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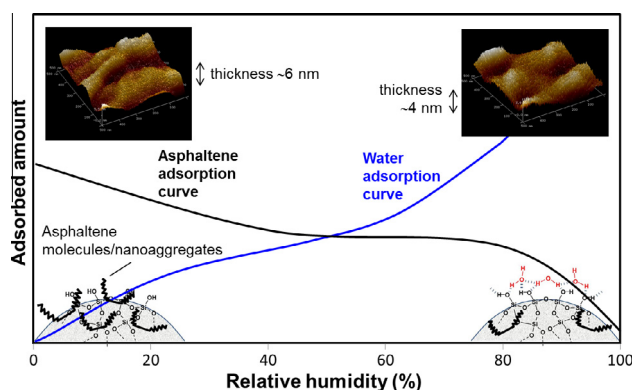
Asphaltene adsorption on quartz sand in the presence of pre-adsorbed water



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GRAPHICAL ABSTRACT



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ABSTRACT

Background and hypothesis: In the oil industry, asphaltenes are known for their tendency to aggregate in solution and to deposit on surfaces, with both properties being connected with operational problems associated with recovery, production and refining. Interactions involving asphaltenes and other crude oil components have been a major aspect of investigation in attempting to understand the full nature of these problems. Water is implicated in asphaltene behavior in solution, for example, where it has been found to delay the deposition of asphaltene aggregates. At interfaces, there is evidence that water-in-crude oil emulsion stability is enhanced through asphaltene-water interactions, and there have been a few reports that asphaltene adsorption on mineral surfaces is reduced in the presence of water. We consider the latter aspect, because the instances of reduced adsorption to date have not attempted to quantify the effect. Previous studies showed that vapor-phase adsorption of organic molecules is reduced in the presence of pre-adsorbed water and we were interested to determine whether the same is true for liquid-phase adsorption of asphaltenes.

Experiments: The surface of quartz sand was controlled by pre-adsorption of water from different relative humidity (RH) environments as the water adsorption isotherm is known from previous studies. These pre-conditioned sand samples were used as substrates for the adsorption from toluene solutions of *n*-heptane-precipitated asphaltenes (C7A) from an Athabasca oil sands bitumen. To supplement the adsorption behavior, atomic force microscopy (AFM) images were taken of the resultant sand grains at 0 and 80% RH, and low-field NMR was used to estimate the sand wettability.

Findings: Asphaltene adsorption on sand is sensitive to surface-adsorbed water, with ~4-fold reduction in adsorption when increasing the RH from 0 to 100%. This is in general agreement with previous vapor-phase adsorption of small organic molecules, and is therefore believed to be the first

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demonstration of the effect of pre-adsorbed water on adsorption from solution. Asphaltene adsorption as a function of RH is the converse of literature water adsorption isotherm data. Three asphaltene adsorption regions have been tentatively identified based on water adsorption behavior and the literature interpretation of water structure on quartz: the highest asphaltene adsorption occurs at very low RH, decreasing to a near-constant value in the range ~40–80% RH, followed by a rapid decrease beyond 80% RH. Further analysis strongly suggests that asphaltene adsorption decreases linearly with the thickness of the adsorbed water film. The effects of RH on asphaltene adsorption are also reflected in AFM images and NMR wettability results.

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1. Introduction

Asphaltenes are separated from crude and residual oils by precipitation with alkane solvents. They are a heterogeneous class of molecules which contrast sharply in polarity and structure from the majority of the crude oil components, which accounts for their predisposition to self-aggregation and adsorption at surfaces. In practice, this leads to undesirable consequences, amongst which are deposition and wettability modification during crude oil extraction, production and refining.

A typical chemical analysis of a petroleum asphaltene is ~80% C, ~8% H and ~12% heteroatoms (O, N and S), with minor contributions from coordinated heavy metals. The asphaltene skeleton consists of a planar polycyclic aromatic 'nucleus' with varying degrees of aliphatic and alicyclic hydrocarbon substitution. The heteroatoms are variously distributed throughout the structure depending on the crude oil source and provide an intrinsic degree of surface activity.

Although asphaltenes are not surface-active to the same extent as classical surfactants, they do share the properties of self-aggregation and adsorption at different surfaces, including water [1].

Since water is known to be an integral part of all crude oil reservoirs, it cannot be ignored when considering surface and colloidal chemical aspects of crude oil recovery and processing. Workers in this field will be particularly familiar with the presence of water as a discrete phase in water-in-crude oil emulsions, owing to the necessity to dehydrate the oil before it can be exported or refined. For this reason, systems containing water dispersed as microscopic droplets in crude oil are now relatively well understood, and adsorption of asphaltenes at the oil/water interface is considered to be an important emulsion stabilization mechanism, since despite only a modest reduction in oil/water interfacial tension, strong interfacial films develop over time [2–4]. It is possible that water plays an active role during asphaltene stabilization of macroscopic w/o interfaces, promoting the formation of asphaltene networks [5]. Irreversibly-adsorbed films of this type produce viscoelastic barriers which enhance the kinetic stability of water-in-crude oil emulsions [6] and are seen at aqueous interfaces of retracted pendant drops of crude oil [7] and asphaltene solutions in toluene [6,8].

Self-aggregation, whether at interfaces or in solution, is understood to result from π - π stacking of the asphaltene polycyclic aromatic regions [9], although electrostatic and H-bonding contributions involving water have also been identified in model asphaltene systems [10–12]. This latter view supports other results from simulation and experiment, that low water concentrations promote asphaltene nanoaggregation in toluene solution [13], which is suggested to involve intermolecular H-bonded water bridges and asphaltene heteroatoms, e.g. $[A_1O \cdots H-O-H \cdots NA_2]$ or similar (the subscripts denoting different asphaltene molecules).

Likewise, solubilization of water in toluene increases in the presence of dissolved asphaltenes [14,15]. However, the counterintuitive

finding that the adsorption capacity decreases with increasing asphaltene concentration has been explained by Andersen and coworkers as indicative of water binding to polar sites on the exterior of asphaltene nanoaggregates [15].

From the foregoing it appears that there are a number of examples where asphaltene/water interactions are implicated in the behavior of crude oils, and for which further understanding at the molecular or nano-scale is required. The present work considers a particular example of this, namely the effect of water on asphaltene adsorption on quartz sand. Although our interest stemmed originally from the structure of oil sands, it will be relevant to sandstone reservoirs in general. In the case of oil sands, however, the structure has long been thought of as consisting of bitumen separated from the sand surface by a thin (few nm) layer of water [16–19].

In such systems, it is important to understand how the presence of water might affect the adsorption behavior of crude oil components, such as asphaltenes. It is generally considered [20,21] that deposition of asphaltenes on mineral surfaces is an important mechanism to explain wettability changes occurring in the reservoir [22–24], with the most polar asphaltene fractions showing the greatest effects [25]. This is significant, since understanding the factors that affect reservoir wettability, including the effect of water, should aid efforts to improve crude oil recovery.

Asphaltenes adsorb at solid surfaces [1], essentially to produce monolayers of nanoaggregates, the latter comprising stacks of ~6 asphaltene molecules, according to the Yen-Mullins aggregation model [26]; further aggregation of nanoaggregates to form clusters at sufficiently high concentrations leads to thicker adsorbed layers [27,28]. According to Adams' comprehensive review on asphaltene adsorption, by assuming 3 nm asphaltene (nano)aggregates with a density of 1200 kg/m³, the maximum surface coverage for an asphaltene monolayer is calculated to be ~3.6 mg/m² [1]. The same review included a brief discussion of the effects of water on asphaltene adsorption on mineral surfaces, with the conclusion that water reduced adsorption due to competition for surface sites.

Here, we focus on this aspect in particular. Collins and Melrose were the first to question whether the presence of water on mineral surfaces would modify asphaltene adsorption [17]. They found that for kaolinite, asphaltene adsorption decreased from 30 mg/g (dry clay) to 22 and 13 mg/g after the pre-addition of 2.3 and 6.6% water, respectively [17]. Saada et al. [29] concluded that asphaltene adsorption from water-saturated toluene onto the clays kaolinite and illite is related to differences in clay hydrophilicity – the more hydrophilic the clay (illite), the lower was asphaltene adsorption. Previously, Menon and Wasan [30] reached a similar conclusion for sodium montmorillonite, for which asphaltene adsorption was reduced significantly on this hydrophilic clay in the presence of pre-adsorbed water. Alipour Tabrizy et al. [31] found that the effects of humidity ('dry' versus 'wet') on asphaltene adsorption were different for calcite, quartz and kaolinite. Adsorption increased by ~60% for calcite, whereas quartz and kaolinite showed decreases of 23% and 16%, respectively.

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