



## Spectroscopic Studies of Petroleum Crudes: Implications for Crude Quality and Enhanced Oil Recovery (EOR)

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### Keywords

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### Summary

Petroleum crudes exhibit various physico-chemical conditions during production from subsurface reservoirs to surface installations. The present work is an attempt to characterize petroleum crudes for enhanced oil recovery (EOR). Two different oils from two different fields of Cambay Basin were studied using spectroscopic measurements. Fourier transformed infrared (FTIR) spectroscopy of the bulk crude (dead oil) helped to characterize in term of components particularly saturated and unsaturated aliphatic structures with functional group present in the study sample. We have also studied fluorescence behavior of the extracted oil in the micellar systems (with polar surfactant) using a steady-state measurements. The extracted oil shows different emission peaks with varying excitation wavelength for both the crudes, which indicates the presence of various aromatic hydrocarbon compounds (mainly 2-, 3- and 5 fused aromatic ring structures) in the extracted oil. In this study, we have established that the intrinsic fluorescence of the crude oil can monitor its interaction with surfactant self-assemblies (micelle) of different charges (cationic-cetyltrimethylammonium bromide i.e. CTAB and anionic-Sodium dodecyl sulfate i.e. SDS). The study concludes that the fluorescence spectroscopy can be one of the useful techniques to investigate the interaction of the luminescent petroleum materials with various surfactants in different physico-chemical conditions for designing EOR method.

### Introduction

To bridge the gap between energy demand and supply for sustainable development, enhanced production of petroleum crudes from the existing reservoirs is very much dependent on the understanding of the recovery processes from subsurface reservoirs. Thus, the characterization of crude oil and its interaction with reservoir rock up to the molecular level is a key factor for designing the enhanced oil recovery processes [Steffens et. al., 2010; Sotelo et. al., 2008]. Out of the most commonly used EOR methods, chemical methods with surfactants, polymers and alkalis are gaining importance where surfactants-assisted methods are expected to play a major role in future crude oil production. The surface activity of the ionic liquid reduces the interfacial tension in the oil-water interface and could be used in an EOR process to increase the production during exploitation of the reservoirs [Lago et al., 2012; Mosayeb et.al. 2012]. Murillo-Hernandez and Aburto (2011) explained the ability of some ionic liquids to solubilize heavy hydrocarbon compounds (asphaltenes, PAH, paraffins) effectively reduces the viscosity of the liquid and enhances the mobility of the crudes in the reservoir (rock) system. To analyze and understand the effectiveness of a surfactant, it is very crucial and critical to have the knowledge of the phase behavior, i.e solubilisation, micro-emulsion formation, flow properties within the reservoir system containing oil, water and injected fluids (with surfactants). In this work, we have used two crude oils from Cambay basin reservoirs and performed FTIR study on the neat crude oil and steady state fluorescence spectroscopy study on diluted crudes using polar surfactant as dilutants. Both the spectroscopic studies

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help to characterize the crudes in the form of composition and quality.

### Materials and Methods

Two crude oil samples (S1, S2) were obtained from two reservoirs of Cambay basin, Gujarat, India. FTIR-ATR analysis was done with Perkin Elmer FTIR-ATR spectrometer version 10.4.2. ATR cell equipped with a diamond crystal with a refractive index of 2.4. The spectra were obtained as a result of accumulation of four (4) scans with a resolution of 4  $\text{cm}^{-1}$ . The transmittance was measured at room temperature keeping a pressure of 20- 80 psig and covered a range of wavenumber 4000-400  $\text{cm}^{-1}$ .

For the fluorescence study the two oil samples were taken in four different beakers (each oil in 2 beakers) and each of the oil samples were diluted (1:2000) with 100 millimolar aqueous solutions of cationic (CTAB) and anionic (SDS) surfactants. The solutions were kept overnight under magnetic stirrer. After stirring the solutions, it was filtered through a 0.45mm filter paper to obtain a clear solution. Perkin Elmer LS55 was employed using 300 nm and 350 nm excitation wavelength and emission (fluorescence) spectra was recorded with wavelength range from 200 – 700 nm with 20 nm intervals, 2.5 nm excitation and 2.5 nm emission slit and a scan rate of 500 nm/min. Cuvettes (10 mm  $\times$  10 mm) were used to hold the solution.

### Results and Discussions

In the IR spectra the most intense peaks appeared around 3000 $\text{cm}^{-1}$ : C-H antisymmetric and symmetric stretching in aliphatic at 2954-2930 $\text{cm}^{-1}$ , 2920-2917  $\text{cm}^{-1}$  and 2859-2849  $\text{cm}^{-1}$ . There were also intense peaks at 1463-1462  $\text{cm}^{-1}$  and 1377  $\text{cm}^{-1}$  corresponding to  $\text{CH}_3$  antisymmetric deformation,  $\text{CH}_3$  symmetric in aliphatic compounds respectively. Other less intense peaks at the region of 1634-1630 $\text{cm}^{-1}$  and 720-719  $\text{cm}^{-1}$  were indicating N-H deformation (Amide II band) in primary amides and  $\text{CH}_2$  rocking in methylene chains in hydrocarbon [Lambert, J. B. et.al., 1987; Melendez, L.V., et.al., 2012 ]. In S2 oil, one characteristic weak broad peak was found near 616 $\text{cm}^{-1}$  indicative of S-C stretching band which was completely absent in S1 oil sample [Lambert, J. B. et.al., 1987]. Thus S2 contains more sulfur than S1. This observation is further supported

by the results from the sulfur in oil analyzer, model no. Horiba SLFA-2800 (S1-0.029 % and S2-0.085%).

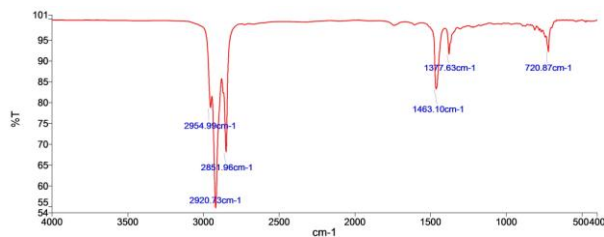


Fig. 1 (i)

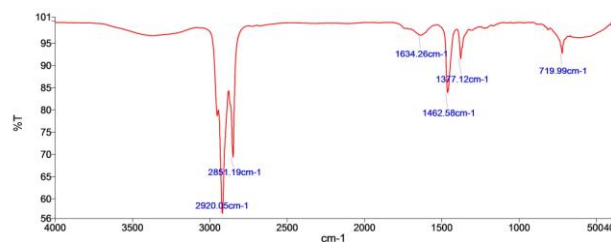


Fig. 1 (ii)

Figure 1: Infrared spectrum of (i) S1 and (ii) S2 sample oil.

The N-H deformation in primary amides and S-C stretch were indicating aromatic compounds or NSO components and the S2 sample is rich with the aforesaid groups compared to S1 sample.

The crude oils were typically excited within a range of ultra-violet (UV) wavelengths i.e. from 300-400 nm and fluoresce in the visible wavelength ranges from 400- 600 nm. Observation under UV excitation enhances the visualization of the structures of chromophores, the light incorporating group of the molecules while the emission (fluorescence) spectra provide the information of various aromatic and asphaltene structures [Groenzin, H. and Mullins, O. C., 2007; Ruiz-Morales, Y., 2007]. We have looked for the fluorescence emission spectra because only small chromophores emit short wavelength light. The emission spectra of the diluted oil samples are obtained by employing two fixed excitation wavelength of 300 nm and 350 nm which are presented in fig1 and 2 and the peak values are provided in Table 1.

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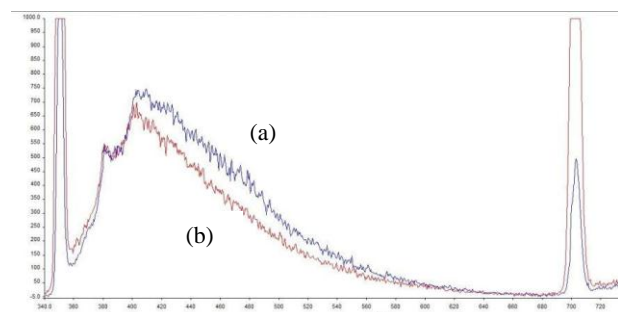
Table1: Peak wavelength and intensity values from the fluorescence spectra of S1 and S2.

| S1 crude oil        |                 |           |                 |           |
|---------------------|-----------------|-----------|-----------------|-----------|
| Ex. Wave length(nm) | SDS             |           | CTAB            |           |
|                     | Wavelength (nm) | Intensity | Wavelength (nm) | Intensity |
| 300                 | 372             | 466       | 430             | 200       |
|                     | 410             | 425       |                 |           |
|                     | 690             | 150       |                 |           |
| 350                 | 380             | 525       | 380             | 550       |
|                     | 404             | 640       | 404             | 750       |

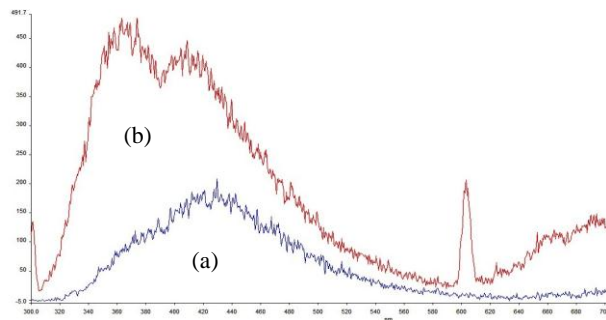
| S2 crude oil |     |     |     |     |
|--------------|-----|-----|-----|-----|
| 300          | 330 | 735 | 370 | 725 |
|              | 346 | 900 | 404 | 550 |
|              | 358 | 760 | 414 | 550 |
|              | 636 | 100 | 632 | 150 |
|              | 670 | 210 | 666 | 350 |
|              | 684 | 225 | 684 | 310 |
| 350          | 382 | 110 | 370 | 350 |
|              | 404 | 115 | 380 | 600 |
|              |     |     | 407 | 675 |
|              |     |     | 425 | 550 |

The peak wavelength values of the sample oils clearly indicate that the surfactants were incorporated mainly 3 and 5 fused aromatic ring (FAR) structures



Wavelength (nm)

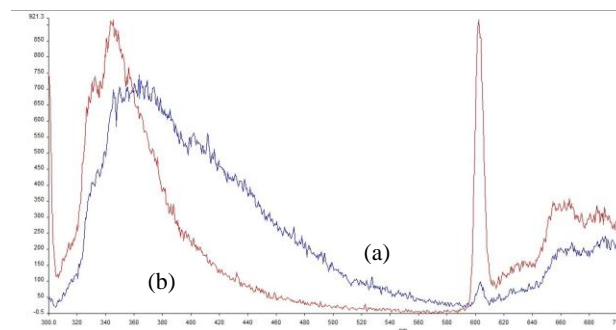
Fig. 2 (i)



Wavelength (nm)

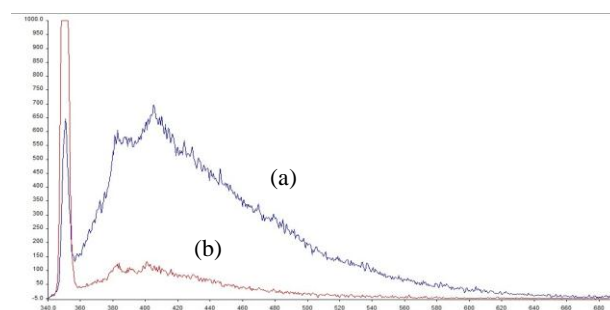
Fig. 2 (ii)

Figure 2: The fluorescence emission spectra of S1 treated with (a) CTAB and (b) SDS for (i) excitation at 300 nm and (ii) excitation at 350 nm.



Wavelength (nm)

Fig. 3 (i)



Wavelength (nm)

Fig. 3 (ii)

Figure 3: The fluorescence emission spectra of S2 treated with (a) CTAB and (b) SDS for (i) excitation at 300 nm and (ii) excitation at 350 nm.

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Table 2: Range of peak wavelength values of fluorescence spectra for aromatic hydrocarbon in solution.

| Fused aromatic structure (FAR) | Names        | Wavelength (nm) |
|--------------------------------|--------------|-----------------|
| Single benzene ring structure  | Benzene      | 250-300         |
| 2- benzene ring structure      | Napthalene   | 300-365         |
|                                | Fluorene     | 302-370         |
| 3-benzene ring structure       | Anthracene   | 372-460         |
|                                | Phenanthrene | 348-407         |
|                                | Napthacene   | 460-580         |
| 4-benzene ring structure       | chrysene     | 380-400         |
|                                | Pyrene       | 370-400         |
|                                | Pentacene    | 620-750         |
| 5-benzene ring structure       | Perylene     | 450-495         |

5 fused aromatic ring (FAR) structures from the S1 oil sample and 2, 3 and 5 FAR structures from the S2 oil sample [ Table 2; Kasha, M., 1960].

In S1, SDS incorporated 3 and 5 FAR structures in a significant amount (inferred from the high peak intensity value) compared to CTAB. On the contrary, in S2, SDS incorporated 2 FAR structures in the miceller structure in a significant manner (inferred from the high peak intensity value) and a few amount of 5 FAR structures whereas CTAB incorporated 3 and 5 FAR ring structures relatively in larger amount than SDS but almost failed to incorporate 2 FAR structures. From both the spectroscopic study, it has been found that the S2 oil is simultaneously enriched with the long chain structure i.e. FAR structures and NSO components. It is also clearly seen that SDS has a selective size preference during micelle formation.

### Conclusions

Both the spectroscopic studies ensure that there is a sharp compositional variation between two oil samples where S2 is richer with NSO components than S1. From this work it has been understood that SDS has a greater efficiency for incorporating small aromatic structures and CTAB has a tendency to pick up large aromatic structures. So, during EOR by surfactant flooding, selection of proper surfactant should be based on the composition of the oil and fluorescence study can be useful for this purpose.

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