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Study of surface-active compounds in Sanand field crude oil

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Abstract

The crude oil sample collected from Sanand oilfield was analyzed chemically and infrared spectroscopically after vacuum distillation and liquid chromatographic separation. It was concluded that the crude oil sample contained anion active surfactants primarily of naphthenic acid type present mainly in the resinous chromatographic fraction which provides most of the surface-active properties to the crude. These naturally occurring surfactants are believed to influence formation of oil/water emulsion and the extent of paraffin deposition of pipe wall. It may also have bearing on the prospect of caustic flooding as tertiary recovery method.

Key words: Surface-active compounds, fractional distillation, adsorption-chromatography, dye-complexes, naphthenic acids.

1. Introduction

Crude petroleum is known to contain considerable quantities of polar surface-active substances which accumulate at oil/water interface[1] and get adsorbed as monolayer on a high energy solid surface decreasing its surface-free energy[2]. Zisman *et al*[3] showed that the adsorption of these compounds may change the wettability characteristic of a solid surface turning it from oil wet to water wet. Cole and Jessen[4] and Ehrig[5] showed that surface wettability can have a profound-effect on the magnitude of paraffin deposition, and Parks[6] and Zisman[7] demonstrated that the presence of certain adsorbed film on a metal surface would reduce the adherence of paraffin to the surface. According to Dodd[8], Patton[9] and Hasiba[10] about 12.5% of the film forming material consists of higher molecular weight aliphatic hydrocarbons while the rest are asphaltenes and resins along with free naphthenic acids, acid anions and their salts.

The molecule of a surface-active substance is formed by combining one or more lipophilic chains and one or more hydrophilic groups. The extent of surface activity is determined by the nature and ratio of lipophilic and hydrophilic groups. The hydrophilic groups include electrically-charged groups *i.e.* ionic groups as well as uncharged polar molecules. The lipophilic (hydrophilic) rest of the molecule can be formed from the entire variety of aliphatic-aromatic and aromatic structures. The anion active tensides are the compounds having polar anion active groups *i.e.* -COOH, $-OSO_3H$, $-SSO_3$, $-SO_3H$, etc. The qualitative

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test for the presence of tensides, is the neutralization of hydrophilic character by salt formation with an oppositely charged ionic-active dye[11]. Methylene blue which is a cation-active dye has been used successfully for the detection and separation of anion-active surfactants from the bulk of resins[11].

Different kinds of carboxylic acids including fatty acids are present in crude oil. Carboxylic acids with one or more polymethylenic rings, are the most effective emulsifying agents. Naphthenic acids comprised the bulk of typical carboxylic acids which form various acid derivatives (salts, esters and amides, etc.) during interfacial deposition due to the fact that carboxylic group in the molecule is bound to the naphthenic ring, not directly, but *via* an aliphatic bridge of varying length[12].

The objective of the present investigation is to separate and identify the surface-active compounds in the oil collected, so as to get an insight into the possible treatment for demulsification as well as the suitability of the oil for caustic flooding operations. The crude oil was fractionated, first by vacuum distillation and then by column chromatography. The extracts were analysed both chemically and infrared spectroscopically to identify the suspected components.

2. Experimental

A 5-litre sample of crude oil was distilled under atmospheric and reduced pressure distillation according to ASTM D 1160-57T method with the help of a fractional distillation unit manufactured by Scientific Apparatus Manufacturing Co. Bombay (Cat. No. 27). Atmospheric distillation was conducted at a reflux ratio of 2:1 up to 200° C boiling point. Vacuum distillation was done at a reflux ratio of 1:10 at a pressure of 2 mm Hg. In order to avoid cracking of higher molecules, the temperature of the still pot was never allowed to exceed 260° C. Boiling points obtained at subatmospheric pressures were converted to equivalent atmospheric boiling points by using the vapour pressure chart (53-12) for petroleum hydrocarbons[13].

The fractions obtained in the boiling ranges 300-340° C, 340-375° C and > 375° C (residuum) were subjected to further fractionation by the modified technique of dual column liquid chromatography (ASTM 2007 - 62T). Before chromatographic analysis the residuum was dissolved in *n*-pentane and subjected to centrifugation at 25000 rpm at ambient temperature for approximately 20 minutes. The resulting *n*-pentane insoluble material constitutes the asphaltene fraction. The dual-column of the liquid adsorption chromatography apparatus consists of an upper column containing 30/60 mesh neutral-baked Fuller's earth, and a lower column containing 100/200 mesh silica gel topped with a layer of Fuller's earth. The following three fractions were obtained after charging the *n*-pentane-crude oil mixture through the column.

(i) Saturated paraffins - The eluant passed through both the columns.

(ii) Resins - The fraction adsorbed on the clay in upper column.

(iii) Aromatics - The fraction which passed through upper column but got adsorbed on silica gel in the lower column.

The desorption of resins and aromatics from the upper and lower columns respectively was carried out by a mixture of acetone and benzene (1 : 1). The fractions of saturates, resins and aromatics were obtained quantitatively after complete evaporation of solvents on a water bath. All distillates with boiling point > 300° C, residuum and their chromatographic fractions were subjected to quantitative elemental determination and infrared spectroscopic analyses. Quantitative estimations of C,H,O,N, and S elements in the fractions were conducted as per the methods of Vogel[14]. The infrared spectra were obtained with the help of infrared spectrophotometer model Perkin Elmer 577 Grating IR.

The IR spectra of asphaltene and dye-complex were taken on KBr pelletes whereas spectra for the rest were obtained by thin film formation on NaCl plates. The interpretation of infrared spectra is based on published literature recommendations[15–17].

3. Theoretical analysis

The special characteristics of the crude oil sample are recorded in Table I. The original sample was in liquid state having small percentage of water. The graphical presentation of atmospheric equivalent boiling point *vs* percentage distilled (Fig. 1) indicates the volatile nature of the crude; as only 27.2% was left as residuum after distillation. The major components of the crude oil sample belong to the range between 260-375° C having carbon atom number range approximately C_{15} - C_{23}. The chromatographic analyses, recorded in Table II, show that the residuum contains 36.0% by weight of asphaltene which is rather high. No asphaltenes were detected in any fraction with the boiling point less than 375° C. The saturate (paraffins) fraction decreases in amount (weight per cent) with increase in boiling point whereas the resin and aromatic components increase with the increase in boiling point. The high percentage of asphaltene and resin in the residuum indicates the asphaltic nature of the crude[18].

Table I

Special characteristics of original crude oil

Sl. No.	Particulars	Values
1.	Type of sample	Well head crude
2.	Region and payzone	Western Region, Single Sand Third Zone
3.	Depth of the well	1360 m
4.	Bottom hole pressure	128 - 130 kg/cm^2
5.	Bottom hole temperature	85° C at 1350 m
6.	Well head pressure	28 kg/cm^2
7.	Bottom sediment and water	8%
8.	Paraffin content	20%
9.	Specific gravity	0.9266
10.	Pour point	10° C
11.	Cloud Point	15.6° C
12.	Project	ONGC Project, India.

Table II

Chromatographic analysis
(Expressed in weight per cent)

Sl. No.	Fraction	Asphaltenes	Saturates	Resins	Aromatics	Loss
1.	Residuum > 375°C	36.00	27.50	16.00	20.50	—
2.	Distillates 340-375°C	—	77.90	1.40	20.10	0.60
3.	Distillate 300-340°C	—	79.40	0.50	18.10	2.00

Table III

Elemental analysis of petroleum fractions
(Expressed in weight per cent)

Sl. No.	Fraction	C	H	O	N	S	C:H
1.	Original crude	84.62	13.21	0.30	1.31	0.54	0.533
2.	Residuum > 375°C	84.10	10.80	0.69	2.73	1.63	0.648
3.	Distillates 340-375°C	83.76	11.30	0.60	2.63	1.64	0.617
4.	Distillates 300-340°C	84.10	11.70	0.55	2.06	1.51	0.598
5	Asphaltenes	83.10	8.10	1.28	4.27	2.75	0.854
6.	Saturates > 375°C	85.91	14.02	—	—	—	0.510
7.	Resins > 375°C	83.27	8.80	1.38	3.56	2.67	0.788
8.	Aromatics > 375°C	33.18	10.60	1.60	2.16	2.36	0.653
9.	Saturates 340-375°C	35.53	14.14	—	—	—	0.505
10.	Resins 340-375°C	84.90	10.00	0.70	2.24	2.16	0.700
11.	Aromatics 340-375°C	85.00	11.72	0.50	1.48	1.30	0.604
12.	Saturates 300-340°C	85.74	14.22	—	—	—	0.502
13.	Resins 300-340°C	86.26	10.14	0.50	1.56	1.50	0.708
14.	Aromatics 300-340°C	85.14	11.63	0.20	1.40	1.25	0.610
15.	Isolated naphthenic acid	85.50	13.20	1.20	—	—	0.515

Elemental analyses of the fractions (Table III) show that the saturate fractions contain no oxygen, nitrogen and sulphur. Their C:H ratios close to 0.5, indicate the presence of long aliphatic hydrocarbons ($C_n H_{2n+2}$) both with straight and branched chains together with alkylated naphthenes. The aromatic fractions are found to contain oxygen, nitrogen and sulphur. The C:H ratios in this case lie in the range of 0.60 - 0.65 which is relatively low when compared to 1.0 (for C_nH_{2n-2}) for a single aromatic ring. Therefore, it can be inferred that the majority of compounds in the aromatic fractions possess not more than two rings substituted by both straight and branched aliphatic side chains or rings of naphthenic character. Resins and asphaltenes contain higher amount of oxygen, nitrogen, and sulphur than aromatics. The C:H ratios of resins (0.70 - 0.79) indicate the possibilities of higher content of condensed aromatic rings associated with aliphatic and polar functional groups in the molecules. The C:H ratio of asphaltene was found to have the highest value of 0.854,

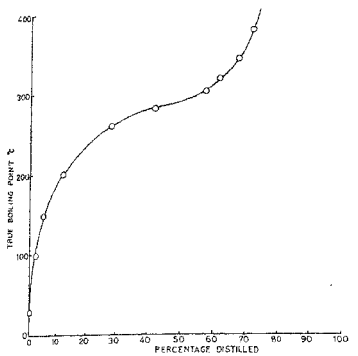

FIG. 1. Distillation curve true boiling point *vs* percentage distilled.

probably due to higher aromaticity of the molecules. A comparison of C:H ratios of all fractions give an expected correlation with the amount of saturated hydrocarbons, that is, higher the content of saturated compounds in a fraction lower is the atomic C:H ratio. Also, aromaticity of successively increasing boiling fractions increases as evidenced by increase in C:H ratio.

The infrared spectra of fractions show that most of the structures absorbing radiations in the region between 5000 and 1333 cm^{-1} produce absorption bands which are virtually independent of the rest of the molecule. All fractions are observed to indicate strong absorption bands characteristic of C-H stretching between 2941 and 2857 cm^{-1}; in the region of 1471-1449 cm^{-1} related to $-CH_2-$deformation and asymmetric $-CH_3$ deformation, and one between 1389 and 1370 cm^{-1} related to symmetric $-CH_3$ deformation. These bands are characteristic of hydrocarbons. The band at 1614 cm^{-1} is due to aromatic ring vibrations while the pattern of bands between 907 and 741 cm^{-1} show the substitution on the aromatic rings. The doublet at 735 and 719 cm^{-1} is always due to long paraffinic chain $(-CH_2-)_n$ but in crystalline form.

Figure 2 shows the infrared spectra of distillates 300-340°C, 340-375°C and residuum > 375°C. The spectra show - OH stretching as a wide band at 3500 cm^{-1}, $-CH_3$; $>CH_2$ and $\rightarrow$ CH stretching in the form of sharp intensity triplets between 2980 and 2890 cm^{-1}, C = C stretching vibration of aromatic ring at 1614 cm^{-1}, $>CH_2$ bending – overlapped with C – C stretching as sharp intensity doublet in the region of 1471–1449 cm^{-1}, the medium intensity of $-CH_3$ bending at 1400 - 1390 cm^{-1}, C – O stretching at 880 cm^{-1} C = C skeleton vibration at 813-800 cm^{-1} and $(>CH_2)_n$ stretching at 746-725 cm^{-1} as medium bands where $n > 4$. The increasing intensities of the spectrum I, II and III at 1614, 880, 813 and 746 cm^{-1} bands indicate the increasing aromatics and paraffinic characters with respect to increasing boiling

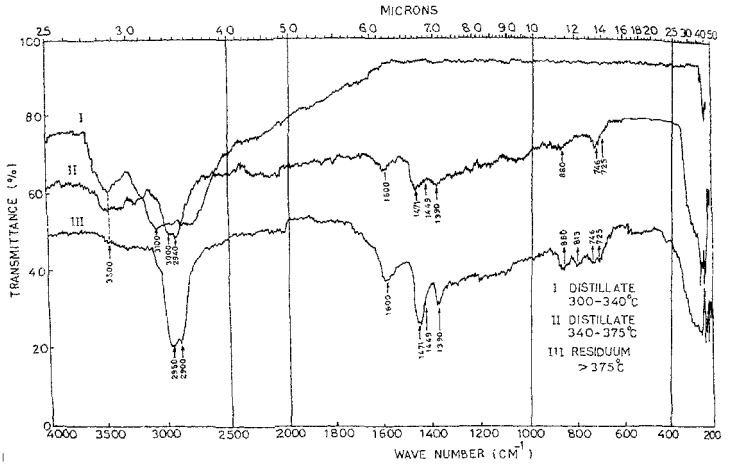

FIG. 2. Infrared spectra of distillation fractions.

point of the fractions. The intensities at 813 and 746 cm^{-1} bands are increased relative to 725 cm^{-1} band with increase in boiling point so that the three are almost equal in residuum > 375° C. The behaviour confirms asphaltic nature of the crude due to increasing $(> CH_2)_n$ rock bending of solid paraffinic chains.

Figure 3 records the infrared spectra of chromatographic fraction of residuum > 375° C *i.e.* asphaltenes, saturates, resins and aromatics. The spectra indicate −OH stretching at 3333 cm^{-1} (spectra III, IV) and sharp triplets of $-CH_3$, $> CH_2$ and → CH stretching between 3000-2800 cm^{-1}. The sharp peak at 1714 cm^{-1} (spectrum III) show C = O stretching of saturated aliphatic acids in resins. The aromatic characteristics are shown by C = C stretching of conjugated aromatic rings between 1614 and 1598 cm^{-1} wave numbers. In spectrum II the absence of absorption peaks in the region of 1680−1500 show the non-aromatic and non-olefinic behaviour of saturates. It confirms that cracking of higher molecules has fully been avoided during the fractional distillation. The high intensity doublets in the 1470-1450 cm^{-1} region are due to $> CH_2$ and $-CH_3$ (asym.) bending, while $-CH_3$ (sym) bending is shown in the region of 1390-1380 cm^{-1} as sharp intensity peaks. The weak intensity bands at 1010 cm^{-1} show C-O stretching of carboxylic group. The weak bands between 980−800 cm^{-1} wave numbers are correlated with naphthenic ring vibrations of 5- or 6-membered rings. The sharp intensity triplet of spectrum III between 790 and 780 cm^{-1} shows the mono-,di-and tri-substituted aromatic rings with alkyl substitution at ortho-, meta-and para-positions. The aliphatic characteristics of all fractions are observed by sharp (doublet or singlet) peaks at 725 cm^{-1}, which is due to $(> CH_2)_n$ stretching, where $n > 4$. Thus

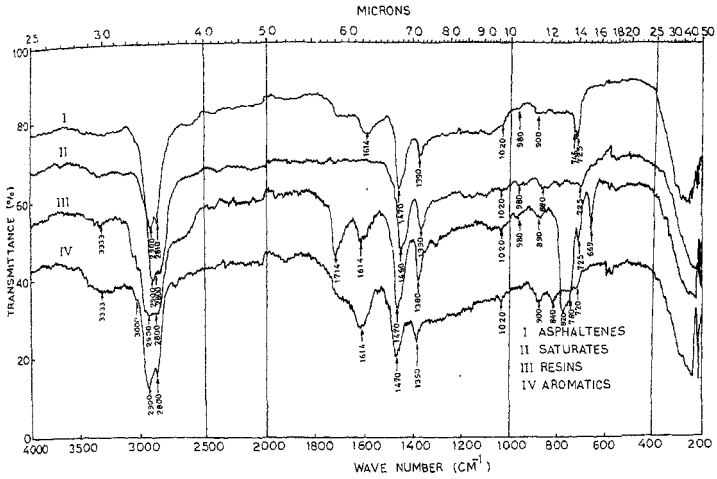

FIG. 3. Infrared spectra of chromatographic fractions (residuum > 375 °C).

the presence of carboxylic group conjugated aromatic and naphthenic ring with polyalkyl substituted chains on the resin molecules and non-aromatic/non-olefinic characteristics of saturated paraffins have been substantiated by the spectral analysis.

The presence of carboxylic group was detected in residuum and resins by qualitative and quantitative observations. The residuum was further examined for interface activity by Burger's method of dye-complex formation and it was found that anion-active surfactants are present in residuum and resin fractions. The neutralised dye-complex was separated from the solution of resins by the interaction of methylene blue dye (by precipitation with oppositely-charged tensides through neutralisation of polar-active charge).

Figure 4 contains the infrared spectra of methylene-blue dye complex of anhydrous anion-active surfactants and isolated naphthenic acid sample. The spectra shows the $-OH$, $-CH_3$, $>CH_2$ and $\rightarrow CH$ stretching bands at 3333, 2941, 2890 and 2780 cm^{-1} wave numbers respectively. 1700 cm^{-1} vibration gives $C=O$ stretching of saturated cycloaliphatic acids. The doublet at 1620 and 1600 cm^{-1} shows $C=C$ stretching of non-conjugated and conjugated aromatic ring vibrations. 1580 cm^{-1} peaks give indication of phenyl ring conjugated with the group having lone pair electrons (in naphthenic acid sample only). The doublet at 1410-1420 cm^{-1} shows the dimeric-OH in plane bending coupled with C-O stretching (in naphthenic acid sample). The peaks at 1390 cm^{-1} is for-CH_3 bending deformation. The broadening of the band from 1130 to 1020 cm^{-1} shows $\rightarrow CH$ banding of phenyl ring overlapped with

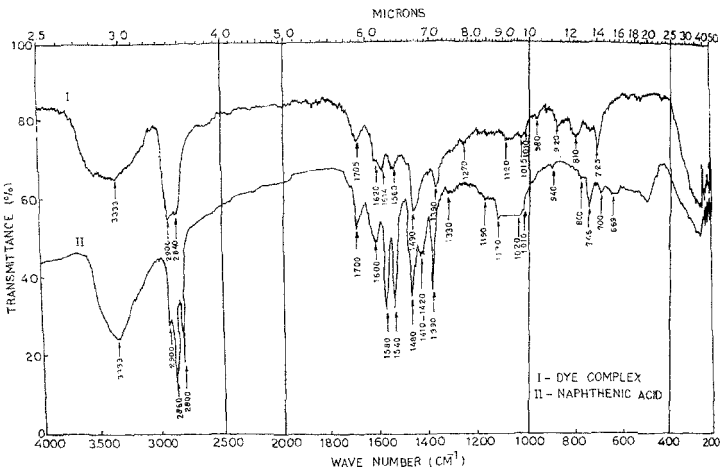

FIG. 4. Infrared spectra of dye complex and naphthenic acid.

isopropyl group $\frac{CH_3}{CH_3}>CH$ stretching. The peaks at 940 cm^{-1} show the naphthenic characteristic of the molecules and in the region of 740-714 cm^{-1} show $(>CH_2)_n$ stretching where $n>4$. Thus it can be inferred that the naphthenic acid sample contains $-COOH$ active group with conjugated and non-conjugated type of aromatic and naphthenic rings along with the long paraffinic substituted chain.

Since resins are known to possess polar-active groups, this fraction was further subjected to the process of isolation of naphthenic acids by the method of adsorption of cycloparaffinic rings on alumina chromatographic column[19]. The resins were distilled with sodium hydroxide at a reduced pressure of 1 mm Hg up to 375° C (atmospheric boiling point). The residuum consisted of sodium salt of carboxylic acid along with the hydrocarbons. Free carboxylic acid was isolated by treating the alkaline residuum with dilute H_2SO_4. The mixture of these acids and hydrocarbons was dissolved in benzene and the solution was passed through a column filled with aluminium oxide. Desorption was carried out in the following order: benzene; alcohol - benzene (1:1); and benzene - acetic acid (3:1) mixtures. The first fraction was free from acid, second fraction contained only traces of the acid while the third fraction which consisted almost exclusively of acids was collected after complete evaporation of the solvents. This fraction was confirmed as napthenic acids. The physical and chemical characteristics of the isolated naphthenic acid fraction were as follows:

Physical state

(a) Brown in colour, semi-solid, lighter than water, water insoluble but soluble in polar organic solvent.

(b) Physical properties: melting point 45°C, boiling point 437.8°C, cloud point 43.9°C.

(c) Chemical properties

(i) Confirmed presence of - COOH group with the sodium bicarbonate test.

(ii) Turns thymol blue indicator into red purple colour, indicating the high activity of anionic tensides.

(iii) The chloroform solution forms blue-green precipitate with the interaction of methylene-blue dye.

(d) Characterization

(i) Elemental analysis of the isolated sample shows G:H ratio 0.571 which indicates lower aromaticity and approximately correlating with the Cn H_{2n-8} O_2. The sulphur and nitrogen elements were found absent in the isolated sample.

(ii) The infrared spectra of isolated sample (fig. 4) show the presence of carboxylic group. Bands arising from the superposition of C = O, C – O, C = C, C-OH, O-H vibrations. Of the five characteristics, three—3333, 1420 and 1010 cm^{-1}—are associated with carboxyl O-H vibration; O-H stretching vibrations lie near 3333 cm^{-1}. The band at 746 cm^{-1} shows the absorption of four or more methylenic group. The bands between 1593 and 700 cm^{-1} show the acidic and naphthenic character of the molecule.

4. Conclusion

The crude oil sample of Sanand oil field is highly volatile and asphaltic in nature. Because of high API gravity and low pour point, the crude is in liquid state at normal temperature. The largest number of components of the crude have boiling point in the range 300-375°C. The surface-active agents present in this crude oil sample are anionic in nature. The molecules of naphthenic acids comprising bulk of the surface-active material deposited at oil/water interface would cause the decrease in interfacial tension of the system thus acting as an emulsifying agent.

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