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Characterization of aromatic fractions separated from the heavy residual fractions of four crude oils having different geological origins by HPLC and NMR

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ABSTRACT

Four crude oils having different geological origins such as DK (Sylhet limestone and Langpar), SL (Oligocene), JN (lower Miocene) and KMC (upper to middle Miocene) were taken from four different locations and distilled at atmospheric pressure up to 300 degrees C. Aromatic fractions were separated from the 300 degrees C+ fractions (feedstock) by medium pressure liquid chromatography (MPLC). The separated aromatic fractions were characterized by high performance liquid chromatography with photo diode array detector (HPLC-PDA) for aromatic group type analysis and by ^{1}H and ^{13}C NMR for aromatic structure type analysis. Different aromatic groups like mono-, di-, tri-, tetra etc. were separated and quantified by HPLC. The combined gained information from NMR analysis provided reliable average structural parameters. These included estimation of aliphatic and aromatic content, average paraffinic chain length, polyaromatic compounds etc.

KEYWORDS

SARA;
HPLC;
MPLC;
^{1}H NMR;
^{13}C NMR;
Phenanthrene.

1. INTRODUCTION

Compositional analyses of heavy petroleum fractions play a decisive role in improving refinery operations, saving energy resources and in mitigating pollution problems. However, knowing every detail is often impossible because of the enormous complexity of heavy petroleum fraction and the limitation of our measuring techniques[1]. Over the years numerous separation schemes have been developed where petroleum hydrocarbons are separated into main groups like saturates, aromatics, polars and asphaltenes. The molecular weight, elemental analysis, group type analysis, distribution of types of carbon chain analysis as well as average structural parameters are studied by different techniques such as solvent extraction, adsorption, IR spectroscopy, Gas Chromatography (GC), Gas Chromatography-Mass Spectroscopy (GC-MS), HPLC and NMR (^{1}H and ^{13}C) spectroscopy etc. But each scheme has its own limitations. Recently TLC-FID has gained recognition for the analysis of heavier petroleum fractions where saturates, aromatics, polar and asphaltenes (SARA) was obtained quantitatively[2].

For a long period aromatic hydrocarbons were separated from crude oil by using adsorption column chromatography[3]. The quantification of the total aro-

matics as well as of their sub fractions (mono-, di-, tri-, etc.) are performed gravimetrically. Long analysis time and incomplete separation between the specific groups are the main problems reported for these methods. The derived aromatic fraction can be further characterized using analytical methods such as gas (GC-MS)[4-7] and HPLC-MS[8]. But high boiling point, poor thermal stability are the main drawbacks for their analysis.

A great number of HPLC analytical procedures have been reported in the literature concerning the separation of crude oils and oil fractions[9-16]. Incomplete separation between the aromatic groups that can be achieved with the current analytical columns is among the main problems encountered. The elution time of these groups depends on the number of aromatic rings and on the type and the number of the substituents present in the molecule. The elution time of the aromatics depends mainly on the number of the condensed rings contained, while the presence of paraffinic and naphthenic substituents in a molecule increases and reduces its retention time, respectively. The overlapping between the different groups influences the quantitative results as it is difficult to determine accurately the peak area of each specific group. Hardware and software approaches can be employed to improve the resolution of the HPLC analysis. The hardware approach involves optimization of the chromatographic conditions (column, type of solvent, flow rates, etc.), while the software approach utilizes multi-channel detection that allows the overlapping components to be distinguished by their individual spectrum patterns. In this communication, four crude oils having different geological origins were distilled at atmospheric pressure up to 300^0C. The 300^0C+ fractions were taken as feedstock. Saturates, aromatics, resins and asphaltenes (SARA) fractions were separated from the feedstock by normal phase HPLC. The separated aromatics were further analyzed by reversed phase HPLC and NMR spectroscopy and the polyaromatic hydrocarbons were quantified on the basis of their ring structures by reversed phase HPLC.

2. EXPERIMENTAL

2.1. SARA Analysis of the feedstock by MPLC

A 5% solution of the deasphaltened fractions of different feedstock was prepared in HPLC grade hexane. 500µl of the solution was injected to the HPLC system consisting of a DYNAMAX SD-300 pump, MERCK L-7490 refractive index detector and a VARIAN Pro Star UV-VIS detector. Two columns were used for the separation of saturates, aromatics and resin. A pre-column for retention of resin fraction and a main column for separation of saturates and aromatics. The pre column was manually packed with silica gel 100 (70-230 mesh ASTM) which was initially heated at 200^0C for 1hour and then at 600^0C for two hours to deactivate the silica gel, the main column used was Lobar 310-25 Lichroprep Si (40-63) having a column dimension of OD: 13 and ID: 10.The solution was initially allowed to pass through both the columns at solvent (HPLC grade Hexane) elution rate of 1ml/min for 25 mins. After 25 mins. the pre-column was disconnected from the solvent line, allowing the solvent path through the main column only with the help of a valve. The saturated hydrocarbons eluted prior to the aromatics from the main column. The saturates were collected in a conical flask. After complete elution of the saturates fraction from the main column i.e. when the saturates peak comes to the baseline as detected by the RI detector, the flow of solvent was reversed with a back flushing valve to hasten the elution of aromatics fraction. The aromatics fraction was collected in a conical flask. The solvent from both the flask was removed by a rotary evaporator. Finally the saturates and aromatics fractions were transferred to a pre-weighed beaker with a little dichloro methane. The dichloromethane was removed from the beaker by heating the beaker on a water bath. The final weight of the beaker was then taken. Resins from the pre column were separated by a mixture of dichloromethane and methanol (95:5)v/v in another pre-weighed beaker. And final weight of the beaker was taken as above.

2.2. Analysis of aromatic fractions by reversed phase HPLC-UV-PDA

A 10% solution of the aromatic fraction was made in Acetonitrile. 20µl of the solution was injected in the HPLC system consisting of Dionex P680 HPLC pump, Dionex PDA-100 photodiode array detector, Shodex RI-71 refractive index detector, Dionex oven and Dionex UCI-100 universal chromatography interface.

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The sample was eluted through a C18-5 (15cm X 4mm) column by a mixture of Acetonitrile (HPLC) grade and water (HPLC) grade (60:40) ratio. Temperature of the column was kept at 50^0C. The elution rate was 0.5ml/min. Total time of analysis was 150 min. Data acquisition was done by Chromeleon Chromatography management system, version 6.40.

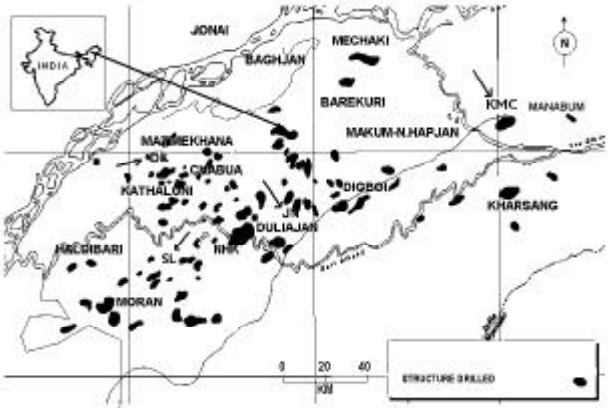

Figure1 : Oilfield map of Assam and Arunachal Pradesh in India

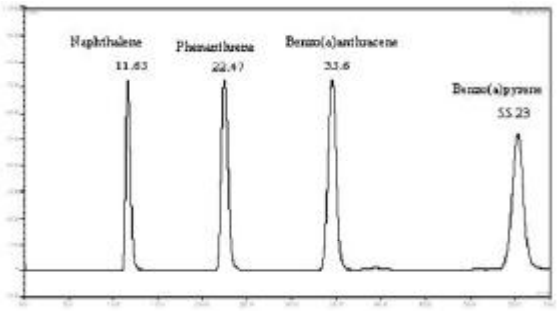

Figure 2 : HPLC chromatogram of aromatic standard

2.3. Analysis of aromatic fractions by NMR

^{13}C and ^{1}H NMR spectra were taken with a Bruker 300 MH_Z instrument using TMS as reference and $CDCl_3$ as solvent.

3. RESULT AND DISCUSSION

3.1. Analysis of aromatics by HPLC

Figure 1 is the map of oilfield locations of Assam and Arunachal Pradesh in North East India showing the locations of crude oils collected for the present studies. The HPLC-UV-DAD chromatogram of aromatics fractions DK, SL, JN and KMC along with standards are presented in figures 3(a-d). A significant number of individual components appear in the elution window of the specific compound groups. From the chromatogram it is very difficult to identify individual compounds due to overlapping of peaks having similar chemical characteristics. But they can be separated into compounds of individual groups like mono, di, tri, tetra etc. aromat-

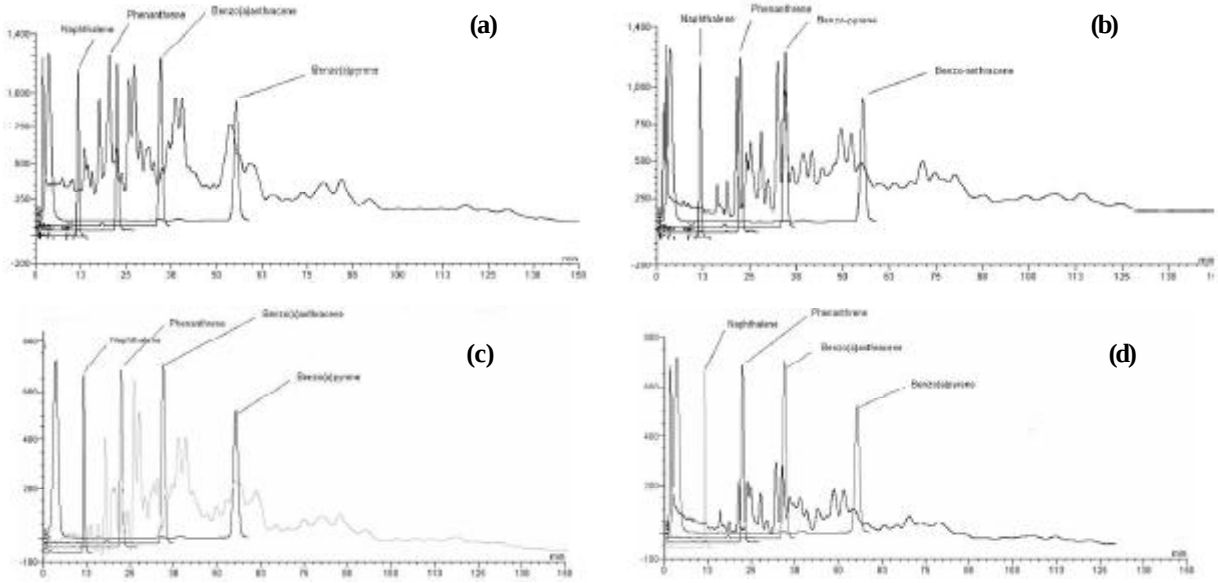

Figure 3: (a) : HPLC chromatograms of DK aromatics and standard; (b) : HPLC chromatograms of SL aromatics and standard; (c) : HPLC chromatograms of JN aromatics and standard; (d) : HPLC chromatograms of KMC aromatics and standard

TABLE 1 : Concentrations of aromatic groups in different aromatic fractions measured by HPLC-UV detector

RT (min)	DK	SL	JN	KMC
0-12 (Mono-aromatics)	12.25	6.81	4.66	3.99
12-22 (Di-aromatics)	16.52	5.28	7.45	5.19
22-35 (Tri-aromatics)	23.77	17.19	22.06	24.13
35-55 (Tetra-aromatics)	30.24	30.67	31.26	38.49
55-150 (Penta+ aromatics)	17.22	40.04	34.59	13.35

TABLE 2: Chemical shifts of proton spectral regions of aromatics

Chemical shifts (ppm)	Assignment	Relative Abundance (%)				
		DK	SL	JN	KMC	VRS
10.7-7.4	Polyaromatic	19.42	27.64	26.4	26.44	4.7
4.3-2.4	α to Aromatic CH_2	20.39	19.51	26.4	25.62	7.4
2.4-2.0	α to Aromatic CH_3	8.74	3.25	4.8	1.65	7.4
2.0-1.09	Paraffinic CH_2	50.48	44.71	41.6	45.45	64.43
1.09-0.5	Paraffinic CH_3	0.97	4.87	0.8	0.83	23.48
Caliphatic/Caromatic		1.1	0.98	0.74	0.86	4.5
Average chain lngth		4	3	4	3	11

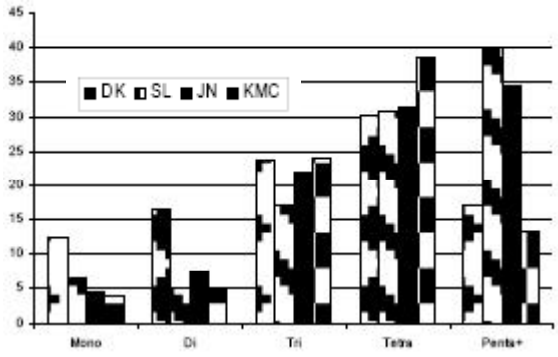

Figure 4 : Concentration of aromatic groups in different aromatic fractions

ics by comparing with the standard compounds representing different groups. For the same reason unsubstituted compounds like naphthalene, phenanthrene, benzo(a)anthracene and benzo(a)pyrene was taken as representative compounds for di-, tri-, tetra-, and penta- aromatic compounds. Approximate separation and calculation of the peak areas of a group of peaks falling into a particular group of compound can be calculated by comparing with the retention times of the standard compounds. As presented in the figure1, the elution time of di, tri-, tetra and penta aromatics are 11.65, 22.47, 35.6 and 55.23 respectively. Peaks falling within the retention times 0.0-11.65 min may be approximately taken as coming from momo-aromatic compounds. Likewise peaks within 11.65-22.47, 22.47-35.6, 35.6-55.23 and 55.23 min onwards can be taken as di-aromatic, tri-aromatic, tetra-aromatic and penta-aromatic and higher compounds. Keeping this assumption the relative concentration of mono-, di-, tri-, tetra- and penta- and higher aromatics are evaluated and presented in TABLE 1. It is observed from the TABLE 1 that all the four reduced crude oils contain compounds of all the different aromatic groups but to different extent. The graphical representation of different aromatic groups present in the different feedstock is presented in figure 4. From the Figure it is observed that for JN there is a linear rise of concentration from mono to penta aromatic groups. DK and KMC aromatic fractions contain highest concentration of tetra-aromatic ring compounds. JN and SL contain more penta and higher aromatic groups than the other polyaromatic groups. Majority of the aromatic compounds are found to be penta+ ring structures. Separation of penta aromatics and higher was not resolved.

3.2. Analysis of aromatic fractions by NMR

Kapur et al[17] estimated the total aromatics in the vacuum gas oil region while Hassan et al[18] characterized Arabian heavy crude oils with the help of NMR spectroscopy. NMR, especially, the combination of ^{1}H-NMR and ^{13}C-NMR and elemental analysis allows the determination of numerous average structural groups in petroleum[9]. The ^{1}H NMR spectra of aromatic fractions of DK, SL, JN and KMC are shown in figures 5(a-d). The distribution of aromatic protons, H_{ar} (7.2-9.0) and aliphatic protons, H_{al} (0-4.0) for each fraction is shown in TABLE 2. The aliphatic region, has been further divided into three parts: Hα (δ:2.0-4.0) are the protons attached to a saturated carbon atom in α-position with respect to an aromatic ring; Hβ (δ:1.0-2.0) are the protons attached to paraffinic methylenes, naphthenes, and methyls or methylene protons β, or further away from an aromatic ring; Hγ (δ:0.5-1.0) are the protons of paraffinic methyls and methyls γ, or further away from the aromatic ring. It is observed that the appearance of intense signal in the chemical shift region of 0.5-1.09 ppm in the proton NMR spectra indicates the presence of ∂-CH_3 group of an alkyl chain attached to the aromatic ring system. The -CH and -CH_2 groups present in the alkyl chain appears in the chemical shift

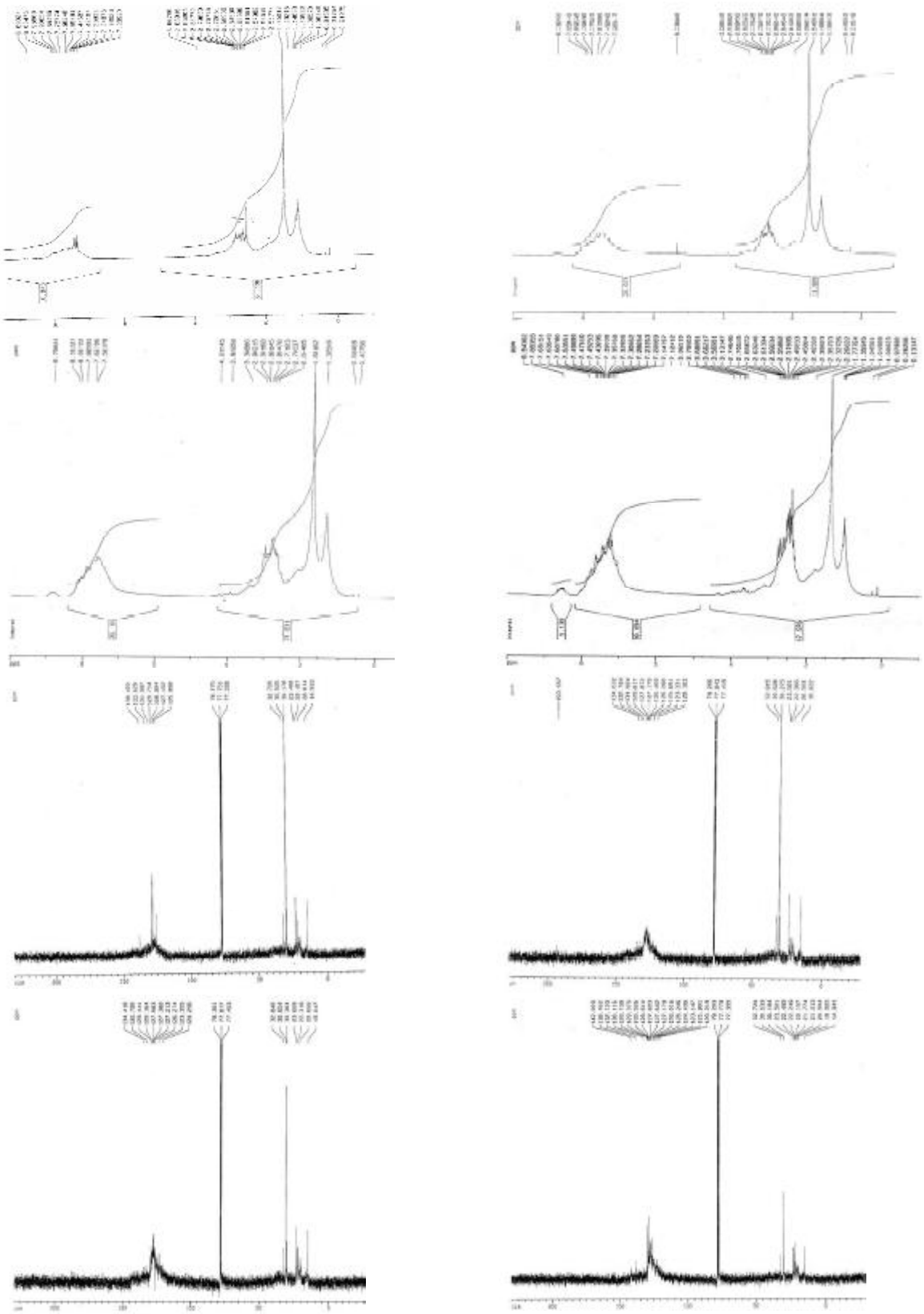

Figure 5 : (a) 1H NMR spectra of DK aromatics; (b) 1H NMR spectra of SL aromatics; (c) 1H NMR spectra of JN aromatics; (d) 1H NMR spectra of KMC aromatics; (e) 13C NMR spectra of DK aromatics; (f) 13C NMR spectra of SL aromatics; (g) 13C NMR spectra of JN aromatics; (h) 13C NMR spectra of KMC aromatics

TABLE 3: Chemical shifts of carbon spectral regions of aromatics

Chemical shifts (ppm)	Assignment	Peak height (cm)				
		DK	SL	JN	KMC	VRS
142.0	Alkyl (other than methyl) substituted aromatics	-	-	-	0.6	-
138.4	Naphthenic substituted aromatic	1.2	-	-	1.0	-
132.7	Most internal aromatic C	0.8	1.1	1.1	0.7	-
130.1	-do-	4.1	-	-	2.9	-
129.4	Aromatic C-H	4.6	1.6	2.1	1.4	-
128.6	-do-	-	-	-	1.5	-
127.8	-do-	-	1.8	2.5	3.3	-
127.2	-do-	1.3	1.9	2.8	1.5	0.5
126.2	-do-	2.3	1.5	2.0	1.8	-
125.3	-do-	-	-	-	2.0	-
124.4	-do-	-	-	-	1.9	0.5
123.3	-do-	-	1.2	1.8	1.1	-
121.8	-do-	-	-	-	0.7	-
120.2	-do-	-	0.9	1.1	0.7	-
32.8	CH in chain next to CH_3	2.3	2.4	2.0	1.7	-
30.5	CH_2 in ethyl group α to an aromatic ring	12.8	12.8	10.5	4.6	1.0
30.2	-do-	2.6	2.4	2.4	1.7	-
28.6	-do-	-	-	-	-	6.3
28.3	-do-	-	-	-	-	1.0
28.0	-do-	-	-	-	-	0.5
23.5	CH2 next to terminal CH_3 in chains ? 6	3.2	3.6	3.2	1.6	-
22.4	α- CH3 not shielded by adjacent groups	-	-	2.0	1.9	-
22.1	-do-	1.9	1.3	-	0.9	2.3
20.6	aromatic attached.CH_3	-	1.3	1.5	0.8	-
20.0	-do-	1.1	-	-	0.7	-
19.6	-do-	-	-	-	0.7	-
14.9	CH_3 gamma or further from aromatic ring	3.1	3.4	2.9	1.7	-
13.1	-do-	-	-	-	-	2.2

region 1.0 to 2.0 ppm. The chain may be attached either to α-naphthenic ring of aromatics or to the mono or polyaromatic ring. It is also observed from the Table 2 that contribution of ∂-CH_3 group is a minor only for all the aromatic fractions. Its relative abundance is approximately 1% in all the aromatic samples. It is probably due to fewer number of side chains attached to the aromatic rings. The benzylic Ar-C-H (2.2-3.0ppm) for KMC and JN appears to be greater than the other two aromatic fractions indicating more number of side chains attached to the aromatic rings in KMC and JN aromatics. Number of carbon atoms in the side chain is determined by the method adopted by Sarpal et al.[19] and presented in the TABLE 3. This indicates that these aromatics have very few number of chains attached to the aromatic rings. Carbon chain attached to the aromatic rings was further identified by ^{13}C NMR spectroscopy. In all the spectra figures 5(e-h) there are two distinct parts: the aliphatic region, 0-70 ppm and the aromatic region, 110-160 ppm. The general characteristics of all the spectra appear to be similar. The resonances in the aliphatic region are due to linear or branched alkanes attached to aromatic rings. The peaks at 14, 23, 32 and 30 are traditionally assigned to terminal C_1, C_2, C_3 and central methylene groups of paraffinic chains[20]. The intensity of the signal at 30 ppm decreases in the order SL>DK>JN>KMC indicating a decreasing trend of the length of side chain attached to the aromatic ring. Methyl substituted aromatic rings indicated by signal around 20 ppm[21] appears to be highest for KMC followed by JN, SL and DK. If the paraffinic chain is branched with a methyl group at some position then the substituted carbon absorb at 33.0 ppm. The branched methyls appear at 19.7 ppm. Appearance of signals at both these positions confirms methyl branching in the paraffinic chain attached to the aromatic ring. No. of such branches is more for DK and SL followed by JN and KMC. In VRS these signals are absent indicating absence of methyl branching in paraffinic chain. Signal in the region (17.6-14.7 ppm) indicates the presence of β- CH_3 group atta β-CH_2 or isobutyl –CH_3 group attached to aromatic ring. The aromatic region contains sharp peaks for DK and KMC whereas no or low intensity peaks are observed for SL and JN respectively in that region. The aromatic region consists of signals due to several types of aromatic carbons attached to hydrogen, $C_{ar\text{-}H}$; to alkyl groups (except methyl), $C_{ar\text{-}alk}$; to methyl group, $C_{ar\text{-}me}$; and in bridgeheads either with aromatic rings or with naphthenic rings, $C_{ar\text{-}H}$ 120.2-129.4 ppm, (TABLE 3) for KMC is highest followed by JN, SL and DK. This indicates that KMC have highest aromaticity followed by JN, SL and DK.

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Signal at 142.2 for alkyl substituted aromatics ($C_{ar\text{-}alk}$) is observed in KMC aromatics only. $C_{ar\text{-}b}$ is absent for SL and JN aromatics indicating no bridgehead carbons in these aromatics. The hump which forms underneath the sharp peaks, is allotted to naphthenic groups[22]. Although α and β to aromatic paraffinic chains also contribute to the signal in this region, it is still a useful indicator of the naphthenic content.

4. CONCLUSION

Separation of aromatic fraction by MPLC from heavy residue of crude oil resulted very good separation of aromatic portion without contamination of saturated hydrocarbons. The purity of aromatic fraction can be checked by TLC-FID. HPLC-PDA analysis of aromatic fraction gives quite accurate concentrations of different aromatic groups present in heavier fractions of crude oil. In all the aromatic fractions the concentration of monoaromatic compounds are found to be quite less than the other polyaromatic groups. DK and KMC contain highest amount of tetra-aromatic compounds whereas SL and JN contain more pentaaromatic+ compounds compared to other aromatic group of compounds. NMR analysis of aromatic fraction is very useful for identifying different classes of aromatic compounds and determination of the number and length of the paraffinic chain attached to the aromatic rings. The length of side chain attached to the rings is in the order SL>DK>JN>KMC.

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