



## Full Length Article

# Adsorption kinetics of asphaltenes at oil/water interface: Effects of concentration and temperature



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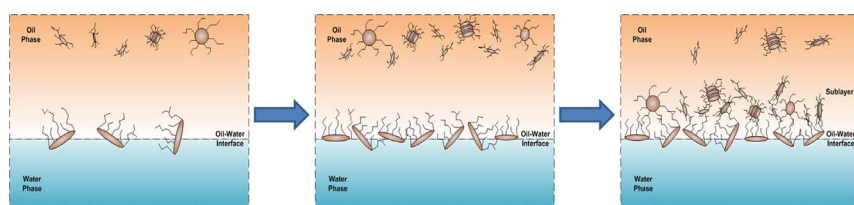
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Asphaltenes are the heaviest components in crude oil. It is generally believed that asphaltenes adsorbed at oil/water interface can form a protective layer to stabilize the water-in-oil or oil-in-water emulsions. In this work, the effects of asphaltene concentration and temperature on the dynamic interfacial tension (IFT) of oil (i.e., toluene)/water interface were systematically investigated using a pendent drop shape method. The adsorption process shows three stages as a function of adsorption time. In Regime I, the reduction kinetics of IFT is diffusion-controlled, during which asphaltenes are adsorbed to the oil/water interface spontaneously. The interfacial diffusion coefficient of asphaltenes to the oil/water interface was found to increase with increasing temperature and decreasing asphaltene concentration, which is much lower than the bulk diffusion coefficient predicted by the Stokes–Einstein equation. In Regime II, the steric hindrance arisen from the adsorbed asphaltenes at oil/water interface from Regime I tends to inhibit further adsorption of asphaltenes to the interface. In Regime III, continuous adsorption of asphaltenes to the sublayer of the interface and reconfiguration of adsorbed asphaltenes or asphaltene aggregates occur, contributing to the continuous but very slow reduction of dynamic interfacial tension. Our results provide useful insights into the adsorption kinetics and adsorption mechanism of asphaltenes at oil/water interfaces under different asphaltene concentration and temperature conditions, with implications to many related interfacial phenomena (e.g., emulsion stability) where asphaltenes are present in oil production.

**Abbreviations:** IFT, interfacial tension; CNAC, critical nanoaggregation concentration; CCC, critical clustering concentration

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## 1. Introduction

As one of the most problematic components in crude oil or oil products, asphaltenes have attracted much research interest in petroleum industry [1–5]. Asphaltenes are conventionally defined as a solubility class that is soluble in aromatic solvents (e.g., toluene), but insoluble in light n-alkanes (e.g., n-heptane). Asphaltenes are the heaviest and polar components consisting of aromatic hydrocarbon rings with peripheral aliphatic chains, containing heteroatoms such as N, O and S as well as metal elements such as V, Ni and Fe [6–7]. According to the Yen–Mullins model [8], asphaltene molecules comprise polyaromatic cores (consisting of an average number of six fused rings) and aliphatic chains. Several asphaltene molecules may stack to form nanoaggregates, on condition that asphaltene concentration exceeds the critical nanoaggregation concentration (CNAC), due to intermolecular interactions such as the  $\pi$ - $\pi$  interaction. Asphaltene nanoaggregates can further form clusters when the asphaltene concentration is higher than the critical clustering concentration (CCC) [9].

In the oil industry, the formation of water-in-oil emulsion is highly unavoidable and undesirable in the transporting pipelines and downstream refinery equipment [10]. Emulsified water carrying dissolved salts contributes to serious corrosion problems and has a negative influence on the quality of oil products. Asphaltenes are believed to play a crucial role in the stability of the water-in-oil emulsion system. It has been reported that the irreversible adsorption of asphaltenes significantly stabilizes the water-in-oil emulsions along with other components such as resins [11], mineral particles [12] and solids-like waxes. Asphaltenes are reported to be responsible for the rigid film formed at the oil/water interface [13–15] which can hinder drop contraction [13,16] and inhibit drop coalescence.

The interfacial properties of oil/water interfaces in the presence of asphaltenes are important for many interfacial phenomena in oil production. The adsorption of asphaltenes to oil/water interfaces and interfacial tension (IFT) has received considerable attention. The adsorption time of asphaltenes at the initial stage, when IFT dropped drastically, was reported to decrease from more than 1000 s to  $\sim$ 100 s with increasing asphaltene concentration [17–18]. Previous studies on the adsorption kinetics of asphaltenes at oil/water interface [19–21] suggest that the adsorption is diffusion controlled in the initial stage (short time regime). However, it has been widely acknowledged that dynamic IFT decreases with aging time (e.g. hours), whereas the long-term adsorption kinetics of asphaltenes still remains unclear. In addition, despite much effort and considerable progress, there is still no agreement in the literature on the reduction kinetics of the IFT and associated interaction mechanism of asphaltenes [18,20,22–23].

Understanding the influence of temperature on the adsorption kinetics of asphaltenes at oil/water interfaces and the interfacial properties is very important in many industrial operations. For example, in surface mining of oil sands industry, bitumen is extracted using hot water (at 40–80 °C) from oil sands [24]. However, there are only limited studies on the effect of temperature on the interfacial behaviors (e.g. interfacial rheology, interfacial tension) of asphaltenes at oil/water interfaces [25–31]. Yarranton et al. [26] reported that the surface pressure isotherm and modulus (interfacial rheology) of oil/water interface with adsorbed asphaltenes were not significantly different at 23 °C and 60 °C. However, it was reported in two other studies [27,28] that IFT values decreased considerably at temperatures elevated over a wider range of 23 °C–125 °C. These previous studies on the effect of temperature mainly focused on the IFT values or interfacial rheology of oil/water interface with asphaltenes, while no report is available about the temperature effect on the adsorption kinetics of asphaltenes at oil/water interfaces.

In this work, the adsorption kinetics of asphaltenes at oil/water interfaces under elevated temperatures has been systematically investigated. The pendant drop shape method was used to obtain the dynamic IFT curves to investigate the influences of concentration and

temperature, and dynamic light scattering was employed to provide complementary information regarding the states of asphaltenes in bulk solutions. Our results provide useful insights into the effects of asphaltene concentration and temperature on the adsorption kinetics and adsorption mechanism at oil/water interfaces, with implications for an improved understanding of the properties of emulsions and oil/water interfaces in oil production.

## 2. Materials and methods

### 2.1. Materials

Throughout the study, Milli-Q water (Millipore deionized with a resistance of  $\geq$  18.2 M $\Omega$ -cm) was used to prepare the aqueous solution. HPLC grade of n-heptane, toluene and methylene chloride were purchased from Fisher Scientific Canada and used as received. NaCl solution was prepared by adding NaCl into Milli-Q water to the desired concentration. High-purity NaCl was obtained from Sigma-Aldrich USA and used as received.

### 2.2. Sample Preparation

#### 2.2.1. Asphaltenes extraction

Asphaltenes were extracted from a crude oil sample according to ASTM IP143 procedure [30]. Briefly, n-heptane was used to mix with crude oil sample at an n-heptane/crude oil ratio of 30:1 (ml/g) and then the mixture was refluxed under stirring for 1 h. The mixture was placed in a refrigerator and was allowed to cool down for 2.5 h. To obtain raw asphaltenes, the mixture was filtered first and then extracted with n-heptane for 1 h using a Soxhlet extractor to remove n-heptane-soluble components completely. After that, methylene chloride was utilized to extract asphaltenes from the residual filtrate. The obtained asphaltenes in methylene chloride solution were concentrated and then dried under nitrogen flow. The extracted asphaltenes were carefully sealed and stored in the refrigerator before use.

#### 2.2.2. Solution preparation

Asphaltenes were initially dissolved in toluene to prepare a 2000 mg/L stock solution. To prepare different concentrations of asphaltene solution, the stock solution was sonicated for 5 min before diluting it with toluene to a desired asphaltene concentration. The concentration of asphaltene solution used in this study ranged from 50 mg/L to 2000 mg/L. Before each use, the diluted asphaltene solutions were sonicated for 5 min and degassed for another 5 min to eliminate possible bubbles which might form in the oil droplet at elevated temperatures during interfacial tension measurements [32–33]. Fresh asphaltene solutions were prepared and used in all experiments.

### 2.3. Interfacial tension (IFT)

The dynamic IFT between oil and brine water was measured by the pendant drop shape method using a goniometer (Ramé-hart Instrument Company, USA). High salinity and high temperature conditions are commonly encountered in reservoirs, and high-salinity flooding has been also used for enhanced oil recovery [34–37]. In this study, to better understand the properties of oil/water interface under high salinity conditions, sodium chloride solution of fixed concentration (i.e., 1 M) was used as brine water. During a typical experiment, the oil phase (asphaltene solution) was loaded into a syringe, which was connected to a U-shaped needle. The U-shaped needle was immersed into a fused quartz cell filled with brine solution. A syringe pump was used to generate asphaltene droplets (with a controlled volume of 10–20  $\mu$ L) [38]. IFT was determined by analyzing the drop profile captured by a camera, based on the Young–Laplace equation [39]. IFT data were collected every two seconds for 2 h.

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