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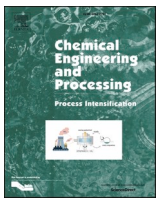

A mechanistic study of the synergistic and counter effects of ultrasonic and solvent treatment on the rheology and asphaltene structure of heavy crude oil

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ABSTRACT

Production from heavy oil reservoirs faces challenges, such as accumulating heavy hydrocarbon materials like asphaltenes near the wellbore, resulting in low recovery rates. To enhance recovery and prevent formation damage, methods often focus on reducing oil viscosity. Solvents and ultrasonic waves have proven effective in this regard, though challenges related to asphaltene aggregation and structural changes persist. This study explores the impact of simultaneously applying ultrasonic radiation and solvents on crude oil's viscosity and asphaltene structure. Toluene and n-heptane, representing aromatic and paraffinic solvents, were employed. Viscosity measurements and Fourier transform infrared spectroscopy tests were conducted on sonicated crude oil diluted with solvents and solvent-diluted crude oil subjected to sonication. Results were compared to untreated and separately treated crude oil samples. The study found that the most effective viscosity reduction method involved blending sonicated oil with toluene under optimal radiation time and concentration conditions. Two primary mechanisms for viscosity reduction were identified. Firstly, there was the dissolution and aggregation of asphaltene clusters. Secondly, chemical changes in asphaltene molecular structure were observed, altering the ratio of aromatic rings to aliphatic chains. This research offers potential insights into how ultrasonication and solvation interact to modify crude oil structure.

1. Introduction

Heavy oils are typically defined as liquid petroleum with a viscosity exceeding 100 cP and API in the range of 10° and 20° at reservoir conditions [1]. Various approaches have been utilized to enhance production from heavy oil reservoirs, primarily focusing on viscosity reduction, the most effective of which are thermal methods. However, the applicability of thermal recovery techniques for reservoirs with special characteristics, such as low thickness, low rock thermal conductivity, bottom water zone, etc., remains challenging [2–5]. In addition, energy consumption and environmental pollution are the main concerns of thermal methods. On the other hand, near-wellbore formation damage induced by, e.g., asphaltene/wax deposition and mud invasion, can significantly reduce oil recovery [6–8]. As a result, many studies have investigated effective and innovative techniques useful for heavy oil recovery and the cleanup of near-wellbore damage.

The solvent-based processes have shown promising results as alternatives to thermal methods with potential applications for enhanced oil recovery (EOR) with less energy use and reduced environmental pollution [2,9-11] and removing asphaltene damage from near-wellbore regions [12]. Several mechanisms have been reported for increasing oil recovery, such as the dilution effect and viscosity reduction [13], oil swelling and possible asphaltene precipitation [14], and water-oil IFT reduction in carbonated smart water EOR [15]. The main concern of using hydrocarbon solvents containing n-alkanes is that asphaltene precipitation and deposition can clog reservoir rock pores and reduce permeability, hence oil production [16].

In addition to solvent-based techniques, numerous studies have documented the utilization of ultrasound for enhancing heavy oil recovery and well stimulation over the past two decades [17–23].

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Ultrasonic radiation has some advantages over conventional IOR methods, e.g., reduced formation damage with low environmental pollution [19,22,24], well stimulation without stopping the oil production (economic benefits), and exact stimulation of selected parts of the oil reservoir. Applying ultrasonic waves can induce notable alterations in the physical and chemical properties of both crude oil and reservoir rock [25,26]. This influence of ultrasonication on the fluid and rock properties in the reservoir is related to the type of fluids and rock and also the wave power [27,28]. The main underlying mechanisms of ultrasonic-assisted oil recovery and near-wellbore stimulation include crude oil viscosity reduction, breakdown of asphaltene aggregates, demulsification, desalination, vibration, changes in the IFT between oil and water, changing the reservoir rock wettability, and increasing in reservoir rock permeability [26,29-34]. Numerous investigations have particularly centered on examining how ultrasonic irradiation affects the viscosity of crude oil and its asphaltenes [35–41].

The primary determinant of recovery from heavy oil reservoirs lies in the viscosity of the oil, as it governs the flow rate and, consequently, the economic feasibility of production. In this regard, heavy components of crude oil, particularly asphaltene constituents, significantly impact the oil viscosity [42–44]. While numerous studies have individually investigated the impacts of solvents and ultrasonic radiation on crude oil properties, a pertinent question arises regarding the combined influence of multiple solvents (such as aromatic and n-alkane hydrocarbons) and ultrasound on the evolution of crude oil viscosity and asphaltene aggregates for the purposes of enhanced oil recovery (EOR) and well stimulation. This is a complex problem, particularly when paraffinic diluents are used as a solvent, and there is a need to carefully address and understand the issue of asphaltene stability (flocculation and collapse) in terms of ultrasonication-solvent interactions.

This paper is a continuation and extension of our previous work [45] in order to investigate the effects of the simultaneous use of ultrasonic radiation and solvents of varying types. The focus of this study is to explore the reduction of heavy oil viscosity through ultrasonic assistance in the presence of aromatic and paraffinic solvents. Our approach involves several key steps. Initially, we measure the viscosity of heavy oil immediately after terminating ultrasonic irradiation and again after a 24-hour irradiation period to determine the optimal radiation duration. Subsequently, we assess how the viscosity of the crude oil changes when mixed with varying volume percentages of solvents (specifically, toluene and n-heptane). We identify the precipitation onset point of asphaltenes when paraffinic solvent is introduced. We examine the viscosity of oil samples treated with ultrasound and blended with solvents to evaluate the combined (synergetic and/or counter) effects of ultrasonication and solvation on oil viscosity. Finally, to gain insights into the alterations in crude oil constituents resulting from the combined sonication and solvation, we employ optical microscopy and Fourier transform infrared spectroscopy (FTIR). We provide detailed explanations of the relationship between viscosity changes and the alterations in the physical and chemical structure of the oil. The outcomes of this research offer valuable insights into the synergistic or counteractive effects of ultrasound and solvents on heavy oil properties. These findings could have practical implications for addressing near-wellbore formation damage induced by asphaltenes and enhancing heavy oil recovery.

2. Materials and methods

2.1. Materials

In this study, we used the same crude oil that was used in our previous study [45]. The crude oil was sourced from a field in southwestern Iran. Table 1 provides details on the physical properties and composition of this crude oil. It is worth noting that the crude oil under investigation falls into the category of heavy asphaltenic oil. To lower its viscosity, we employed 99 % pure normal heptane (Merck, Germany) and toluene (Merck, Germany).

2.2. Experimental apparatus and procedure

Fig. 1 illustrates the schematic representation of the experimental setup employed in this study. Ultrasonication of the crude oil was conducted using an ultrasonic generator (Topsonics, Model: UHP-400) with an output power capacity of up to 100 W and a maximum frequency of 20 kHz. The Brookfield DV-III Ultra viscometer was utilized to measure the oil viscosity. We used a high-resolution optical microscope (Nikon E-200, Japan) to visualize the oil asphaltene aggregates before and after the ultrasonic treatment. To investigate the individual and combined impacts of ultrasonication and solvation on asphaltene molecular bonds, we analyzed both untreated and treated oil samples (treated with ultrasonic waves and solvents) using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The FTIR measurements were conducted using a Bruker Tensor II spectrometer (Bruker Optik, Germany). The experimental procedure adopted in this study is outlined as follows. Initially, the crude oil was transferred into 50-mL glassware beakers. We measure the viscosity of crude oil samples subjected to ultrasonic waves at a frequency of 20 kHz and an output power of 100 W for varying durations of irradiation. For each irradiation time, we conduct viscosity measurements in two steps. First, we measure the oil viscosity immediately after discontinuing the ultrasonic radiation, prior to allowing the oil to cool down to ambient temperature. In the second step, we assess the viscosity of the oil after it has cooled down for 24 h post-radiation. These dual measurements aid in pinpointing the optimal radiation duration, where viscosity reaches its minimum value. Subsequently, we measured the viscosity of the original crude oil blended with different volume percentages of solvent. During this phase, we identify a specific solvent concentration, referred to here as the 'optimum solvent concentration,' at which asphaltene precipitation commences for the paraffinic solvent (i.e., n-heptane). Following this determination, we measure the viscosity of the diluted crude oil with the solvent at the optimum concentration while subjecting it to ultrasonic irradiation at the previously established optimal radiation duration. Once again, we conduct viscosity measurements immediately after halting the radiation and after 24 h of radiation exposure. All experiments are conducted at an ambient temperature of 22 °C and atmospheric pressure. Finally, we employ optical microscopy and FTIR analysis to assess alterations in the physical and chemical attributes of the oil samples subjected to various treatment scenarios, as detailed in Section 2.3.

2.3. Description of the treatment scenarios

In this study, we used ultrasonic radiation and solvents to assess the evolution of the rheological behavior and asphaltene structure of heavy

Table 1
Properties of the crude oil employed in this research. The data was reproduced from [45].

Density (g/cm^3)	Oil gravity (API)	Viscosity (cP)	Bubble-point pressure (psi)	SARA analysis (wt.%)			
				Saturated	Aromatic	Resin	Asphaltene
0.94	19.0	145 (25 °C)	995 (45 °C) 1265 (110 °C)	43.4	35.6	12.9	8.1

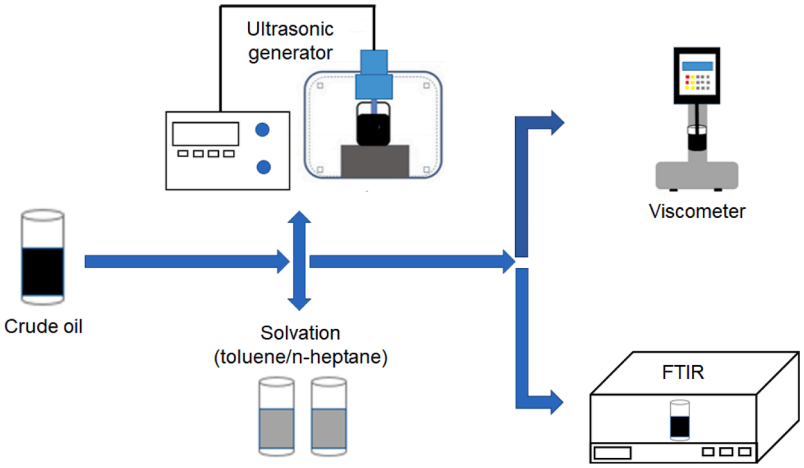

Fig. 1. An experimental setup diagram utilized to explore the synergistic effects of ultrasound and solvent on oil viscosity.

crude oil. To accurately evaluate the synergetic and counter effects of the combined use of ultrasound radiation and solvation of crude oil with aromatic and paraffinic solvents, all possible treatments can be classified into 8 treatment scenarios, as described in detail in Table 2. The treatment scenarios described in Table 2 essentially represent the following general cases:

(1) Scenario I shows the original crude oil sample (non-irradiated solvent-free state). The scenario is referred to as the *reference crude oil*.
(2) Scenarios II and III represent the solvation (or dilution) of the original (non-irradiated) crude oil in aromatic (i.e., toluene) and paraffinic (i.e., n-heptane) solvents, respectively. These scenarios are called the *solvation of crude oil*.
(3) Scenario IV indicates irradiated solvent-free (non-diluted) crude oil. This is referred to as *ultrasonic radiation of crude oil*.
(4) Scenarios V and VI represent crude oils initially subject to ultrasonic radiation and then blended (diluted) with aromatic and paraffinic solvents, respectively. These scenarios are referred to as *irradiation-then-dilution-treated crude oil*.
(5) Scenarios VII and VIII illustrate crude oils that are initially blended (diluted) with aromatic and paraffinic solvents, respectively, before they are radiated with ultrasound waves. These scenarios are referred to as *dilution-then-irradiation-treated crude oil*.

Table 2
Description of the treatment scenarios considered in this study to assess the impacts of the combined use of ultrasonic radiation and solvation of crude oil with aromatic and paraffinic solvents on the oil viscosity and asphaltene structure.

	No irradiation	Irradiation
No dilution	**Scenario I:** Non-irradiated, non-diluted crude oil (Original crude oil sample)	**Scenario IV:** Irradiated, non-diluted crude oil
Dilution	**Scenario II:** Diluted non-irradiated crude oil with aromatic solvent	**Scenario V:** Irradiation-then-dilution-treated crude oil with aromatic solvent
	Scenario III: Diluted non-irradiated crude oil with paraffinic solvent	**Scenario VI:** Irradiation-then-dilution-treated crude oil with paraffinic solvent
		Scenario VII: Dilution-then-irradiation-treated crude oil with aromatic solvent
		Scenario VIII: Dilution-then-irradiation-treated crude oil with paraffinic solvent

3. Results and discussion

3.1. Influence of ultrasound on the crude oil viscosity without solvent effect

As described in our previous work [45], the crude oil samples with the same volume (50 cm^3) were exposed to ultrasonic waves at a frequency of 20 kHz and output power of 100 W for varying radiation durations (2, 4, 6, …, 18 min). Measuring the crude oil temperature exhibited a continuous rise with increasing ultrasonic radiation time before reaching a point where the temperature was stabilized. Fig. 2(a) shows the measured viscosity of the crude oil immediately after we ceased the ultrasonic radiation and before the oil cooled down. It is worth noting that Fig. 2 was reproduced from our previous paper [45] for comparisons with the individual and combined effects of solvents and ultrasound on crude oil viscosity. Our findings revealed a significant reduction in oil viscosity due to ultrasonication. Specifically, as the radiation time increased up to a certain threshold, viscosity decreased substantially by up to 47 %. Beyond this critical point, viscosity exhibited a more moderate increase. The most pronounced reduction in viscosity occurred when the oil was exposed to radiation for 8 min. Previous research has proposed that ultrasonic-induced viscosity reduction arises from the complex interplay of two phenomena. Firstly, there are the mechanical (or thermal) effects of the waves, involving mechanisms like acoustic cavitation, mechanical vibration, and the dissipation of acoustic energy [39,46-49]. During cavitation, the heating collapse forms large bubbles, so suspension conglomerates disintegrate [50]. Secondly, there are the chemical effects, wherein ultrasound directly impacts the molecular structure of the oil, primarily through the breakdown of asphaltenes and heavy molecules into lighter ones [25, 38].

In addition to the immediate viscosity measurements taken after ceasing the radiation (as depicted in Fig. 2(a)), we also measured the viscosity of the oil after it had cooled down due to heat dissipation to the surroundings, following 24 h of radiation exposure [45]. It was observed that the oil's viscosity had increased to some extent during this post-radiation period. This can be attributed to the reduction in molecular vibrations due to the radiation's shock removal, which altered

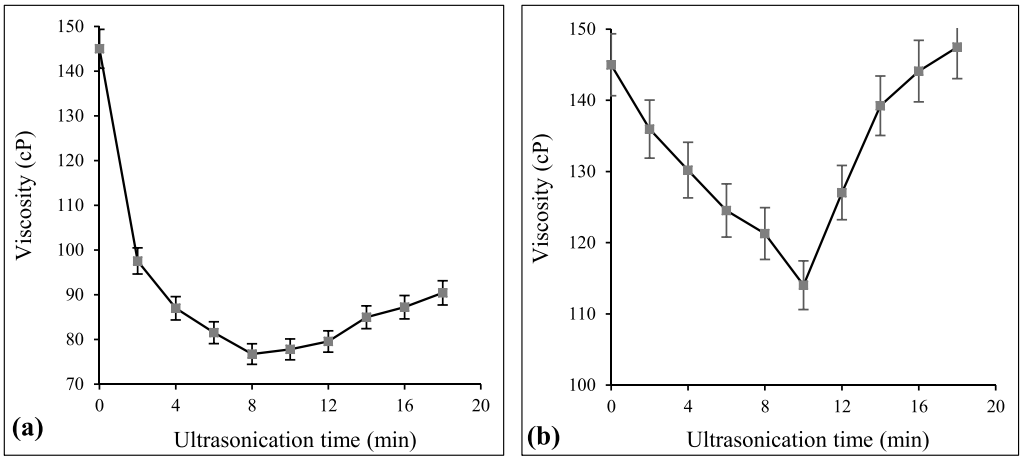

Fig. 2. (a) The oil post-radiation temperature and viscosity versus ultrasonic radiation time (before the oil cooled down); (b) the cooled-down oil viscosity after 24 hrs of ultrasonic radiation. Both figures were reproduced from Razavifar, et al. [45].

the molecular arrangement and, consequently, increased viscosity. Furthermore, it is important to note that the post-radiation oil viscosity did not return to its initial level; instead, it remained either lower or higher than the original oil viscosity, depending on the duration of radiation. This phenomenon can be linked to permanent changes in the composition and molecular structure of crude oil, particularly the physical and chemical cracking of asphaltenic aggregates [38,45]. Referring to Fig. 2(b), it becomes evident that there exists an optimal radiation time at which the post-radiation oil viscosity reaches its minimum value. Our findings indicated this optimal radiation duration as 10 min, resulting in a permanent 21 % reduction in crude oil viscosity. It's important to emphasize that the optimum radiation time is unique and depends on the physical and chemical characteristics of the oil, including the asphaltene content, as well as the specific radiation frequency and power settings. Table 3 provides a comparison of the optimum radiation time obtained in this study with a few results reported in the literature. It is argued that the final cooled-down post-radiation viscosity of crude oils is the outcome of complex interactions between the breakdown of heavy molecules, the boiling effect, and the recombination of heavy components, particularly asphaltene aggregates [51].

A typical viscosity response accompanied by a schematic of the main mechanisms behind the evolution of viscosity is illustrated in Fig. 3. The initial oil viscosity is marked by point A. The viscosity decreases early during the ultrasonication of the crude oil (point B). But, after stopping the radiation and cooling the oil by heat transfer, viscosity starts to increase and continues to rise (point C). Throughout ultrasonic irradiation, several factors contribute to the reduction in viscosity. These factors include the breakdown of heavy components in crude oil, notably asphaltene constituents, a decrease in asphaltene aggregate size, and an increase in internal friction due to the dissolution of suspended particles [38,39,44]. At point B, which corresponds to the optimal radiation duration, we observe the most extensive cracking of heavy components within the crude oil and the least recombination of these components. This results in the minimum viscosity attained during the process. As evident from Table 3, the optimum radiation time depends on the crude oil characteristics (°API and asphaltene content) and the wave properties (frequency and power). When ultrasonication is terminated, reattachment of asphaltenic components [38], evaporation of light hydrocarbon components, i.e., the boiling effect [52], conversion of resin molecules to asphaltenes [53], and heat loss to the surroundings play main roles in increasing the oil viscosity.

Table 3
A comparison of optimum ultrasonic radiation time and the percentage of viscosity reduction in this work and other studies.

API	Asphaltene Content (%)	Ultrasonic frequency (Hz)	Ultrasonic power (W)	Optimum Radiation time (min)	Reference
13.85	Not reported	24	280	5	[52]
21.66	8.81	45	1.8	45	[54]
12, 20	12.3, 10.2	45	75	10, 40	[38]
29.1, 15.9	2.9, 12.1	20	80,100,160	1–3	[55]
31.1	19.45	46	50	8	[35]
27.9	5.3	20	40	2.5	[41]
19.0	8.1	20	100	10	This work

For a more rigorous assessment of the impact of ultrasonic power on fluid viscosity, it is advisable to examine how viscosity evolves concerning power density, representing the ultrasonic wave power per unit volume of the irradiated fluid. We conducted viscosity measurements on oil samples subjected to ultrasonic treatment with varying volumes. Specifically, ultrasonic waves at 20 kHz/100 W were applied to samples with volumes of 50, 100, and 150 cm^3 for the determined optimal radiation duration of 10 min. Once again, viscosity measurements were taken immediately after discontinuing the radiation (under high-temperature conditions) and after 24 h of radiation (under ambient or low-temperature conditions). In Fig. 4, the measured viscosity is depicted as a function of power density. It becomes apparent that lower power density corresponds to a milder decrease in viscosity. This observation is attributed to the diminishing impact of ultrasonic wave energy as the sonicated volume increases. Notably, our findings reveal that the disparity between viscosity under high and low-temperature conditions enlarges as ultrasonic power density rises.

3.2. Effect of solvent on the crude oil viscosity without ultrasonic radiation

Two different solvents, i.e., toluene, a typical aromatic solvent, and n-heptane, a typical n-alkene or paraffinic solvent, were chosen to assess the sole effect of solvent as well as the simultaneous influence of ultrasonication and solvent on the crude oil viscosity. It is known that aromatics such as toluene can easily dissolve asphaltenic components of crude oils, while asphaltene is not soluble in paraffinic hydrocarbons such as n-heptane [56]. In this part, the crude oil samples were blended with the solvents at different volume percentages ranging from 2 % to 24 %. Fig. 5 depicts the viscosity measurements of the crude oil when blended with solvents at different concentrations. Note that the data for (n-heptane+crude oil) was reproduced from our previous work [45] for comparison purposes. The data in Fig. 5 demonstrate that introducing solvents into the crude oil reduced oil viscosity. This reduction can be

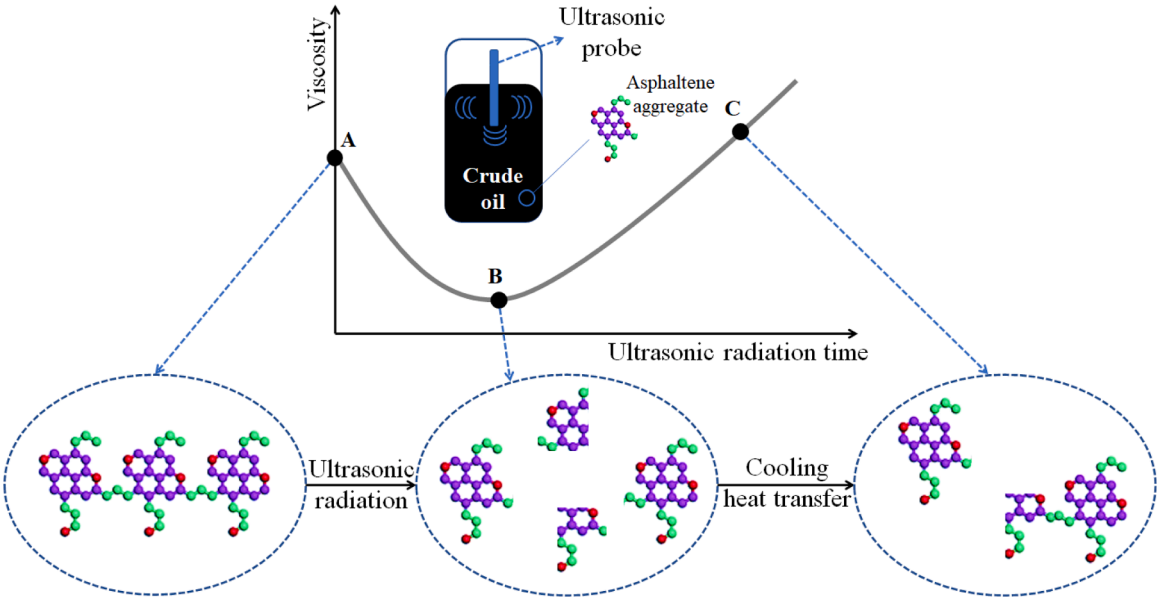

Fig. 3. A typical viscosity response as a function of ultrasonic radiation time. Ultrasonic irradiation of the oil results in.

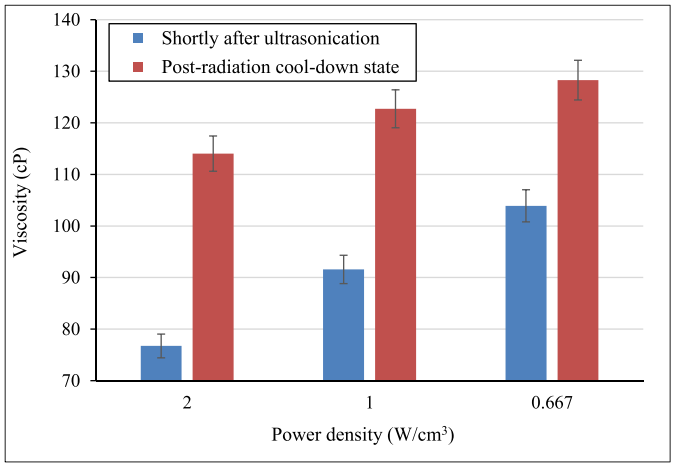

Fig. 4. The measured oil viscosity for various wave power densities. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

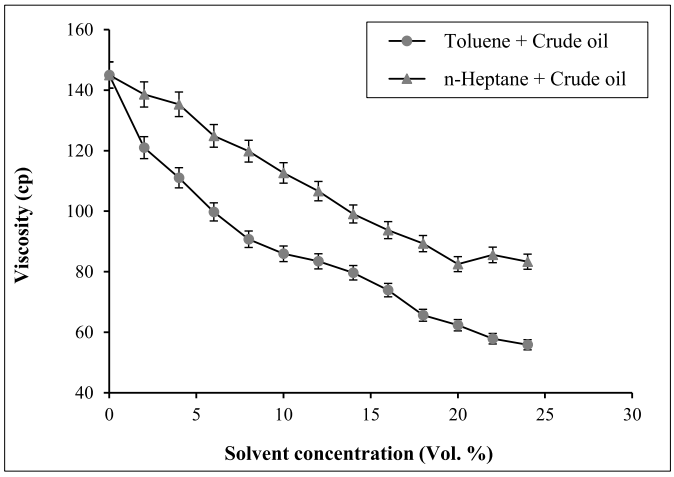

Fig. 5. Effect of dilution of the crude oil with the solvents on the oil viscosity. The data for (n-heptane+crude oil) was reproduced from Razavifar, et al. [45].

attributed to both the dilution effect, involving the mixing and diffusion/dispersion of the solvent within the heavy oil, and the interactions between the solvent and asphaltenes [57–59].

The nature of molecular interactions that occur in crude oil-hydrocarbon solvent blends has been discussed in several studies [60, 61]. Two observations can be clarified in Fig. 5. First, toluene reduced the viscosity more than n-heptane at the same volume percentage. A second significant observation is that the continuous decline in viscosity ceased when the n-heptane concentration reached 20% vol. At this juncture, a slight upturn in viscosity became noticeable before further reductions were observed with additional n-heptane. This distinct turning point is commonly denoted as the onset of asphaltene flocculation. At this stage, the suspended asphaltene particles, also called colloids, begin to influence the oil's flow characteristics, leading to an increase in viscosity [62,63]. The observation was confirmed in other studies, such as [64]. We found 43 % and 57 % reductions in the viscosity by adding 20 vol.% of n-heptane and toluene, respectively. For further investigations of this study, we opted for a uniform volume of 20 % by volume for the solvent (toluene/heptane) to facilitate a meaningful comparison of solvent effects on crude oil properties. While it was found that toluene exhibited a continuous reduction in oil viscosity with increasing concentrations, we adopted 20% vol of the solvent as the optimal concentration.

3.3. *Investigation of the combined influence of ultrasonic waves and solvent on oil viscosity*

In this section, we examine the combined impact of ultrasound and solvent on crude oil viscosity. These findings hold the potential for enhancing ultrasonic-assisted heavy oil recovery or addressing issues related to asphaltene-induced near-wellbore formation damage through solvent flooding. To align with the objectives of this study, we designed two distinct experimental procedures. In the first scenario, we initially mixed the crude oil samples with 20 vol.% of either toluene or n-heptane. Subsequently, we exposed 50 cm^3 of the diluted oil to ultrasonic waves for the optimized duration of 10 min. Viscosity measurements were then taken immediately after the ultrasound treatment and again after 24 h of ultrasonication. This approach is denoted as the 'dilution-then-irradiation-treated crude oil' (as outlined in Table 2). In the second

scenario, the crude oil samples were first subjected to ultrasound treatment for the optimized duration before blending them with 20 vol. % of solvents while in the cooled-down state. This methodology is termed the "irradiation-then-dilution-treated crude oil" (as detailed in Table 2). In essence, in the first case, we diluted the crude oil with solvents prior to ultrasonication, while in the second case, we performed the opposite sequence of actions.

The results of the viscosity measurements for all the scenarios outlined in Table 2 are presented in Fig. 6. It is noted that the results of scenarios I, II, IV, and V were previously reported in our previous paper [45] and they are used here for comparison purposes and mechanistic evaluations. Key findings from Fig. 6 can be summarized as follows. It is important to note that all percentage values mentioned here are in reference to the original, non-irradiated crude oil viscosity (as indicated in Table 1) unless explicitly stated otherwise.

(1) In the absence of ultrasonication, a substantial reduction in viscosity (ranging from 43 % to 57 %) was observed in the diluted crude oil containing 20 vol.% of solvents when compared to the undiluted crude oil. Due to its solubility characteristics and asphaltene content, toluene exhibited a more pronounced viscosity reduction than n-heptane.
(2) Diluting the non-irradiated oil with toluene resulted in a greater viscosity reduction compared to both the undiluted, radiated oil and the radiated, diluted oil with n-heptane.
(3) Ultrasonication of the diluted crude oil with solvents led to a 10 % reduction in viscosity compared to diluted oil without ultrasonic treatment.
(4) In terms of the original, non-irradiated crude oil, ultrasonication of the diluted crude oil resulted in a significant viscosity reduction of 48 % and 61 % for n-heptane and toluene, respectively. Interestingly, dilution of the ultrasonically treated crude oil caused an even greater decrease in viscosity, amounting to 66 % and 68 % for n-heptane and toluene, respectively.
(5) A comparison between the sonicated crude oil and the sonicated diluted oil shows that adding the solvent assisted in the intense radiation-induced cavitation. It is hypothesized that the solvation of the crude oil reduced the heavy constituents and increased the volatile components; hence, more intense cavitation occurred due to sonication. This hypothesis was further investigated and confirmed by the FTIR measurements (see Section 3.5).
(6) The most substantial oil viscosity reduction was observed in diluted irradiated crude oil with toluene (scenario V in Table 2).

3.4. Characterization of the asphaltene aggregates under ultrasonic and solvent effects by optical microscope

We utilized a high-resolution microscope to visualize the asphaltene aggregates within the crude oil both before and after ultrasonic radiation for the optimized duration of 10 min. Fig. 7(a)–reproduced from our previous paper [45] for comparison purposes–presents a microscopic image of the non-radiated undiluted crude oil, revealing the presence of relatively large asphaltene aggregates. In contrast, Fig. 7(b and c) displays images of the ultrasonically treated diluted crude oil containing 20 vol.% of toluene and n-heptane, respectively. Clearly visible is the considerable reduction in aggregate sizes resulting from ultrasonic radiation, primarily achieved by breaking down clusters and reducing asphaltene content through mechanisms such as asphaltene re-dissolution and the conversion of asphaltene molecules into lighter aromatics [65]. A comparison between Fig. 7(b) and Fig. 7(c) highlights the presence of larger asphaltene aggregates when the crude oil was mixed with n-heptane.

3.5. Characterization of the oil structural changes under ultrasonic and solvent effects by FTIR spectroscopy

So far, our investigations have revealed that the combined impacts of ultrasonic radiation and paraffinic solvents on crude oil viscosity encompass two opposing aspects. At specific concentrations, paraffinic solvents like n-heptane induce asphaltene flocculation and precipitation within the oil, thereby increasing viscosity. Conversely, ultrasonication of crude oil breaks down heavy components and reduces the size of

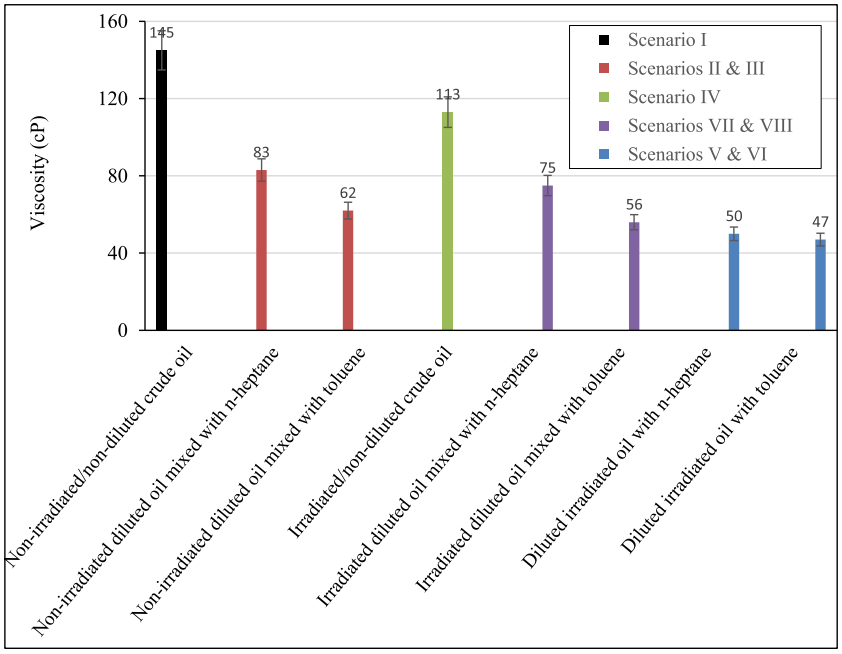

Fig. 6. A comparison of the measured viscosities of the irradiated diluted/non-diluted oil samples with solvents with the cases of non-irradiated diluted/non-diluted oil samples. Note that the radiation was applied for the optimum radiation time of 10 min, and the dilution of the samples was carried out to give solutions with 20 vol.% of the solvents. It is noted that the irradiated oil viscosity was measured when the samples were cooled down to the ambient temperature. It is noted that the results od scenarios I, II, IV, and V were reproduced from Razavifar, et al. [45] for comparison purposes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

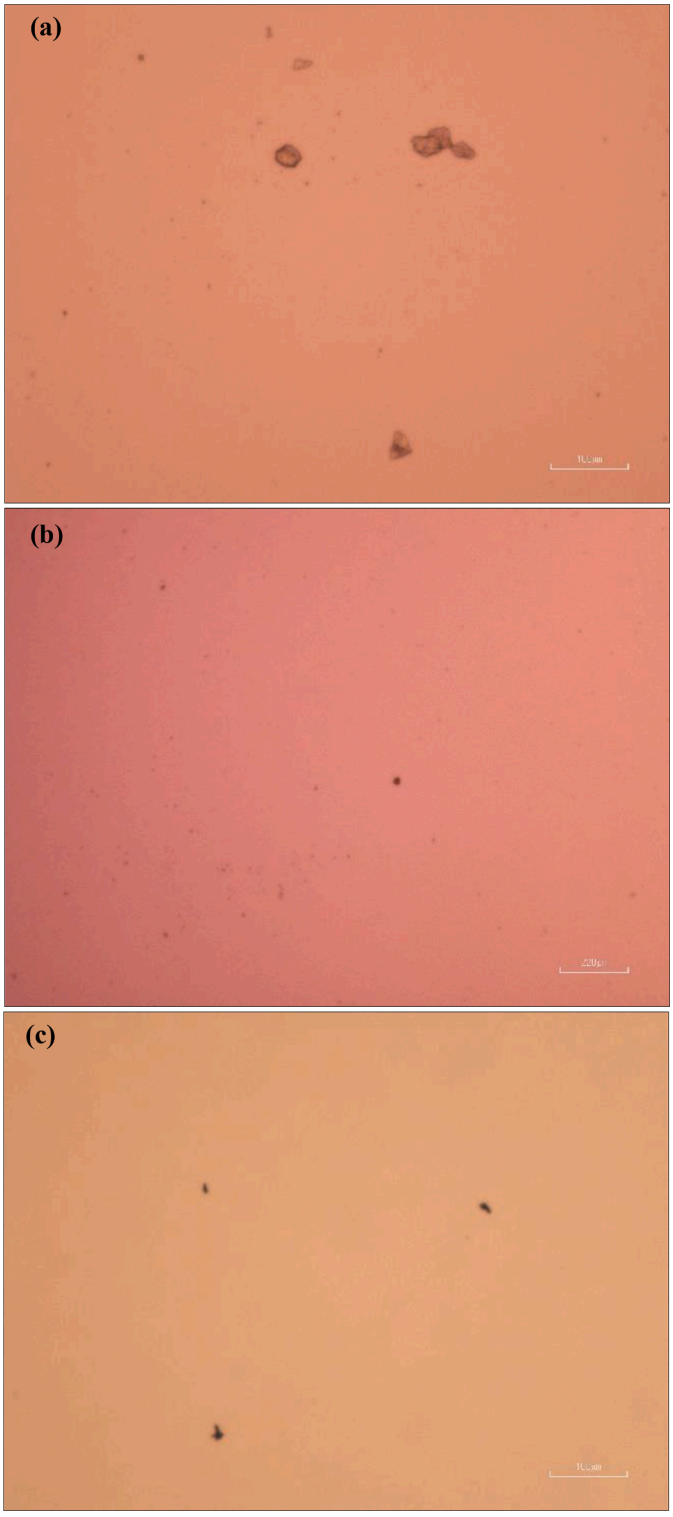

Fig. 7. Microscopic images of (a) the original (non-radiated and undiluted) crude oil, reproduced from Razavifar, et al. [45], (b) ultrasonically-treated diluted crude oil with toluene, and (c) ultrasonically-treated diluted crude oil with n-heptane.

heavy aggregates. To gain a deeper understanding of the synergistic and/or antagonistic interactions between ultrasonication and solvents (both aromatic and paraffinic) on crude oil viscosity and asphaltene structures, we conducted FTIR measurements across all scenarios outlined in Table 2. FTIR is an effective method for analysis of the evolution of functional groups in crude oils [66]. It is worth noting that ultrasonic irradiation was carried out for the optimal duration, and solvent blending was performed at the optimal concentration of 20 %. The FTIR spectrum analysis was based on the comparisons of peak heights observed in each specific wavenumber range.

Fig. 8 displays the FTIR spectra of non-radiated and ultrasonically treated crude oil samples, both in their pure form and blended with solvents. These FTIR measurements unveiled the evolution of functional groups within the asphaltene structure of crude oil due to ultrasonication and/or dilution with solvents (paraffinic/aromatic). Remarkably, we observed similar FTIR spectra and peak patterns across all scenarios, with some pronounced peaks in cases where toluene was used as the solvent (Scenarios II, V, and VII). Our evaluation of the resulting FTIR spectra focuses on specific wavenumber ranges, guided by findings in [65,67,68], which highlight the major peaks observed in Fig. 8:

- **FTIR Range 1 (2800–3000 cm^{-1}):** The peak around 2900 cm^{-1} in this range corresponds to an aliphatic sp^3 C–H stretching band. According to Fig. 8, the peaks in this region (2800–3000 cm^{-1}) are the strongest for all scenarios, excluding the cases where toluene was used as a solvent.
- **FTIR Range 2 (1300–1700 cm^{-1}):** In this range, the peak at approximately 1600 cm^{-1} corresponds to a sp^2 aromatic C = C ring stretch, while the peak at approximately 1450 cm^{-1} is attributed to an aliphatic sp^3 C–H.
- **FTIR Range 3 (400–900 cm^{-1}):** Within this range, the peak at approximately 750 cm^{-1} signifies the out-of-plane bonding vibration of an aromatic sp^2 C–H bond.

To assess the combined impacts of ultrasonics and solvents on the crude oil structure, we compared the FTIR responses of ultrasonic radiation of crude oil, solvation of crude oil, irradiation-then-dilution treatment of crude oil, and dilution-then-irradiation treatment of crude oil, as depicted in Fig. 9. These comparisons were made with the original crude oil as a reference state. For a more comprehensive understanding and assessment, we provided the FTIR spectra of toluene and n-heptane, retrieved from the NIST Chemistry WebBook (https://webbook.nist.gov/ chemistry), in Fig. 10. Assuming that peak heights in an FTIR spectrum reflect the content of functional groups [67], we conducted a quantitative analysis of the molar ratio of aromatic rings (as indicated by the peak of sp^2 C=C vibrating at ~1600 cm^{-1}) to aliphatic side chains (represented by peaks of sp^3 C–H appearing at ~2900 cm^{-1} and ~1450 cm^{-1}), based on the most prominent peaks observed in the FTIR bands shown in Fig. 9 [67,69]. The results of the molar ratio of aromatic rings (1600 cm^{-1}) to aliphatic chains (2900 cm^{-1} and 1450 cm^{-1}) for the original (reference) crude oil and the oils treated with ultrasonic waves and/or paraffinic and aromatic solvents are reported in Table 4. It is noted that the data presented in Table 4 were calculated based on the most intense peaks within the FTIR bands, as follows:

- 2800–3000 cm^{-1}: The most prominent peaks were identified at a wavenumber of 2921 ± 1 cm^{-1}.
- 1300–1700 cm^{-1}: The strongest peaks were located at wavenumbers of 1602 ± 3 cm^{-1} and 1457 ± 2 cm^{-1}.
- 400–900 cm^{-1}: The most intense peaks were observed at a wavenumber of 725 ± 3 cm^{-1}.

Based on the FTIR measurements (Fig. 9 and Table 4), the key findings can be summarized as follows:

- A comparison between Scenarios I and IV reveals that the ratios of aromatic rings to aliphatic chains underwent significant changes (often reductions) due to ultrasound application at the optimal radiation time. This suggests that the sonication of crude oil effectively

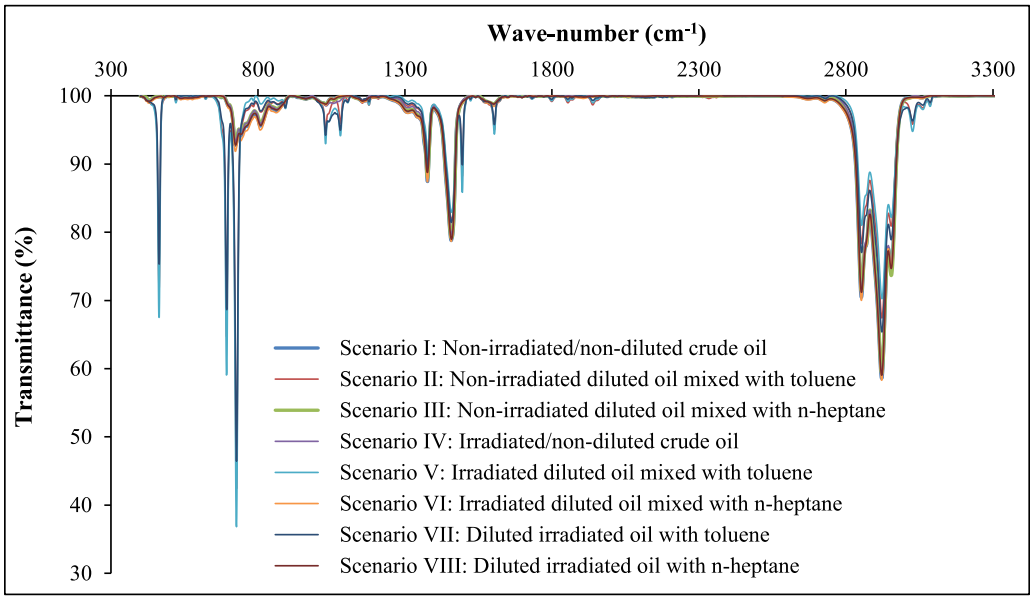

Fig. 8. The FTIR spectra of untreated and ultrasonically treated crude oil samples free from or blended with solvents. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

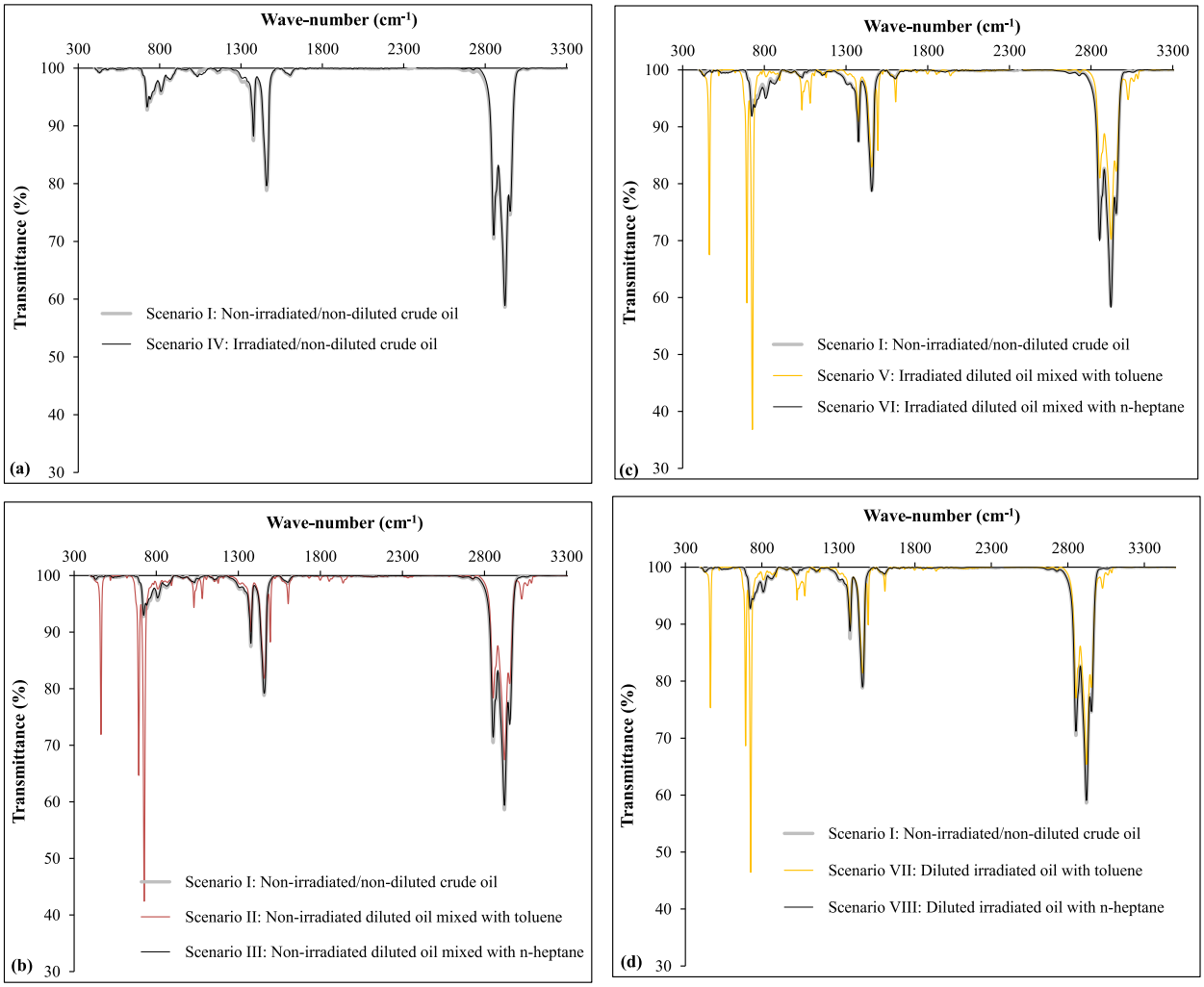

Fig. 9. Comparisons of the FTIR spectra of the original crude oil with (a) the ultrasonically treated oil, (b) non-radiated oil diluted with solvents, (c) ultrasonically treated diluted oil, and (d) diluted ultrasonically treated oil.

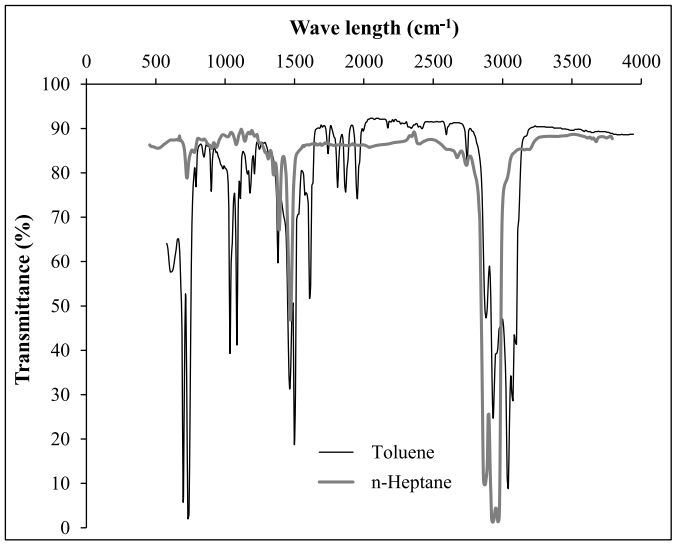

Fig. 10. FTIR spectra of toluene and n-heptane, retrieved from the NIST Chemistry WebBook (https://webbook.nist.gov/chemistry).

fractured the aromatic rings within the oil's structure, resulting in a relative reduction in oil viscosity (Fig. 6).

- Solvation of crude oil in toluene notably decreased the ratios of aromatic rings to aliphatic chains, primarily because of the efficient dissolution of heavy components in aromatic-based solvents. This aligns with the substantial decrease in viscosity observed in diluted crude oil with toluene, as depicted in Fig. 6. This behavior was not observed when dissolving crude oil in n-heptane, as asphaltene components are insoluble in paraffinic solvents.
- A comparison between the case of dilution-then-irradiation-treated crude oil (Scenarios VII and VIII) and the radiated crude oil (Scenario IV) or untreated crude oil (Scenario I) indicates a further reduction in the molar ratios of aromatic rings to aliphatic chains, especially when toluene-diluted crude oil was sonicated (corroborated by the viscosity reduction in Fig. 6).
- The most significant decrease in the ratios of aromatic rings to aliphatic chains was observed in the case of irradiation-then-dilution-treated crude oil with toluene (Scenario V), consistent with the lowest viscosity found in diluted-irradiated oil with toluene in Fig. 6.

In conclusion, for optimal crude oil viscosity reduction, the oil should first be diluted with toluene at the optimal concentration, followed by ultrasonication for the recommended duration. Our FTIR results indicate that one of the primary factors contributing to viscosity reduction is the reduction of aromatic rings relative to aliphatic chains within the crude oil structure. Some discrepancies observed in Table 4 compared to the viscosity reduction results (Fig. 6) may arise from overlooking the influence of other minor peaks (i.e., other functional groups in the crude oil structure) in the FTIR spectra, as depicted in Fig. 9. It is essential to note that the disparities between the data in Table 4 and the results in Fig. 6 stem from the complex interplay between factors such as the boiling effect, chemical breakdown of heavy molecules, and the physical disintegration and reformation of heavy components, particularly asphaltene aggregates. FTIR measurements primarily shed light on changes in the chemical structure of heavy oil, including alterations in heavy oil constituents like asphaltenes.

3.6. *Discussion: mechanism of viscosity reduction when simultaneously using ultrasound and solvent*

To sum up our findings thus far, we found that the combined effects of ultrasound and paraffinic solvents on crude oil viscosity involve two contrasting sides. Paraffinic solvents induce asphaltene flocculation and precipitation within the oil at specific concentrations, leading to increased viscosity. On the other hand, ultrasonication of crude oil breaks down and chemically converts asphaltene aggregates. This study explored two primary experimental scenarios: (1) dilution of crude oil with solvent followed by ultrasonication of the diluted oil, and (2) ultrasonication of crude oil followed by dilution of the ultrasonically treated crude oil. Notably, the second scenario resulted in a more significant viscosity reduction for both toluene and n-heptane. In essence, the solvation of ultrasonically treated crude oil with hydrocarbons proved to be the most effective in reducing viscosity.

The complexities associated with relating the properties of dispersed asphaltene particles to the viscosities of colloidal crude oil and the thermodynamic analysis of phase separations in crude oil's heavy components are beyond the scope of this work. Interested readers can refer to relevant literature for an in-depth exploration of this topic [63,70,71]. In this study, our aim is to propose a hypothesis elucidating the mechanisms behind the synergistic effects of ultrasound and solvent on crude oil viscosity, focusing on the oil's asphaltene structures. To achieve this, it is crucial to have a clear understanding of the asphaltene aggregation process in crude oil. Asphaltene possesses notable characteristics to form aggregates within crude oil and hydrocarbon solutions. Under unfavorable conditions, asphaltene molecules assemble into colloids, which can then further aggregate into clusters or flocs [72]. It is important to emphasize that the size of asphaltene aggregates is strongly influenced by factors such as the type of solvent, the asphaltene content of crude oil, and temperature [72]. In our study, we observed that adding n-heptane to crude oil increased the size of asphaltene aggregates while solvating the crude oil with toluene decreased the size of asphaltene particles. This aligns with findings from other studies [73,74].

On the one hand, solvent-induced asphaltene micellization and flocculation are pivotal aspects in the evolution of crude oil viscosity. Therefore, it is imperative to consider both colloidal stabilization and solvation. On the other hand, several studies have confirmed that ultrasonic radiation reduces the size of asphaltene flocs and aggregates [25,37,75,76] and chemically converts asphaltene into resin and lighter hydrocarbons [77]. The reduction in asphaltene aggregate sizes depends on the radiation time, with the optimum radiation time leading to minimized asphaltene flocculation rates and floc sizes. Our FTIR

Table 4
The estimated molar ratio of aromatic rings to aliphatic chains based on the FTIR measurements for the reference crude oil and the crude oils treated with ultrasonics and/or solvents.

Ratio	Reference crude oil Scenario I	Solvated crude oil Scenario II	Scenario III	Radiated Crude oil Scenario IV	Irradiation-then-dilution-treated crude oil Scenario V	Scenario VI	Dilution-then-irradiation-treated crude oil Scenario VII	Scenario VIII
$\frac{sp^2C=C}{sp^3C-H}\left(\frac{1600cm^{-1}}{2900cm^{-1}}\right)$	1.683	1.405	1.664	1.667	1.343	1.688	1.465	1.673
$\frac{sp^2C=C}{sp^3C-H}\left(\frac{1600cm^{-1}}{1450cm^{-1}}\right)$	1.250	1.161	1.248	1.240	1.138	1.252	1.176	1.251

measurements in this study underscore the importance of changes in the chemical structure of heavy oil, alongside the key role played by physical effects in breaking down heavy component aggregates and facilitating dissolution and precipitation processes. According to the FTIR results, one of the primary mechanisms driving crude oil viscosity reduction through the simultaneous use of ultrasound and solvents involves reducing the molar ratio of aromatic rings relative to aliphatic chains in the asphaltene structure of crude oil.

4. Summary and conclusions

This study investigated the simultaneous effects of ultrasound and both aromatic (toluene) and paraffinic (n-heptane) solvents on the viscosity and asphaltene structure of a heavy crude oil (19 °API, 8 % asphaltene). Our findings revealed a complex interplay of synergistic and antagonistic interactions among various physical and chemical changes in the oil properties caused by ultrasonic waves, shock removal, dissolution of heavy oil components, and asphaltene aggregate precipitation. For our specific crude oil, we experimentally determined the optimal conditions, including a 10-minute ultrasound treatment (using 100 W and 20 kHz) and a 20 vol.% solvent concentration, which minimized viscosity before any increase. We devised eight experimental scenarios, considering the use or absence of ultrasound and aromatic or paraffinic solvents, as well as the order of sonication and solvation. All measurements were conducted under these optimal conditions.

Our viscosity measurements indicated that solvent addition had a more significant impact on reducing viscosity than ultrasonication alone. Compared to the original, untreated crude oil, the lowest viscosity was achieved when the radiated crude oil was mixed with toluene under optimal conditions, resulting in a 68 % reduction in viscosity. This scenario, referred to as "'irradiation-then-dilution treatment of crude oil in aromatic solvents," demonstrated superior performance. Notably, the effectiveness of the "dilution-then-irradiation treatment of crude oil" was similar to dilution without ultrasonication. Optical microscopy confirmed that the amount and size of asphaltene aggregates in the toluene-treated "irradiation-then-dilution" crude oil were significantly smaller than in other cases. Our study identified two main mechanisms for reducing the viscosity of heavy asphaltenic crude oil through combined ultrasound and solvent treatment. First, it involved the dissolution and aggregation of asphaltene clusters, which were influenced by the solvent type and asphaltene content/structure in the crude oil. The second mechanism pertained to a chemical change in the asphaltene molecular structure. In our specific crude oil, we observed alterations in the ratio of aromatic rings to aliphatic chains. Notably, the most effective viscosity reduction was achieved when sonicated oil was blended with toluene. These findings have practical applications, particularly in addressing real-world challenges like the cleanup of near-wellbore formation damage caused by factors such as asphaltene/wax deposition and enhancing heavy oil recovery.

CRediT authorship contribution statement

Jafar Qajar: Conceptualization, Methodology, Validation, Supervision, Writing – review & editing. **Mehdi Razavifar:** Investigation, Formal analysis, Writing – original draft. **Masoud Riazi:** Supervision, Methodology, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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