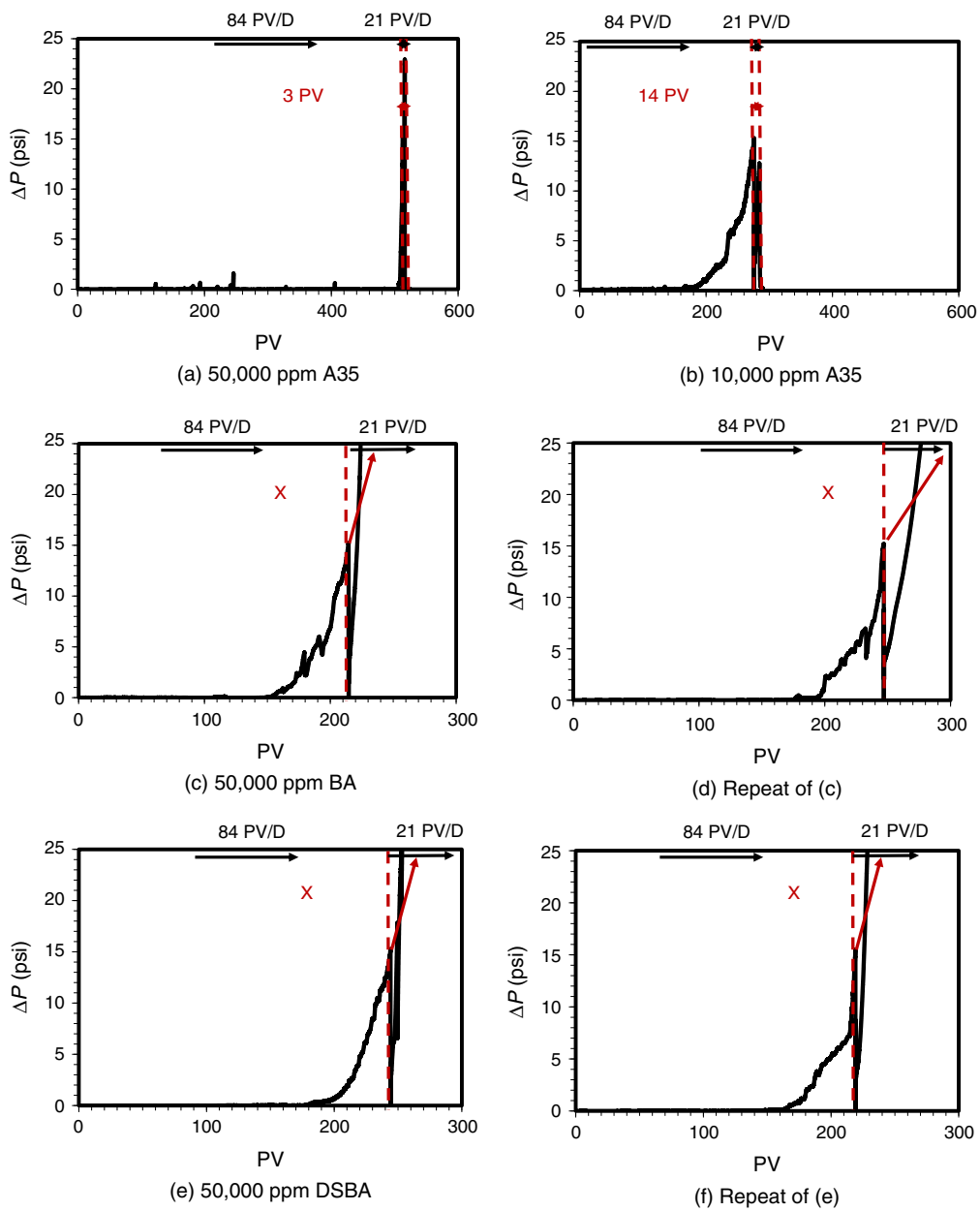
Fig. 10—Pressure drop vs. PV flow with MN-132 oil: (a) 10,000 ppm BA, (b) repeat of (a) run, (c) 50,000 ppm DBSA, (d) repeat of (c) run, (e) 10,000 ppm DBSA, and (f) repeat of (e) run.
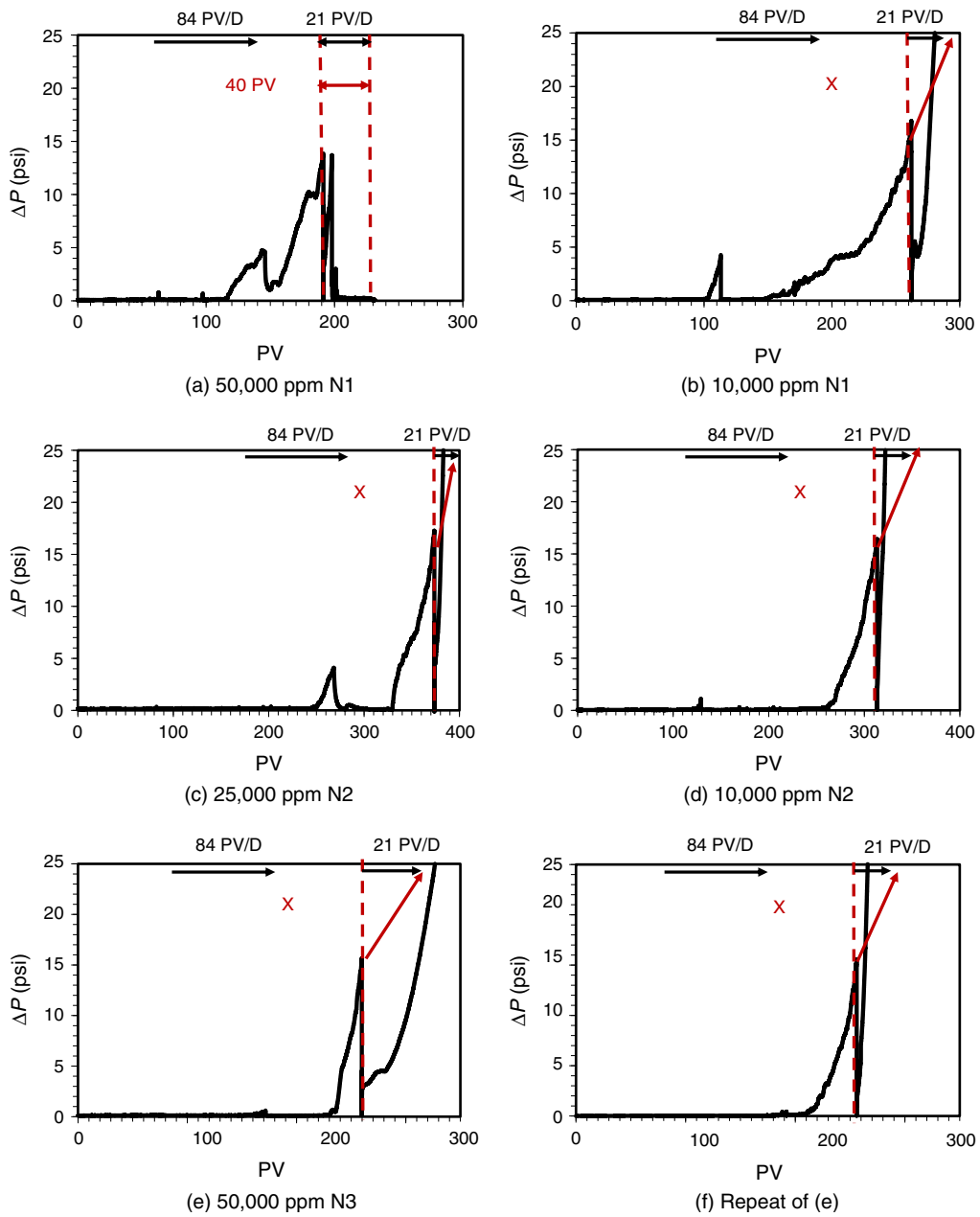
Fig. 11—Pressure drop vs. PV flow in BAB oil: (a) 50,000 ppm N1, (b) 10,000 ppm N1, (c) 25,000 ppm N2, (d) 10,000 ppm N2, (e) 50,000 ppm N3, and (f) repeat of (e) run. X denotes that the chemical is not effective.

Fig. 12—Pressure drop vs. PV flow in BAB oil: (a) 50,000 ppm A35, (b) 10,000 ppm A35, (c) 50,000 ppm BA, (d) repeat of (c) run, (e) 50,000 ppm DBSA, and (f) repeat of (e) run. X denotes that the chemical is not effective.
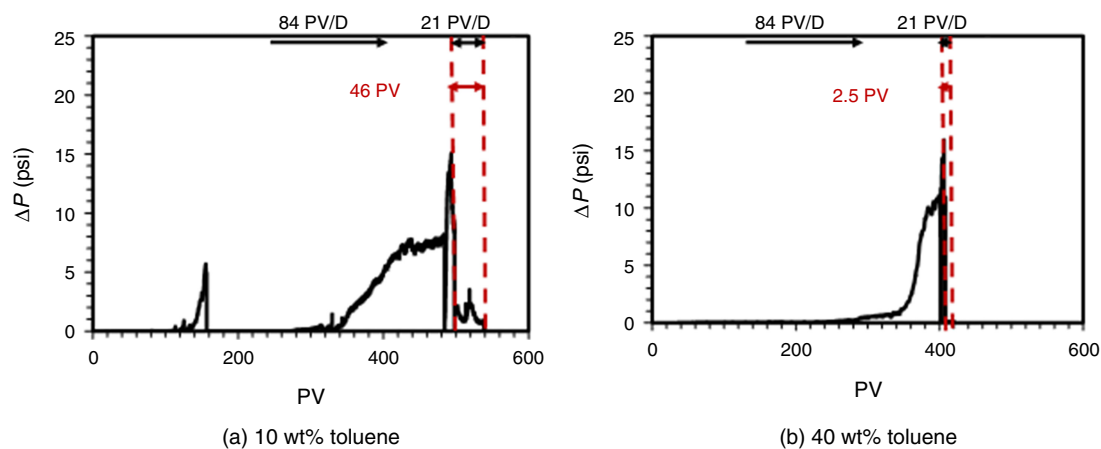
Fig. 13—Pressure drop vs. PV flow with toluene in MN-132 oil: (a) 10 wt%, and (b) 40 wt%. Removal period is shown in red.
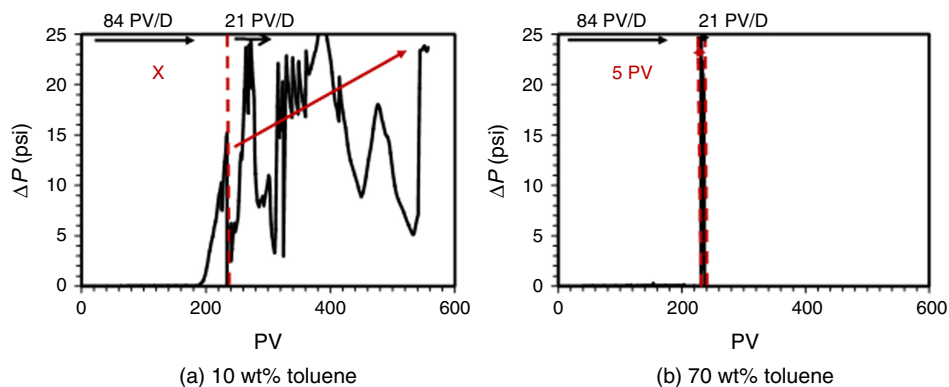

Fig. 14—Pressure drop vs. PV flow with toluene in BAB oil: (a) 10 wt%, and (b) 70 wt%. X denotes that the chemical is not effective.
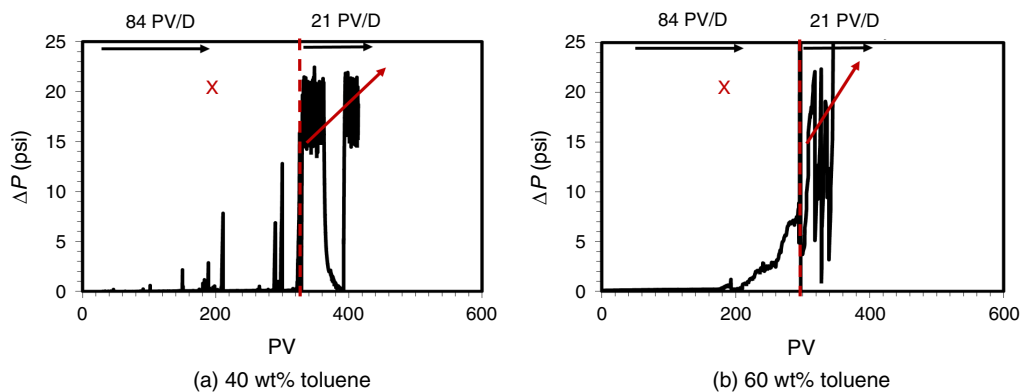

Fig. 15—Pressure drop vs. PV flow: (a) 40 wt% toluene in BAB oil and (b) 60 wt% toluene in BAB oil. X denotes that the chemical is not effective.
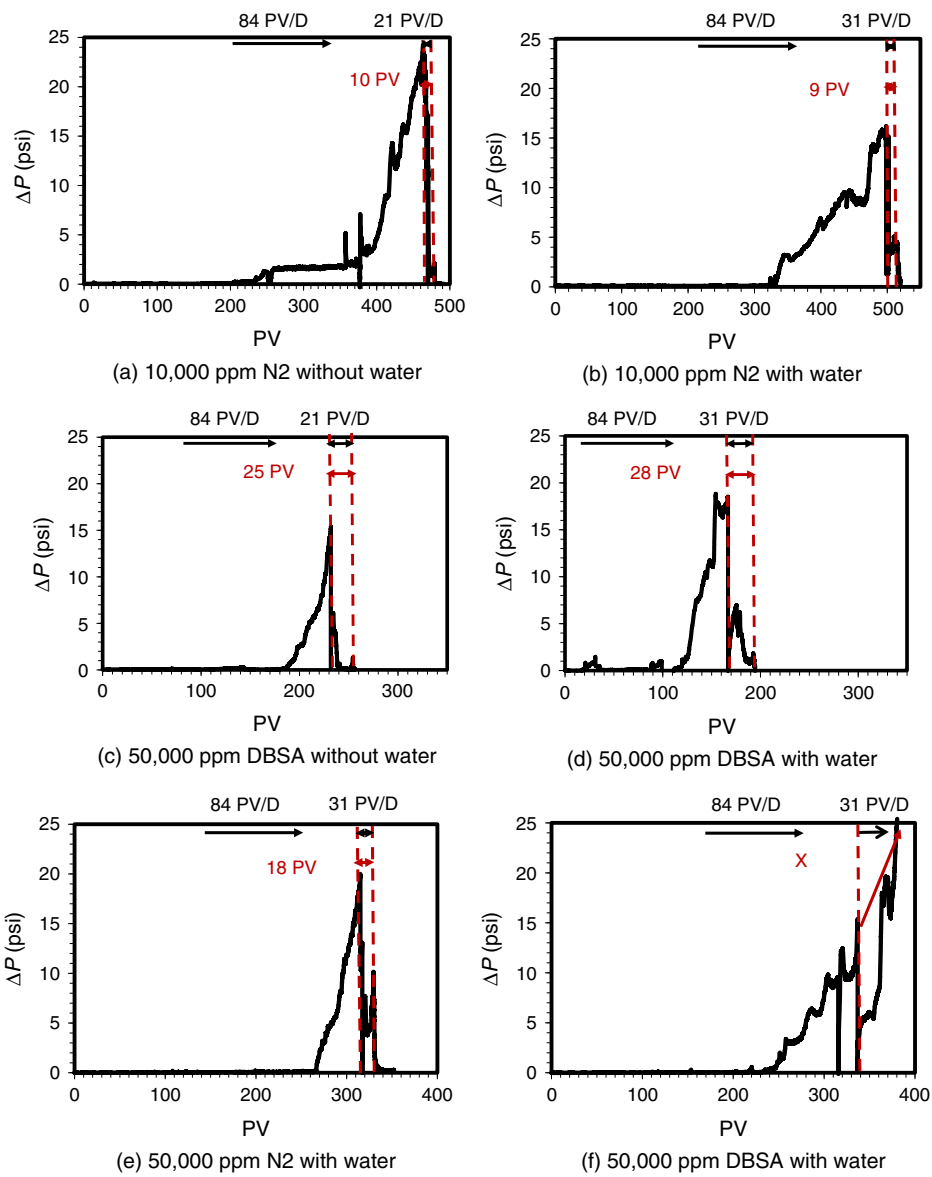
Fig. 16—Pressure drop vs. PV flow in MN-132 oil : (a) 10,000 ppm N2, (b) 10,000 ppm N2 with 50 vol% water, (c) 50,000 ppm DBSA, (d) 50,000 ppm DBSA with 50 vol% water, with BAB oil mixed with 50 vol% water for (e) 50,000 ppm N2, (f) 50,000 ppm DBSA. X denotes that the chemical is not effective.
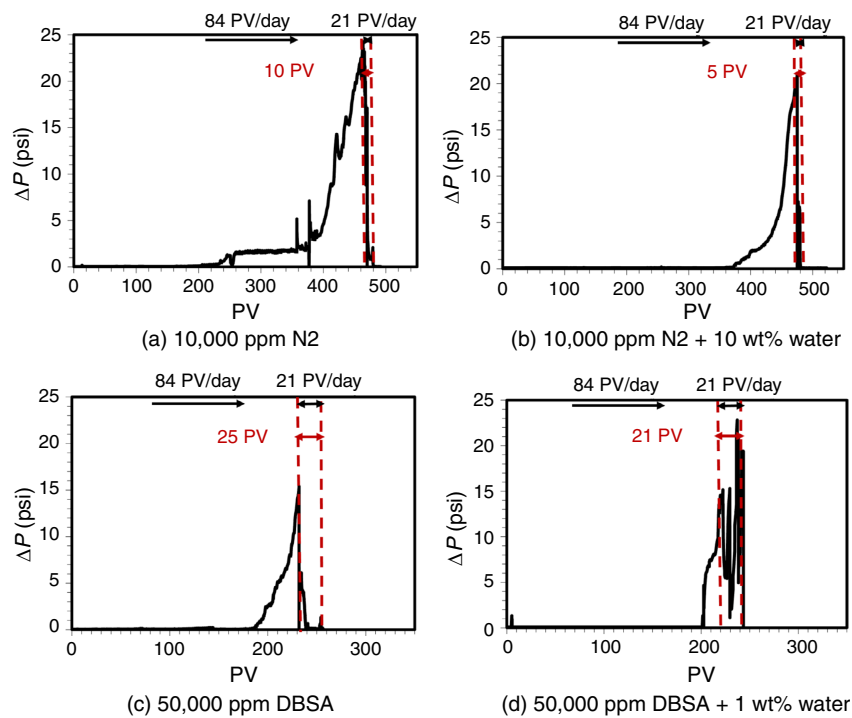
Fig. 17—Pressure drop vs. PV flow (a) 10,000 ppm N2 in MN-132 oil, (b) 10,000 ppm N2 in MN-132 oil with 10 wt% water, (c) 50,000 ppm DBSA in MN-132 oil, and (d) 50,000 ppm DBSA in MN0132 oil with 1 wt% water.
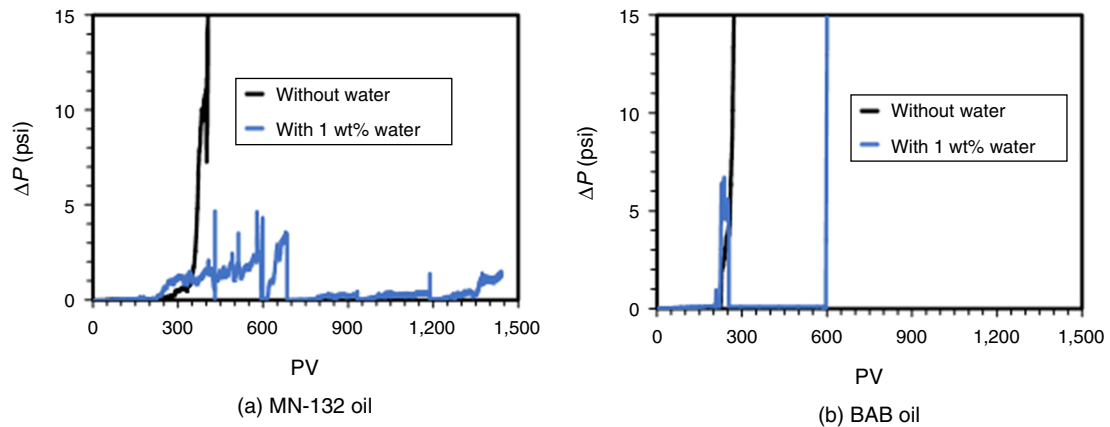

Fig. 18—Pressure drop profiles due to asphaltene deposition without water and with 1 wt% water: (a) MN-132 and (b) BAB oil.

Oil Sample	Functional Molecule	Chemical Conc. (ppm)	pH
	–	–	6.9
	N1	10,000	6.8
	N2	10,000	6.9
MN–132	N3	10,000	6.9
	BA	10,000	6.9
	DBSA	50,000	2.3
	A35	10,000	6.5
	–	–	6.9
	N2	50,000	6.9
BAB	DBSA	50,000	2.1
	A35	10,000	6.5

Table 4—pH of water equilibrated with oil samples.

Conclusions

On the basis of extensive flow measurements, we have found two functional molecules that are effective in two different crude oils. We perform both static vial tests and dynamic flow tests using six nonionic, weakly ionic, and ionic surfactants. The effect of water on the performance of selected surfactants has also been studied. Following conclusions are drawn:

1. One nonionic surfactant N2 and one ionic surfactant A35 at 1 wt% dissolved in two crudes are found to be very effective to remove the deposited asphaltene. These surfactants are superior to DBSA, which is commonly regarded to be an effective molecule in asphaltene deposition removal.

2. In flow testing, all the surfactants remove the deposition in the flowline in the crude with less severe asphaltene aggregation. In the other crude with relatively higher precipitated asphaltene network, only two surfactants (N2 and A35) remove deposition. The ionic surfactant A35, at 1 wt% dissolved in the crude, is found to be the most effective chemical in asphaltene deposition removal for both the crudes.

3. Surfactants at ten to seventy times lower concentrations than toluene are found to remove the deposited asphaltenes. This is the first report of effective surfactants in asphaltene deposition removal in flowlines at very low concentration compared to DBSA.

4. Water is found to have a significant effect on delaying deposition, which reconfirms the past work.

5. Water does not have an appreciable impact on the effectiveness of the functional molecules in the removal of asphaltene deposition.

   In future we plan to investigate using brine of various salinities and salt compositions and test its effect on surfactant performance to remove asphaltene deposition. Additionally, asphaltene deposition and removal in reservoir rock will also be studied by performing coreflooding experiments.

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