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Characterization of rock-fluid and fluid-fluid interactions in presence of a family of synthesized zwitterionic surfactants for application in enhanced oil recovery

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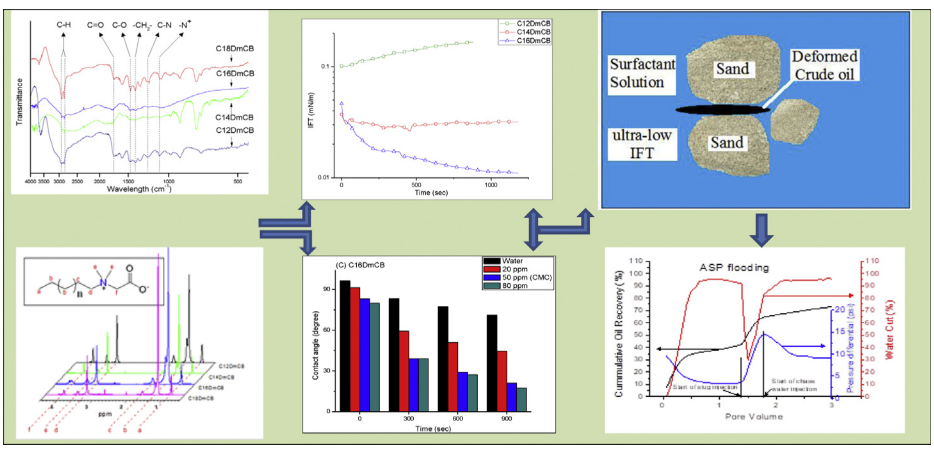
GRAPHICAL ABSTRACT



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ABSTRACT

Zwitterionic surfactants are gaining importance for their application in enhanced oil recovery (EOR) because of their favourable thermodynamic and surface properties. A family of carboxybetaine based surfactants with hydrophobic tail length of 12, 14, 16 and 18 carbons were synthesized and characterized by FTIR and ^{1}H NMR spectroscopy. Critical micelle concentration (CMC) of the surfactants were found to be very low as compared to the conventional surfactants and thermodynamic studies revealed better surface and micellization activity. Salt tolerance study and Krafft point analysis indicated the suitability of the surfactants in the harsh reservoir conditions. Reduction of interfacial tension (IFT) between crude oil and surfactant solutions significantly decreased with increase in carbon chain length. Presence of salt and alkali were found to have synergetic effect in IFT reduction by the surfactants. Phase behaviour study showed formation of Winsor type III microemulsion which is desirable to displace the trapped oil by miscibility mechanism. The surfactants were also found to be effective in altering the wettability of oil-wet rock to water-wet, resulting better oil recovery. Sand pack experiments showed an additional oil recovery of 30.82% of original oil in place (OOIP) by injection of a small pore volume of surfactant slug in combination with alkali and polymer.

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1. Introduction

Current petroleum industry scenario of high demand and limited reserves forces the industry to extend their production towards enhanced oil recovery (EOR) techniques. EOR comprises of injection of chemicals, gases and use of thermal methods for oil recovery. Chemicals such as surfactants, polymer and alkali are injected which recovers oil by reduction of interfacial tension (IFT) and reducing mobility ratio [1]. Surfactants are amphiphilic compounds having polar hydrophilic head and hydrophobic tail of carbon chain. Hydrophobic part of the surfactant is responsible for adsorption of surfactant at oil-water interface and reduction of IFT between oil and water [2]. Surfactant also adsorbs on the reservoir rock surface by hydrophilic and hydrophobic interaction and changes its natural wetting property [3]. Oil trapped in the narrow pores of the reservoir forms oil bank in front of the surfactant flood front and is thus produced from the production well [4].

The surfactants are classified based on the charge of hydrophilic head as anionic surfactant with negatively charged hydrophilic head, cationic surfactant with positively charged hydrophilic head, zwitterionic surfactant with hydrophilic head having both positive and negative charges and non-ionic surfactant having no charge on the hydrophilic part of the surfactant. The solubility, surface activity and micelle formation are the primary properties of the surfactants. These properties of surfactant are mainly dependent on both the hydrophilicity of its head and the hydrophobicity of its tail. Surfactants with larger carbon chain have more hydrophobicity and have lower critical micelle concentration (CMC) [5] and surfactants with a larger head group have more hydrophilicity, thus have better water solubility and form smaller micelles [6]. Zwitterionic surfactants which have larger hydrophilic head have properties such as better water solubility and temperature stability [7]. The cationic part of the hydrophilic head can be ammonium or pyridinium ion and the anionic part can be phosphate, carbonate, sulfonate or sulfate. Larger separation between cationic and anionic moiety will affect the overall size of the hydrophilic head and cause an increase in its CMC [8]. Zwitterionic surfactants have been investigated for its applicability in EOR and ultralow IFT have been achieved for carboxybetaine [9] and sulfobetaine [10] based zwitterionic surfactants.

The aim of this paper is to synthesize a family of carboxybetaine based zwitterionic surfactant with varying hydrophobic tail length of 12, 14, 16 and 18 carbons. The synthesis of surfactants was done by quaternizing tertiary amines of different carbon chain lengths by sodium chloroacetate. The synthesized surfactants were characterized by FTIR and ^{1}H NMR spectroscopy and their solubility in water was tested by Krafft temperature analysis and salt tolerance test. To check for the applicability of surfactants in chemical EOR, their IFT reduction tendency, phase behavior and wettability alteration effectiveness were evaluated. Finally, sand pack experiments were conducted to test the recovery of trapped oil by injection of surfactant slug along with alkali and polymer.

2. Materials and methodology

N,N-dimethyldodecylamine (purity > 96%), N,N-dimethyltetradecylamine (purity > 90%), N,N-dimethylhexadecylamine (purity > 98%) and N,N-dimethyloctadecylamine (purity > 90%) were purchased from TCI Chemicals and quaternized by quaternizing agent sodium chloroacetate (purity > 98%) bought from Sigma Aldrich to synthesize four zwitterionic surfactants of different carbon chain lengths. Methanol (purity > 99.8%) bought from SRL Chemicals was used as solvent in synthesis procedure. For purification of synthesized surfactant chloroform (purity > 99%) purchased from Rankem Chemicals was used. For testing the effect of concentration of salt and alkali, NaCl (purity > 99%) brought from Rankem Chemicals and Na_2CO_3 (purity > 99%) brought from SRL Chemicals were used respectively. All chemicals procured were used without any further purification. Double distilled water was used in synthesis procedure and for the preparation of solutions.

Table 1
Zwitterionic surfactants and their respective reactants.

n	Reactant	Product
8	N,N-dimethyldodecylamine	N-Dodecyl-N,N-dimethyl-2-ammonio-1-ethanecarbonate (**C12DmCB**)
10	N,N-dimethyltetradecylamine	N-Tetradecyl-N,N-dimethyl-2-ammonio-1-ethanecarbonate (**C14DmCB**)
12	N,N-dimethylhexadecylamine	N-Hexadecyl-N,N-dimethyl-2-ammonio-1-ethanecarbonate (**C16DmCB**)
14	N,N-dimethyloctadecylamine	N-Octadecyl-N,N-dimethyl-2-ammonio-1-ethanecarbonate (**C18DmCB**)

The detailed method of synthesis of carboxybetaine based zwitterionic surfactant may be found elsewhere [11]. In the present study, sodium chloroacetate (0.12 mol) was mixed with corresponding tertiary amines (0.1 mol) of chain lengths of 12, 14, 16 and 18 carbons in a solvent mixture of methanol and water (Vmethanol:Vwater = 1:4). The reaction mixtures were refluxed for 12 h at 75 °C. White residues were obtained by distillation of the solvent and excess tertiary amines from the respective reaction mixtures. Chloroform was added and filtered to remove unreacted sodium chloroacetate and NaCl formed during the reaction. The filtrates were distilled to remove chloroform and dried to obtain the desired end products. Fig. 1 shows the reaction scheme for the synthesis of the zwitterionic surfactants. Table 1 shows the names of the zwitterionic surfactants synthesized by quaternization of the respective tertiary amines.

The characterization of the synthesized surfactants was done by FTIR and ^{1}H NMR spectroscopy. FTIR of the surfactants was performed using PerkinElmer Spectrum-2 spectrophotometer using KBr pellets. Chemical structure of synthesized surfactant was also confirmed using ^{1}H NMR by Bruker AVANCE III 500 MHz FTNMR spectrometer using $CDCl_3$ as solvent.

Surface tension of the surfactants was measured to find their respective CMCs and the adsorption and thermodynamic parameters of the surfactants were calculated. Surface tension values of different surfactants at different concentration were measured by pendant drop method using Drop Shape Analyser (Kruss DSA25S, Germany). Drop of surfactant solutions was suspended at the tip of needle and images captured were analyzed to measure the surface tension of the solution. Surface tension readings were plotted against the concentration of surfactant in solution to evaluate the CMC of the surfactant. The instrument was calibrated using distilled water before taking readings. The calibration of the instrument and all measurements were taken at 30 °C.

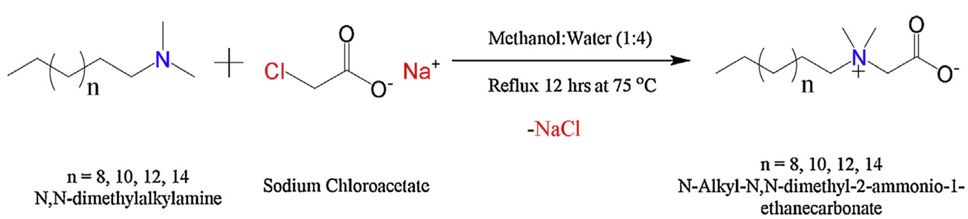

Fig. 1. Reaction scheme for the synthesis of the zwitterionic surfactants.