Full Length Article

Steady-state and time-resolved fluorescence spectroscopic study of petroleum crudes in aqueous-surfactant solutions: Its implications for enhanced oil recovery (EOR) during surfactant flooding

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ARTICLE INFO

ABSTRACT

Surfactant flooding, a widely used chemical enhanced oil recovery (EOR) method, involves reduction of interfacial tension of the crude oil-aqueous surfactant system. During the surfactant flooding micelle structures have been formed in aqueous media where crude oil components are entrapped inside it. The nature of the surfactants in the aqueous injection fluids and the crude oil compositions are the key controlling factors for understanding the efficacy of the surfactant flooding during EOR. Therefore, understanding of the molecular level interaction between crude oils and aqueous surfactant solutions is very crucial for designing injection fluids during surfactant flooding for subsurface reservoirs having different types of crude oils. Two crude oils (Cambay basin, India) and three surfactants: cationic (cetyltrimethylammonium bromide i.e. CTAB), anionic (sodium dodecyl sulfate i.e. SDS) and neutral (Triton X-100 i.e. TX100) were used in this study for understanding their interaction behavior. The chemical characterization by various analytical methods supports the presence of different sizes of the fused aromatic ring (FAR) associated with the polycyclic aromatic hydrocarbons (PAH) of the used crude oils. In this study, we have investigated the type of oil components present in the micelles formed by the surfactant solutions of various charges using steady-state and time-resolved fluorescence spectroscopic measurements. The extracted oil components in the micelles of different charges show different emission peaks with varying excitation wavelength and different fluorescence lifetime, indicating incorporation of PAH with variable sizes of FAR. Ionic surfactants (CTAB and SDS) are more compatible to exploit small (2–3 FAR) as well as medium (4–7 FAR) PAH structures whereas non-ionic surfactant (TX100) dominantly entraps medium PAH structures within their micelles. This study established that the intrinsic fluorescence of the crude oil can monitor its interaction with surfactant micelle of different charges and helps to design effective injection fluids for optimized crude oil recovery during surfactant flooding.

1. Introduction

With the increasing energy demand, various conventional enhanced oil recovery (EOR) methods have been applied for the optimization of production from subsurface hydrocarbon reservoirs. Out of the most commonly used EOR methods, chemical methods with surfactants are gaining importance for easy application in reservoirs having a wide range of crude oil composition [1]. The use of surfactant-assisted methods began in late 1920's to early 1930's in EOR fields [2] and it is expected to play a major role in enhancing crude oil production in future days. Surfactant flooding is based on injecting an aqueous solution with low concentration of surfactant into the subsurface petroleum reservoirs. This flooding results in low interfacial tension between oil and water affecting (in general enhancing) the mobility of the trapped residual oil inside the pore system of the reservoir rocks [3]. In some cases, surfactant reduces the wettability of the grain surfaces which effectively releases the oil retained in the rock pore surfaces [4]. Murillo-Hernandez and Aburto [5] explained the ability of some ionic liquids to solubilize the heavy hydrocarbon compounds (asphaltenes, PAHs, paraffin). This oil solubilization in dilute surfactant solutions effectively reduces the viscosity of the liquid which in turn enhances the mobility of crude oil in the reservoir system. The composition of petroleum crude is a chemical continuum with a gradual increase of molar mass from nonpolar saturates, aromatics to polar resins and asphaltenes. The surfactant molecules form nearly spherical micelles in bulk water with usual size of 1–10 nm. Micelles of TX-100, CTAB, and SDS

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are about 51 Å, 50 Å, and 30 Å, respectively [6,8]. The core of micelle essentially consists of the hydrocarbon chains where charge head groups are projecting outward into the bulk water. Small-angle X-ray and neutron scattering (SANS) studies have revealed the detailed structural information of the variety of micelles [6–8]. Research studies have established the fact that both asphaltenes and resin molecules are present as nano-sized aggregates inside the micelles formed by the surfactants in an aqueous solution [5,9]. In both the work they showed that the state of aggregation as well as the polarity of the micro-environment inside the micelles changes with the concentration and the presence of polar asphaltenes and resins of the crude oil. Thus, the surface activity of the used surfactants in the dilute surfactant solution with the formation of the micellar structure and the nature of their microenvironment are essential for understanding the trapping mechanism of different types of crude oil components.

Petroleum crude oil components exhibit optical property due to the presence of its optically active components. Therefore, different optical spectroscopic methods have been used to detect the nature of aromatic compounds such as polycyclic aromatic hydrocarbons (PAHs) present in crude oils and other carbonaceous materials [10–17] which exhibit excitation in the ultraviolet to visible light and fluoresce in the range of visible wavelength [15–20]. PAH structures generally contain many fused aromatic ring (FAR)s ranging from small to large (max.10 FAR) [21]. The small PAH structures emit at lower wavelength whereas large PAH structures emit at higher wavelength [22]. Moreover, the nature of the fluorescence is completely dependent on the chemical composition (presence of chromophore and quencher concentration) of the crude oil and their physical properties such as viscosity, optical density [15,23–25]. Several optical techniques have been used for characterization of neat and diluted crude oils in terms of the components present and understanding their behavior in different operating conditions [15,16,26–30]. Different modes of fluorescence spectroscopy, particularly steady-state, synchronous scan, and time-resolved fluorescence, are advantageous over the other traditional methods for crude oil analysis as it is non-destructive, versatile and gives a fast response with low cost [31]. Thus, the optical spectroscopic study is gaining importance for application in exploiting crude oils from subsurface reservoirs. However, few spectroscopic studies have been carried out to investigate the interaction of crude oils in the aqueous solutions and the behavior of the nano-sized aggregates formed by the components of crude oils in the micellar environments [5,9]. The steady-state and time-resolved fluorescence spectroscopic studies help to understand the interactions between crude oils and surfactant aqueous solutions, and shed light on the effect of the surfactant charge on the system. This knowledge would be crucial during surfactant flooding for EOR. We have analyzed steady-state and time-resolved fluorescence behavior of two crude oils (Cambay basin reservoirs of India) in three surfactant aqueous solutions for designing effective EOR fluids. The characteristic peak positions in fluorescence emission spectra and the fluorescence lifetime of crude oils diluted with different surfactant solutions vary with the type of aggregates formed within the micelles and the type of PAHs entrapped within them (micellar structures) during the interaction. In this work, we have established that the optical behavior of the crude oils can be used to monitor their interactions with surfactant micelles of different charges. This would have deep-rooted implications in designing effective injection fluids to enhance oil recovery.

2. Materials used and sample preparation

Two petroleum crude oil samples (here labeled as LO1 and HO1) were collected from two different producing reservoirs of Cambay Basin, India. LO1 was provided by Oil and Natural Gas Corporation Limited (ONGC) and HO1 was provided by Gujarat State Petroleum Corporation (GSPC). Three types of surfactants (research grade) namely, anionic (sodium dodecyl sulfate i.e. SDS), cationic (cetyl-trimethylammonium bromide i.e. CTAB) and non-ionic (triton X-100

i.e. TX100), were used for the study. The asphaltenes were separated from the respective crude oils by following ASTM D2007-80 (standard asphaltene separation method from crude oils). It has been found that LO1 crude contains 3 wt% (wt. %) asphaltenes whereas HO1 crude contains 8.9 wt% asphaltenes. The crude oils and their fractionated asphaltenes were chemically characterized with various analytical methods. The crude oil-surfactant aqueous solutions were prepared for understanding the interaction study at molecular level. 100 mM surfactant solutions of SDS, TX100, and CTAB were prepared by dissolving sufficient amount of surfactants in distilled water at room temperature to achieve concentration above 'Critical Micellar Concentration (CMC)'. Sufficient amount of the crude oils were then poured separately into each surfactant solution and kept for overnight stirring. The crude oils in aqueous surfactants solutions were then centrifuged and extensively diluted (with same dilution factor) with the equimolar aqueous surfactant solutions for the optical measurement study for obtaining better spectral signatures.

3. Instrumentation and analytical methods

3.1. Chemical characterization of crude oils and their asphaltenes

The crude oil samples and their solvent separated asphaltene fractions were chemically characterized with the help of thermogravimetry (TG), steady-state and synchronous fluorescence (SSF and SFS) spectroscopy, gas chromatography-mass spectrometry (GC–MS) analysis, and Fourier transform infrared (FTIR) spectroscopic study.

TG analysis of the crude oil samples was carried out in a nitrogen atmosphere with PerkinElmer TGA-50H maintaining the heating rate at $10\,°C\,min^{-1}$ for each sample.

Steady-state emission spectra of diluted bulk crude oil samples and asphaltenes (diluted into toluene in 1:1000) were recorded on a PerkinElmer-LS55 spectrofluorometer employing different excitation wavelengths (320 nm–500 nm). Synchronous fluorescence spectra of same diluted samples (bulk crude oils and asphaltenes) were captured by applying a simultaneous scanning of excitation and emission wavelengths keeping the constant difference of $\Delta\lambda$ (30 nm).

The solvent separated asphaltene samples were analyzed using a PerkinElmer Autosystem XL (GC) and a PerkinElmer TurboMass (MS). The samples were analyzed using a PE-5MS capillary column (30 m × 0.25 mm i.d., × 0.25 μm film thickness). Helium was used as carrier gas with a flow rate of 1 ml/min. The samples were dissolved in toluene and injected by autosampler in pulsed split less mode. The ion source was operated in the electron ionization mode at 70 eV. The temperature of GC oven was held at 80 °C (5 min) and then ramped to 290 °C at 10 °C/min and held for 20 min. The asphaltene fractions were analyzed in full scan mode over a mass range of 20–620 Da. Identification of compounds was based on the comparison of elution pattern and mass spectra with those reported in the literature [32].

FTIR analyses of two neat crude oils and their asphaltenes were done with PerkinElmer FTIR-ATR spectrometer version 10.4.2. The crude oil spectra were obtained as a result of the accumulation of four (4) scans with a resolution of $4\,cm^{-1}$. The transmittance was measured at room temperature covering a range of $4000–400\,cm^{-1}$. The ATR cell was equipped with a diamond crystal having a simple reflection refractive index of 2.4. The angle of incidence of IR beam was 45°.The FTIR spectra of the asphaltene samples were acquired by the same instrument using the KBr pellet technique. The fractionated asphaltenes (from LO1 and HO1) were combined with spectroscopic grade KBr, and pellets were prepared with a hand-held KBr press machine.

3.2. Study of crude oil in aqueous surfactant solutions

Steady-state emission spectra of the crude oil-aqueous surfactant solutions were measured at the different excitation wavelength in a JobinYvonFluorolog 3 fluorimeter employing excitation/emission slit