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Mixed interfaces of asphaltenes and model demulsifiers part I: Adsorption and desorption of single components

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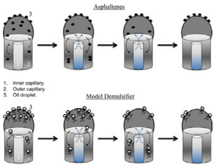
HIGHLIGHTS

- Asphaltenes and Brij®-93 follow Langmuir and Frumkin-type isotherms at liquid–liquid interface.
- Asphaltenes are irreversibly adsorbed at the liquid–liquid interface.
- Brij®-93 is partly desorbed when flushed with pure solvent.

GRAPHICAL ABSTRACT



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ABSTRACT

This article is the first in a series of two aiming to understand the competitive adsorption and desorption dynamics of asphaltenes and a model demulsifier (Brij®-93) at the liquid–liquid interface to broaden the knowledge of the stability of crude-oil emulsions. In this article, the properties of single components are studied. First, the Langmuir and Frumkin isotherms were successfully used to describe the interfacial tension data allowing the determination of the equilibrium adsorption parameters of asphaltenes and Brij®-93. Second, desorption of single compounds (from pure xylene, the adsorption medium) was followed through the use of a double coaxial capillary system. It was found that asphaltenes are irreversibly adsorbed (∼2% amount desorbed) at the oil/water interface even at low surface coverage and adsorption times which confirm the strong interactions present. It was also found that desorption is independent of the pure solvent flow condition and the total volume exchanged. Third, results show that the model demulsifier Brij®-93 is partly desorbed (∼20%) from the oil/water interface. This could be attributed to the distribution of ethyl oxide (EO) groups in the polydisperse sample or to the polydispersity of the aggregates adsorbed which have different adsorption energies. This work provides the fundamental framework for the second part of the series in which adsorption and desorption dynamics of a mixed interface composed of asphaltenes and Brij®-93 will be studied.

1. Introduction

Petroleum extraction is undoubtedly linked to water co-production. Water is present at several stages of the production process and one of the main issues in terms of transportation from the reservoirs to the cracking plants is the formation of emulsions. That is, the stabilization of water-in-oil (W/O) emulsions by crude oil indigenous surfactants such as asphaltenes, resins and naphthenates [1,2]. Asphaltenes are defined as the fraction of petroleum insoluble in *n*-alkane but soluble in toluene (aromatic solvents). Therefore they are not a single chemical compound, but instead a solubility class composed of molecules with different molecular weights and functionalities [3–5]. Asphaltenes are largely responsible for the formation of organic deposits and due to their surface active nature, also responsible for wettability changes of mineral surfaces in the reservoirs [6,7]. It has also been reported that Naphthenic acids [8] are surface active under certain conditions related mainly to pH and that they can influence

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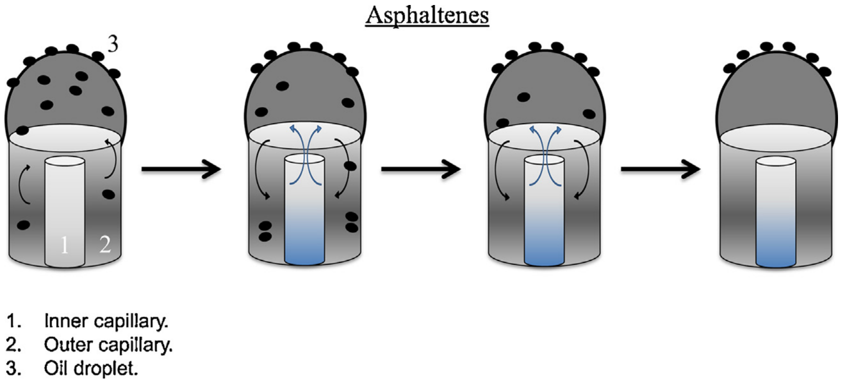

Fig. 1. Coaxial double capillary system showing the desorption process of a surface active molecule that exhibits partly reversible adsorption after the injection of a predetermined volume of pure solvent.

in the stability of emulsions, even if the main mechanisms of emulsion stabilization are attributed to the asphaltenes. The main mechanism of asphaltene-stabilized emulsions is the formation of a rigid and mechanically strong film around the water droplets which prevents them from coalescing [9]. Evidently, stable W/O emulsions are undesired in the oil industry due to high transportation costs, energy demands, corrosion of pipe lines flow assurance issues due to the viscosity increase and subsequent problems in the refining stages. Typical market demands are in the order of 0.5% BSW by volume (bottom, solids, water), which means that efficient and effective methods for removing the water are imperative [10].

Demulsification is the process of breaking emulsions to separate the water from the rest of the crude oil. There are several methods for the separation of water, among them gravitational, centrifugal and electro-coalescence methods. Chemical demulsification refers to the addition of certain chemicals, typically in the order of 1 up to 1000 ppm to promote phase separation by reducing the interfacial tension, thus making it possible for the demulsifiers to mix with the indigenous surfactants (asphaltenes) at the interface [2]. The chemicals (i.e. Demulsifiers) should exhibit both high diffusion rates, so they can quickly go to the interface and interact or compete with the emulsifiers already present [11]; and they should be able to affect the rigid skin that surrounds the water droplets. They can act on the protecting film by changing the elasticity or interfacial viscosity, they can form a film giving rise to an oil-in-water (O/W) emulsion, they can operate as a wetting agent and most of these results being consequences of their interaction with the asphaltene network [12]. The composition of commercially available demulsifiers is broad [11]. Starting with simple organic solvents that dissolve the indigenous surfactants such as benzene, acetone and short-chain alcohols and going up to the category of nonionic surfactants that are known to act as efficient demulsifiers. Members of the latter group include fatty esters, fatty amides, alkyl phenol ethers and polyoxopropylene glycol ethers (PEO-PPO block co-polymers), only to mention some.

Adsorption and desorption kinetics of surface active chemicals can be investigated through dynamic tensiometry, that is, the measurement of the dynamic surface/interfacial tension. When liquid–liquid systems are being studied, a drop of one of the liquids is produced in the second immiscible liquid [13]. This drop can be either pendant or emerging depending on the type of system that is to be studied; it can be either an oil droplet or a water droplet. These drops can nowadays be rapidly analyzed through the use of powerful software coupled with CCD cameras. The technique is commonly known as axisymmetric drop shape analysis (ADSA), and it is widely accepted as a robust and versatile method for measuring the interfacial tension (IFT) [14]. The equilibrium surface/interfacial tension data can be described through adsorption isotherms and equations of state. For instance, the well-known isotherms of Henry, Langmuir, Frumkin and Freundlich have been widely used to describe the adsorption of several surface active compounds onto liquid–air, liquid–liquid and liquid–solid interfaces [15,16].

Several experimental protocols based on the ADSA technique have been proposed to study desorption kinetics or multilayer formation [17–19]. They are of particular interest, mainly because of the ability to follow the interfacial tension as a function of time when the surface active molecules are being desorbed from the interface (see Figs. 1 and 2). The novel coaxial capillary apparatus reported by Ferri et al. [20] and further developed by Kotsmár et al. [21] and Ferri et al. [14] allows the study of convection-enhanced adsorption/desorption kinetics of a liquid–liquid interface. The experimental design consists of a pendant (or emerging) drop formed at the end of a capillary initially at equilibrium with a bulk concentration of surface active molecules. The interface is then driven away from equilibrium by injecting a surfactant free solution (i.e. solvent), thus generating a change in the dynamic interfacial tension [14]. Several factors such as reorganization, multilayer formation, unfolding (proteins), conformations and more importantly the reversibility of adsorption at the interface can also be addressed through this novel method coupled with other studies available in the literature.

This work will elucidate new insight on the coalescence process by studying the interactions present in a mixed interface between asphaltenes and a model demulsifier. This will enhance the understanding of emulsion stability at a molecular level. This is the first part of a series of two publications in which the adsorption and desorption aspects of asphaltenes and Brij®-93 are investigated using a system based on ASDA. First, an analysis on adsorption of single compounds onto liquid–liquid interfaces is performed to obtain equilibrium parameters. Second, using a coaxial capillary system, desorption from a pure solvent is performed to follow the kinetics of the same components (i.e. asphaltenes and a demulsifier). And finally, adsorption isotherms and equations of state are used to describe the IFT versus time data, making it possible to establish the composition at the interface, the percentage of desorption and possible destabilization mechanisms.

2. Experimental

2.1. Asphaltenes

Asphaltenes were extracted by precipitation with *n*-hexane from a chemical-free heavy crude oil of the Norwegian continental shelf. Basic analysis of the crude oil is given in Table 1.To extract the asphaltenes, the crude oil was first heated at a temperature of 60 °C. It was subsequently shaken to ensure homogeneity of the