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Wax adsorption at paraffin oil–water interface stabilized by Span80

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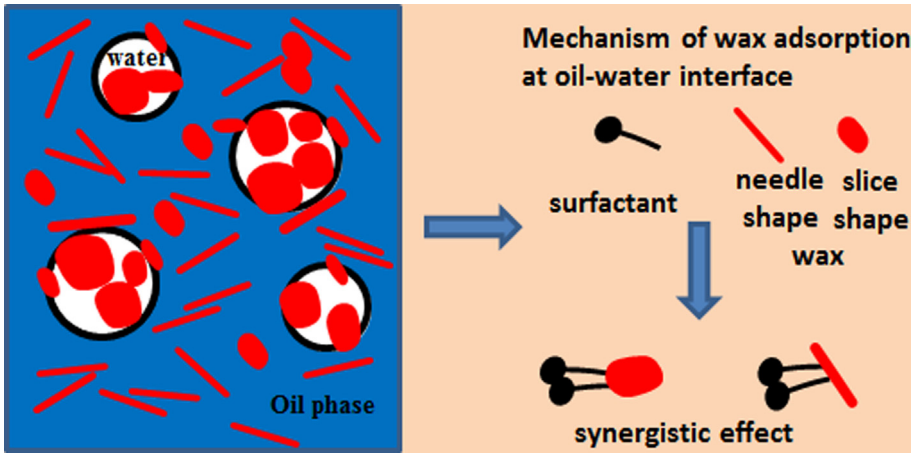
HIGHLIGHTS

- Wax adsorption at oil-water interface has been observed by microscope.
- The mechanism of wax adsorption at oil-water interface has been explained.
- The rheology of oil-water interface has been change by wax adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, wax adsorption at the water–oil interface was studied. Through a polarizing microscope, interfacial adsorption of wax crystals was observed. The cause of the adsorption was proposed to be the synergistic effect between surfactant and wax. An additional experiment, an interfacial rheology test, validated the synergistic effect, showing that wax adsorption enhances the interfacial storage modulus and changes interfacial viscosity. The interfacial storage modulus increased with the decrease in temperature, which implies that the amount of wax adsorption increased at the interface, in agreement with the findings observed with the microscope. Temperature and wax content are two factors that affect interfacial rheology.

1. Introduction

In an oil–water multiphase transportation pipeline, which is unavoidable in deep water oil fields owing to the existence of natural surfactants and flow shear, water can always be dispersed into the oil phase, creating a water-in-oil emulsion. As a result, wax deposition in emulsion systems has been a common problem for the flow assurance industry. However, there is limited research on

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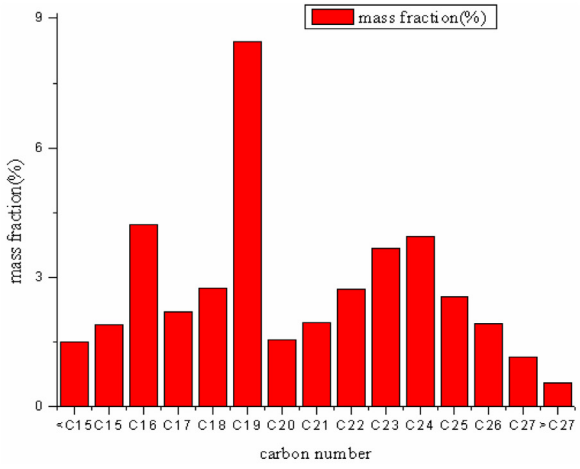
oil–water two-phase wax deposition, and the results obtained by experiments are not consistent [1–7]. Information on the effect of water droplets in the oil phase for the wax deposition process is still lacking. Zheng and Fogler [8] found that dispersed water droplets inhibit wax diffusion by partially blocking its diffusion path and gave the relation between the diffusion coefficient rate and water content of emulsion.

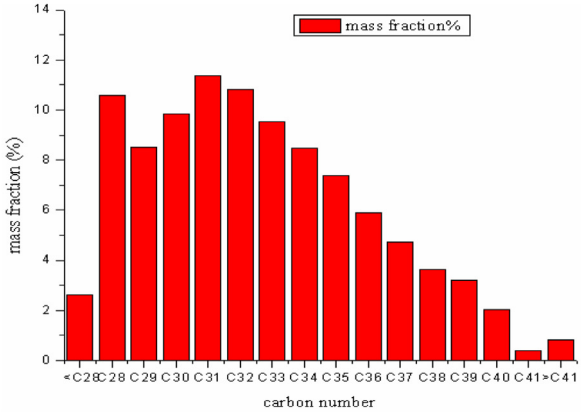
Current studies about the adsorption of natural oil components can be divided into two aspects. On the one hand, there is research that focuses on the adsorption process of asphaltene, which acts as a surface active component and promotes the stability of the emulsion [9–12]. The adsorption of asphaltene at the oil–water interface was interpreted by a Langmuir equation of state (EOS) at the beginning of adsorption, and later adsorption kinetics followed random sequential adsorption (RSA) [13]. On the other hand, the relationship between the wax crystals and the stability of the oil–water emulsion has been carried out. The stability of emulsion can be promoted by fine particles such as wax crystals [14,15], silica [16], clay, and charge latex particles [17], which can hinder the coalescence of the dispersed phase. This type of emulsion is named the Picking emulsion. Binks et al. [18] studied the effect of wax crystals on emulsion stability and found that wax that has cocrystalization with ester or acid molecules can be adsorbed at the oil–water interface. Rousseau et al. [19] found that rapid crystallization of wax in the continuous phase of water-in-oil emulsion was more stable while resisting both coalescence and flocculation than the pre-crystallization of waxy oil. Further, it is important to study whether the presence of oil–water interface has an effect on waxy oil emulsion flow and deposition.

Waxes (long chain alkanes as one component of crude oil) have no interfacial activity, so wax cannot be adsorbed at its interface. However, emulsion contains surfactant and surfactant is amphiphilic; therefore, it is necessary to consider whether the surfactants and the wax have a synergistic effect, which causes the wax to be adsorbed at the oil–water interface indirectly. The interaction of the surfactants with proteins [20,21] or solid particles [22–25] has been extensively studied. For example, a water-soluble surfactant was added to hinder the adsorption of proteins at the oil–water interface to prevent protein gelling [26–28]. Despite the presence of surfactants, the charged solid particles were able to continue reducing the interfacial tension [29], and the inherently hydrophilic particles mixing with surfactants were able to increase their hydrophobicity [16].

To confirm the synergistic effect between wax and surfactant at the oil–water interface, the wax precipitation process in water-in-oil emulsion was observed with a polarizing microscope and the interfacial rheology was investigated to further characterize the interfacial adsorption [30–34].



(a) The carbon number distribution of mineral oil



(b) The carbon number distribution of wax

Fig. 1. The carbon number distribution of (a) mineral oil and (b) wax.
(a) The carbon number distribution of mineral oil.
(b) The carbon number distribution of wax.

Table 1
Wax appearance temperature of paraffin oil with different wax mass percentage.

Paraffin oil	wax appearance point(°C)
5%wax/LP14	30.03
7%wax/LP14	34.11

2. Materials and methods

2.1. Experiment materials

The continuous phase of the W/O emulsion prepared in the experiments was composed of wax and mineral oil (for preparation details, see section 2.2). The wax was supplied by the Daqing Petrochemical Branch Company (Daqing, China). The wax hydrocarbons range was from C28 to C41. The mineral oil LP14, supplied by the Yan Chang Petrochemical Company (Beijing, China), was composed of hydrocarbons C15 to C27 (0.836 g/cm^3, 15 °C). The carbon number distribution of mineral oil and wax is shown in Fig. 1. The surfactant was non-ionic oil-soluble surfactant (sorbitan monooleate, Span80). The required dosage of wax and surfactant was determined by the mass fraction of paraffin oil. Deionized water phase was used for the internal phase and the water content was the volume fraction of total volume of oil and water.

The wax appearance temperature (WAT) of paraffin oil (prepared by wax and mineral oil) with different wax percentage was measured by DSC, and the results are shown in Table 1. The solubility curve of wax is shown in Fig. 2.

An exponential function was used to fit the solubility curve and the results are provided below.

For 5% wax content,

$$C = -0.349 + 0.7119\exp\left(T/15.01\right) \quad (1)$$

For 7% wax content,

$$C = -0.517 + 0.8836\exp\left(T/16.18\right) \quad (2)$$

where C is the solubility of wax, wt%, and T is temperature, °C.