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Fatty acid-asphaltene interactions at oil/water interface

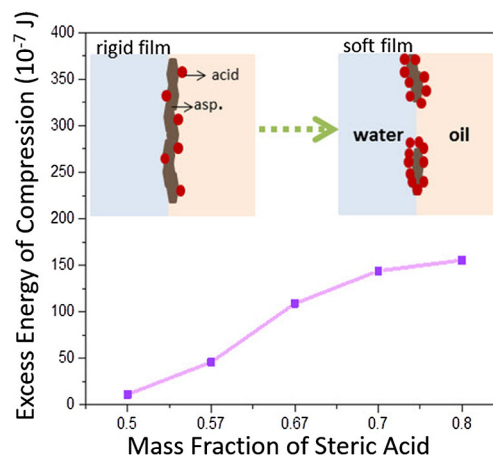
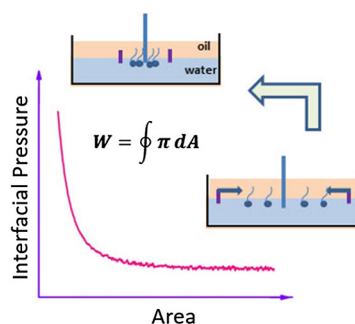
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HIGHLIGHTS

- Studied interactions of asphaltene and model naphthenic acid [stearic acid] at oil-water interface.
- Calculated and investigated excess work of compression for the asphaltene-acid mixed film from their Langmuir trough pressure-area isotherms.
- Identified a decrease in the rigidity of asphaltene interfacial film by stearic acid addition.
- Visualized morphology changes in asphaltene interfacial films with the increase in stearic acid amount using in situ Brewster angle microscope.

GRAPHICAL ABSTRACT

Langmuir Trough Experiments



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ABSTRACT

Asphaltenes have been shown to stabilize water-in-oil or oil-in-water emulsions by forming a viscoelastic interfacial film via molecular aggregation at oil-water interfaces. Natural carboxylic acids (“naphthenic acids”) and their anions present in crude oil are able to compete with asphaltenes to adsorb at the crude oil-water interface, decreasing significantly the crude oil-water interfacial tension. In this study, we designed a group of experiments to systematically probe the molecular interactions of naphthenic acid with asphaltenes at the oil-water interface by studying the Langmuir interfacial isotherms.

Stearic acid as a representative naphthenic acid alone was not able to form rigid films at the toluene-water interface, in contrast to rigid interfacial films of asphaltenes. Upon mixing of asphaltenes with stearic acids, non-ideal (non-additive) behavior of interfacial isotherms was observed. Stearic acid was found to associate strongly with asphaltene molecules at the interface and render the films more expanded and flexible. The reduction in rigidity of interfacial film was found to be directly proportional to the amount of the stearic acid present in the system. Washing experiments by replacement of the top phase with fresh solvent showed irreversible adsorption of both asphaltenes and stearic acids at the toluene-water interface. The softening of interfacial film by stearic acid led to reduced compression energy of the interface, measurable quantitatively by defining the excess work of compression (W_{excess}) as a measure of molecular interactions at the oil-water interface. The calculated W_{excess} was found to increase

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with increasing stearic acid concentrations in the mixture as a result of softened interfacial films. In-situ Brewster angle microscopy visualization revealed a progressive reduction of molecular aggregates at the toluene-water interface with increasing addition of stearic acids.

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1. Introduction

Over the past several decades, increasing consumption of liquid fossil fuels has led to a swift decrease in conventional oil reserves, which prompted the development of unconventional crude oil resources such as shale gas and oil sands deposits [1]. Unlike the conventional oil, unconventional oil reserves are made of heavily biodegraded petroleum, typically with high content of naphthenic acids and/or asphaltenes [2]. The presence of high concentrations of these heavy oil components causes great difficulties in oil production, such as formation of highly stable water-in-oil emulsions. Such emulsions are problematic to downstream operations, which are problematic to downstream operations, such as scaling/fouling and corrosion of equipment in refineries [3–5]. More effective separations of W/O emulsions can help reduce the processing costs and improve the productivity and quality of final products. It is therefore highly desirable if not essential to understand the cause of emulsion stabilization, which allows prediction and mitigation of corresponding adverse effect.

Despite their poor definition as a solubility class of petroleum material that are insoluble in *n*-heptane but soluble in toluene, asphaltenes have been considered as the main component that is responsible for stabilizing W/O petroleum emulsions. Previous studies have shown that upon mixing of water with heavy oil, asphaltenes were the main compounds to produce extremely stable W/O emulsions [6,7]. A popular and well-appreciated notion is that the surface-active asphaltenes are able to adsorb irreversibly at the oil-water interface to form a rigid and protective film surrounding the dispersed water droplets [8,9]. Studies on Langmuir-Blodgett films confirmed the formation of two-dimensional asphaltene layers at the oil-water interface. The asphaltene layers at oil-water interfaces were found to be rigid in nature and of measurable mechanical strength. Once asphaltenes adsorbed at the oil-water interface, the equilibrium becomes heavily shifted in favor of irreversible adsorption due to intermolecular association at the interface. Previous studies have shown such irreversible adsorption of asphaltenes at the toluene-water interface that even replenishing the top bulk toluene with pure toluene does not lead to a noticeable desorption [10,11]. Recent studies further suggested the cross-linking of asphaltene aggregates as the cause of the rigidity of asphaltene films, providing mechanical strength that prevents the coalescence of emulsified water droplets and hence increasing emulsion stability [12–14].

Apart from asphaltenes, the indigenous organic acids together with their corresponding soaps are also known to be surface and interfacially active, contributing to stabilizing W/O petroleum emulsions [15]. In heavily biodegraded crude oil, the acid contents are much higher with species ranging from simple alkyl carboxylic acids to fused ring aromatic acids [2]. Several mechanisms have been discovered to be responsible for the stabilization of water-in-crude oil emulsions. First, the acidic molecules could ionize at the oil-water interface and dramatically lower the interfacial tension (IFT) [16]. Studies have shown that the formation of layered lamellar crystalline films could decrease the probability of water droplets coalescence and stabilize W/O emulsions [17–19]. Another mechanism that has been proved by several studies is the presence of high molecular weight acid species as calcium soaps at oil-water

interface, leading to formation of stable W/O emulsions. One particular case is the tetra-acids with a carbon number of eighty (ARN) [20]. Research has found that calcium naphthenates formed from ARN could accumulate at oil-water interface, leading to the formation of highly stabilized emulsion systems [21,22]. Comparing to the mechanisms of ionization and soap precipitation described above, understanding of acid-asphaltene interactions is less developed. Pauchard and Muller et al. showed that diprotic acids and asphaltenes form integrated films with high dilatational elasticity that stabilize crude oil emulsions [23,24]. However, other studies showed both enhancement and diminution of W/O emulsion stability by different acids. Studies by Gao et al. for example showed a significant reduction in the asphaltene-containing toluene-water interfacial tension and softening of the rigid asphaltene films by naphthenic acid addition that destabilized W/O emulsions [25]. Ese and Kilpatrick demonstrated that β -cholanolic acid could either stabilize or destabilize water-in asphaltene-containing oil emulsions, depending on the pH of the aqueous phase and concentration of the acids in oil [15]. They concluded that naphthenic acids seem to enhance the stability of emulsions at the neutral pH and decrease the stability at the alkaline pH; while asphaltene-like acids could stabilize emulsions under all conditions [26]. It becomes clear that asphaltene-acid interactions at oil-water interface are complex in nature and emulsions could be either stabilized or destabilized with various mechanisms and under different conditions by indigenous surfactants. As a result, asphaltene-acid interactions have to be treated carefully on a case-to-case basis.

In this study, we are presenting experimental results showing interactions between asphaltenes and stearic acid at toluene-water interface. Stearic acid is one type of linear NAs containing 18 carbon atoms. It was chosen to represent naphthenic acid for the following reasons. First, stearic acid has high occurrence in nature with simple molecular structure, which simplifies the explanation of the observed isotherms [27,28]. The linear fatty carboxylic acids were found preferentially adsorb at the oil-water interface than other NAs containing cyclic components, indicating that the stearic acid is more likely the component of crude oil that interacts with asphaltenes at oil-water interface [29]. Since this research is focused on the interactions between asphaltenes and natural acid at the oil-water interface, choosing the linear stearic acid to represent NAs would be a good option. In contrast to other NAs with shorter hydrocarbon chains, stearic acid of long carbon chains has minimal solubility in the water subphase. Therefore, the concentration of acid in water phase can be considered negligible, which greatly simplifies the analysis. Pendant drop tensiometer was used to determine equilibrium time needed for the prepared interface to reach a dynamically stabilized state. The change in the interfacial property of asphaltenes films with the addition of stearic acid at various concentrations was studied using Langmuir interfacial trough technique. Film compression energy was calculated from Langmuir interfacial isotherms to evaluate the degree of acid-asphaltene interactions at oil-water interface. Calculations were based on the assumption that the adsorption of individual components at the interface was solely dependent on the partial concentration of the components in the bulk solution. The variation in compression energy can therefore be considered as a measure of the change in interfacial film properties. Washing experiments

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