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Toward Separation and Characterization of Asphaltene Acid and Base Fractions

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ABSTRACT: Chemical inhibition of asphaltene deposition is considered a cost-effective way to prevent the harsh consequences of asphaltene instability in the produced crude. Thus, a careful screening of asphaltene inhibitors is crucial for an efficient prevention. However, the characteristics of asphaltenes such as their acid−base properties will influence the selection of an asphaltene inhibitor and the inhibition mechanism. Therefore, improved knowledge on asphaltene acidic and basic fractions is important. In this work, the separation of asphaltenes into acid, base, neutral, and amphoteric fractions was performed. Among the existing techniques to fractionate asphaltenes, the method of Ramljack was adopted and applied on a light oil extracted asphaltene. However, this oil was sampled from one of the wells in the Hassi Messaoud field in Algeria that experienced a recurring deposition of asphaltenes. The results of asphaltene fractionation reveal that the half composition of this heavy part of crude oil is active functions gathered acid and base components. However, the main contribution is reported to the neutral fraction. The characterization results of infrared and elementary analyses show that both active fractions are aromatic and polar. Moreover, the acid fraction contains in its structure carboxylic acids, phenols, sulfoxide groups, and aliphatic chains, while the structure of the base fraction contains amines, sulfoxide groups, and aliphatic chains.
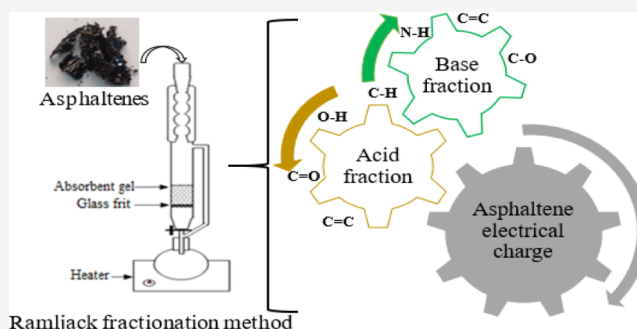
1. INTRODUCTION

Asphaltene deposition can occur when changes in the thermodynamic conditions and the chemical composition upset the chemical equilibrium of the crude oil components, so the system loses its ability to disperse asphaltene particles, and as a result, these carbonaceous components precipitate out of solution.[1]

Depending on the thermodynamic and hydrodynamic conditions, the asphaltene deposits can occur at any part of the production system.[2] The cleaning procedure becomes more complicated when the deposition phenomenon takes place near the wellbore or within the reservoir rock (a form of formation damage).[3,4] In some cases, the buildup of asphaltene deposits can completely plug the petroleum flow, especially, where no control is set up. Basically, there are three methods to treat or mitigate the deposition of asphaltenes: mechanical (scrapers), thermal (hot oil, downhole heater, and heat liberate chemicals), and chemical (solvents, dispersants, and inhibitors).[5] The first two methods are usually applied after the deposition has occurred, while the chemical intervention can be employed before or after the deposition of asphaltenes.

Asphaltenes are brittle solid materials that are dark brown to black in color.[6] They are defined by their insolubility in light paraffinic solvents such as pentane and heptane, but soluble in aromatic hydrocarbons.[7] Chemically, the asphaltene particles are characterized by their high molecular weight and polarity. However, their molecular structure is made up of polycyclic condensed aromatic rings with alkyl chains.[8] Moreover, these properties are not the same for all asphaltenes in crude oils.[9] This is related to the change of crude oil source, solvent, and operating conditions.[10,11]

In general, the asphaltene particles are also known by their acid−base properties due to their highly aromatic character and the presence of peripheral heteroatoms such as sulfur, nitrogen, and oxygen. The acidic character changes according to the origin of asphaltenes,[12] and it is related to the presence of weak acids such as phenols, carbazoles, and indoles. Besides, the presence of amides gives asphaltenes the basic character.[13] Thus, the presence of these various polar and active functions explains the tendency of asphaltenes to associate by hydrogen bonding.[14]
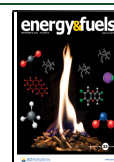
The nonunique properties of asphaltenes make them more complex components,[15] and thus, the choice of a treatment to deal with asphaltene deposition becomes very difficult. Therefore, having knowledge about asphaltene characteristics can be a helpful guide in the selection of asphaltene inhibitors.[16] For example, negatively charged asphaltenes tend to be dispersed by cationic amphiphiles, while positively charged asphaltenes tend to be dispersed by anionic amphiphiles.[17] Moreover, it was demonstrated by Madhi et al.[18] that the acid−base interaction is the stronger contributor to the inhibition mechanism than hydrogen bonding and $\pi-\pi$ interactions.

In 1990, Siffert et al.[12] established the relationship between electrical charge and flocculation of heavy oil distillation residue in organic medium. However, the electrical charge results in an electron transfer between the solid particles and the liquid phase. Indeed, the results of their study indicate that there is an interaction parameter I_{al} between asphaltenes (a) and the dispersion liquid (l) defined as

$$I_{al} = (AN_a)(DN_l) + (DN_a)(AN_l)$$

where AN_a and DN_a are the electron acceptor and donor numbers of asphaltenes, respectively, while AN_l and DN_l are the electron acceptor and donor numbers of the dispersion liquid, respectively. Another interaction parameter I_{aa} between the asphaltene particles has been defined as

$$I_{aa} = 2[(DN_a)(AN_a)]$$

Accordingly, the comparison of these two interaction parameters $(I_{al}$ and $I_{aa})$ allows for the evaluation of the dispersion stability or the flocculation tendency of asphaltenes as follows:

When $I_{sl} > I_{ss} \Rightarrow$, dispersion is stable.

When $I_{sl} < I_{ss} \Rightarrow$, there is asphaltene flocculation.

Based on the results mentioned above, there is a relation between the flocculation of asphaltenes and the surface electric charge in an organic system. In other words, the electric charge on the surface of asphaltene particles is responsible for their stability in the oil. It is important to note that the acidic and basic fractions of asphaltenes represent the acceptor and donor of electrons, respectively.[19] Thus, the distribution of these active fractions in asphaltene particles is a key factor toward the investigation of asphaltene stability from the electrical charge perspective. This can be achieved through the separation of the acidic and basic fractions of asphaltene, which is the aim of this work.

The separation of acids and bases from asphaltenes involves methods based on the chemical properties of these substances. In the literature, three methods can be used to fractionate asphaltenes: USBM−API, SARA, and methods reported by Ramljack et al.

The USBM−API method was developed by the US Bureau of Mines in cooperation with the API, developing a general protocol for the separation and characterization of distillates at a high boiling point of crude (350−370 °C). The crude oil sample is carefully subjected to atmospheric distillation at a maximum temperature of 200 °C. However, the component fractions of the residue are separated according to the protocol shown in Figure 1.[20]

The SARA method has the advantage of fast and standardized analyses. It consists of separating the acid, basic, and neutral nitrogen fractions on a column containing the two ion exchange resins and ferric chloride. Note that the
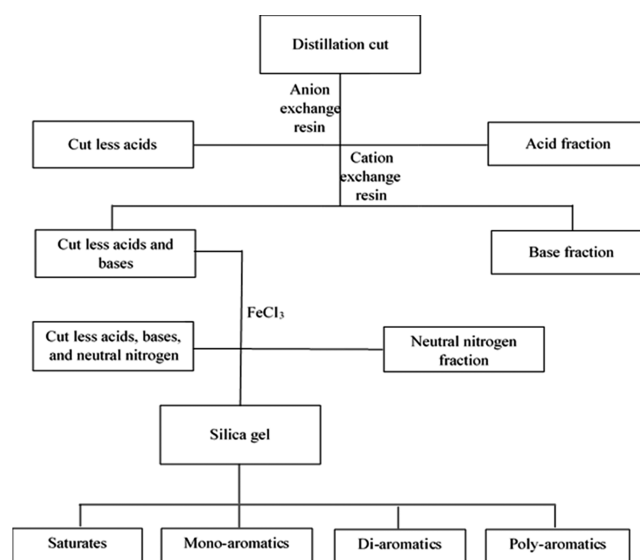

Figure 1. Fraction separation scheme according to the USBM−API standard. "Reproduced from [Jewell, D.; Weber, J.; Bunger, J.; Plancher, H.; Latham, D., Ion-exchange, coordination, and adsorption chromatographic separation of heavy-end petroleum distillates. *Anal. Chem.* **1972**, *44* (8), 1391−1395]. Copyright [1972] American Chemical Society".

nonpolar compounds are separated in another adsorption chromatography column.[21]

The method reported by Ramljack et al.[22,23] allows for the separation and the extraction of the acid and base fractions from petroleum cuts. However, this method has been applied in the literature to fractionate asphaltenes extracted from bitumen[23] and in one case to separate acids from asphaltenes of an Iraq oil.[22] This technique has been developed to separate and extract the acid and base fractions of asphaltenes by introducing some modifications to the method proposed by Jewell et al.[20] The latter has been used to isolate the acid fraction from bitumen and crude oils. The procedure of Ramljak consists of percolating the sample that is already dissolved in chloroform on a column filled with a previously activated gel (Figure 2), where the nature of the gel and solvent varies according to the fraction to be separated.[22,23]

The analysis of the three fraction separation methods led us to adopt the method reported by Ramljack et al. for the following reasons: speed of extraction operations, reduced consumption of solvents, no need for a permanent presence or
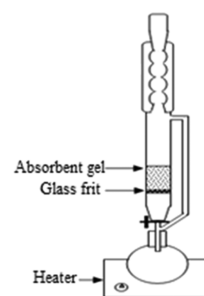

Figure 2. Recycling chromatography column to fractionate asphaltenes. "Reproduced from [Ramljak, Z.; Solc, A.; Arpino, P.; Schmitter, J. M.; Guiochon, G., Separation of acids from asphalts. *Anal. Chem.* **1977**, *49* (8), 1222−1225]. Copyright [1977] American Chemical Society".

CD: Choke diameter change   **WS**: Wire Line scrapping
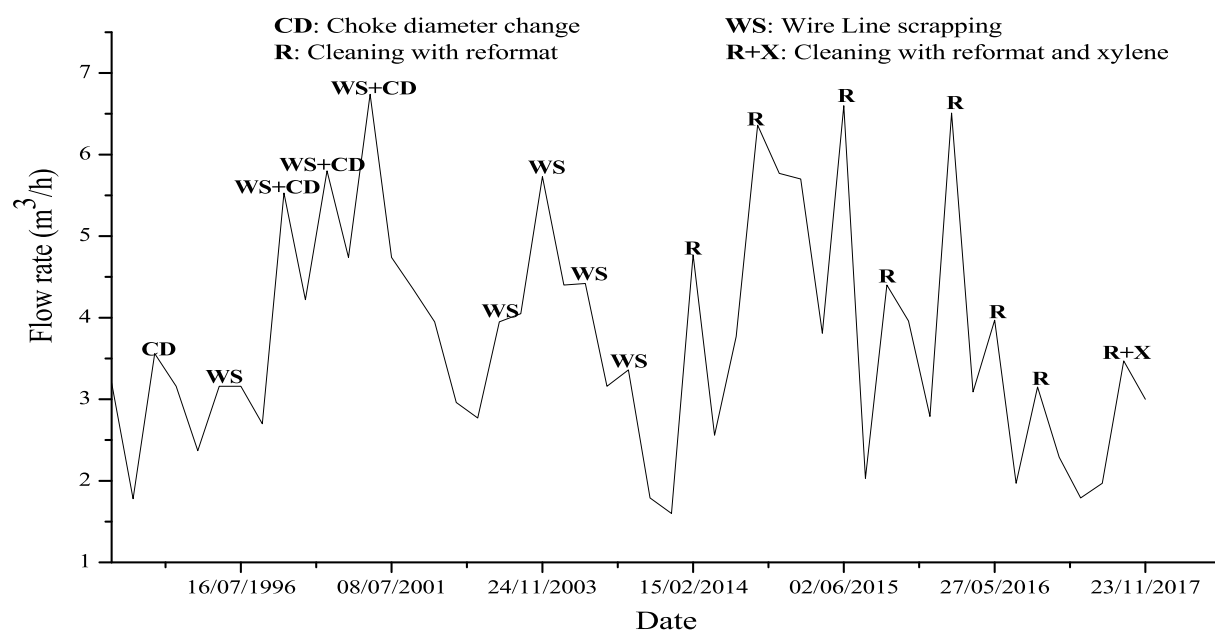**R**: Cleaning with reformat   **R+X**: Cleaning with reformat and xylene

Figure 3. History production of the selected well.

supervision of the operator, and the test sample is 10 times larger than the API process. In API and SARA processes, there is a problem with the decomposition of ion exchange resins in organic solvents, resulting in contamination of the solutes.

In this work, the acid−base properties of asphaltenes are investigated by isolating the acidic and basic fractions from asphaltenes and then characterizing them separately. For this purpose, a nonstabilized crude oil from the Hassi Messaoud field was selected and its asphaltene part was fractionated into acid, base, neutral, and amphoprotic fractions for the first time in the literature. As is known, oil production in the Hassi Messaoud field has been seriously disrupted due to problems of total or partial blockage of the tubings. Indeed, a decrease in the production of the majority of wells in this field has been observed due to asphaltene deposits. Besides reservoir depletion, the deposition of asphaltenes can also be responsible for the decrease in oil production. Although the crude oil from this field contains a very low concentration of asphaltenes, they are unstable, which leads to their flocculation and deposition.[5,24]

2. EXPERIMENTAL METHODS

The selected well is a short radius well. Its reservoir is characterized by a pressure of 297 bars and a temperature of 119 °C. This well is frequently plugged by asphaltene deposits, whereas the production history of this well (Figure 3) describes the severity of the asphaltene problems by the drop in its productivity and the frequency of intervention operations, whether by mechanical scraping with a wire line unit or solvent washing (reformat or xylene).

2.1. Crude Oil Properties. The crude oil was sampled from the wellhead of the selected well, and then it was characterized to define some of its physicochemical properties according to specific standard methods as follows: density at 20 °C (ASTM D4052-11 and ISO12185-96), kinematic viscosity at 20 °C (ASTM D445-06 and ISO 3104-94), total acid number (ASTM D974-04 and ISO 6618-97), sulfur content (ASTM D4294-10 and ISO 8754-03), base sediment and water (ASTM D96 and ISO 9030-90), water content (IP 356), salinity (ASTM D6470), flash point (ASTM D56-05), pour and freezing points (ASTM D97), and metal content (ASTM D6728). Saturated, aromatic, resin, and asphaltene fractions (SARA)

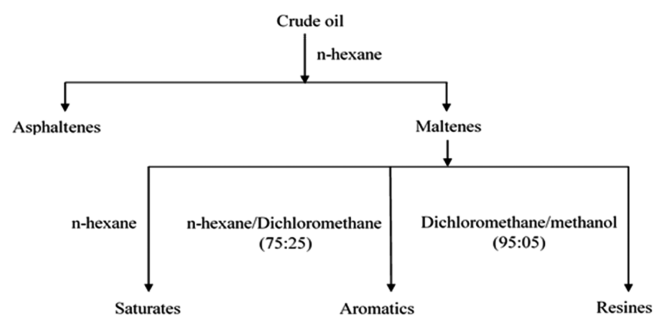were determined using liquid column chromatography according to the protocol illustrated in Figure 4.[5]

Figure 4. SARA separation protocol.

2.2. Asphaltene Characterization and Fractionation. The extracted asphaltene from the oil sample was characterized by determining its elemental composition of carbon, hydrogen, nitrogen, and sulfur, its metal content, and its functional groups using Elementary Vario Micro, Spectroil M spectrometers, and Fourier transform Infrared Sofas IR700, respectively.

The method reported by Ramljak et al.[22,23] that we adopted in this work consists of fixing one of the active fraction (acid or base) via its interaction or affinity with the activated gel (potassium silica or phosphoric alumina) and then eluting the second active fraction with the neutral part by recycling chloroform, as they are not trapped by the packed column. In this selective extraction procedure, the acid fraction will be attracted by the potassium silica, while the base fraction will be attracted by the phosphoric alumina via the electrical charge between the target fraction and the activated column.

To prepare the potassium silica column, a mass of 20 g of silica gel is mixed with 40 mL of a saturated solution of potassium hydroxide (KOH) dissolved in isopropanol (50 g/L) and 100 mL of chloroform. This latter is left to stand for 5 min and then placed in the silica column. The silica treated with potassium is washed by recycling the chloroform for 15 min to remove excess KOH and isopropanol.

Phosphoric alumina gel is prepared by mixing 20 g of alumina gel with 40 mL of phosphoric acid and 100 mL of chloroform. This mixture is left to stand for 5 min and then placed in the column. The alumina treated with phosphoric acid is then washed by recycling the chloroform for 15 min to remove excess phosphoric acid.

A total of 100 mg mass of asphaltenes dissolved in chloroform is loaded onto a column filled with the prepared potassium silica. The extraction of the basic and neutral fractions is performed by recycling chloroform for 5 h. The acid fraction fixed on the potassium silica is then eluted with a mixture of formic acid−methanol−chloroform (50 mL:100 mL) added at the top of the potassium-treated silica column and recycled for 3 h.

To separate the basic fraction from the neutral fraction, the two fractions, base and neutral, recovered from the potassium silica column are loaded onto a column filled with phosphoric alumina. However, the neutral fraction is percolated with 100 mL of chloroform. After that, the basic fraction is eluted by a mixture of pyridine−methanol−chloroform (100 mL:50 mL). This mixture is recycled for 3 h to confirm that all base fraction has been recovered.

Each recovered fraction undergoes solvent distillation by the Buchi R-210 rotary evaporator and is then weighed.

3. RESULTS AND DISCUSSION

The crude oil selected is a light, nonsulfurous crude and does not contain water. It is characterized by its high acidity (TAN > 1). It was reported that acidity of crude oil may arise from two different sources: high sulfur content or the presence of carboxylic acids in crude oil.[25] Due to the low content of sulfur in our oil sample, the acidity is proposed to be due to the presence of carboxylic acids. The content of sediment or impurities in the analyzed oil is negligible as indicated by BSW assay results (Table 1). Generally, the sediments found in

Table 1. Crude Oil Physicochemical Properties

properties	instrument	
density at 20 °C (g/cm³)	Density meter DMA48	0.8274
kinematic viscosity à 20 °C (cSt)	Mgw Lauda viscosimeter	5.448
total acid number (mg KOH/g)	metrohm titration station	1.99
sulfur content (wt %)	sulfur in oil analyzer SLFA-2100 HORIBA	0.1
base sediment and water (%, v/v)		<0.01
water content (%, v/v)		0.1705
salinity (ppm)	Metrohm titration station	40
flash point (°C)	Herzog Tag closed cup	< −5
pour point (°C)	Newlab 1300	−51
freezing point (°C)	Newlab 1300	−54
saturates (wt %)		73.19
aromatics (wt %)		19.28
resins (wt %)		7.20
asphaltenes (wt %)		0.33
CII		2.77

crude oil represent the solid part insoluble in hydrocarbons and water, such as cuttings from the reservoir rock, drilling mud cake, and metals that can cause many problems in the production system (erosion, corrosion, clogging, etc.).

The salts considered in crude oil are chlorides composed essentially of 20% $MgCl_2$, 10% $CaCl_2$, and 70% NaCl. These chlorides are insoluble in oil and their presence in high concentrations of more than 60 mg/L can promote corrosion and clogging of facilities.[26] The results of salinity measurement indicate that this oil is not salty. Moreover, this crude is characterized by a low flash point.

SARA fractionation is a predictive tool widely used to evaluate the stability of asphaltenes in crude oil.[27] The results of characterization by SARA analysis (Table 1) show that this crude is poor in favorable fractions (resins + aromatics) and

rich in unfavorable fractions (saturated + asphaltenes). This means that the solubility parameter of the oil is low despite the high ratio of resins to asphaltenes. It is clear from SARA analysis results that the solubility power of crude oil is reduced due to the high content of saturated hydrocarbons (up to 73 wt %). We note that these light molecules are considered to be a flocculating agent of asphaltenes.[15] Moreover, the value of the colloidal instability index (CII) indicates that the studied oil is very unstable (CII > 0.9).[28]

Metals in crude oil come from several sources, including formation or injection water, solid particles from the reservoir rock entrained by the oil during withdrawal from the well, asphaltene metals contained in the oil, and pipe corrosion products.

The results of measurement of metals content in the oil (Table 2) show that this sample has in its composition

Table 2. Metal Content in Crude Oil

metal	tenor (ppm)
iron	21.8
lead	1.2
nickel	0.4
silicon	2.7
boron	0.4
sodium	24.0
magnesium	4.6
calcium	15.2
zinc	0.4
molybdenum	1.3
vanadium	1.1
total	73.1

different metals with a total of 73.1 ppm. The appearance of high concentrations of sodium and calcium indicates that these crude oils may contain salts. The iron present in this oil sample comes in second class with a fairly high concentration, and its presence can be considered as an indication of corrosion of production tubing; however, the content of asphaltenes that may be responsible for the presence of iron in oil is negligible.

The contents of carbon, hydrogen, nitrogen, sulfur, and oxygen in the extracted asphaltene are shown in Table 3. It is noted that the asphaltenes extracted from crude have a content of 8.83% of heteroatoms. The H/C ratio refers to the aromaticity of the asphaltenes.[29−31] Regarding the hydrogen to carbon atomic ratio (H/C ∼ 1),[32] this sample has a pronounced aromatic character.

Table 3. Results of Elemental Analysis and Metal Content in Asphaltenes

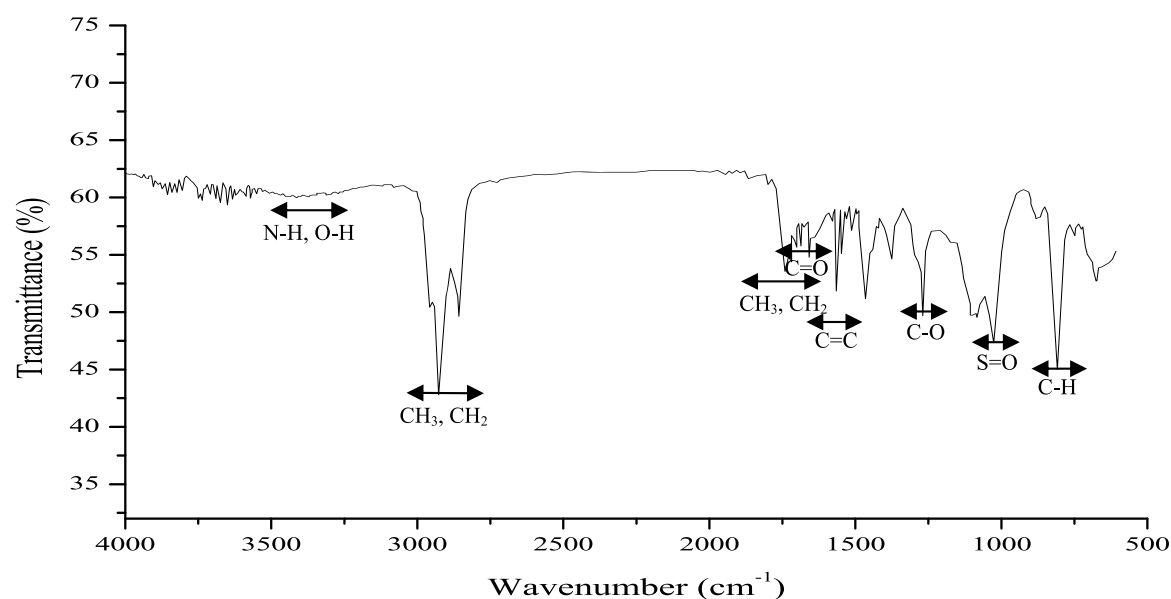| element	weight %
carbon	84.72
hydrogen	6.45
nitrogen	0.51
sulfur	0.74
oxygen (by difference)	7.58
heteroatoms	8.83
H/C	0.91
iron (ppm)	8.4
vanadium (ppm)	0.2
nickel (ppm)	1.1

Figure 5. FTIR spectrum of the extracted asphaltenes.

Table 4. Results of Acid and Base Fraction Extraction From the Asphaltene Sample

extraction order	asphaltenes (mg)	acid fraction (wt %)	base fraction (wt %)	neutral fraction (wt %)	amphoprotic fraction (wt %)
silica−alumina	100	11	40	47	2
alumina−silica	100	12	38	48	2

The metals present in asphaltenes can be used in the self-association of asphaltene molecules.[33] The results presented in Table 3 show that the asphaltene sample contains iron, vanadium, and nickel in different proportions.

The infrared spectrum of the asphaltene sample shown in Figure 5 is similar to those obtained by several authors (Daaou et al.[34] and Larbi et al.[35]). The spectrum shows a low intensity of a band appearing between 3500 and 3100 cm^{-1}, indicating the presence of a small amount of N−H group amines, alcohols, and O−H group phenols. The high absorption bands located at 2856/1376 and 2925/1750 cm^{-1} correspond to the aliphatic alkylene and alkyl groups CH_2 and CH_3, respectively. These asphaltenes contain a significant portion of aromatic rings presented in the C=C and C−H groups at around 1600 and 800 cm^{-1} peaks, respectively.

Based on the wide bands between 1800 and 1000 cm^{-1}, the studied asphaltenes may have different functional groups, such as C=O, and C−O, on the aromatic rings. These functional groups are likely to form hydrogen bonds. The 1030 cm^{-1} peak indicates the presence of a sulfoxide group in the asphaltene sample, and elemental analysis confirms the presence of sulfur in the chemical composition of the asphaltenes studied.

Table 4 summarizes the percolation results of asphaltenes in the silica−alumina direction and the alumina−silica direction. These results show that the decomposition of asphaltenes into acid, base, neutral, and amphoteric fractions do not depend on the direction of percolation; silica−alumina or alumina−silica. The neutral fraction constitutes the dominant fraction in this sample of asphaltenes, followed by the base fraction and then the acid fraction and the amphoteric ones, which can react both as an acid and a base.

The results of the elemental analysis (Table 5) showed that the analyzed acid and base fractions are aromatic and polar

fractions. Moreover, the content of heteroatoms in both fractions exceeds 22% of the total composition.

Table 5. Elemental Analysis of Acid and Base Fractions of Asphaltenes

element	acid fraction	base fraction
carbon (%)	70.45	69.02
hydrogen (%)	6.78	6.31
nitrogen (%)	0.51	2.48
sulfur (%)	0.80	1.03
oxygen (by difference) (%)	21.46	21.16
heteroatoms (%)	22.77	24.67
H/C	1.15	1.09

Figure 6 shows the results of the infrared analysis of the acid fraction of asphaltenes. The spectrum obtained shows a wide absorption between 3600 and 3100 cm^{-1}, indicating the presence of a significant amount of O−H group of carboxylic acids and phenols. Indeed, the results of the elemental analysis of this fraction confirm the existence of these acids by the presence of a significant content of oxygen. Consequently, these carboxylic acids may contribute in the high recorded acidity of the oil.[36] The absorptions at 2925/1638 and 2848/1385 cm^{-1} indicate the presence of the aliphatic groups CH_3 and CH_2, respectively. This acid fraction of asphaltenes has in their structures functional groups C=O between 1750 and 1550 cm^{-1} corresponding to carboxylic acids. A small amount of sulfoxide groups intervenes in the structure of the acid fractions studied by the appearance of a low absorption peak around 1020 cm^{-1}. It should be noted that this sample is characterized by the presence of a significant quantity of aromatics presented essentially by the functional groups C−O, C=C, and C−H between 1800 and 700 cm^{-1}.[37]
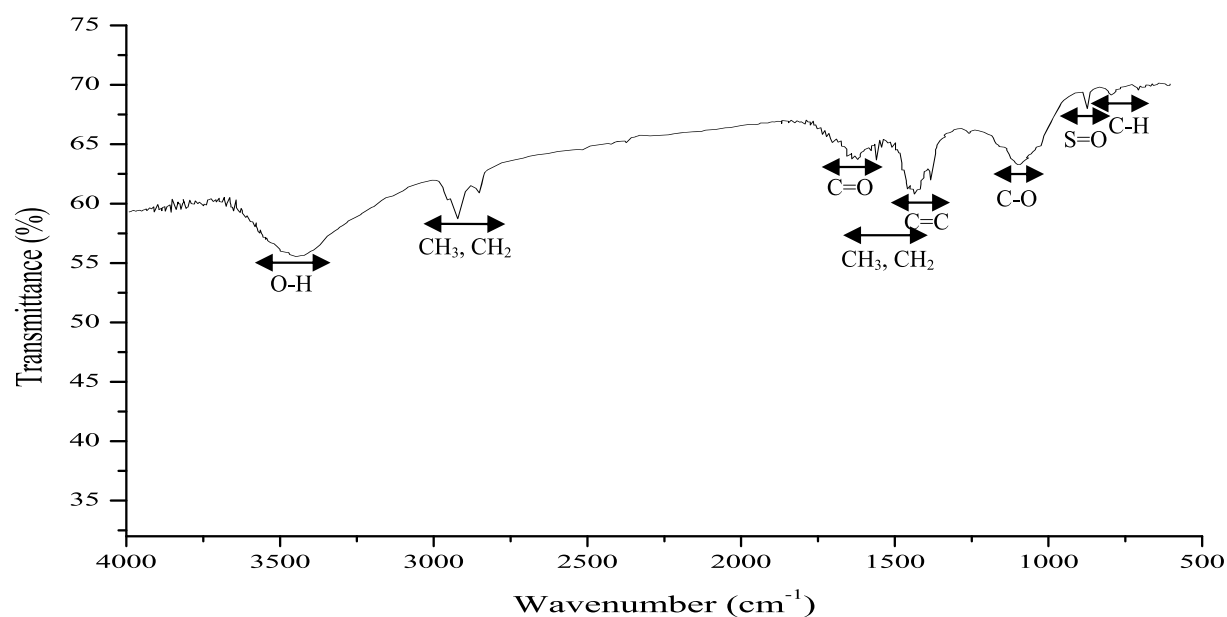
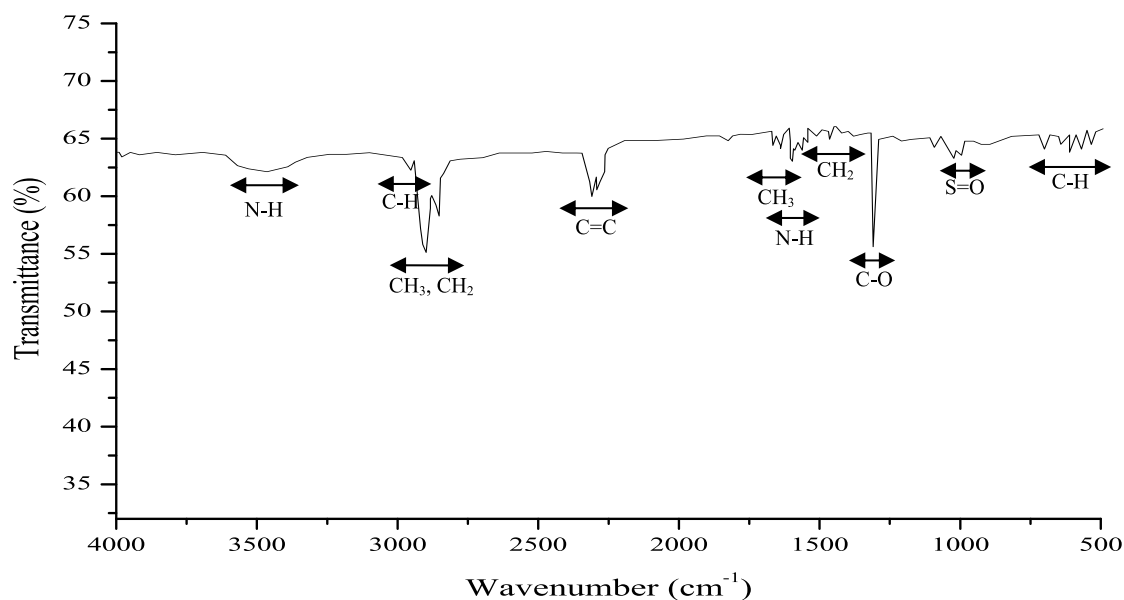**Figure 6.** FTIR spectrum of asphaltene acidic fraction.

Figure 7. FTIR spectrum of the asphaltene base fraction.

The infrared spectrum for the basic fraction of this asphaltene sample is shown in Figure 7, and the characteristic bands of this sample are summarized in Table 6, indicating its relevant functional groups. According to the results obtained, this basic fraction is characterized by the presence of a significant amount of amines, a large amount of aromatics, and an almost negligible amount of sulfur compounds. Moreover, this fraction has aliphatic groups in its structure.

4. CONCLUSIONS

In order to separate and characterize acid and base fractions of asphaltene, one of the Hassi Messaoud oil field wells has been selected based on its long history fighting against the deposition of asphaltenes. However, the sampled oil is light and does not contain impurities in its composition. Nevertheless, this oil is unstable, and it has the tendency to generate

Table 6. Infrared Spectral Range Assignments for the Asphaltene Base Fraction

absorption frequency (cm^{-1})	functional group	base fraction characteristic bands
3600–3150	N–H	3324
3100–3000	C–H	3043
2990–2800	CH_3, CH_2	2901, 2832
2400–2000	C=C	
1800–1620	CH_3	1644
1600–1550	N–H	1591
1500–1320	CH_2	1440
1300–1200	C–O	1249
1150–1050	S=O	1081
1000–650	C–H	966, 860, 792, 735, 671

problems in the production system because of asphaltene deposits according to SARA analysis result.

The oil-extracted asphaltenes are composed of condensed aromatic rings with aliphatic chains and heteroatoms (O, N, and S), where oxygen exists mainly in the hydroxyl groups OH and can be found in the peripheral aromatics or in the aliphatic chains, while nitrogen can be found in the form of pyrrolic or pyridine amines. Sulfur is found in the form of sulfoxide compounds $(RS(=O)R)$. The presence of metals in the asphaltene sample was also revealed such as iron, vanadium, and nickel.

These asphaltenes have been separated into four fractions; acid, base, neutral, and amphoteric, using the method reported by Ramljack et al., which is found as the more practical and economical technique to isolate those fractions among the existing separation procedures. The results of asphaltene fractionation point out that the neutral fraction is the dominant part in the asphaltene sample. Moreover, the acid and basic fractions are aromatic and polar compounds. The first fraction is characterized by the presence of carboxylic acids, phenols, sulfoxide groups, and aliphatic chains, while the second fraction has amines, sulfoxide groups, and aliphatic chains in its structure.

The present work may guide in the selection of asphaltene inhibitors through identifying the dominant active part of asphaltene (acid or base) and neutralizing it via the acid–base interaction by adding a suitable inhibitor. Therefore, adding an acidic inhibitor, such as dodecylbenzenesulfonic acid, benzoic acid, or salicylic acid, to asphaltenes characterized by a high tenor of base fraction can potentially give good inhibition results. These acids are known by the presence of hydroxyl (phenolic) and carboxyl groups in their structure, which enhances their ability to inhibit asphaltenes. Conversely, for asphaltenes that have high acidic fraction content, it will be important to select inhibitors that have in their structure more basic groups such as amine groups.

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Notes

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