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# CHARACTERIZATION OF VIRGIN ASPHALTENES AND ITS SUBFRACTIONS USING UV-VISIBLE AND FTIR SPECTROSCOPY

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## Abstract

Spectroscopic characterization of asphaltene is necessary in order to understand the changes it undergoes when heavy and extra-heavy oil types such as bitumen are subjected to catalytic aquathermolysis. The structural composition of asphaltene and its subfractions were investigated using UV/Visible and FTIR Spectroscopy. Raw bitumen sample was obtained from the bitumen deposit at Mile 2 in Odigbo, Ondo State, Nigeria. The sample was purified and the asphaltene fraction was precipitated with *n*-hexane, the precipitated asphaltene was fractionated into fractions A and B based on their difference in solubility and polarity with hexane/toluene mixture at a fixed ratio. The results showed that virgin asphaltene and its subfractions absorbed light of longer wavelength in the range (465 – 640 nm), indicating that they are made up of polynuclear aromatic compounds. The results also revealed the presence of alkyl side chains and major oxygenated groups in both virgin asphaltene and its subfractions (A and B). In general, asphaltene are complex molecular compound which consists of aromatic moieties with alkyl side chains, polar groups (ester, ether and carbonyl), acidic and basic groups (carboxylic and pyridine) which can interact at certain pH range by accepting or donating protons.

**Keywords:** Asphaltene, Bitumen, Subfractions A and B, UV/ Visible, FTIR,

## 1. Background

Asphaltenes are considered the most complex mixture of carbonaceous macromolecular compounds that have been found to pose many challenges which include obstruction of reservoirs, clogging of wells and pipeline as well fouling and stabilization of oil-water emulsions in the petroleum industry (Galoppini, 1994; Kokal and Sayegh, 1995; Khadim and Sarbar, 1999; Shedid and Zekri, 2006; Ma *et al.*, 2008; Muhammad, 2015). Although, they are usually referred to as the heaviest fraction of petroleum but their solubility-based behaviour encompasses identical substances from coals and bitumen (Behar *et al.*, 1984; William, 1985; Solli and Leplat, 1986) and base on composition the two are very identical (Badre *et al.*, 2006; Muhammad, 2015). The composition of asphaltenes has remained a subject of interest and attention for many researchers (Bunger and Li, 1981; Peters, 1986; Sheu and Mullins, 1995; Sheu, 2002; Sabbah *et al.*, 2011; Mullin *et al.*, 2012; Muhammad and Abbott, 2013; Wu *et al.*, 2013; Muhammad, 2015). **Generally**, asphaltenes macromolecules are considered to be composed of aliphatic side-chains joined to aromatic moieties through C-C, C-O and C-S linkages (Yen, 1974; Peng *et al.*, 1997; Muhammad, 2015). The aromatic moieties are made up of large condensed pericyclic sheets of 4 and 20 rings (Groenzin and Mullins, 1999; Badre *et al.*, 2006; Muhammad, 2015) whereas the alkyl moieties were found between C<sub>3</sub> to C<sub>7</sub> in size (Calemma *et al.*, 1995; Muhammad, 2015), however, homologues occur between C<sub>1</sub> to C<sub>32</sub> (del Rio *et al.*, 1995; Peng *et al.*, 1999; Muhammad and Abbott, 2013; Muhammad, 2015). More so, the aliphatic moieties are known to consist of both acyclic (*n*-alkyl and iso-alkyl) and cyclic (hopanoids, steroids etc.) alkyl groups (Mojelsky *et al.*, 1992; Trifilieff *et al.*, 1992; Peng *et al.*, 1997; Strausz *et al.*, 1999; Muhammad and Abbott, 2013; Muhammad, 2015). The aromatic moieties in a complex asphaltenes structure which are further interconnected to each other by aliphatic bridges (Polymeric structure) are still been study (Bunger and Li, 1981; Hammami *et al.*, 1995; Speight, 2004; Badre *et al.*, 2006; Strusz *et al.*, 2008; Mullins, 2009; Muhammad, 2015). It has been reported that the molecular composition of aliphatic moieties and their stereochemistry are greatly affected by thermal stress (Muhammad and Abbott, 2013; Muhammad, 2015). But the aromatic moieties oxidation by ruthenium oxide makes it impossible to get clear image of the thermal evolution of the asphaltenes (Muhammad, 2015). In this paper, UV/Visible and FTIR Spectroscopy were employed to study virgin asphaltenes and its subfractions (A and B) to better understand the changes that might occur in asphaltenes structure and

composition when heavy and extra oils are subjected to catalytic aquathermolysis.

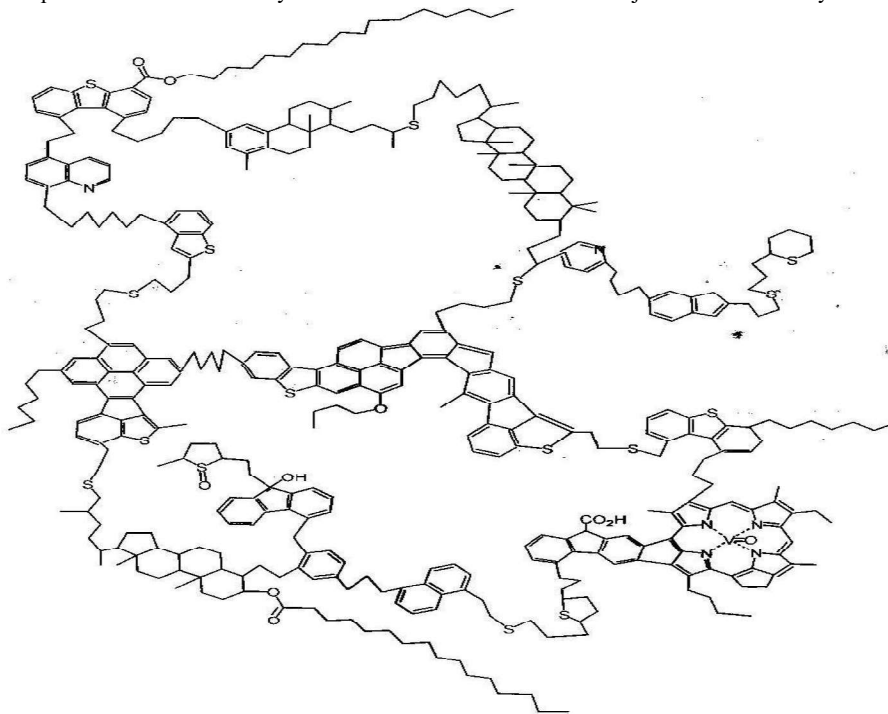


Figure 1: Hypothetical structure of asphaltene (Adapted from Anigbogu, 2011).

## 2. Material and Methods

### 2.1. Sampling

The bitumen sample was collected into a plastic container from the bitumen deposit at Mile 2 in Odigbo Local Government Area, Ondo State located in Nigerian bitumen belt of southwestern Nigeria. The belt lies on the onshore areas of eastern Dahomey (Benin) Basin, with Longitude 3°45'E and 5°45'E and Latitude 6°00'N and 7°00'N (Bakare *et al.*, 2015).

### 2.2. Purification of Raw Bitumen

In order to remove particulate matter, bitumen (40 g) was dissolved with 200 cm<sup>3</sup> of DCM in a beaker using ultrasonicator (DR-LQ20) for 30 minutes. The solution obtained was filtered with a Whatman filter paper and the filtrate was left to dry completely (Muhammad, 2009).

### 2.3. Precipitation of Asphaltenes

Bitumen (1.00 g) was treated with *n*-hexane (40 cm<sup>3</sup>) in a conical flask and was sonicated regularly. Firstly, the bitumen was dissolved with little amount of DCM before the asphaltenes were precipitated with *n*-hexane. The mixture was then stirred for 30 minutes and was allowed to equilibrate for 24 hours. The asphaltenes were recovered from the mixture by centrifuging at 3500 rpm for 10 minutes. The asphaltenes were then re-dissolved with DCM (1 cm<sup>3</sup>) and re-precipitated with *n*-hexane (40 cm<sup>3</sup>). The mixture was sonicated for 10 minutes and the asphaltene was then recovered by centrifugation. This procedure was repeated one more time and the asphaltene recovered was transferred into a pre-weighed beaker with little amount of DCM and left to dry (Muhammad, 2009).

### 2.2.4 Fractionation and Characterization of Asphaltenes

Fractionation of asphaltene was carried out by dissolving certain amount of asphaltene in toluene followed by the addition of *n*-hexane at a ratio of *n*-hexane:toluene (hextol) designed to precipitate only some asphaltenes (Barrera *et al.*, 2013; Yamchi, 2014). Starting the fractionation, a clean beaker (100 cm<sup>3</sup>) was weighed and exactly 3.00 g of asphaltenes was measured into it. Toluene was then added to it and the mixture was left overnight and later placed in an ultrasonic bath (DR-LQ20) for 5 minutes until the asphaltenes completely dissolved.

The corresponding volume of *n*-hexane according to the desired hextol ratio was added and the mixture was sonicated for another 45 minutes. After it was allowed to settle for 24 hours, the solution was centrifuged at 4000 rpm for 5 minutes to separate precipitated asphaltenes from the mixture. Supernatant was decanted and the solid

left was transferred with DCM into a clean beaker and this was named as fraction “A”. The supernatant was then placed in a fumed cupboard to evaporate the hextol and the residue was named as fraction “B”. The two subfractions were allowed to dry until there was no difference in mass (Yamchi, 2014).



Figure 2: Showing flakes of *n*-C<sub>6</sub> asphaltenes obtained from the bitumen

(a) *UV/Visible Spectroscopic Measurements*

Asphaltenes (0.0001 g) was dissolved in dichloromethane (2.00 cm<sup>3</sup>) to obtain asphaltenes solution and was transferred into a cuvet then it was placed in the sample compartment of the UV spectrophotometer. A UV/visible spectroscopic measurement of the solution was made between 400-800 nm on a spectrophotometer (UV-1800). The spectra information gave some insight into the polyaromatic structures in asphaltene and the extent of distribution of polyaromatic condensed ring system (Li *et al.*, 2002). The same procedure was adopted for the characterization of its subfractions.

(b) *FTIR Analysis*

Asphaltene and its subfractions were analyzed on a Fourier transform infrared spectrometer (MB3000). The samples were measured using a transmission technique.

Small quantity of the sample dissolved in dichloromethane was carefully dropped into a firmly packed potassium bromide powder with a syringe. The mixture was ground into fine powder and a pellet was prepared. The infrared spectrum was scanned on the pellet 30 times using a detector at a resolution of 4 cm<sup>-1</sup> in the range 4000 - 750 cm<sup>-1</sup> (Li *et al.*, 2002).

**3. Results and Discussion**

**3.1 Results of Characterization of Asphaltene and its Subfractions**

The results of the experiments conducted are hereby presented:

The UV/Visible spectra of asphaltene and its subfractions are presented in Figure 3(a – c) and were interpreted in Table 1.

Table 1: UV/Visible data of Asphaltene and its subfractions

Asphaltenes					
Virgin		Fraction A		Fraction B	
Absorbance	λ (nm)	Absorbance	λ (nm)	Absorbance	λ (nm)
3.70	510	3.50	570	3.20	465
3.20	515	2.00	575	3.00	470
2.00	520	1.40	600	2.90	475
1.40	530	0.80	640	2.30	480
1.20	535	----	-----	1.50	485

The spectra data of virgin asphaltene and its subfractions (Table 1) shows that they absorbed light in the visible region of the electromagnetic spectrum indicating that asphaltenes are highly unsaturated as shown in the hypothetical structure of asphaltene Figure 1.

The UV/Visible spectra of virgin asphaltene and its subfraction shows that they all contain polynuclear aromatic structures based on their absorbance at the following wavelengths: 465, 470, 475, 480, 510, 512, 520, 530, 570, 575, 600 and 640 nm, respectively.

The fact that asphaltenes are polycyclic aromatic compound, it's obvious that the wavelength of the individual aromatic constituents will vary considerably.

Their light absorption which occurred in the visible region of the spectrum (longer wavelength) suggests the presence of fused benzene rings or polynuclear aromatic system in asphaltene and its subfraction which are unsaturated and highly conjugated in nature. Their absorption is similar to those found in the literature. The range of absorption bands for both virgin asphaltenes and its subfraction are between 465 – 640 nm which correspond to the bands of highly conjugated polynuclear aromatics structures such as **benzenoid**. These are in accordance with asphaltenes and the UV/Visible absorption bands shows resemblance with those described elsewhere (Anigbogu, 2011; Concawe, 2012). The absorption bands which are in the range of 465 – 640 nm for both the virgin asphaltene and its subfractions are within the visible region which characterized the polynuclear aromatic compounds, indicating the presence of chromophore in the asphaltenes (Anigbogu, 2011). In the light of this, asphaltenes are coloured and the chromophore that maybe found in asphaltenes includes: conjugated double bonds involving aromatic hydrocarbon as indicated by the infrared spectra of the virgin asphaltene and fraction B. According to molecular orbital theory, the likely electronic transitions are:  $\delta \rightarrow \delta^*$ ,  $n \rightarrow \delta^*$ ,  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  where  $n$  = non-bonding orbital,  $\delta$  = sigma orbital,  $\pi$  = pie orbital and those with asterisk are antibonding orbitals. The wavelengths of absorption range are in accordance with simple molecular orbital theory assumption. The assumption is that the difference in energy  $\Delta E = \text{HOMO} - \text{LUMO}$  is small.

Therefore the longer the wavelength of absorption, the smaller the energy of irradiation. Hence, exposure of these compounds with small  $\Delta E$  value and longer wavelength of absorption to high irradiation energy will denature them. Thus they could decompose under such condition (Anigbogu, 2011).

In Figure 4(a-c), the infrared spectra of virgin asphaltene and its subfractions are presented and were interpreted in Table 2 based on literature by Silversten and Webster (1998), Pavia *et al.* (2001) and were corroborated by Bakare *et al.* (2015).

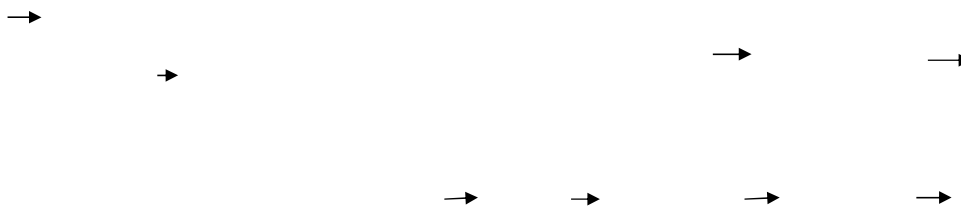


Table 2: Assignment of Functional Groups to FTIR bands in Virgin Asphaltene and its Fractions

Wavenumber (cm <sup>-1</sup> )	Asphaltenes			Interpretation
	Virgin	Fraction A	Fraction B	
3450	+	+	+	O-H stretch (H- bonded)
2925	+	+	+	C-H stretch in alkyl (CH <sub>2</sub> )
2850	+	+	+	C-H stretch in alkyl (CH)
1650	+	+	+	C=O (str.), in carboxylic acids
1500	+	-	+	C=C asymmetric str. in aromatics
1425	-	+	+	CH <sub>2</sub> (def.), in ketone
1350	-	+	-	C-N (str.), in aromatic amine
1275 - 1200	+	+	-	C-O (str.), in ester/ ether
1050	-	+	-	S=O (str.), in sulfoxides
750	+	+	-	C-H (def.), in ring with three adj. H-atoms

+ = present, - = absent, str. =stretch, def. = deformation, adj. = adjacent

The spectra of virgin asphaltene and its subfractions (Table 2) indicate strong and broad band absorption at  $3450\text{ cm}^{-1}$  typical of O-H stretch (H-bonded). The two strong absorptions at  $2925\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  correspond to C-H stretch in ( $\text{CH}_2$ ) and ( $\text{CH}$ ) found in alkyl groups, respectively. The band at  $1650\text{ cm}^{-1}$  may be attributed to C=O (stretch) in carboxylic acids, ketone and amide. A weak band at  $1500\text{ cm}^{-1}$  which could be ascribed to C=C (stretch) in aromatic compounds was present in virgin asphaltene and fraction B but absent in fraction A while a band at  $1425\text{ cm}^{-1}$  which is characteristics of  $\text{CH}_2$  (def.) in ketone was absent in virgin asphaltenes but present in fraction A and B, respectively. Also, the spectra revealed a band at  $1350\text{ cm}^{-1}$  which might be due to the availability of C-N (str.) in aromatic amine was present in virgin asphaltene and fraction B but present in fraction A and the band observed in the range  $1275 - 1200\text{ cm}^{-1}$  could be assigned to C-O (str.) in ester or ether was present in virgin asphaltene and fraction A but absent in fraction B. More so, a strong band at  $1050\text{ cm}^{-1}$  which may be ascribed to S=O (str.) in sulfoxides or sulfonic acids was absent in virgin asphaltene and fraction B and present only in fraction A while an absorption band at  $750\text{ cm}^{-1}$  is a characteristics of C-H (def.) in benzene ring with three adjacent hydrogen atoms was present in both virgin asphaltene and fraction A but absent in fraction B. The IR spectra bands (Table 2) are in conformity with observation of Muhammad (2015) and Bakare *et al.* (2015) in terms of functional groups. The spectra characteristics of virgin asphaltene showed the absence of some functionalities such as S=O and C-N which were present in one of its fractions described the heterogeneity of asphaltene. Although hydrocarbons are consistent with all the spectra, however, the presence of O-H and C=O groups in all the spectra confirmed that asphaltenes as a group are indeed polar because they aid asphaltene molecules in forming a mechanical barrier through hydrogen bonding around the water droplets and prevent coalescence (Li *et al.*, 2002). These infrared results are in accordance with studies on Agbabu Natural Bitumen (Bakare *et al.*, 2015).

#### 4 Conclusions

The results showed that virgin asphaltene and its subfractions absorbed light of longer wavelength in the range (465 – 640 nm), indicating that they are made up of polynuclear aromatic compounds. The results also revealed the presence of alkyl side chains and major oxygenated groups in both virgin asphaltenes and its subfractions (A and B).

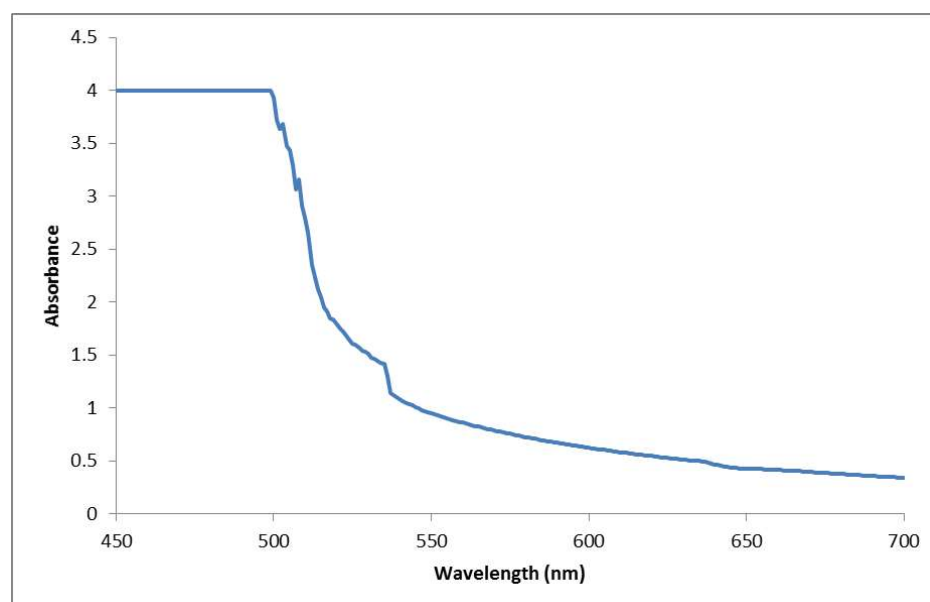


Figure 3a: UV- Visible spectra of virgin asphaltene

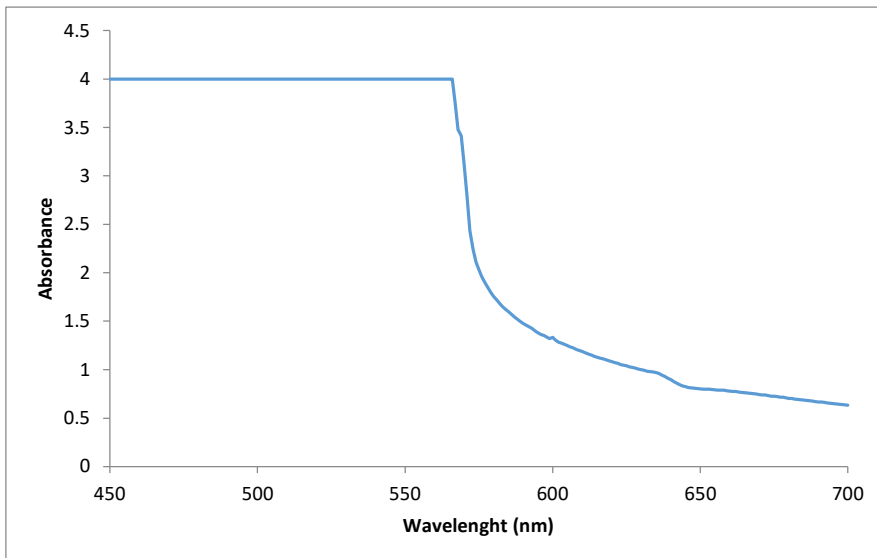


Figure 3b: UV-Visible spectra of asphaltene fraction A

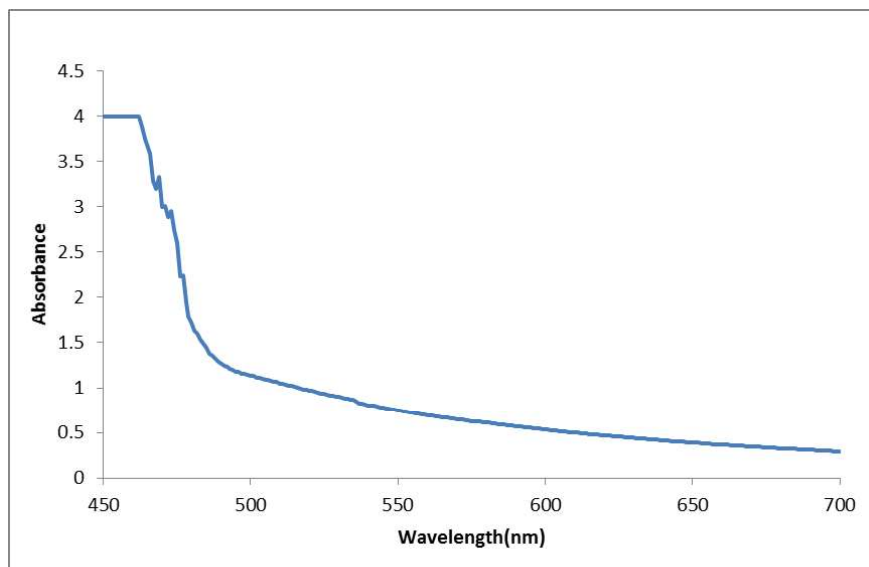


Figure 3c: UV-Visible spectra asphaltene fraction B



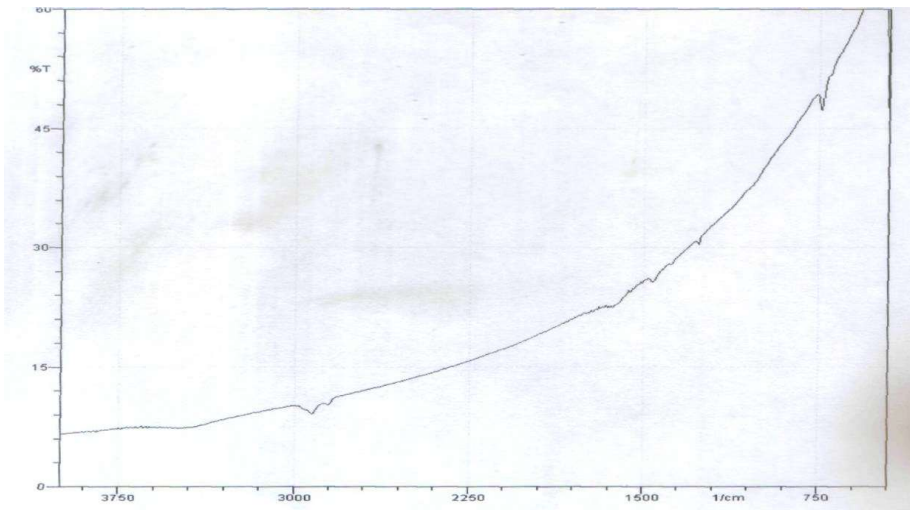
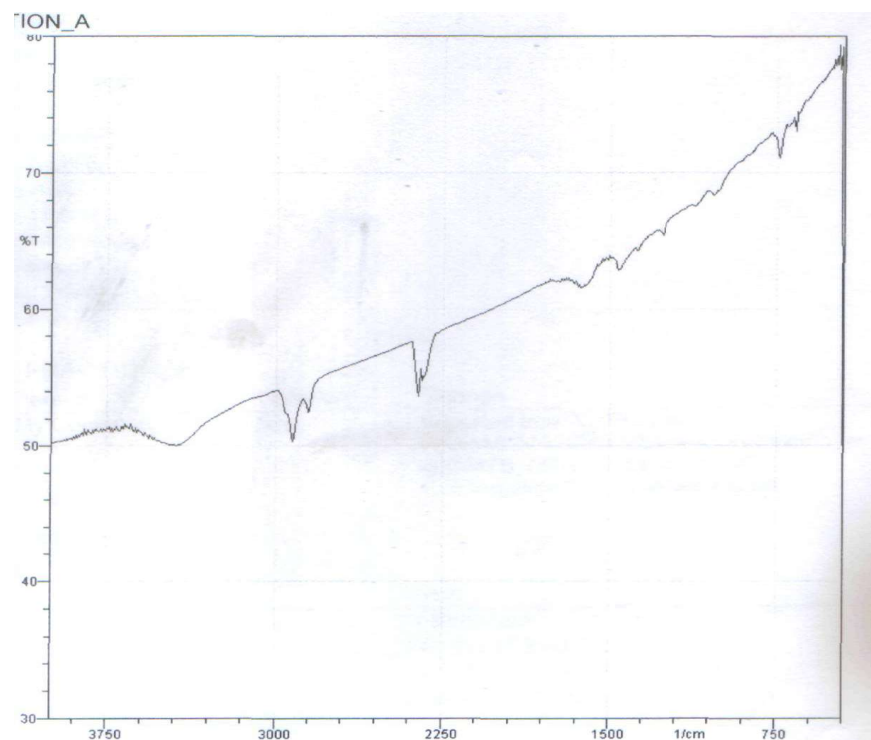


Figure 4a:  
FTIR spectra of virgin

asphaltene



asphaltene fraction A

Figure 4b:  
FTIR spectra of

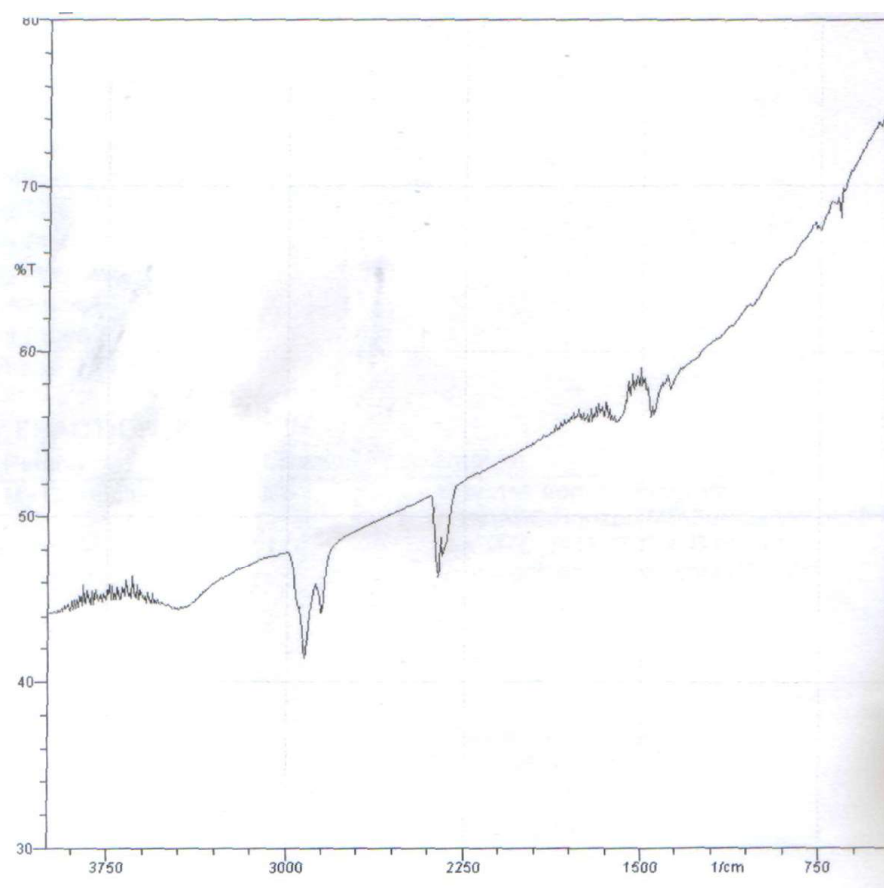


Figure 4c: FTIR spectra of asphaltene fraction B

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