Partition Performance of Biological Sulfonate Synthesized from Waste Cooking Oil by Sulfonation in Oil and Water

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Abstract. Biological sulfonate was synthesized from waste cooking oil by sulfonation. Fourier transformation infrared spectrometer was employed to characterize biological sulfonate. The influences of the surfactant concentration, alkali concentration and emulsification on the partition coefficient of biological sulfonate in oil and water were investigated. The experimental results show the waste cooking oil can react with the fuming sulphuric acid to successfully produce biological sulfonate. The partition coefficients of biological sulfonate have a small decrease when biological sulfonate concentration is more than 0.2%. Adding alkali to biological sulfonate solution or emulsifying biological sulfonate solution and crude oil can both improve the partition coefficients of biological sulfonate in oil and water, and the variation law of the partition coefficients with the concentration of biological sulfonate remain unchanged. By contraries, after adding alkali to solution and emulsifying it with crude oil, the partition coefficients of biological sulfonate will increase with the increase of surfactant concentration.

Introduction

At present, surfactant flooding agents such as petroleum carboxylate, petroleum sulfonates, alkylbenzene sulfonate, lignin sulfonate, etc. have been used in tertiary oil recovery in China[1]. The raw materials for the synthesis of these surfactants were mainly from by-products gained in petroleum refining[2]. Consequently, these surfactants were difficultly biodegraded in natural condition, and would lead to produce environmental pollution. Their proportion in the total production of surfactants has declined gradually[3]. Biomass resources were used to replace fossil resources as a raw material for surfactants[4]. Natural oils have become one of the research hotspots in synthesis of surfactant because of its large production, low cost and environmental friendliness[5]. In particular, the use of waste cooking oil to synthesize surfactant could provide a solution for food safety and environmental pollution brought by waste cooking oil[6].

The interfacial tension between surfactant flooding system and crude oil was usually required to reach the ultra-low interfacial tension of 10⁻³ mN/m, which was one of the important indicators for evaluating and screening surfactant flooding agents, and determined the oil displacement efficiency[7]. It was difficult to reach the ultra low interfacial tension of 10⁻³ mN/m between single surfactant solution and crude oil. Usually, different surfactants or surfactant and alkali were combined to reduce the interfacial tension between oil and water to the ultra-low interfacial tension of 10⁻³ mN/m by synergistic effect. After the surfactant solution was in contact with oil phase, the surfactant molecules were adsorbed into the oil-water interface until the adsorption reached the equilibrium. Then, the concentration of surfactant in oil and water no longer changed, and the interfacial tension between oil and water reached the equilibrium value. Shan suggested the partition coefficient was used to described this state, which was defined as the ratio of the surfactant concentration in oil phase to that in water phase. Simultaneously, the partition coefficient could also reflect the ability of surfactant to reduce the interfacial tension between oil and water. A tremendous amount of researches
in this area have been carried out by many scholars. W.D. Liu et al.[8] studied the partition rules of surfactant in oil and water for alkali/surfactant/polymer system, and investigated effects of alkaline concentration, type and emulsification on the partition coefficients as well. Z G Ye et al.[9] determined the partition coefficients of trace surfactant in oil and water by spectrophotography. Y Zhang et al.[10] researched influences of oil to water ratio and stirring time on the partition coefficients of surfactant in oil and water for alkali/surfactant/polymer system, and compared the partition coefficients of single surfactant system, surfactant/polymer system and alkali/surfactant/polymer system. The above studies were mainly related to surfactants synthetized by by-products gained in petroleum refining. In this paper, biological sulfonate would be synthesized from waste cooking oil by sulfonation. Then, influences of surfactant concentration, alkali concentration and emulsification on the partition coefficients of biological sulfonate in oil and water would be investigated, compared with petroleum sulfonate provided by oilfield.

Experimental

Materials and Instruments

The waste cooking oil was purchased from Zoushan Huan Xin Waste Oil Recycling factory (Zoushan, China), petroleum sulfonate and the degassed crude oil were provided by the Number One Oil Exploding Companies of the Daqing Oil Field. Methyl alcohol, chloroform, methylene blue (MB), thymol blue (TB), hexadecyl trimethyl ammonium bromide (CTMAB), dichloromethane, ethanol were purchased from the Sinopharm Chemical Reagent Co., Ltd (Beijing, China, AR grade).

The instruments used in this study were as follows: Prestige-21 Fourier transformation infrared spectrometer (Shimadzu Corporation, Japan), TE412 electronic balance (Sartorius Company, Germany), J-HH-2A thermostatic waterbath (Shanghai Hao Zhuang Instrument Co., Ltd, China), THZ-82 cyclotron oscillation thermostatic waterbath (Jiangsu Changzhou Jintan Precision Instrument Manufacturing Co., Ltd, China).

Preparation and Characterization of Biological Sulfonate

A certain proportions of the waste cooking oil and the organic solvent were added to flask with three necks. Then, the waste cooking oil was quickly stirred to completely dissolve in the organic solvent for forming the reaction solution. A certain volumes of fuming sulphuric acid were slowly added to the reaction solution at room temperature, which was quickly stirred for heat dissipation at the same time. After all the fuming sulphuric acid was added, the reaction solution was heated to the reaction temperature of sulfonation. When the reaction ended, the NaOH solution was slowly added to the reaction solution for hydrolysis and neutralization until the reaction solution was alkaline. The reaction solution was diluted with distilled water, fully stirred, and then divided to obtain light brown products by separating funnel. The light brown products were processed by reduced pressure distillation to remove the solvent and water, and then get the orange biological sulfonate.

The Fourier transform infrared (FT-IR) spectra of the waste cooking oil and biological sulfonate were recorded on a Prestige-21 Fourier transformation infrared spectrometer in the region of 4000-400 cm\(^{-1}\) with a resolution ratio of 4 cm\(^{-1}\) and a scanning times of 70.

Measurement of the Partition Coefficients of Biological Sulfonate

The biological sulfonate solution and petroleum sulfonate solution at different concentrations (0.05%, 0.1%, 0.15%, 0.2%, 0.25%, 0.3%, 0.4%) were prepared to investigate the effect of the surfactant concentration on the partition coefficient. The same volumes of biological sulfonate solution or petroleum sulfonate solution and crude oil were put into different conical flasks with cover. These conical flasks with cover had been placed for 7 days in the thermostatic waterbath at a temperature of 40°C. Then, the concentrations of biological sulfonate and petroleum sulfonate in water phase were directly determined by two-phase titration method, and they in oil phase were calculated by the initial

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concentration subtracting the concentration in water phase. The partition coefficients of biological sulfonate and petroleum sulfonate in oil and water phases can be defined as follows:

\[
\lambda = \frac{C_O}{C_W}
\]

Where, \( \lambda \) is the partition coefficient of the surfactant in oil and water phases; \( C_O \) and \( C_W \) are the surfactant concentration in oil phase and in water phase, respectively.

The alkalis were added into biological sulfonate solution and petroleum sulfonate solution in order to study the effect of alkali at different concentrations (0.5%, 1.0%, 1.5%) on the partition coefficient.

The conical flasks with cover loaded with the surfactant solution and crude oil had been placed for 7 days in the cyclotron oscillation thermostatic waterbath at a temperature of 40°C for investigating the influence of emulsification on the partition coefficient. In the course of the experiments, the oscillation had been kept so that the oil could fully get in touch with the water by way of forming the emulsion.

Results and Discussion

Structure Characterization of Biological Sulfonate

The FT-IR spectra of biological sulfonate and waste cooking oil were shown in Figure 1. The FT-IR spectrum of waste cooking oil shows that the peak at 3010 cm\(^{-1}\) is assigned as the stretching vibration of C–H bond in the unsaturated carbon chain, the peak at 1652 cm\(^{-1}\) is assigned to the stretching vibration of C=C bond, and the peaks at 1377 cm\(^{-1}\) and 720 cm\(^{-1}\) are due to the bending vibration of C–H bond in the unsaturated carbon chain. The above peaks are the characteristic absorption peaks of olefin, which disappear in the FT-IR spectra of biological sulfonate yet. At the same time, the FT-IR spectrum of biological sulfonate shows the peak at 3473 cm\(^{-1}\) is assigned to the stretching vibration of O–H bond, the peak at 1221 cm\(^{-1}\) is due to the asymmetric stretching vibration of –SO\(_3\)– bond, the peak at 1083 cm\(^{-1}\) is assigned as the symmetric stretching vibration of –SO\(_3\)– bond, and the peak at 648 cm\(^{-1}\) is assigned to the stretching vibration of –C–S– bond. Consequently, these results demonstrate that the unsaturated C=C bonds of waste cooking oil do have a sulfonating reaction with SO\(_3\), and the product obtained is a kind of biological hydroxy sulfonate.

![Figure 1. FT-IR spectra of waste cooking oil and biological sulfonate.](image)

Influence of Surfactant Concentration on Partition Performance

The partition coefficients of biological sulfonate and petroleum sulfonate at different surfactant concentrations were shown in Figure 2. As seen in Figure 2, the partition coefficients of biological sulfonate and petroleum sulfonate decrease with increasing surfactant concentration. When the surfactant concentration is less than 0.2%, the partition coefficients decrease rapidly. However, when the surfactant concentration is higher than 0.2%, the partition coefficients decrease slowly. It can be explained that the surfactant molecules migrate spontaneously from the water phase to the oil-water
interface due to hydrophobic interaction of lipophilic group of the surfactant molecules after the surfactant solution is in contact with the crude oil. Therefore, most of the surfactant molecules in the water phase are aggregated on the oil-water interface. With the increase of the surfactant concentration, more and more surfactant molecules are adsorbed on the oil-water interface until the surfactant molecules reach the adsorption equilibrium. Then the amount of the surfactant molecules is no longer changed on the oil-water interface, and yet the surfactant concentration in the water phase increases gradually, resulting in the decrease of the partition coefficient of the surfactants in oil and water. The partition coefficients of biological sulfonate and petroleum sulfonate have similar changing laws, and the partition coefficients of biological sulfonate in oil and water are lower than those of petroleum sulfonate. This proofs that the ability of biological sulfonate reducing the interfacial tension between oil and water is stronger than that of petroleum sulfonate at the same concentration.

![Graph](image)

Figure 2. Partition coefficient of the surfactants in oil and water at different concentrations.

**Influence of Alkali Concentration on Partition Performance**

The variations of the partition coefficients of biological sulfonate and petroleum sulfonate at different alkali concentrations were shown in Figure 3(a) and (b), respectively.

![Graphs](image)

(a) Biological sulfonate

(b) Petroleum sulfonate

Figure 3. Influence of alkali concentration on partition coefficient of the surfactants in oil and water.

These figures show the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water decrease rapidly in the initial stage at the same concentration of alkali with increasing surfactant concentration. But when the surfactant concentration is higher than 0.2%, the partition coefficients decrease slowly. This suggests that alkali can promote the aggregation of the surfactant molecules to the oil-water interface. Moreover, the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water will have a small increase with the increase of alkali concentration. It can be explained that the ion intensity in the water phase increases with the increase of alkali concentration to strengthen the repulsion between the surfactant molecules so that more surfactant molecules are clustered to the oil-water interface, resulting in the decrease of the surfactant concentration in water phase. Thus, the partition coefficients of biological sulfonate and petroleum
sulfonate in oil and water will be increased. The variation law of the partition coefficients of biological sulfonate in oil and water is basically the same as that of petroleum sulfonate. However, the partition coefficient of biological sulfonate is greater than that of petroleum sulfonate at the same alkali concentration because of better ability for biological sulfonate in reducing the interfacial tension between oil and water.

**Influence of Emulsification on Partition Performance**

After the surfactants and crude oil being emulsified, the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water without alkali were shown in Figure 4(a). These figures show the variations of the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water with the surfactants concentration remain constant before and after the surfactants and crude oil being emulsified. That is, the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water decrease with increasing surfactant concentration. However, the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water after the surfactants and crude oil being emulsified are higher than before the surfactants and crude oil being emulsified. It can be explained that the contact interfaces of the surfactant and crude oil increase in the emulsification process of the surfactants and crude oil, resulting in the increasing number of the surfactant molecules adsorbed on the oil-water interface. Then, the surfactant concentration decreases in water phase, leading to increase the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water.

![Figure 4. Influence of emulsification on partition coefficient of the surfactants in oil and water.](image)

After the surfactants and crude oil being emulsified, the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water with alkali concentration of 1.0% were shown in Figure 4(b). These figures show the variations of the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water with the surfactants concentration have distinct difference by joining alkali in the surfactant solutions to emulsify the crude oil. After the surfactants and crude oil being emulsified, the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water increase with increasing the surfactant concentration, and the partition coefficients of biological sulfonate in oil and water are still higher than those of petroleum sulfonate as well. It can be explained that alkali can react with the crude oil to generate the active substance, which can cooperate with the surfactants to form more stable emulsion. Consequently, the surfactant concentration in water phase decreases, resulting in increasing the partition coefficients of the surfactants in oil and water. Especially, the volumes of the emulsion formed increase and the surfactant concentration in water decreases with the increase of the surfactant concentration. Thus, the partition coefficients of biological sulfonate and petroleum sulfonate in oil and water increase with the increase of the surfactants concentration.
Summary
The biological sulfonate was successfully synthesized from waste cooking oil by sulfonation. The FT-IR spectrum of biological sulfonate demonstrates that the unsaturated C=C bonds of waste cooking oil can react with SO₃ to produce a kind of biological hydroxy sulfonate. The partition coefficients of biological sulfonate in oil and water decrease with increasing surfactant concentration. The partition coefficients decrease rapidly with the surfactant concentration of less than 0.2%, while they decrease slowly with the surfactant concentration of higher than 0.2%. When alkali was added to the surfactant solution, the partition coefficients of biological sulfonate in oil and water will have a small increase with the increase of alkali concentration. Biological sulfonate being emulsified with crude oil will lead to an increase of the partition coefficients of biological sulfonate in oil and water. When alkali is added to biological sulfonate solution and then emulsified with crude oil, the partition coefficients of biological sulfonate will increase with the increase of surfactant concentration.

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References