



Synthesis and physicochemical performance evaluation of novel sulphobetaine zwitterionic surfactants from lignin for enhanced oil recovery



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ABSTRACT

Lignin sulphobetaine zwitterionic surfactants (LSBA) were successfully synthesized by a cost-effective three-step route containing sulfonation, quaternization and alkylation reaction from renewable alkali lignin. The synthesized surfactants were characterized by FT-IR, UV and ¹H NMR analysis. The physicochemical properties of synthesized surfactants had been tested to investigate the effectiveness of LSBA surfactants for enhanced oil recovery (EOR). The hydrophile lipophile balance (HLB) values of LSBA-1, LSBA-2 and LSBA-3 were 14, 11 and 10, respectively. LSBA surfactants exhibited high surface activity with low surface tension and the critical micelle concentration (cmc) of LSBA-1, LSBA-2 and LSBA-3 were 4.36×10^{-4} mg/L, 4.45×10^{-4} mg/L and 1.04×10^{-3} mg/L, respectively. The dynamic interfacial tension (IFT) between the crude oil from Huabei and Xinjiang oilfields (China) and the LSBA solution was measured. Compared with Huabei crude oil, LSBA surfactants showed better interfacial activity on Xinjiang crude oil. LSBA surfactants reduced the IFT between Xinjiang crude oil and brine down to ultra-low ($<10^{-3}$ mN/m) under weak alkaline conditions.

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1. Introduction

In recent years, more and more attention has been paid to surfactant flooding recovery, which is one of the promising chemical methods for enhanced oil recovery (EOR) [1–3]. Surfactants can not only decrease the oil/water interfacial tension (IFT) but also improve the capillary number, making the residual oil trapped in reservoir flow, thus the efficiency of oil recovery can be improved greatly [4–6]. At the present stage there are a lot of serious problems in surfactant flooding, such as adsorption loss, large dosage and high cost, which obviously limit the wide application of surfactants in EOR [7]. Therefore, the research and development of high efficiency and low-cost oil-displacing surfactants has become one of the major challenges for the scientific workers. The production of eco-friendly green surfactants which make full use of natural renewable resources and the green chemical synthesis technology are the hotspot and primary development direction for the current oil-displacing surfactants [8,9].

As the second abundant renewable resource in the nature, lignin is a kind of biopolymer composed by benzene propane monomer on earth after cellulose [10–12], which is expected to play an important role in

the near future as a raw material for the production of bio-products. Most industrial lignins are produced as a by-product during the paper pulping process with a large volume of approximate 50 million tons each year [13]. And the majority of them are burnt or drained directly into rivers and lakes as waste, which not only cause the waste of resources but also seriously pollute the environment [14,15]. In addition, the molecular structure of lignin on the benzene ring and the side chains contains a number of different functional groups, such as methoxyl group (–OCH₃), hydroxyl (–OH), carbonyl group (–CO–), alkyl and so on, which can be modified through a variety of chemical reactions [16–18]. The water solubility and interfacial activity of lignin will be affected by the introduction of the hydrophilic and lipophilic groups [19, 20]. Therefore, the surfactants synthesized from the biodegradable and low-cost lignin will be one of the most promising applications in EOR.

Lignosulfonate is the first surface active component applied in surfactant flooding, but the industrial lignosulfonate has strong hydrophilic groups without long-chain of lipophilic group, which leads to the inhibition of interfacial activity of lignosulfonate [21]. Therefore, the lignosulfonate cannot decrease the IFT to ultralow level ($<10^{-3}$ mN/m) between oil and water when used alone, it usually need to be compounded with other main surfactants to form oil-displacing surfactants with better interfacial performance [22,23]. In order to improve the interfacial performance of the surfactants synthesized from lignin,

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a wide range of synthesis techniques such as sulfonation, alkylation, oxidation, amination and carbonylation have been developed to alter the molecular structure of alkali lignin [24–28]. However, most of these methods can only improve the oil-soluble of lignin surfactants and the existing lignin surfactants are in general relatively hydrophilic, the modified lignin surfactants used alone still cannot decrease the IFT of oil-water to ultralow level. Moreover, multiple steps, the high modification cost and special equipments are also needed in these techniques.

In the last decade zwitterionic surfactants have attracted the attention of researchers for their adaptability in EOR [29–31]. The superior properties of zwitterionic surfactants, such as good biodegradability, salt resistance, high temperature resistance, good water solubility and enough lipophilicity and good synergistic effect with some nonionic and anionic surfactants, which enable them to be effective on increasing the oil recovery efficiency [32–34]. At present, there are many different zwitterionic surfactants synthesized and the demand for this kind of surfactant is increasing each year. However, the relatively high cost of zwitterionic surfactants limits their large-scale application in EOR compared to other types of surfactants. At present, the synthesis and performance research of zwitterionic surfactants are the focus of attention for researchers, and little attention has been paid to study and synthesis of zwitterionic surfactants from low-cost and renewable lignin. Sulphobetaine and their derivatives are a class of zwitterionic surfactants containing quaternary ammonium cation and sulfonic acid anion, with excellent stability under acidic and alkaline conditions.

In the present work, a new cost-efficient and high performance zwitterionic surfactants from alkali lignin as raw materials were successfully synthesized by an economic pathway, in which a three-step procedure was involved. First, the alkali lignin was selectively oxidized and sulfonated with hydrogen peroxide and sodium sulfite to obtain the product lignosulfonate. Second, (2, 3-epoxypropyl) alkyl dimethyl ammonium chloride (ADAC) was prepared by the reaction of long alkylchain dimethyl tertiary amine and epichlorohydrin. Last, this intermediate ADAC was subsequently reacted with phenolic hydroxyl groups of lignosulfonate to synthesize lignin sulphobetaine zwitterionic surfactant (LSBA). Thus, both long alkylchain and amine functional groups were introduced into the lignin molecules to improve the surface activity and solubility of lignin surfactants. The structures of target products LSBA were analyzed by FT-IR, UV and ^1H NMR. The hydrophile lipophile balance (HLB) experiments for LSBA surfactants were examined. The surface active and interfacial behavior of LSBA surfactants were also evaluated by surface tension and interfacial tension measurements, respectively.

2. Experimental procedures

2.1. Materials

Alkali lignin was provided by Shandong paper mills of China. Hydrogen peroxide (30 wt%), sodium sulfite, epichlorohydrin, sodium hydroxide, sulfuric acid, hydrochloric acid, sodium carbonate, isopropanol and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Decyldimethyl tert-amine, dodecyldimethyl tert-amine, tetradecyldimethyl tert-amine, p-hydroxybenzoic acid, *N*, *N*-dimethylformamide and tetra-*n*-butylammonium hydroxide were purchased from Sigma Chemicals. All the chemicals were analytical pure grade.

Partially hydrolysed polyacrylamide (HPAM, $M_w = 1800 \times 10^4$) was given from Beijing Hengju Chemical Group Co., Ltd., China. Two kinds of dewatered and degassed crude oil were provided by Xinjiang and Huabei oilfields, China. The density of crude oil from Xinjiang and Huabei oilfields was 0.85 g/cm³ and 0.78 g/cm³, respectively. The ionic composition of simulated brine from different oilfields was shown in Table 1.

Table 1

Composition of simulated brine from Huabei and Xinjiang oilfields, China.

Oilfield	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	CO ₃ ²⁻ (mg/L)	HCO ₃ ⁻ (mg/L)
Huabei	53.6	22.0	3900.7	32.2	4737.5	117.5	–	1925.9
Xinjiang	56.9	13.4	2085.0	–	2577.0	131.6	5.8	1156.9

2.2. Methods

2.2.1. Synthesis of oxidized sulfonated lignin

The quantitative lignin (40 g) dissolved with 300 mL deionized water was added into a three-necked round-bottom flask equipped with a stirrer. After the pH of solution being adjusted to 12 with sodium hydroxide solution, 6 g hydrogen peroxide was added into the flask at 70 °C for 1 h with stirring. Then the sodium sulfite (8 g) was added into the reactor and the reaction continued for 1 h at 180 °C. After the reaction, the pH of resulting mixture was adjusted to 2 with dilute sulfuric acid and the precipitation was separated by centrifuge. Thus, a brown power of oxidized sulfonated lignin was obtained after drying in a vacuum oven.

2.2.2. Synthesis of (2, 3-epoxypropyl) alkyl dimethyl ammonium chloride

The epichlorohydrin (9.25 g) and hydrochloric acid (4.38 g) were added into a three-necked round-bottom flask and agitated at 25 °C for 30 min, then decyldimethyl tert-amine (18.54 g) was added dropwise in 20 min after the reaction temperature was went up to 40 °C. After that, the pH of the mixed solution was adjusted to 9 with sodium hydroxide solution and the reaction continued for 2 h at 50 °C. Thus the intermediate (2, 3-epoxypropyl) decyldimethyl ammonium chloride (ADAC-1) was obtained after cooling to room temperature.

By varying the carbon chain length of tertiary amine, the intermediates ADAC-2 and ADAC-3 were synthesized according to the above synthetic pathway using the dodecyldimethyl tert-amine and the tetradecyldimethyl tert-amine, respectively.

2.2.3. Synthesis of lignin sulphobetaine zwitterionic surfactant

In a 500 mL round-bottom flask, 25.4 g oxidized sulfonated lignin which was dissolved in 200 mL acetone was added and the temperature of the mixture was raised to 40 °C gradually. Then the pH of solution was adjusted to 12 by adding sodium hydroxide and insulation for 30 min in order to fully dissolve the oxidized sulfonated lignin in acetone. After that, the intermediate ADAC-1 (30.81 g) was added dropwise into the flask with stirring after the reaction temperature increased up to 50 °C and the reaction was carried out for 2.5 h at 50 °C. After removing the solvents by rotary evaporator under reduced pressure, the 200 mL isopropanol was added into the mixture and refluxed at 70 °C for 3 h to filter off inorganic salts. Then the mixture was neutralized by distilled water and dried in a vacuum oven at 60 °C for 20 h, a light brown solid powder of lignin sulphobetaine zwitterionic surfactant (LSBA-1) was obtained.

The products LSBA-2 and LSBA-3 were synthesized according to the above synthetic method using the intermediates ADAC-2 and ADAC-3, respectively.

2.2.4. Chemical analysis

Fourier transform infrared spectroscopy (FT-IR) (Thermo 6700, USA) was employed to characterize the structures of alkali lignin and synthesized LSBA surfactant by potassium bromide (KBr) pellet method in the range of 500 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Ultraviolet spectrum (UV) measurements were performed in a Lambda UV-Visible Spectrometer (Perkin-Elmer co., America). Element analyses of alkali lignin and LSBA surfactant were carried out on the Vario ELL III type element analyzer (Elementar Co., Germany). Nuclear magnetic resonance (NMR) spectroscopy was used to obtain the ^1H NMR spectra of

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