Journal of Molecular Liquids 266 (2018) 43–50

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Effect of internal olefin on the properties of betaine-type zwitterionic surfactants for enhanced oil recovery

S.M. Shakil Hussain, Muhammad Shahzad Kamal *, Lionel Talley Fogang

Center for Integrative Petroleum Research, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

ARTICLE INFO

Article history:
Received 2 March 2018
Received in revised form 30 May 2018
Accepted 8 June 2018
Available online 18 June 2018

Keywords:
Betaine
Formation brine
Heat stability
Surface properties
Enhanced oil recovery

ABSTRACT

In this report, four in-house synthesized betaine-type zwitterionic surfactants containing unsaturated and saturated hydrophobic tail as well as carboxylate and hydroxy-sulfonate head groups were investigated. The two surfactants containing unsaturated tail showed excellent solubility in deionized water, sea water (57,643 ppm) and formation water (213,734 ppm). However, the other two surfactants containing saturated tail exhibited poor solubility regardless of the nature of the head group, and hence they were not evaluated further. The thermogravimetric analysis results of the surfactants containing unsaturated tail revealed excellent short-range heat stability and the major weight loss was observed above 200 °C. The surfactants containing unsaturated tail exhibited excellent long-range heat stability and the FTIR and NMR spectral characterization of the aged sample of surfactants in seawater for 15 days at 90 °C showed no change in chemical structure. The critical micelle concentration (cmc) of the surfactants decreased by increasing the salinity of the water. However, hydroxy sulfobetaine showed lower cmc value (1.78×10^{-5} mol/L) compared to the carboxybetaine (1.88×10^{-5} mol/L). Moreover, surface tension corresponding to cmc (γ_{cmc}) increased by increasing the salinity of the water. Rheological studies of the polymer-surfactant hybrid demonstrated that the increase in the surfactant concertation in deionized water lowers the viscosity and storage modulus of the polymer; however, in sea water, the surfactant addition showed negligible effect. The betaine-type zwitterionic surfactants exhibited excellent salt tolerance, surface, and thermal properties and may be a material of choice for enhanced oil recovery in harsh condition reservoir.

1. Introduction

High salinity and high temperature reservoirs possess a large amount of world's residual fossil fuel [1]. The oil recovery technique is usually classified into three stages namely primary, secondary, and tertiary [2–6]. In primary recovery, the crude oil naturally produces or sometimes artificial lift devices are used. In secondary recovery, water is injected to push the oil to the surface. It is well understood that 20% to 40% of the crude oil from an oil field can be recovered by utilizing primary and secondary enhancement techniques and a major part of reservoir oil is unswept and left in the reservoir [7]. Using tertiary oil recovery, also called enhanced oil recovery (EOR), 30% to 60% additional oil can be obtained [8]. The chemical EOR technique involves the use of alkaline, surfactant, and polymer. Such technique has been applied industrially with huge economic and technical success in various oilfields [9].

Surfactants have been used successfully in different oilfield applications such as well stimulation, drilling fluids, acid diversion, and EOR [10–12]. Surfactant flooding is one the important EOR technique and almost 20% of the original oil in place (OOIP) can be produced by applying suitable surfactant [13]. Stability of surfactant under high salinity and high temperature conditions is a challenging task. An appropriate surfactant for EOR applications should have high thermal stability, compatibility with the applied polymer, low retention (<1 mg/(g of rock)), salt tolerance, and low interfacial tension (IFT) [14]. The main objective of surfactant flooding is to switch the rock wettability from oil-wet to water-wet and to lower the (IFT) among crude oil and brine [15, 16]. A suitable surfactant for EOR should have good surface properties including low IFT and low cmc, compatible and soluble with reservoir brine, thermally stable, and interact with other chemicals such as polymers.

In comparison with different classes of surfactants such as nonionic, cationic, and anionic surfactants, the zwitterionic surfactants exhibit several interesting properties because of their unique structure [17]. For instance, petroleum sulfonate (anionic surfactant) has been extensively applied in EOR. However, anionic surfactants have very low salt tolerance and elevated Krafft point which limits their application particularly in high salinity reservoir [16]. On the contrary, zwitterionic surfactants contain both anionic and cationic moieties in their molecular structure and displayed thermal

* Corresponding author.
E-mail address: shahzadmalik@kfupm.edu.sa (M.S. Kamal).

https://doi.org/10.1016/j.molliq.2018.06.031
0167-7322/

stability, good water solubility, biodegradability, low toxicity, and excellent salt tolerance [18]. Moreover, betaines are a novel class of zwitterionic surfactants and found to be stable in the presence of high temperature, pH range, and electrolyte concentration [13]. We recently observed that the oil recovery by injecting betaine-type zwitterionic surfactant solution and the surfactant-polymer hybrid in solution was 8% and 21%, respectively using Indiana limestone core [19, 20]. Due to such properties, research must focus on the investigation of zwitterionic surfactants for EOR application especially in high salinity (220,000 ppm) and high temperature conditions.

In our previous report, we observed that the betaine-type surfactants with a long hydrophobic tail (≥C18) showed poor solubility in water [21]. Due to this reason, most of the investigations have been confined to a hydrophobic tail length smaller than C18 [22]. However, the carbon-carbon double bond in the hydrophobic tail of the surfactant offset the poor solubility by decreasing Krafft temperature (T_k) of the surfactant [23].

In this report, we studied the physicochemical properties of four in-house synthesized betaine-type zwitterionic surfactants namely: stearyl dimethyl amidopropyl carboxybetaine **1** (SDAB), oleicyl dimethyl amidopropyl carboxybetaine **2** (ODAB), stearyl dimethyl amidopropyl hydroxy sulfobetaine **3** (SHSB), and oleicyl dimethyl amidopropyl hydroxy sulfobetaine **4** (OHSB) (Fig. 1). We systematically studied the effect of carbon-carbon double bond (internal olefin) in the hydrophobic tail of the surfactants by comparing two sets of surfactants (SDAB vs ODAB and SHSB vs OHSB) which differ with each other by carbon-carbon double bond in the hydrophobic tail (Fig. 1). The SDAB and SHSB exhibited poor solubility in all kind of water, and hence they were not evaluated further. However, the ODAB and OHSB showed good solubility in DW, SW, FW, and we further evaluated the effect of head group (carboxylate vs hydroxy-sulfonate) by means of heat stability (both short-range and long-range), surface tension, and rheological properties.

2. Experimental

2.1. Materials

The zwitterionic surfactants (SDAB, ODAB, SHSB, and OHSB) were synthesized by adopting the method reported in the literature [22, 24]. Oleic acid (biochemical, 92%), stearic acid (biochemical, 99%), 3-(dimethylamino)-1-propylamine (Aldrich, 99%), sodium fluoride (ACS, 99%), sodium chloroacetate (Aldrich, 98%), 3-chloro-2-hydroxypropanesulfonic acid sodium salt (Aldrich, 95%) were used as acquired. Solvents were purified through distillation for the synthesis. One commercial AM-AMPS copolymer was utilized to identify the compatibility and interaction of the surfactants with the polymer. The AM-AMPS copolymer was provided by SNF Floerger (France) had 8 million Dalton molecular weight along with 25% degree of anionicity. The structures of the synthesized surfactants (SDAB, ODAB, SHSB, and OHSB) and AM-AMPS copolymer are given in Fig. 1. Table 1 described the composition of synthetic SW and FW using commercial salts such as NaCl, $NaHCO_3$, Na_2SO_4, $MgCl_2$, and $CaCl_2$. All salts were purchased from sigma Aldrich.

2.2. Analytical equipment

The structure of the in-house synthesized surfactants (SDAB, ODAB, SHSB, and OHSB) was confirmed by NMR and FTIR. The ^1H NMR and ^{13}C NMR techniques were measured on a Jeol NMR instrument (500 MHz) using $CDCl_3$ as a solvent and chemical shifts reading were obtained in ppm. The FTIR results were acquired using FTIR instrument (16F model of Perkin-Elmer). The values were recorded in cm^{-1}.

2.3. Thermogravimetric analysis (TGA)

The TGA analysis was done on SDT Q600 machine from TA instruments by warming (10 °C/min) and the experimental temperature

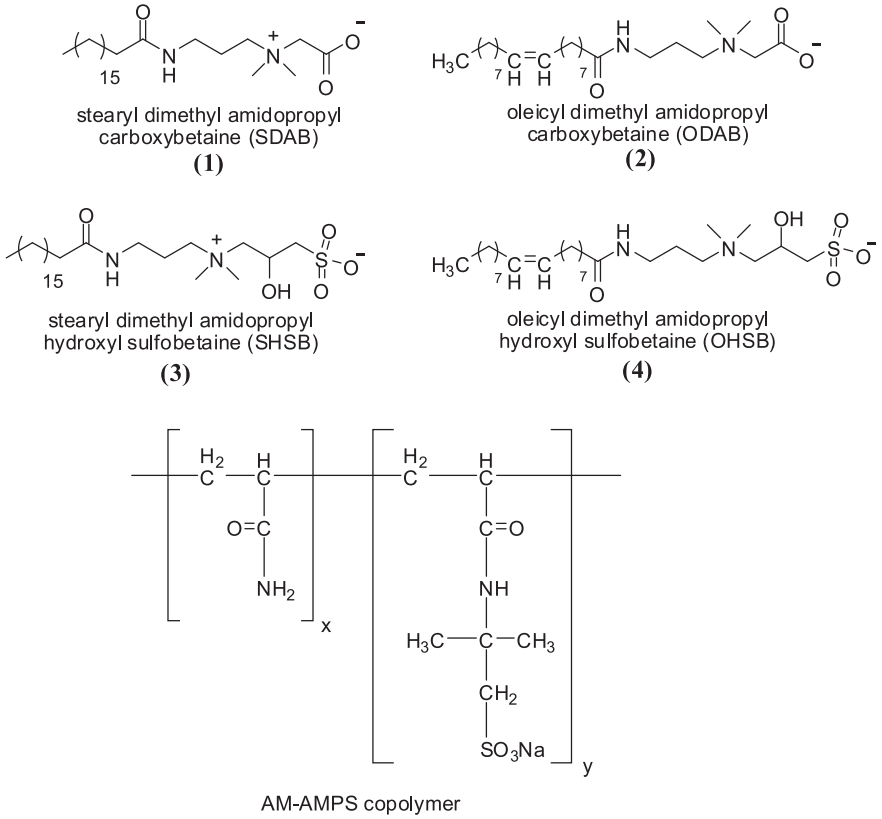

Fig. 1. Chemical structures of the synthesized surfactants (**1**–**4**) and commercial AM-AMPS copolymer.