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Systematic investigation of the synergistic effects of novel biosurfactant ethoxylated phytosterol-alcohol systems on the interfacial tension of a water/model oil system

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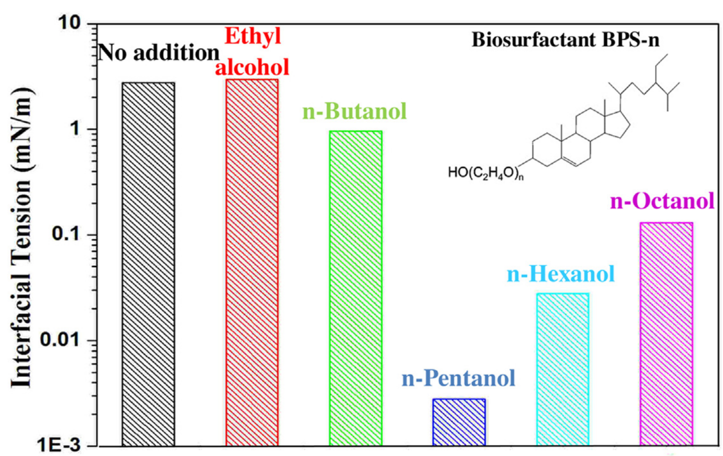
HIGHLIGHTS

- Biosurfactant ethoxylated phytosterols are used in chemical EOR for the first time.
- Cosurfactant alcohols show the synergistic effects with the BPS-30 in IFT reduction.
- There is a close relationship between the IFT reduction and the alcohol chain length.
- Ultra-low IFT can be achieved with the assisted of cosurfactant *n*-pentanol.

GRAPHICAL ABSTRACT



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ABSTRACT

Increasing attention has been paid to the potential applications of biodegradable or natural surfactants in various fields, including chemical enhanced oil recovery (EOR), since the use of eco-friendly chemical processes was first proposed. The novel nonionic biosurfactant, ethoxylated phytosterols (BPS-n), was introduced to chemical EOR for the first time. The BPS-n showed a satisfactory ability to reduce the interfacial tension (IFT) between water and a model oil (*n*-octane) when the effects of BPS-n concentration, salinity and temperature were investigated. Several typical alcohols have been used as cosurfactants to further reduce the IFT through synergistic effects with BPS-30. Interestingly, there may be a close relationship between the ability to reduce the IFT and the hydrophobic chain length of the alcohol. Based on the adsorption and stereo-hindrance effect, we proposed a reasonable explanation for this relationship.

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1. Introduction

It is estimated that approximately 60% of the crude oil in reservoirs remains available for further use after conventional primary and secondary oil recovery. Enhanced oil recovery (EOR) is playing an increasingly significant role in the improvement of oil production [1]. Several EOR methods have already been employed to extract residual oil, and surfactant flooding is a commonly used technique [2–10]. Surfactants can increase oil recovery by reducing the oil/water interfacial tension (IFT) or modifying the wettability [2–7]. It is well known that the application of surfactants can effectively increase oil recovery and add huge economic benefits. However, there are a few essential problems that must be addressed immediately, such as the environmental effects and the ability to reduce IFT [11].

Several groups have paid more attention to investigating environmentally friendly and efficient surfactants for chemical EOR since the topic of "green" chemistry and chemical engineering was first proposed [12–23]. Li et al. reported the adsorption kinetics of phospholipid biosurfactants at the oil/water interface [13]. Then, they further investigated the effects of protein on the phospholipid biosurfactant monolayer at the air/water or oil/water interface [14–17]. Recently, Ahmadi et al. studied the ability of a natural surfactant with micro-sized particles of mulberry leaf to reduce the IFT between kerosene and water and found that the sweep efficiency can be increased from 49% to 66.8% of Original Oil In Place (OOIP) with the assistance of surfactant flooding [22]. In most of the above reports, the surfactants were directly extracted from the leaves or flowers of natural plants and were not further purified. The impure surfactants are not beneficial for studies of the action mechanism, which can influence their applications in development. To avoid this vital problem, we attempt to employ the typical nonionic biosurfactant ethoxylated phytosterols (BPS-n) in chemical EOR. The BPS-n is produced by the physical pressing of corn or soybeans. Due to their remarkable nutritional and medicinal value, BPS-n has been referred to as "the key of life". Moreover, the defined molecular structures of BPS-n aid in the intensive investigation of their action mechanism.

A large number of reports have demonstrated that the IFT reduction of oil/water systems is the basic mechanism of surfactant flooding and that reducing IFT by two or more orders of magnitude can improve the oil recovery efficiency by tens of percent [4]. Thus, the IFT is generally desired to be lower than 10^{-2} mN/m in the practical applications. Due to the molecular structure of natural surfactants, the IFTs in the previous literature rarely achieved such a low value [18–23]. The addition of cosurfactant may be an effective way to further decrease the IFT, and alcohols with short chains are the most common cosurfactants [24–29]. The structure of the cosurfactant is similar to that of the surfactant. However, the cosurfactant cannot form micelles because of either poor water solubility or weak hydrophobic interaction. The introduction of cosurfactant to the surfactant and aqueous solution/oil system can increase the interfacial fluidity and molecular disorder, leading to a further reduction of the IFT. Iglauer et al. found that alkyl polyglycoside microemulsion consisting of an alcohol cosurfactant could decrease the IFT values of a water/oil system to 0.01 mN/m or less. The oil recovery was as high as 85% of OOIP by the coreflood test [25]. Then, Jeirani et al. decreased the IFT values to 0.0001 mN/m and increased the total oil recovery to 87% with the assistance of triglyceride-cosurfactant combinations [26].

Herein, we introduced the novel nonionic biosurfactant BPS-n to the new field of chemical EOR, which has rarely been reported. Then, we systematically investigated the effects of several factors (BPS-n concentration, salinity and temperature) on the IFT between BPS-n aqueous solutions and model oil (*n*-octane). Moreover, the cosurfactant alcohols with different chain lengths were added to further decrease the IFT.

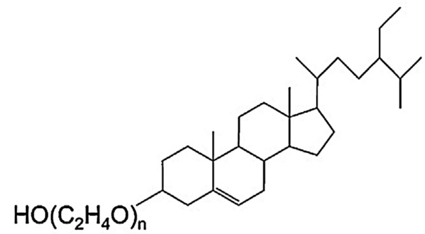

Fig. 1. The molecular structure of the biosurfactant ethoxylated phytosterols (BPS-n, n = 10, 20, 30).

2. Experimental

2.1. Chemicals

The biosurfactant ethoxylated phytosterol (>98%, BPS-n, n = 10, 20, or 30, where n is the number of oxyethylene units, Fig. 1) was a kind gift from Nikkol, Japan. Sodium chloride, *n*-octane, ethyl alcohol, *n*-butanol, *n*-pentanol, *n*-hexanol, and *n*-octanol were purchased from Shanghai Chemical Reagent Company. All chemicals were analytical grade and used as received.

2.2. Measurement of interfacial tension

The interfacial tension between the model oil and water were directly measured via the spinning drop method on a TX-500C spinning drop interfacial tension apparatus (American CNG Company) as previously described [2]. The aqueous solution was primarily filled in the glass tube. Then, a droplet model oil was injected into the centre of the water phase. Finally, the interfacial tension was measured at the fixed rotating velocity (5000 rpm) at the given temperature.

3. Results and discussion

In the present study, *n*-octane was selected to replace the typical mixture of crude oil to eliminate the effects of asphaltene and other impurities.

3.1. The effects of biosurfactant ethoxylated phytosterols (BPS-n) on the interfacial tension (IFT) of water/n-octane

As shown in Fig. 2, there is a distinctly decreasing tendency for the three IFT curves with increased concentrations of the BPS-n aqueous solutions. Further, the IFT curves for BPS-20 and BPS-30 are almost coincident. This result suggests that the reduced level of the IFT is well below the BPS-n concentration of 1000 mg/L, whereas the reduced level is moderate above that concentration. The three types of biosurfactant ethoxylated phytosterols, BPS-10, 20, and 30, can effectively reduce the IFT of water/n-octane from 25.56 mN/m to 8.01 mN/m, 2.56 mN/m, and 2.76 mN/m, respectively. The main difference among the three biosurfactants is the length of the hydrophilic ethoxylated chain, which greatly affects the interfacial activity of the surfactant. This requires the hydrophilic property to be roughly equal to the hydrophobic property for the surfactant to best reduce the IFT. For BPS-10, the short hydrophilic ethoxylated chain is not beneficial to the interfacial absorption, which leads to a higher IFT value. Increasing the hydrophilic chain length (BPS-20, 30) can further enhance the interfacial activity, resulting in a lower IFT value.

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