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Studies on the physicochemical properties of synthesized tailor-made gemini surfactants for application in enhanced oil recovery

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ABSTRACT

In this study, the physicochemical properties of a series of synthesized cationic gemini surfactants with different aliphatic carbon spacer lengths were investigated as an effective, unconventional chemical agent for practical application in enhanced oil recovery (EOR) from mature reservoirs. The self-aggregation property at low concentrations was confirmed by tensiometry measurements. Critical micelle concentration (CMC) values increased with temperature rise. Thermal stability experiments showed no surfactant degradation over a long time period. The surfactants showed good tolerance to salt addition, confirming their functionality even under high salinity conditions. Rheological studies discussing the effect of the nature of micelles on the viscosity of surfactant solutions was studied as a function of concentration and temperature. Ultra-low interfacial tension (IFT) values of the order of 10^{-2} to 10^{-3} mN/m was obtained at the oil-aqueous interface. Zeta potential and contact angle measurements revealed favorable rock alteration from intermediate-wet to water-wet state by the mechanism of ion-pair interactions. Sandpack flooding studies using surfactant-polymer formulations yielded additional oil recoveries of 29.83%, 31.73%, 33.83% and 34.55% for 14-3-14, 14-4-14, 14-5-14 and 14-6-14 systems respectively.

1. Introduction

In the face of current global scenario, crude oil is one of the economically mature markets that have the potential to solve the energy crisis problem. Petroleum reservoir essentially comprises of a substantial pool of hydrocarbons in porous rock formations that can be extracted by the application of different oil recovery techniques. Though primary and secondary methods are employed for oil recovery, nearly two-thirds of the original oil in place (OOIP) still remain unrecoverable in a mature reservoir. Chemical enhanced oil recovery (EOR) techniques normally involve the injection of specifically designed chemicals to alter the properties of reservoir fluids. Modifications in the chemical molecular structure (in the synthesis stage) hold the key to achieving enhanced interfacial and wettability alteration properties in oil-rock-surfactant aqueous systems [1–5]. Gemini surfactants belong to a unique class of surface-active agents, consisting of two hydrophobic tails and two hydrophilic heads connected by a spacer chain. In addition to their self-aggregating capacity at low concentrations, gemini surfactants show far superior properties in comparison to conventional monomeric surfactants [6]. Recent studies show that their unique traits may well prove to be crucial in modern day EOR operations [7–9]. Previous studies showed that they have the ability to reduce IFT at the crude oil-aqueous interface [10,11]. Rock-wetting characteristics in the presence of gemini surfactant solutions are investigated in earlier reports [12]. Wettability alteration occurs due to interactions that primarily exist between the alkyl tail of the gemini surfactant and certain crude oil components [13]. Alam and Siddiq [14] reviewed the interfacial and rheological properties of gemini surfactant solutions as a function of concentration. Being relatively new in the field of surfactant science and newer in petroleum industry, gemini surfactants have enormous potential for application in oil recovery processes.

Four 14-s-14 cationic gemini surfactants (s = number of aliphatic carbon atoms in spacer chain) were synthesized and characterized. Critical micelle concentration (CMC) values were measured by surface tensiometry at different temperatures. Thermal stability and salt tolerance levels at CMC solutions were studied to check for suitability of GSs under high temperature, high salinity conditions. Viscosity measurements were performed for a wide range of surfactant concentrations. Interfacial behavior at the interface between crude oil and surfactant solution was studied by spinning drop technique. Wettability alteration behavior was investigated by zeta-potential and contact angle measurements to explain the oil-displacing ability of surfactant solutions from the rock surface. Chemical flooding experiments were conducted to determine the tertiary oil recovery percentages in sandpack systems.

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2. Experimental section

2.1. Materials

1,3-Dibromopropane, 1,4-Dibromobutane, 1,5-Dibromopropane and 1,6-Dibromohexane were obtained from TCI Chemicals. *N*,*N*-dimethyltetradecylamine was purchased from Sigma Aldrich. Crude oil was collected from Ahmedabad oil field. The oil has a total acid number of 0.044 mg KOH/g, kinematic viscosity of 61.47 cSt and gravity of 23.55° API at 303 K. Partially hydrolyzed polyacrylamide (PHPA) was used for preparation of surfactant-polymer (SP) mixtures. Double distilled water was used in all experiments.

2.2. Surface tension measurements for CMC determination

Surface tensions for GS solutions were measured using Du Noüy method in Easy Dyne K20 Tensiometer (Kruss, Germany). A platinum ring was slowly lifted from the surface of GS solution. After each measurement, the platinum ring was cleaned thoroughly by burning in a Bunsen burner flame and the instrument was calibrated using standard pure solvent. Critical micelle concentration (CMC) values corresponding to the lowest surface tension were measured. Each test was repeated three times to achieve reproducibility of results. Accuracy of readings was found in the range $\pm$ 4%.

2.3. Thermal stability of GS solutions

The surfactant solution at CMC was constantly heated at 90 °C in a 2-neck R.B. flask, with a condenser attached to one neck to prevent loss due to evaporation and a syringe fitted with another neck for collecting aged GS solution. Solutions obtained from flask were quenched with ice-cold water and finally tested for IFT at different time intervals over a period of 15 days.

2.4. Rheological studies

Viscosity measurements were carried out using a Bohlin Gemini 2 Rheometer (Malvern Instruments Limited, UK). Variation of viscosity with concentration was analyzed at a shear rate of 100 s^{-1}. The viscosity values of all GS solutions were measured at 303 K, 323 K and 343 K.

2.5. Salt tolerance studies

The NaCl concentration for pure GS solutions at corresponding CMC was increased to check for tolerance levels at different temperatures. The solutions were initially prepared and then allowed to centrifuge for 15 min at 2500 rpm. Salt tolerance at elevated temperatures was studied by heating the aqueous solutions to 343 K to check for precipitate formation.

2.6. IFT measurements at the oil-aqueous interface

The interfacial tension (IFT) between crude oil and aqueous GS solutions was measured by spinning drop method in a SVT20 tensiometer (Dataphysics, Germany). A drop of crude oil was injected into a capillary tube containing surfactant solutions with different gemini concentrations. Then, the sample solutions were rotated at 3500 rpm and value of IFT studied by fitting the oil drop profile under these conditions. Before each measurement, the capillary tube was first rinsed with toluene or benzene (non-polar solvent) to remove residual crude oil. Then, the tube was cleaned with acetone for removal of salt or surfactant traces. The capillary tube was then dried, prior to next measurement. Each oil-aqueous system was analyzed until a constant IFT value was observed. The IFT experiments were performed at 303 K, 323 K and 343 K.

2.7. Wettability alteration analysis

2.7.1. FTIR spectroscopy of dry and oil-wet quartz rock

FTIR analysis of quartz powder before and after treatment with crude oil was performed to study the mechanism of oil-imbibition on quartz surface. 1 g of dried quartz powder was homogeneously mixed with 2 g crude oil to prepare oil-wet powder and then kept for 48 h at 333 K in vacuum dryer for ageing process. The aged sample was finally studied for IR spectra in Perkin Elmer Spectrum 2 analyzer using KBr pellets.

2.7.2. Zeta potential measurements

Zeta-Meter System 4.0 was used for the measurement of zeta potential. For zeta analysis of oil/GS systems, 2% crude oil was stirred thoroughly in corresponding aqueous GS solution. For rock/aqueous systems, 2 g of quartz powder was mixed in 500 ml of distilled water, followed by sonication for 30 min using Fisher brand Model FB15051. The prepared suspensions were stabilized for 1 h and finally tested for varying concentrations of GSs at 303 K. Both dry and oil-wet quartz powder samples were used to study their interactions with GS molecules in zeta potential studies. Each solution is placed in a viewing chamber and an electric field is activated for potentiometric measurements. Using the micro-electrophoresis principle, the electrophoretic velocity of the colloids is directly proportional to the zeta potential. Direction of particle movement indicates the charge type on the suspended quartz particles.

2.7.3. Contact angle studies

A quartz specimen was cut in the dimension of 25 × 25 × 5 mm using a trimming machine, followed by burnishing with a grinding tool to obtain a smooth flat surface. The surface roughness was further minimized using polishing tools. The rock was cleaned with double distilled water and acetone, followed by vacuum drying for 24 h to remove any adsorbed contaminants. The dried quartz sample was aged in crude oil for 30 days at 343 K to change the wettability nature to intermediate-wet. Dynamic contact angle values were measured using a Drop Shape Analyzer (Kruss DSA25, Germany) by sessile drop method. The oil-wetted rock sample was placed in the temperature-humidity chamber to control the temperature of the surroundings. 5 μl of a surfactant solution was dropped onto the rock surface to study the dynamic contact angle values. After each measurement, the temperature-humidity chamber was exposed to ambient conditions to restore its internal humidity. An original surface area of rock was selected for each new measurement to prevent contamination by aqueous solution traces.

2.8. Sandpack flooding experiments

Flooding tests were performed to determine the recovery efficiency of different chemical slugs using sandpack system [15,16]. The flooding set-up consists of core holder, displacement pump (Teledyne Isco), chemical solution cylinder and fraction collector. Core holder geometry with a length of 45 cm and radius of 3.5 cm was selected. The core holder was tightly packed with 60–70 mesh uniform grains of sand and saturated with 1.0 wt% brine solution. A pressure of 30 psig was applied and the absolute permeability was calculated using the Darcy's Eq. (1).

$$q = \frac{kA}{\mu}\frac{dp}{dx} \tag{1}$$

where, q is the volumetric flow rate (cm^3/s), A is the total cross-sectional area of the sandpack system (cm^2), μ is the fluid viscosity (cp), $\frac{dp}{dx}$ is the pressure gradient (atm/cm) and k is the permeability in Darcy. After brine saturation, the sandpack was flooded with crude oil to irreducible water saturation and left for 6–7 days to allow the oil to effectively wet the sandpack. Then, the slug was introduced into the