Controlled Releases of Asphaltene Inhibitors by Nanoemulsions

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ABSTRACT: Asphaltene precipitation is usually responsible for many flow assurance problems such as wettability changes and pore clogging in reservoirs, fouling in wellbore tubings and production surface facilities. This study develops a novel approach by using nanoemulsions (NE) for controlled delivery and release of asphaltene inhibitors (AI) to minimize asphaltene precipitation with reduced AI amount. LUMiSizer was utilised to study the effectiveness and performance of controlled release by three cases on asphaltene sedimentation: i) strong organic acids (dodecyl benzene sulfonic acid, DBSA), ii) nanoemulsions (blank NEs), and iii) nanoemulsions loaded with DBSA (DBSA NEs). The experiments suggested that the optimum inhibitor concentration for completely stabilizing asphaltene were 4 vol. % for DBSA. This amount of inhibitor can be significantly reduced by ~ 20 times by using the DBSA NEs, and the release time can be greatly extended. A mechanistic understanding of the controlled release effect is proposed based on interfacial properties and electron microscopic studies, which is related to the hydrophilicity of DBSA and the strong intermolecular interactions among all DBSA NE's components and the asphaltene molecules.

KEYWORDS: Controlled release ; asphaltene inhibitor, nanoemulsions, asphaltene precipitation and stability

1 INTRODUCTION

Asphaltene can be defined as a poly-disperse distribution of the heaviest and most polarizable fraction of the crude oil that is insoluble in low-molecular-weight alkanes, such as n-pentane and n-heptane, but completely soluble in aromatic hydrocarbons, such as benzene and toluene [1]. Asphaltene fraction is formed of associated systems of polynuclear aromatics bearing alkyl side chains, organic molecules containing oxygen, nitrogen, and sulfur as well as vanadium and nickel porphyrins are also present in asphaltenes [2]. Asphaltene is usually responsible for many flow assurance problems like wettability changes and pore clogging in reservoir rocks, and fouling in wellbore tubing and production surface facilities [3]. One of the greatest challenges related to asphaltenes is the instability, which results in precipitation in reservoirs, wells and facilities, severely impacting the oil production quality and economics. Asphaltene instability begins with the onset of insolubility, followed by the formation of colloidal scale particles, which aggregate and ultimately sediment out of solution. Asphaltene aggregation is attributed to intermolecular attractive interactions arising from charges on the rings as a result of the presence of dissociated ions, along with acid and basic functional groups, containing heteroatoms (N, S, and O). Nitrogen is mainly contained within the rings, in either pyrrolic structures (acidic) or pyridinic structures (basic). Sulfur is present in thiophenic structures, while oxygen appears in hydroxyl, carbonyl, and carboxylic groups [4]. Thereby, the dissociation of charged ions must cause opposite surface charges on asphaltenes. Basic functional groups (e.g., pyridinic groups) should generate negative charges in nonpolar medium, whereas hydroxyl groups in carboxylic acids, alcohols, and phenols as well as mercapto groups (associated with mercaptans) and organic sulfides would produce positive charges [5]. The time

required for asphaltenes to fully separate can be increased by varying solvent compositions, indicating that the delay of instability is possible [6].

Chemical treatment is considered as one of the most common strategies to prevent asphaltene precipitation. Asphaltene inhibitors (AI) are designed to interact with asphaltene to inhibit precipitation, aggregation and deposition, and ensure enhanced flow. Even though this approach is widely used in oilfields, it has a major problem due to the loss a large amount of chemicals inside reservoir, resulting in high treatment cost. [7]. For instance, the cost of chemical additive injection in Middle Eastern fields is in the range of USD $ 31,000 ~$ 46,000 per well per year [8]. In a study investigating the chemical amount required for controlling asphaltene precipitation, Subramanian et al. [9] reported that at an addition of 5 wt. % of dodecyl benzene sulfonic acid (DBSA), the asphaltene precipitation could be completely controlled. Similarly, Ortega et al. [10], suggested that the attachment of DBSA to asphaltene molecules with 3 wt % DBSA could noticeably improve the rheological properties of bitumen. Hashmi et al. [11] studied the capability of commonly available surfactant aerosol-OT (AOT) to stabilize asphaltene suspensions in heptane. Regardless of the amount of AOT, however, the sedimentation behaviour of asphaltene was similar to that of in the absence of surfactant. Even with 20 wt. % of AOT in solution, samples collapsed within the first hour after the preparation, which indicated that it was not effective in stabilizing asphaltenes. Moreover, aromatic solvents like toluene dissolve asphaltenes, but only at very high concentrations, i.e., nearly 50% by weight [11].

Using high concentrations of inhibitor tends to produce self-associations in the bulk rather than adsorption on asphaltene, reducing their effectiveness [12, 13]. More recently, attention has focused on increasing the effectiveness of inhibitors by increasing the adsorption of scale

inhibitors on rock surface, hence increasing the lifetime of a squeeze treatment [14].These studies include: (i) mixing cations or Fe (II) ions with the scale inhibitor to provide better retention than using the inhibitor alone [15], (ii) adding pH modification chemicals to the inhibitor via a temperature dependent material such as urea, (iii) using mutual solvents (such as the small alkyl glycols) to change the rock wettability (more water wet) [16], and (iv) using kaolinite or other clay to enhance the inhibitor adsorption [17]. These studies, however, only showed limited reduction in the amount of inhibitors. An attempt to further reduce the amount of scale inhibitors has been done by Zhang et al., in 2016 [18] by using reverse micelles as non-aqueous scale inhibitor delivery vehicles for oilfield mineral scale control. In addition, a systematic study of the effectiveness of using oil-in-water nanoemulsions in breaking down asphaltene emulsions was reported by Souza et al. [19, 20].

Application of controlled delivery and release of oil chemicals can be of tremendous value, in both upstream and downstream, where asphaltene precipitation can have unfortunated consequence. While the concept of controlled release has been widely used in nanomedicine area, with many successful applications, it has never applied for asphatene inhibitors. This work proposes a novel concept to encapsulate and control the release of asphaltene inhibitors by using nanoemulsions (NEs), which could i) improve the stability of the asphaltene, ii) reduce the usage of inhibitors, and iii) extend the treatment time via slow release of inhibitors. As an example study, a conventional inhibitor, dodecyl benzene sulfonic acid (DBSA), is used as model inhibitor. The effect of asphatene stability and controlled release effect via nanoemulsions are examined by the centrifugal method in three case studies, i) with pure inhibitors (DBSA), ii) with blank NEs, and iii) with NE loaded with DBSA (i.e. DBSA NE).

2 EXPERIMENT AND METHODS

2.1 Materials and samples preparation

2.1.1 Materials

Analytical grad materials including crude oil, xylene (> 98.5%), n- heptane (extra pure ≥ 98), Toluene (extra pure ≥ 98), dodecyl benzene sulfonic acid (DBSA), Tween 80 (sorbitan monooleate), and sodium benzene sulfonic acid (SDS) were purchased from Sigma-Aldrich company. Chemical structure of materials employed is illustrated in (Fig.S1) (In the supporting information).

2.1.2 Preparation of oil-in-water NEs

The properties and stability of the final NEs are largely dependent on the preparation procedures and techniques applied. Oil in water NEs with and without DBSA were prepared. At the beginning, the formation consisting of DBSA was dissolved in xylene and mixed together by stirring using a magnetic stirrer at 1000 rpm at room temperature for 24 hour until a clear sample was obtained. At the same time, another sample consisting of non-ionic surfactant (Tween 80), anionic surfactant (SDS) and deionized water were mixed together by using the magnetic stirrer for 24 hour as well to ensure complete dispersion and dissolution. In the next step, the mixture of (deionized water, surfactants) was added slowly to the mixture of xylene and DBSA. Then, the samples were pre-homogenized by a high shear mixer (IKA T2S digital/Ultra- Turrax) for 4 minutes (~3000rpm) for each sample to improve the mixing and size distribution. After that, the samples were treated by an ultrasonic probe for 8 minutes per sample, amounting to 2 minutes of actual sonication for 4 times (i.e., 1 minute without sonication between two actual sonications). The amplitude for sonication was about 20%, the power was 26 watt, and the energy about 2000

J for each cycle. The procedure was implemented carefully to ensure the oil inside the NE has not been evaporated by the high temperature, which generated by high energy sonication. The low weight percent of oil was selected in order to minimize the effect of droplet coalescence and the mass of the surfactants was tasted to be in excess for the smallest emulsion produced.

The composition of the dispersions used to prepeare blank NEs were at a concentrations of 7 vol.% xylene (oil phase), 10 vol.% mixed surfactants (9.9 vol.% Tween 80 and 0.1 vol.% SDS), and 83 vol.% deionized water, while DBSA NEs were composed of: 1 vol.% DBSA, 7 vol.% xylene, 10 vol.% mixed surfactants, and 82 vol.% deionized water. The droplet size for blank NE, and 1 vol. % DBSA NE were about 20 and 22 nm respectively.
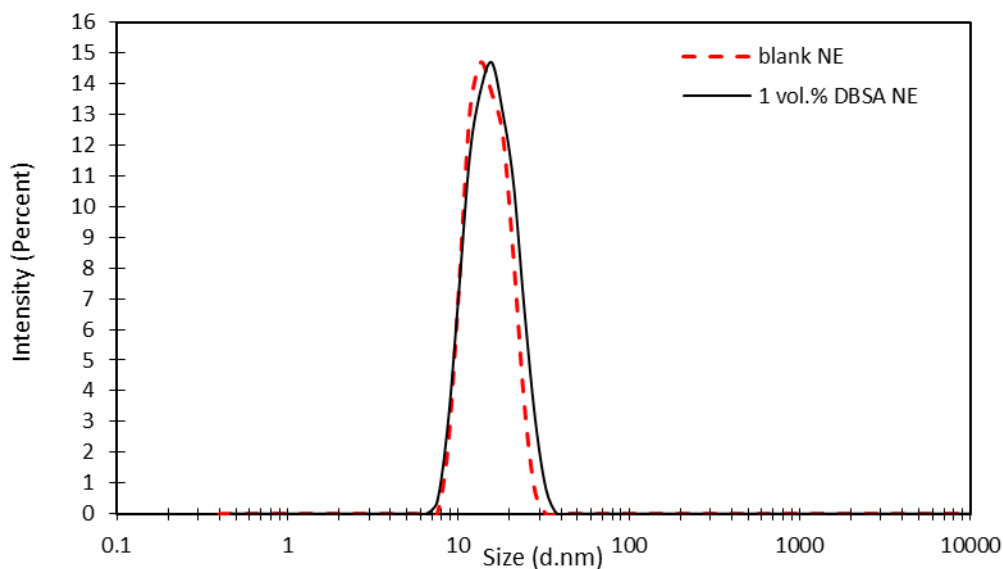
Fig. 1: Droplet size for blank NE, and DBSA NE (containing 1 vol. % DBSA).

2.2 Methods and measurements

2.2.1 Asphaltene extraction and preparation of asphaltene solution

The separation of asphaltenes was carried out according to ASTM D2007 by mixing crude oil with n-heptane at a volume ratio of 1:40, which is known to destabilize asphaltenes and to give rise in asphaltene precipitation [21]. The mixture was allowed to equilibrate after stirring and left overnight at room temperature. It was then filtered under vacuum using 0.2 µm pore size Whatman filter paper. Next, the filter cake was repeatedly washed with n-heptane to remove any resins until the effluent from the filter became colourless. Finally, the asphaltenes were recovered from the filter cake by dissolution in toluene and then dried after toluene evaporation. The asphaltene solution containing 0.5 w/v % of the asphaltene was prepared in a mixture of two solvents, n-heptane and toluene (Heptol), in different portions, which will be detailed below.

2.2.2 Infrared spectroscopy and elemental analysis

Infra-red spectrometry allows investigating the functional groups present in a sample. The elemental composition (C, H, N, O, S) of the Iraqi asphaltene were determined by Elemental Analyser (CHNS-O).

2.2.3 Refractive index

Refractive index (RI) was measured for asphaltene at 298.15 K with an automatic refractometer (Rudolph Research Analytical model J357). The measurement is based on the detection of the critical angle of a light emitting diode at which there is no refracted light.

2.2.4 Analysis of droplet size and polydispersity index

The droplet size and size distribution for the NEs prepared with different concentrations of dispersant were measured approximately 2-5 hours after the preparation by a laser diffraction method (i.e., Zetasizer Nanoseries ZS, Malvern Instrument, Worcestershire, UK). NE droplet

size was determined by 3 measurements and calculated as the mean diameter of the volume distribution (MV).

$$MV = \frac{\sum Vi\, di}{\sum Vi}$$ (1)

where V_i is the volume percentage between droplet sizes and di is the diameter of droplets. About 1 ml of sample was placing in a disposable cuvette (12.5 x 12.5 x 45 mm). All NEs were stored at 25 °C and samples were withdrawn periodically for droplet size determination.

2.2.5 Separation analysis

Sedimentation (precipitation) analysis was performed by an analytical centrifuger (LUMiFuge, LUMiSizer; LUM, Germany). This multi-sample analytical centrifuger display in situ the change of particle concentration instantaneously by NIR-light transmitted across the full length of the samples. The analytical centrifuges allow measuring the extinction profiles during centrifugation over the whole sample length. In each measurement, 400 µL of the asphaltene solution (asphaltene in 60:40 Heptol) was pipetted into a polycarbonate transparent cell with a 2 mm path length. Real-time transmission profiles across the sample were recorded at certain time intervals during the centrifugation. The sedimentation velocity was determined. Measurement scheme of the multisample analytical centrifuge with photometric detection is shown in (Fig. 3). Parallel NIR-light is passed through the sample cells and the distribution of local transmission is recorded at pre-set time intervals over the entire sample length.
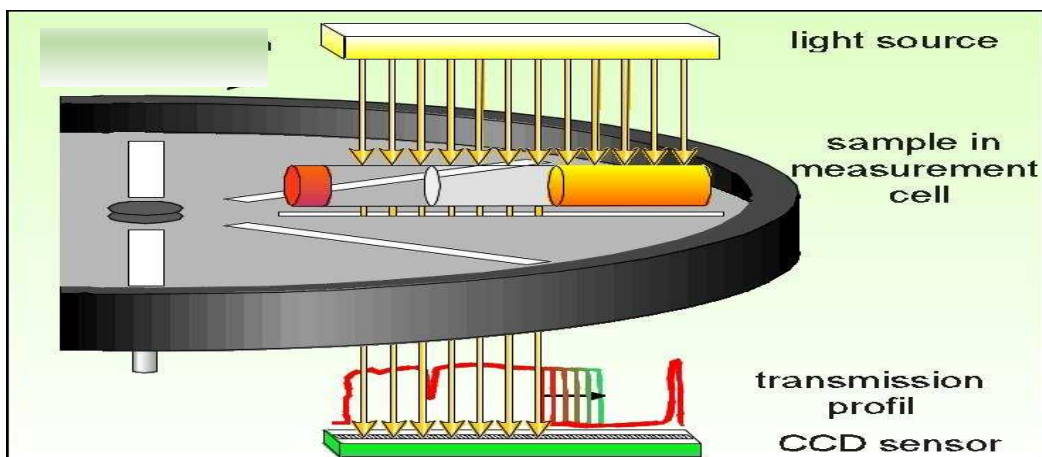
Fig. 3: Measurement scheme of the multisample analytical centrifuge.

2.2.6 Asphaltene dispersant/inhibitor release

Release studies of DBSA were performed using a dialysis bag method. Dialysis membranes which were soaked overnight having a pore size of 8 KDa (Sigmae Aldrich Co., Madrid, Spain) was used for this study. The dialysis bag was filled with known amount of DBSA NEs, which was immersed into 300 mL of Toluene/ethanol mixture (7:3 in volume) [22,23].The mixture was rotated at 700 rpm at 37 C° [24]. A total of 1 mL of sample was collected at predetermined time interval and equal volume of releasing medium was replaced. DBSA was quantified using UV-visible spectrophotometry, at the wavelength of 320 nm, on the basis of previously prepared calibration curve using the following equation:

$$DBSA\ released\ (\%) = \frac{DBSA\ in\ media}{Total\ DBSA\ added} \times 100 \tag{2}$$

2.2.7 Analysis of asphaltene size and interfacial tension

The morphology of the asphaltene particles was examined using dynamic optical imaging (Malvern Instrument Morphology G3S Microscope (Instrument AG, Renens, Switzerland)) and

using a transmission electron microscope (FEI Titan Themis Cubed 300 TEM). Interfacial tensions were measured using a KSV CAM 200 optical tensiometer.

3 RESULTS AND DISCUSSION

3.1 Analysis of asphaltene

Asphaltenes are composed of fused benzene rings with aliphatic chains, heteroatoms (O, N, and S), and metals (Fe, V, and Ni) [25]. In asphaltenes, oxygen exists mostly in OH groups and can be found in peripheral aromatics or in aliphatic chains. Nitrogen can be found in pyrolic (5-member ring) or pyridinic (6- member ring) form. Whereas sulfur mostly exists as thiophene (5-member ring), sulfide type groups (RSR), or sulfoxide (RS (= O) R) [26]. Infrared (IFR) spectroscopy, which shows characteristic peaks that correspond to the modes of functional groups, is one of the most-well known tools for assessing the structure and functional groups for asphaltene. The current study of using IFR spectroscopy found that asphaltene molecules consisted mainly of linear, branched, and naphthenic hydrocarbons attached to large aromatic clusters. Fig.4 shows that the asphaltene sample consisted of aromatic, aliphatic hydrocarbons, sulfoxide, and aliphatic primary amines functions. In the aliphatic, C-H stretch range and CH_3 stretching dominated over CH_2. Table (1) shows the properties and SARA analysis of the crude oil, whereas Table (2) shows the elemental analysis of the crude oil and asphaltene by the elemental analyzer. One advantage of determining the functional groups and hetroatoms is to understand the mechanism of asphaltene stability by intermolecular interactions between these functional groups and hetroatoms with asphaltene dispersant molecules.
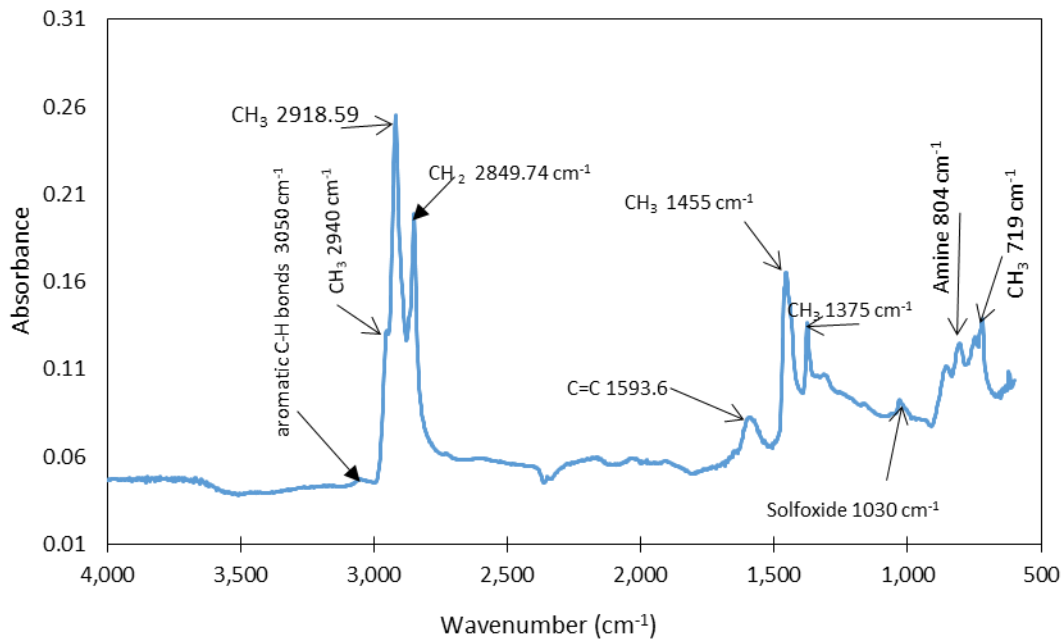
Fig. 4 Infrared spectroscopy analyses of asphaltene.

Table 1: Properties and SARA analysis for the crude oil.

Property of the Crude oil	
Density, API	18.96
Density at 20 ℃, g cm^{-3}	0.936
Density at 15 ℃, g cm^{-3}	0.939
Viscosity at 25 ℃, mPa s	76
Viscosity at 50 ℃, mPa s	28
Total acid number, mg KOH g^{-1}	0.47
Asphaltenes, % m m^{-1}	3.6
Resins, % m m^{-1}	15.0
Saturates, % m m^{-1}	54.4
Aromatics, % m m^{-1}	27.0

Table 2: Elemental analysis of the crude oil and its asphaltene.

Samples	N (wt. %)	C (wt. %)	H (wt. %)	S (wt. %)	O (wt. %)
Asphaltene	0.80	78.64	7.56	9.04	1.21
Crude oil	0.24	81.15	10.3	2.08	2.03

3.2 Asphaltene precipitation test in n-heptane/toluene mixture (heptol)

The precipitation of asphaltene involves a complex interactions among a variety of intermolecular forces, such as dispersion and van der Waals forces [27]. Gray et al. [28] proposed several mechanisms for asphaltene self-association including acid-base interactions, hydrogen bonding, metal coordination complexes, and interactions between cylcoalkyl and alkyl groups to form hydrophobic pockets driven by van der Waals interactions, in addition to aromatic $\pi - \pi$ stacking. They suggested that all of these mechanisms interact to form a complex mixture of asphaltene nano-aggregates, leading to precipitation eventually. In order to find a practical way to prevent or treat the potential problems due to asphaltene precipitation, it is necessary to determine the amount of n-heptane, which affects the stability properties of asphaltenes. It has been proposed that the refractive index, which is an indicator of the extent of the intermolecular attractions between asphaltene molecules, is a proper property to describe the asphaltene precipitation from a crude oil-hydrocarbon mixtures [29,30].. The refractive index function can be calculated by:

$$RF_n = \frac{(n^2-1)}{(n^2+1)} \tag{5}$$

where RF_n is the refractive index function and n is refractive index.

In previous studies [29, 30], n-heptane was added to the crude oil or asphaltene and a linear relationship was found between the refractive index function, and the concentration of

heptane for toluene/heptane mixture (see supporting information (Fig.S1)). However, in the present study, the asphaltene with toluene/heptane mixture where asphaltene particles precipitate out from the solution, a gradual deviation from the linear relationship, Fig. 5, was observed. This deviation in the refractive index function at high n-heptane concentrations is caused by the formation of asphaltene particle flocculation and precipitation . Therefore, the point at which a departure from a linear trend on refractive index is observed is defined as the "onset precipitation point". Before the onset , asphaltenes were inherently stable and do not precipitate. This value was then used to calculate the parameters such as solubility blending and insolubility numbers [31] (see section S1 and (Fig. S2) in the supporting information).

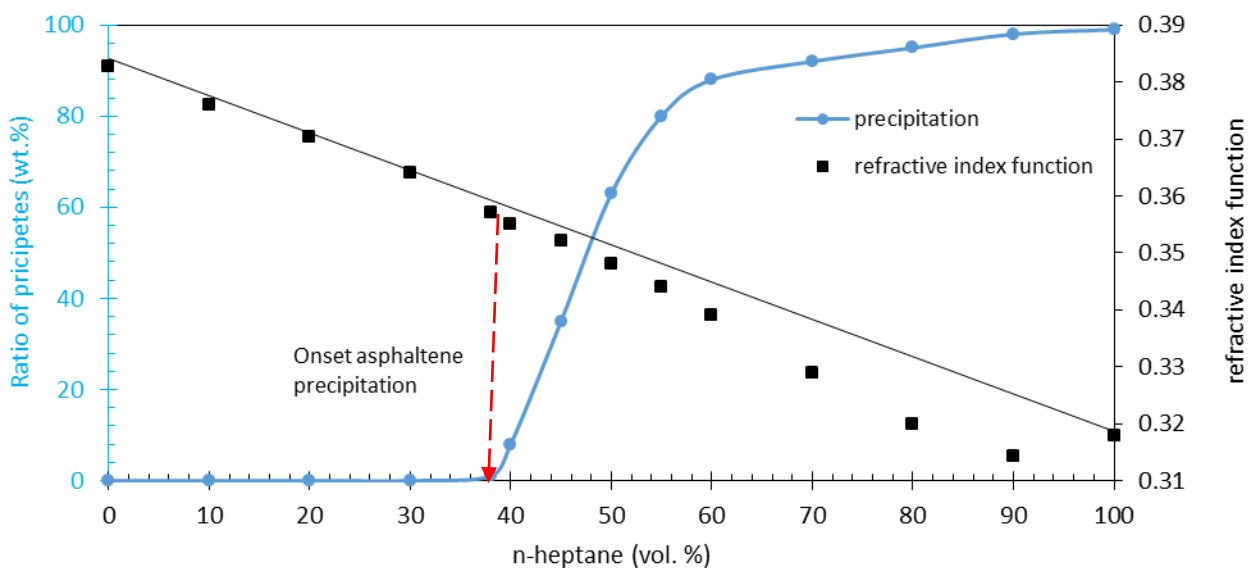Fig.5: Asphaltene precipitation ratio for the asphaltene mixed with n-heptane. Precipitation onset occurs at 38.2 vol % of n-heptane.

3.3 Asphaltene stability performance by analytical centrifugation

An analytical multi-sample centrifugation technique, the LUMiSizer, has been recently used to characterize the stability of colloidal dispersions for early formulation stability within shorter

timescales [32,33]. However, this technique has received little attention in the field of asphaltene sedimentation (or precipitation). By observing the asphaltene particles front moving as the sedimentation occurs, it is possible to characterize the stability of asphaltene and determine the optimum concentration of additives which affect the stability. The centrifugation method is adopted in this work to examine the effect of controlled release by investigating the stability of asphaltene particles by three case studies: i) with pure DBSA, ii) with blank NE, and iii) with DBSA NE, as below.

3.3.1 Asphaltene stability with pure DBSA

Asphaltene stability and sedimentation velocity with DBSA was investigated first. From the data in (Fig. 6a), it is clear that the DBSA can enhance the asphaltene stability. The results demonstrate that the sedimentation of asphaltene without DBSA showed a high bed sediment from 24 mm (initial uniform dispersion height) to 0.8 mm (packed bed height) within 7 minutes, resulting in a quick formation of aggregation into larger structures, settling faster. It also shows that the sedimentation process decreases with the increase of DBSA concentration until approaching to a plateau value. For samples with a concentration ≤ 4 vol. % DBSA, the asphaltene particles are sterically stabilized by the presence of extended DBSA molecules on the asphaltene particle surface and the precipitation high is reduced to 0.21 mm within 24 minutes. Under this condition, as the centrifugal field is applied, the individual particles gradually settle over long time and are able to arrange into a very close packed bed (see (Fig.S3) in the supporting information). However, with increasing the concentration of DBSA over 4 vol. %, the sedimentation only increased slightly, which is due to the self-association of DBSA.

3.3.2 The effect of nanoemulsion on asphaltene precipitation

The settling data for asphaltene particles with and without NEs is considered in (Fig.6b). It is obvious that the sediment time is seen to progress in a linear fashion with all volume fractions of blank NEs. For samples, with a volume fraction < 20 % (80 µl NE), a transition to a settling regime is seen after a finite time, and only a small change in the sediment height is observed over extended times. At 20 % NE, the rate of settling reduces and the time for sediment consolidation increases, i.e. within 16 minutes. Therefore, these findings suggest that the NEs have a moderate influence on asphaltene stabilization comparing with using the optimum concentration of DBSA (4 vol. %). The stability behaviour can be attributed to the presence of blank NEs components such as water, mixed surfactants, and xylene that interact with asphaltene molecules.

3.3.3 The effect of DBSA nanoemulsion on asphaltene precipitation

DBSA NE in this study consists of four components: xylene, DBSA soluble in xylene, mixed ionic and non-ionic surfactants (SDS and Tween-80), and water, and the detailed compositions are shown in Table 5. Nanoemulsions with 1 vol. % DBSA remain homogeneous without any observable sediment for weeks, and is used for the centrifugation tests, as shown in (Fig. 6c). It can obvious seen that the sedimentation velocity in the case of using small volume fractions of DBSA NE (5 and 10 vol. %) are considerably slower than that of pure asphaltene solution. For asphaltene sample with a volume fraction 20 vol. % DBSA NE (i.e., containing 0.8 µl DBSA), there is a significant reduction in the final settling height , which decreases from 0.8 mm to 0.2 mm, and the sedimentation time increases from 390 sec to 1470 sec comparing to pure asphaltene solution. . This is indicative of reduced settling velocities of asphaltene particles. A possible explanation for these results are due to the intermolecular interaction between DBSA NE components and asphaltene molecules. It may be assumed that, in this case, the DBSA was

progressively released from NE and interact with asphaltene molecules, leading to a slower settling.
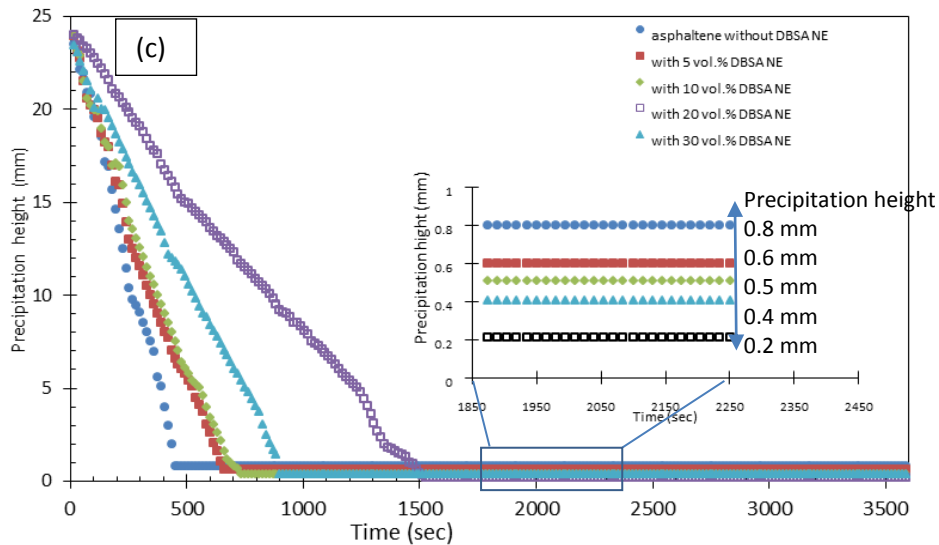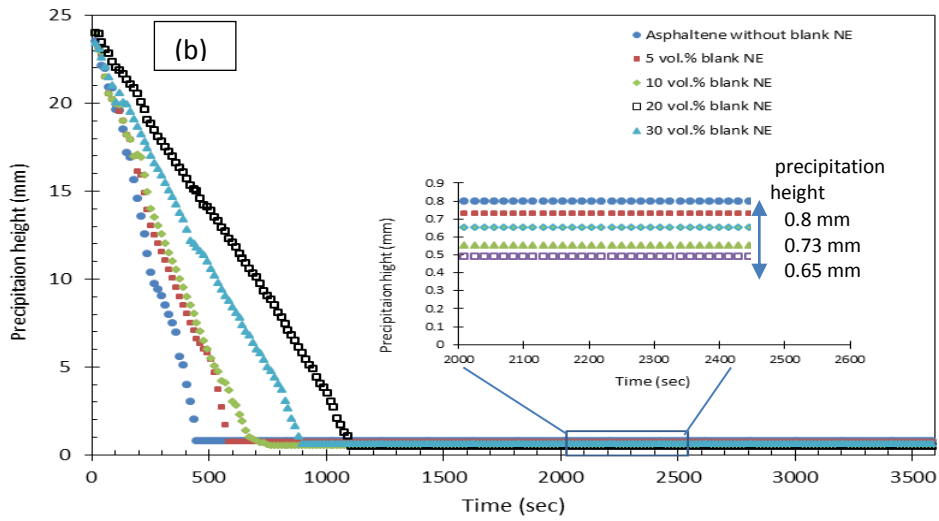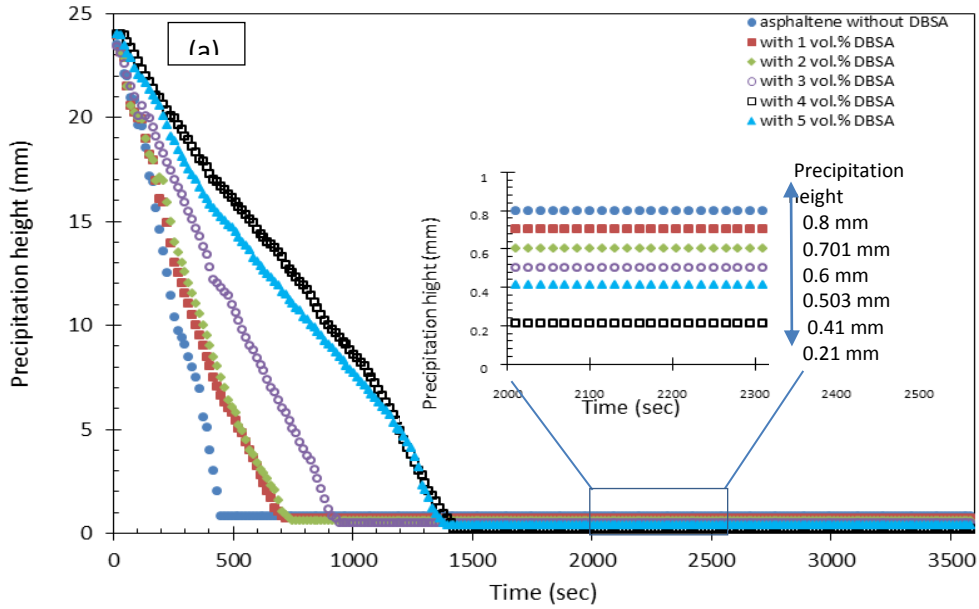
Fig. 6: Precipitation profiles for asphaltene solution with and without different volume fractions of (a) DBSA, (b) blank NEs, and (c) DBSA NEs. The data indicate sedimentation rate and the final height of the precipitation.

Fig.7 further compares the four cases under the optimum conditions, which shows that asphaltenes treated by 20 vol. % DBSA NE has similar effect as that of 4 vol. % DBSA. The treatment by 20 vol. % blank NE still has some effect but less stronger the other two. To illustrate the effect of imhibitor (i.e. DBSA) reduction, the instability index and sedimentiaon velocity are plotted as a function of DBSA volume. Using 20 vol.% DBSA NEs (i.e., containing 0.8 µl DBSA) give nearly the same values of instability index and the sedimentation rate as that of 4 vol.% DBSA (i.e., about 16 µl). Therefore, the amount of asphaltene inhibitor (% R_{AI}) is decreased by 95%. Although DBSA NEs contain different chemicals such as xylene, surfactants, and DBSA, the total chemicals (% R_{TC}) are again lower than 4 vol.% DBSA by a factor of 10%, as shown in clearly in the detailed mateirals balance are shown in Tables 3,4, and 5. Using NEs for DBSA delivery can significantly reduce the inhibitor and chemical amounts.

The ability of NE to deliver DBSA is further examined by determining the inhibitor release as shown in (Fig. 8). This procedure is similar to drug release in the area of nanomedicine [22, 23, 24]. The release rate is calculated from the slope of the released amount-time profiles of DBSA. The obtained results indicate that it is possible to obtain an effective and prolonged inhibitor release. By using NEs, it takes ~ 1450 seconds under centrifugal force to reach a nearly 100% release of DBSA. The amount of DBSA contained in both studies was 1 vol. % (i.e, 0.3 ml DBSA dissolved in 30 ml of DBSA NE and xylene). The data presented in (Fig. 8) also confirmed the improvement of DBSA release by NEs and the released of DBSA is much higher from nanoemulsion (99%) than that from xylene (13%). This can be due to the high lipophilicity of the DBSA, i.e., a higher affinity to the xylene than receptor solution (medium). Moreover the

enhanced diffusion from the nanoemulsion may be due to the large surface area of the droplets and the presence of surfactant, which reduce the interfacial tension.
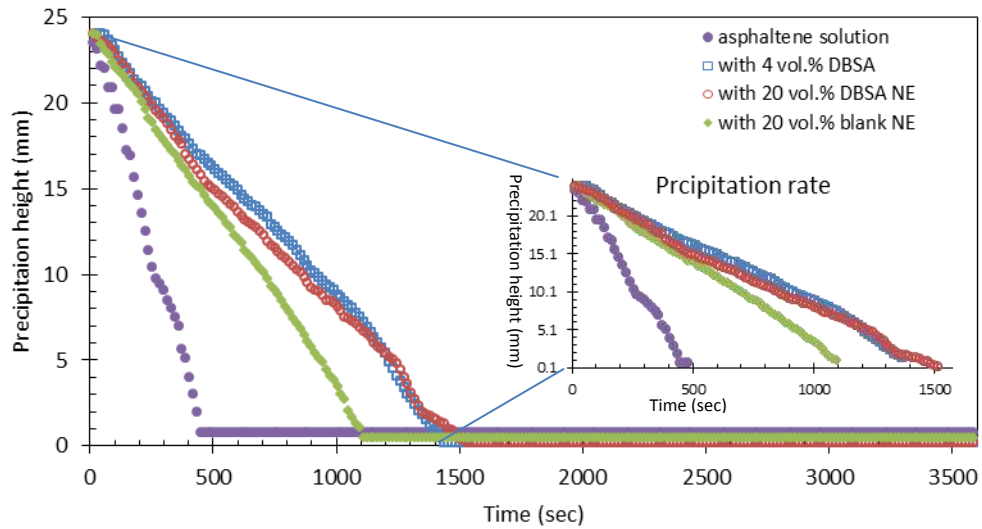

Fig. 7: The precipitation rate and the effect of optimum concentrations of DBSA, blank NE, and DBSA NE on asphaltene precipitation.
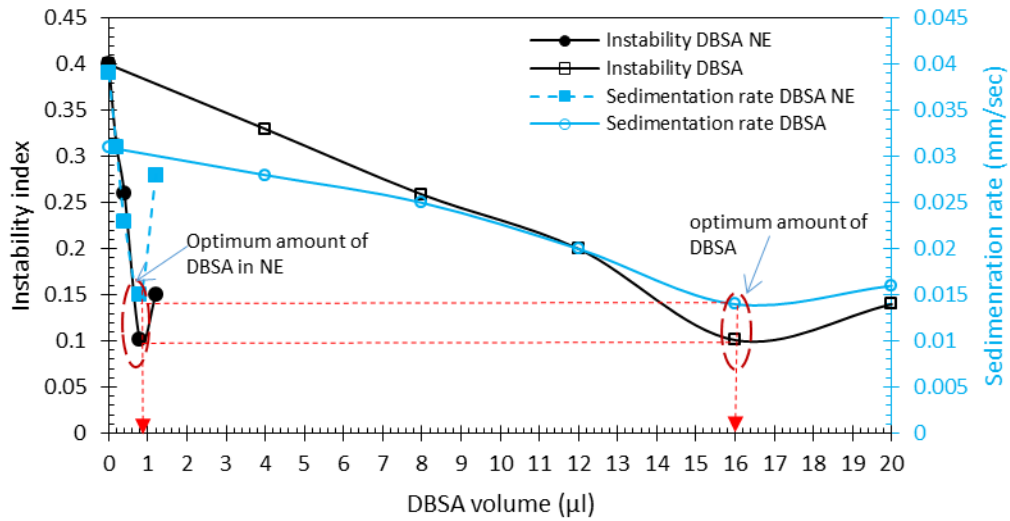

Fig. 8: Instability index and sedimentation rate for asphalting solution with different amounts of DBSA and DBSA NEs.

Table 3: Volume and volume fraction of DBSA.

DBSA	Vol. DBSA (µL)
1 vol.%	4.0
2 vol.%	8.0
3 vol.%	12.0
4 vol.%	16.0
5 vol.%	20.0

Table 4: Blank NE components and material balance.

Vol%. of blank NE	Vol. of blank NE (µL)	xylene vol.%	Vol. xylene (µL)	Tween 80 vol.%	Vol. Tween 80 (µL)	SDS vol. %	Vol. SDS (µL)	Water vol.%	Vol. Water (µL)
5	20	7	1.4	9.9	2.475	0.1	0.02	83	16.6
10	40	7	2.8	9.9	3.96	0.1	0.04	83	33.2
20	80	7	5.6	9.9	7.92	0.1	0.08	83	66.4
30	120	7	8.4	9.9	11.88	0.1	0.12	83	99.6

$$*: \quad vol.\,of\,component = \frac{Total\,volume\,of\,sample\,x\,vol.\%}{100}$$

$$**: \%\,R_{TC} = \left(\frac{Total\,chemicals\,vol.\,without\,nanoemulsion - Total\,chemicals\,vol.with\,nanoemulsio}{Total\,chemicals\,vol.\,without\,nanoemulsion}\right) x\,100\%$$

$$\%\,R_{AI} = \left(\frac{vol.without\,nanoemulsion - vol.with\,nanoemlsion}{vol.without\,nanoemulsion}\right) x\,100\%$$

Table 5: DBSA NE components and material balance.

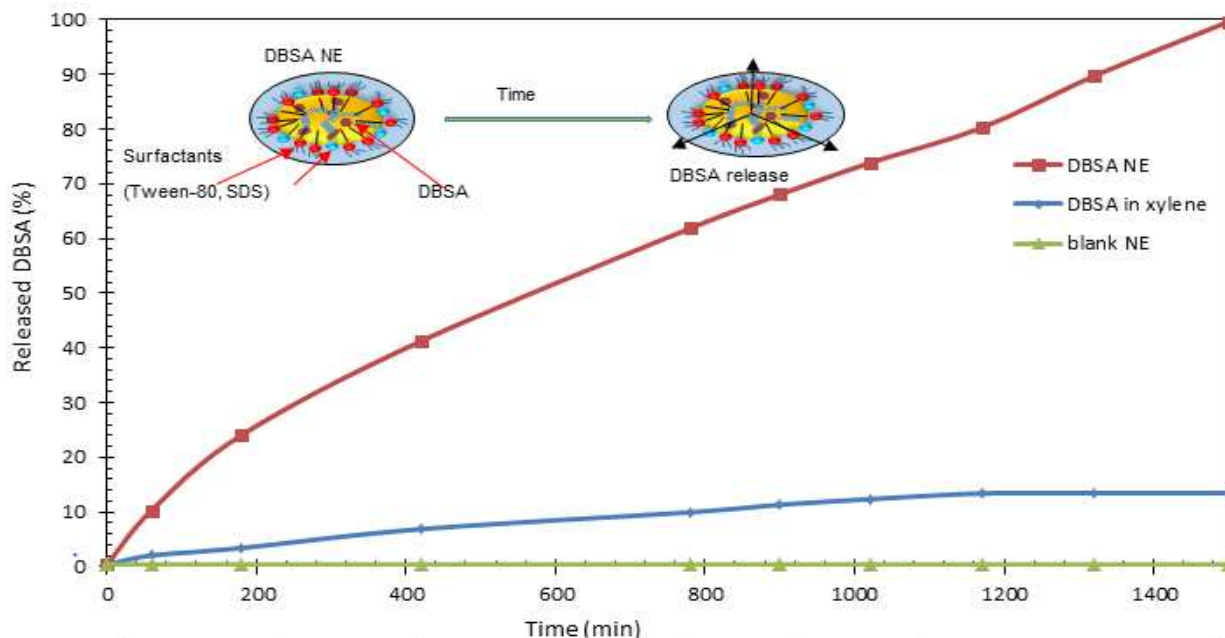| Vol.% of DBSA NE	Vol. of DBSA NE (µL)	xylene vol.%	Vol. xylene (µL)	Tween 80 vol.%	Vol. Tween 80 (µL)	SDS vol.%	Vol. SDS (µL)	DBSA Vol.%	Vol. DBSA (µL)	Water vol.%	Vol. Water (µL)	% R_AI*	% R_TC**
5	20	7	1.4	9.9	1.98	0.1	0.02	1.0	0.2	82	16.4	98.7	74.4
10	40	7	2.8	9.9	3.96	0.1	0.04	1.0	0.4	82	32.8	97.5	55.0
20	80	7	5.6	9.9	7.92	0.1	0.08	1.0	0.8	82	65.6	95	10.0
30	120	7	8.4	9.9	11.88	0.1	0.12	1.0	1.2	82	98.4	92	< 1

Fig. 9: Release profile of DBSA from NE and xylene.

3.3.4 Potential asphaltene stability mechanisms

3.3.4.1 Intermolecular interaction between asphaltene and the presence of DBSA, blank NEs, and DBSA NEs.

The DBSA's head group plays a major role in the asphaltene stabilization. Consequently, the presence of sulfonic acid groups ($-SO_3H$) is required for DBSA to effectively interact with asphaltenes. The interaction between DBSA and asphaltenes has been extensively studied in the literature [5, 38, 39, 40], which showed that the DBSA concentration and the chemical and structural properties of asphaltenes are major controlling variables. The intermolecular interaction takes place through the protonation of heteroatoms functional groups in the asphaltenes, which are positively charged, while proton-donor DBSA molecules become negatively charged ions. Hence, this process leads to an ion pair with a strong ionic bonding,

able to promote further electrostatic interactions with other ion pairs in neighbouring molecules/aggregates [11, 38, 39, 41].

Nevertheless, as the DBSA concentration rises, a greater number of DBSA molecules are attached to the available sites on asphaltene molecules/aggregates, up to either completion or unreachability of any available site as a result of steric hindrance by already attached DBSA molecules in the vicinity. This process progressively leads to the full coverage of aggregates, hindering interactions between asphaltene molecules as well as inhibiting aggregation [42, 43]. This strong acid-base interaction results in the attachment of the dispersant's sulfonic acid group to asphaltenes and makes DBSA a very effective asphaltene stabilizer [44, 45].

In addition of the DBSA's head group, DBSA's tail length plays a key part in the asphaltene stabilization. DBSA's tail length (12 carbon atoms) can provide a steric-stabilization effect to prevent asphaltenes from aggregating [42]. When the alkyl tail has six carbon atoms or more, this polar moiety becomes sufficiently large to form a stable aliphatic layer to prevent asphaltene particles from aggregation. As the length of the asphaltene inhibitor tails increases, the steric exclusion effect becomes successively important [39]. Figure (10 a) shows proposed intermolecular interactions mechanism between asphaltene and DBSA molecules.

In the case of using blank NE, NEs in this study consist of three components, which are: oil phase (xylene), surfactants (Tween 80 and SDS) and water. The first systematic study of using NE for demulisifacation of water/oil emulsions or asphaltene emulsions was reported by Souza et al. [19, 20]. In order to understand the effect of blank NE on asphaltene precipitation, we focus on the effect of each component in the NEs on asphaltene particles. Water can appear in three different forms in oil systems: solubilized, emulsified, or free water. Non-polar oils dissolve very small amounts of water depending on the saturation limit of the type of oil. Beyond the

saturation limit, water becomes either emulsified when surfactants are added or separated as free water [46, 47]. According to Sjöblom et al. [46] and Aslan et al. [47], water delays the precipitation of asphaltene, which could be due to i) water forms a layer around asphaltene and prevents asphaltene from precipitation or ii) water molecules act as a bridge between asphaltene molecules via hydrogen bonds between water molecules and heteroatoms in asphaltenes. Another component in NE may affect asphaltene precipitation is xylene, which is one of the most effective solvents for asphaltenes [48]. Moreover, Souza et al [19] suggested that the diffusion of the surfactant molecules to the water/oil interface can reduce the aggregation size of the asphaltene. Therefore, in this study, it was found that the use mixed surfactants (Tween 80 and SDS) as well as xylene and water in NE can provide good interactions with asphaltene molecules.

In addition to the effect of blank NE components, the DBSA NEs contain DBSA in the oil phase can modify the colloidal structure of asphaltene by promoting the interactions between the asphaltene molecules and the components of DBSA NEs. For example, the hydroxyl group in the chain length can form H- bonding with water or surfactants, whereas the nitrogen in the aromatic core can provide acid−base as well as H-bonding interactions with DBSA. This process can provide very strong and different bonding interaction between asphaltene/DBSA NE components such as: acid-base interaction, hydrogen bond, polar-π interaction, cation-π interaction and aromatic − aromatic interaction. These interactions can promote further electrostatic interactions with other ion pairs. Therefore, using a small amount of DBSA (1 vol. %) with other components in the DBSA NEs is sufficient to produce a complete coverage of the individual aggregates. Figure (10 b) shows proposed chemical mechanism for molecular assembly of DBSA NE

components: DBSA, xylene, Tween 80, SDS, and water to an active site at the asphaltene molecular structure, through very strong interactions.

3.3.4.1 Intermolecular interaction between asphaltene and the presence of DBSA NEs.

The DBSA NEs can modify the colloidal structure of asphaltene by promoting the interactions between the asphaltene molecules and the components of DBSA NEs (i.e., DBSA, xylene, surfactants (Tween 80 and SDS) and water). The DBSA is the most important component of DBSA NE and its head group plays a major role in the asphaltene stabilization. Consequently, the presence of sulfonic acid groups ($-SO_3H$) is required for DBSA to effectively interact with asphaltenes. The interaction between DBSA and asphaltenes takes place through the protonation of heteroatoms functional groups in the asphaltenes, which are positively charged, while proton-donor DBSA molecules become negatively charged ions. Hence, this process leads to an ion pair with a strong ionic bonding, able to promote further electrostatic interactions with other ion pairs in neighbouring molecules/aggregates [11, 38, 39, 41, 42,43,44,45]. In addition of the DBSA's head group, DBSA's tail length plays a key part in the asphaltene stabilization. DBSA's tail length (12 carbon atoms) can provide a steric-stabilization effect to prevent asphaltenes from aggregating [42]. When the alkyl tail has six carbon atoms or more, this polar moiety becomes sufficiently large to form a stable aliphatic layer to prevent asphaltene particles from aggregation. As the length of the asphaltene inhibitor tails increases, the steric exclusion effect becomes successively important [39]. Figure (10 a) shows proposed intermolecular interactions mechanism between asphaltene and DBSA molecules.

The second component in DBSA NE may affect asphaltene precipitation is xylene, which is one of the most effective solvents for asphaltenes [48]. The third component is surfactant; Souza et al [19] suggested that the diffusion of the surfactant molecules to the water/oil interface can

reduce the aggregation size of the asphaltene. Therefore, in this study, it was found that the use mixed surfactants (Tween 80 and SDS) in DBSA NE can provide good interactions with asphaltene molecules. In addition, water can appear in three different forms in oil systems: solubilized, emulsified, or free water. Non-polar oils dissolve very small amounts of water depending on the saturation limit of the type of oil. Beyond the saturation limit, water becomes either emulsified when surfactants are added or separated as free water [46, 47]. According to Sjöblom et al. [46] and Aslan et al. [47], water delays the precipitation of asphaltene, which could be due to i) water forms a layer around asphaltene and prevents asphaltene from precipitation or ii) water molecules act as a bridge between asphaltene molecules via hydrogen bonds between water molecules and heteroatoms in asphaltenes.

This system can provide very strong and different bonding interactions between asphaltene and DBSA NE components such as: acid-base interaction, hydrogen bond, polar-π interaction, cation-π interaction and aromatic – aromatic interaction. These interactions can promote further electrostatic interactions with other ion pairs. For example, the hydroxyl group in the chain length can form H- bonding with water or surfactants, whereas the nitrogen in the aromatic core can provide acid−base as well as H-bonding interactions with DBSA. Therefore, using a small amount of DBSA (1 vol. %) with other components in the DBSA NEs is sufficient to produce a complete coverage of the individual aggregates. Figure (10 b) shows proposed chemical mechanism for molecular assembly of DBSA NE components: DBSA, xylene, Tween 80, SDS, and water to an active site at the asphaltene molecular structure, through very strong interactions.
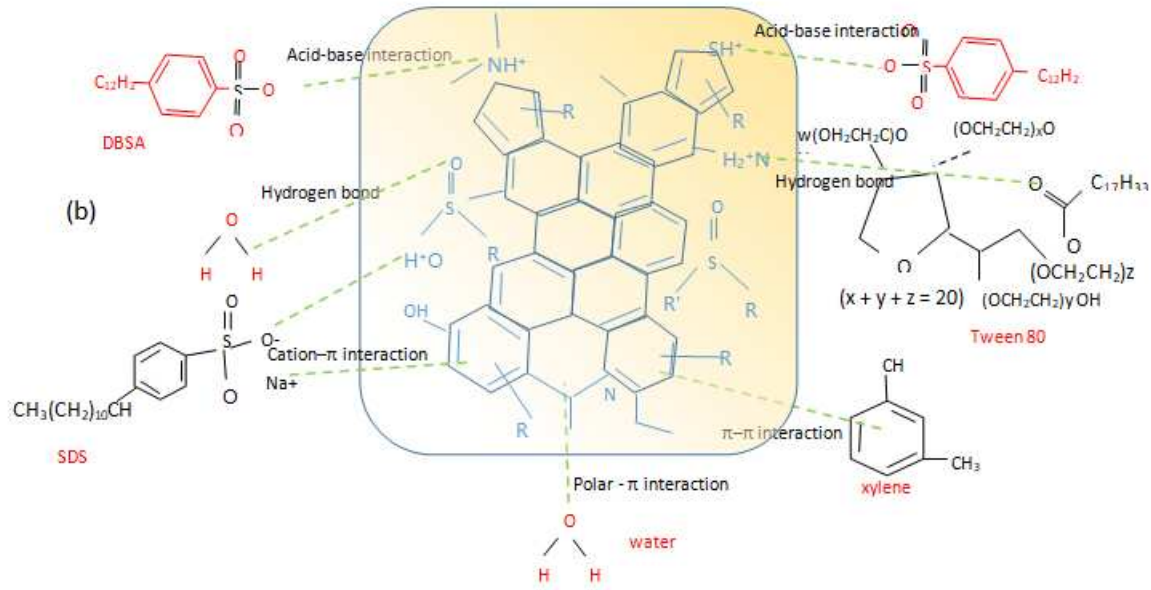
Fig. 10: Proposed chemical mechanism for molecular assembly. (a) shows a schematic asphaltene molecule with a heteroatomic nitrogen protonated at sufficiently DBSA concentration and (b) attachment of DBSA NE components: DBSA, xylene, Tween 80, SDS, and water to an active site at the asphaltene molecular structure, through very strong interactions, the heteroatomic such as nitrogen, oxygen, and sulfur groups are all protonated.

3.3.4.2 Water /asphaltene dispersion interface in the presence of the nanoemulsions.

To evaluate the influence of the blank NEs and DBSA NE and their composition on the asphaltene aggregates/ clusters present at the water/ oil interface, the interfacial tension (IFT) was studied. Fig.11 shows the IFT for four cases, i) water / Heptol mixture (60:40 vol.%), ii) water with and without surfactants / asphaltene solution (asphaltene in 60:40 Heptol), iii) blank NE / asphaltene solution and iv) DBSA NE / asphaltene solution. Interestingly, the IFT of water/Heptol was decreased from 28.0 to 22.0 mN m^{-1} when the asphaltenes were added to Heptol.

In the case of using blank NE or DBSA NE in asphaltene solution, the addition of 1vol. %
DBSA did not cause a significant change in the IFT . Thus, DBSA is likely located inside
nanodroplets (in xylene) and stabilised by mixed surfactants, which acts as a very good carrier
for DBSA. DBSA NEs shows a strong tendency to migrate and adsorb at the water/oil interface
due to the large surface area of the droplets and the presence of ionic / non-ionic surfactants,,
which reduces the IFT to 3.7 mN m^{-1}. [19, 20]. This interfacial activity explains the
effectiveness of DBSA NE in controlling asphaltene precipitation, as it allows the displacement
of asphaltenes from the water−oil interface, thereby stabilizing the asphaltene in solution.
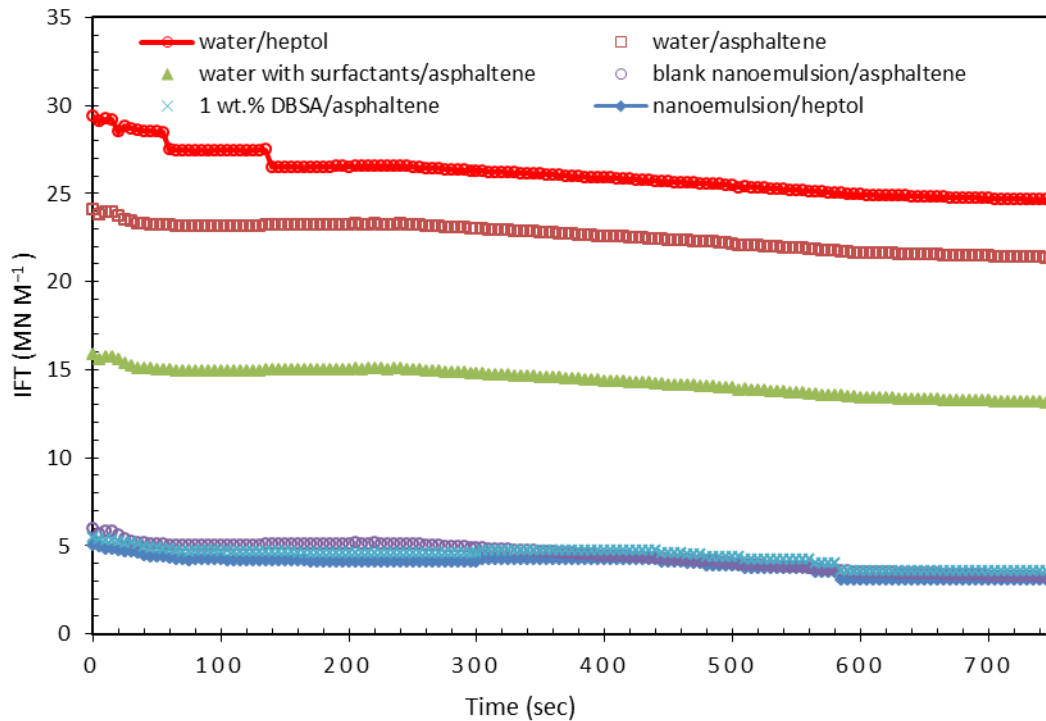Subseuqently DBSA is slowly released and interact with asphaltene molecules.

Fig.11: Water/oil interfacial tensions in the presence or absence of NEs containing 10 vol. %

surfactants with 7 vol. % xylene.

3.3.4.3 Controlled release of DBSA and its effect on asphaltene stability.

Two possible mechanisms can be used to explain the role of DBSA NEs to control asphaltene precipitation in both oil phase and water/oil interface. The first mechanism may be occurred in the oil phase (asphaltene in 60:40 Heptol), i.e., the bulk effect. The water phase (oil-in-water NEs) forms a layer around the asphaltene particles. Nanodropletes adsorb on asphaltene particles due to its high lipophilicity and higher affinity to the asphaltene as well as its small size (about 20 nm). Figure (12 b) shows the micrograph obtained from morphology G3S microscope for the asphaltene with DBSA NEs before the centrifugation. It is obvious that asphaltene particles are surrounded by water phase (i.e., containing DBSA NEs). However, very long chains of asphaltene flocculates linked together (like filaments) were clearly observed before centrifugation experiment.

When asphaltene with DBSA NEs are centrifuged , the stresses exerted on the asphaltene particles with NEs can be amplified and may make Tween 80 molecules move towards the water phase (i.e., around asphaltene particles) due to its affinity toward water, leaving oil droplet uncovered. As a result, the DBSA inside oil droplets can be released to interact with asphaltene particles, hence preventing asphaltene precipitation. Figure (12 C) shows the TEM micrographs obtained for the asphaltene with DBSA NEs after the centrifugation, which shows that asphaltenes are formed by nanometric particles having a diameter of around 5 to 30 nm with a large distance in between. Evidence here confirms that the DBSA NEs are able to reduce asphaltene particles from precipitate and form good dispersion in the medium, due to the effectiveness of DBSA NEs for asphaltene stabilization.

The possible second mechanism occurs at the water/oil interface, i.e. the surface effect, as described in the section 3.3.4.2. Therefore, DBSA NEs (containing DBSA dissolved in xylene)

and surfactants are able to displace all the asphaltenes from the interface via the release of DBSA and other components from DBSA NEs. Therefore, DBSA NEs interact with asphaltene aggregates/ clusters at the oil/water interface due to the high lipophilicity and higher affinity to the oil than water, which consequently keep asphaltene particles in the solution with smaller average size.
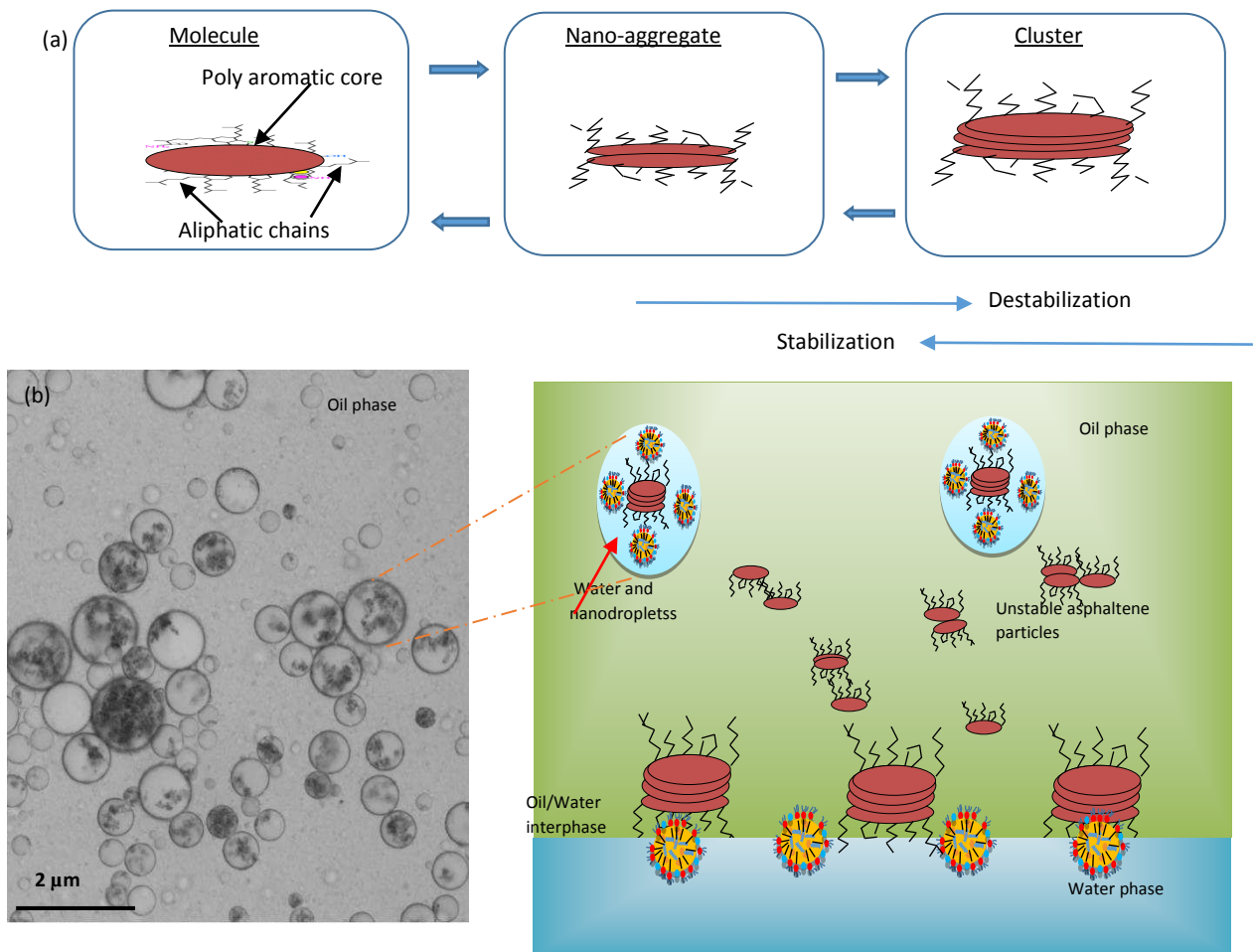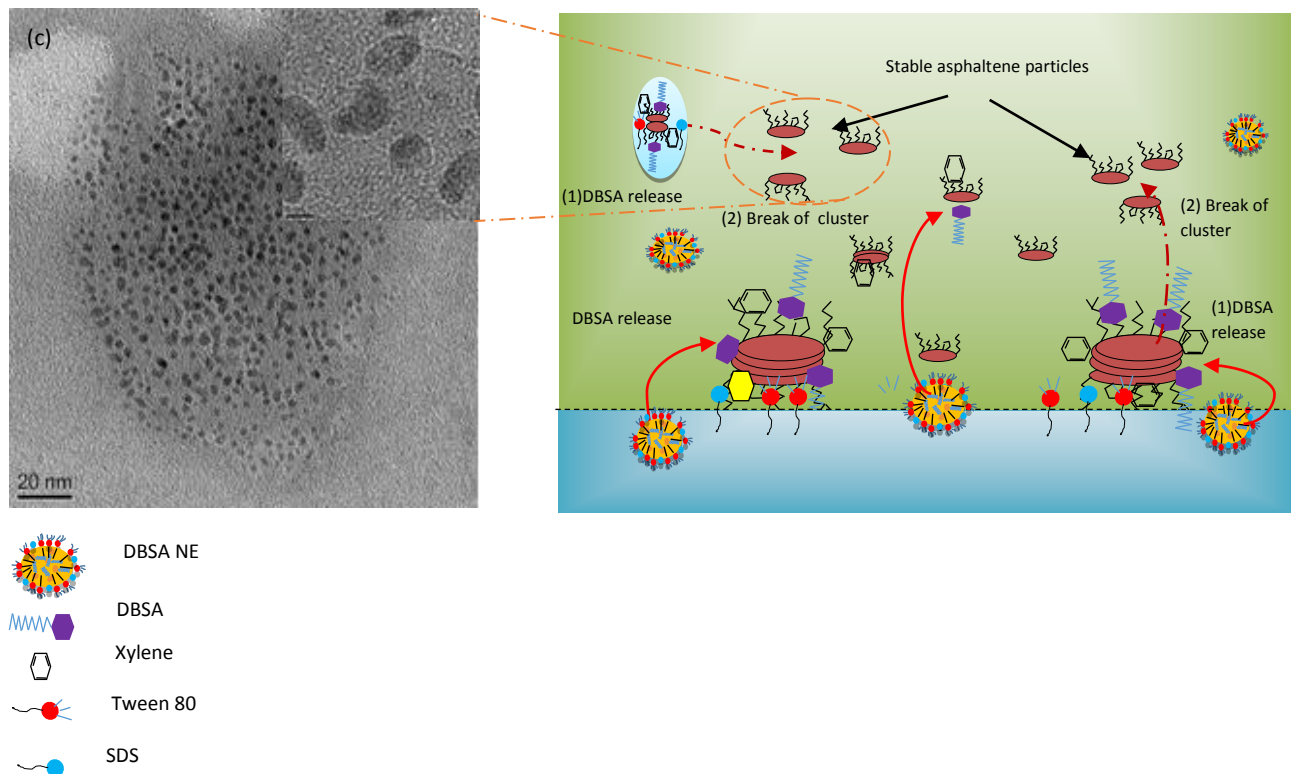
Fig. 12 The mechanism scheme of (a) asphaltene molecule and formation of aggregates and clusters; (b) G3S morphology micrographs obtained for the asphaltene with DBSA NEs before centrifugation; (c) TEM micrographs obtained for the asphaltene with DBSA NEs after centrifugation and releasing DBSA from DBSA NEs.

4 CONCLUSION

This study explored the concept of controlled delivery of asphaltene inhibitors by using nanoemulsions. Centrifugal experiments confirmed the validility of the new concept:

- NEs allow significant reduction of inhibor and chemical amounts in stabilizing the asphaltene. The inhibitor amount and total chemical usage can be reduced by 95 and 10 % respectively comparing with the case of using pure DBSA.

- NEs allows a signicant delay of asphaltene precipitation, i.e. a delay from pure asphaltene solution of 450 sec to 1400 sec in the presence of NEs.

- The presence of DBSA NE also reduced the precipitation thickness of asphaltene up to 75 %.

- The release of DBSA from NE depends on the interactions of surfactants used for the fabrication of NEs, and the subsequent change of the overall polarity and hydrophobic characteristics.

- Both the surface effect and bulk effect were contributing to effectiveness the NE in releasing inhibors, including the migriton of NEs to the water/oil interface and slowly release of chemcials at the interace, and the formation of hydration layers around asphltene particles in the bulk.

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