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Understanding Mechanisms of Asphaltene Adsorption from Organic Solvent on Mica

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ABSTRACT

The adsorption process of asphaltene onto molecularly smooth mica surfaces from toluene solutions of various concentrations (0.01 - 1 wt%) was studied using a Surface Forces Apparatus (SFA). Adsorption of asphaltenes onto mica was found to be highly dependent on adsorption time and concentration of the solution. The adsorption of asphaltenes led to an attractive bridging force between the mica surfaces. The adsorption process was identified to be controlled by diffusion of asphaltenes from the bulk solution to the mica surface with a diffusion coefficient on the order of 10^{-10} m^2/s at room temperature, depending on asphaltene bulk concentration. This diffusion coefficient corresponds to a hydrodynamic molecular radius of approximately 0.5 nm, indicating that asphaltene diffuses to mica surfaces as individual molecules at very low concentration (e.g. 0.01 wt%). Atomic force microscopy (AFM) images of the adsorbed asphaltenes on mica support the results of the SFA force measurements. The results from the SFA force measurements provide an insight on the molecular interactions (e.g. steric interaction, bridging attraction as a function of distance) of asphaltenes in organic media and hence their roles in crude oil and bitumen production.

Keywords: asphaltenes, adsorption, interaction forces in solvent, Surface Forces Apparatus

INTRODUCTION

Interfacial phenomena govern the properties of solids, liquids and gases in pharmaceuticals, food products, cosmetics, and petroleum processing, to name a few. From interfacial studies, one can determine the fundamental mechanisms and kinetics of film formation, surfactant adsorption, and film rupture that ultimately govern the behaviour of dispersion systems. Of extreme importance in the petroleum industry is the formation of stable water-in-oil (w/o) emulsions that result from the adsorption of bituminous compounds at an oil-water interface. The interactions and assembly of adsorbed molecules or their aggregates lead to formation of a protective layer that resists droplet-droplet coalescence.[1–11] Stable emulsions have been a major challenge in petroleum production, affecting process throughput and downstream operations such as upgrading. It is necessary to develop knowledge on the formation of these protective layers to design suitable protocols for film disruption and prevention of stable emulsion formation.

Polyaromatic asphaltenes containing a significant fraction of heteroatoms such as oxygen, nitrogen and sulphur are commonly considered the problematic component of crude oil and bitumen. They readily partition at the liquid-liquid and solid-liquid interfaces. The complex nature of asphaltene molecules makes it difficult to define their molecular structures. As a result asphaltenes are poorly defined as a solubility class material that is soluble in toluene but insoluble in alkanes such as *n*-heptane.[12,13] Due to the presence of heteroatoms, asphaltenes are partially polar, and have a tendency to adsorb at the oil-water and oil-solid interface.

The adsorption of asphaltenes on solids such as pipelines and clay particles create added processing difficulties. While pipeline deposition can lead to pipe plugging, adsorption onto clay solids modifies their wettability, decreasing efficiency of oil liberation from the solids and increasing solids partitioning at the oil-water interface.[14-20] In oil production, the formation of a

complex multiphase dispersion layer in the middle of oil-water separation vessel, known as rag layers, is frequently encountered.[21,22] The rag layers are extremely stable multiemulsions with the stabilizing species identified as surfactants, asphaltenes and inorganic fine particles. The inorganic fine particles are predominantly iron-containing solids that readily associate with organic compounds such as asphaltenes to form biwettable solids which preferentially stabilize w/o emulsions. The presence of this highly viscous rag layer with medium density prevents the separation of emulsified water from oil or vice versa.

The adsorption of asphaltenes on mineral surfaces has commonly been studied by quantitatively determining the amount of asphaltene adsorbed using i) solution depletion method,[23,24] ii) quartz crystal microbalance,[25,26] iii) photothermal surface deformation spectroscopy[27] and iv) thermal gravimetric method, or qualitatively by contact angle measurements.[16,17] Common clay minerals used in adsorption studies are kaolinite, illite, montmorillonite, mica and chlorite. The common non-clay minerals used in adsorption studies are quartz, calcite, feldspar, limestone, and dolomoite. Dudasova et al.[28] studied the adsorption of asphaltenes from five different petroleum sources onto different organic surfaces and observed Langmuir-type adsorption. They concluded that the adsorption depends more upon the solid surface than upon the origin of the asphaltenes and that the heteroatomic species in asphaltenes were important for surface adsorption. According to Buckley,[29] the driving force for asphaltene adsorption on inorganic solids in the absence of water is mainly through polar interactions between oil and a solid, which leads to surface precipitation of asphaltenes. Mica, because it can be cleaved to provide uniform and molecularly smooth surfaces has been used to study asphaltene adsorption.[14,30] Recently, Adams published a comprehensive review on the chemical and physical nature of asphaltenes and

corresponding characteristics of asphaltene adsorption.[37] The above research provided valuable information on stabilization mechanisms and adsorption kinetics of asphaltenes.

Due to the complexity of asphaltene molecules and limitations of some of the techniques described, probing molecular mechanisms of asphaltene adsorption on inorganic solid surfaces from organic solvents and subsequent association remains rather limited. In all of these studies, asphaltenes are extracted from crude oils and solubilised in mixtures of toluene and *n*-alkanes. According to Buckley,[28] the driving force for asphaltene adsorption on inorganic solids in the absence of water is mainly through polar interactions between oil and a solid, which leads to surface precipitation of asphaltenes.

Determining the organization of asphaltenes at a solid-liquid interface has been the subject of numerous studies generally involving determination of adsorption isotherms. Several authors have reported Langmuir-type adsorption isotherms, indicating the formation of a monolayer of asphaltenes at the toluene-quartz interface.[17,29] Whereas, others have found stepwise or linear increase in adsorption, suggesting a multilayer adsorption process, for example, toluene to glass, and toluene to quartz/dolomite/kaolin/calcite.[27,30,31] Ellipsometry studies confirmed the presence of multilayer asphaltenes adsorbed on solids.[32] Acevedo et al.[27,33] suggested that a weakly aromatic asphaltene that is stable in its crude oil would form a single layer whereas a strongly aromatic asphaltene, which exhibits a tendency to precipitate, would form a multilayer.

The kinetic aspect of asphaltene adsorption on metal surfaces has also been studied. With quartz crystal microbalance measurements, Xie and Karan[34] showed that the initial asphaltene adsorption process on gold surface is controlled by the diffusion of asphaltenes from the bulk solution to the substrate surface. The equilibrium state is then reached only after an extended

adsorption period, which can be as long as several days, as also observed by Acevedo et al.[33] Using solution depletion method, Goual et al.[26] determined two distinct regimes of asphaltene adsorption on silica surface as a function of asphaltene concentration: at low bitumen concentration, the system did not reach a steady-state of adsorption because the adsorbed amount of asphaltenes was still increasing linearly even after 8 h of adsorption; whereas at high bitumen concentration a steady-state of adsorption was reached after just few min (<2 min). The authors proposed that the transition between these two regimes could be due to the stabilization of asphaltenes by increased amount of resins at high bitumen concentrations, better solubilisation of asphaltene would prevent any further adsorption.

In a previous study,[14] we measured the interactions between asphaltene-asphaltene surfaces in toluene and heptane using a surface forces apparatus (SFA). Strong steric repulsion was observed between asphaltene surfaces which are responsible for preventing water droplets from coalescing and leading to a stable emulsion. In the present study, we investigate the adsorption mechanisms of asphaltenes (from bulk solution) to hydrophilic solid surface and the associated molecular interactions.

Due to its unique ability to measure simultaneously the interaction force, F, as a function of the absolute surface separation, D, and the local geometry of two interacting surfaces (the local radius R or contact area) at a force sensitivity of <10 nN and an absolute distance resolution of ~0.1 nm *in situ* and in real time, SFA has been extensively used in studying governing forces of many biological and non-biological systems.[36-39] SFA is one of the most powerful techniques for the research objective of this study. The force-distance curves or so-called force profiles obtained from SFA measurements could provide important information on build-up kinetics of adsorbed layers via accurate and absolute film thickness measurement, and properties of adsorbed layers

such as asphaltene-asphaltene interfacial energy and molecular conformation changes of the adsorbed asphaltene layers through the force measurement.

MATERIALS AND EXPERIMENTAL METHODS

Materials. Vacuum distillation feed bitumen was provided by Syncrude Canada Ltd., Alberta, Canada. Asphaltenes were precipitated from bitumen by adding 40 times of n-heptane to bitumen by volume. The asphaltenes used in this work were prepared using well-established procedures reported elsewhere.[40] The elemental analysis showed C, H, N, O and S compositions of the Asphaltenes being ~79%, 8%, 1.2%, 1.3% and 7.6% by weight, respectively. Asphaltene solutions were prepared using as received High-Performance Liquid Chromatography (HPLC)-grade toluene (Fisher). Solutions were prepared fresh and mildly sonicated for 15 min prior to their use. Muscovite mica sheets were purchased from S & J Trading Inc. (Glen Oaks, NY).

Sample preparation. Muscovite mica can be easily cleaved to obtain large atomically smooth surfaces, allowing to prepare reproducible clean substrates. The cleaved mica basal planes are similar to many clay basal surfaces. A thin layer (~500 Å) of silver was coated on one side of the cleaved thin mica sheets of a few microns thick. With the silver facing down, the mica was glued onto cylindrically shaped silica glasses before loading them in the SFA chamber. For the SFA experiments, a desired asphaltene solution was injected to fill the gap between two closely placed mica surfaces in the SFA chamber. The chamber was sealed and saturated with the vapor of the same solvent.

Surface Forces Measurements. The SFA is an ideal technique for exploring the adsorption kinetics and interactions between the adsorbed asphaltene layers.[14,36-39,41,42] During the force measurements, if the surface separation D is much smaller than local radius of curvature R, the

surface interaction of the crossed-cylinder configuration in SFA is equivalent to that between a sphere of the same radius and a flat surface.[36] The surface separation and deformation is monitored in real time and in situ by Multiple Beam Interferometry (MBI) using Fringes of Equal Chromatic Order (FECO).[43,44] The interaction forces are determined by the measured deflection of the calibrated force-measuring springs. The interaction force *F(D)* between two crossed-cylinder surfaces can be converted to the interaction energy per unit area of two flat surfaces, *W(D)*, using the well-established Derjaguin approximation.[43-47]

$$F(D) = 2\pi R W(D) \tag{1}$$

The adhesion energy per unit area between two surfaces of the same materials in solvent, W_{ad}, can be determined from the pull-off force, F_{ad} (the force required to separate the surfaces from adhesive contact), by: [43-47]

$$W_{ad} = 2\gamma = F_{ad}/1.5\pi R \tag{2}$$

In this study, the reference distance (D = 0) was set as the adhesive contact between the two bare mica surfaces in air prior to injecting the asphaltene solution between the surfaces. During a typical force measurement, the normal force-distance profile (*F vs. D*) was obtained by an initial approach to a "hard wall" or "confined layer thickness", followed by separation of the two surfaces (note: the "hard wall" distance or the "confined layer thickness" in this study is defined as the mica-mica separation distance or thickness of confined asphaltenes which barely changed with increasing the normal load or pressure).

AFM Imaging. AFM topographical images of the sample surfaces were obtained using an Agilent 5500 Molecular Imaging Microscope (Agilent Technologies, Inc., Chandler, AZ), operated under AAC mode in air. The AFM images were used to observe changes in structure,

coverage, relative layer thickness and aggregate size of adsorbed asphaltenes. Silicon nitrate cantilevers with a nominal resonance frequency of 300-350 kHz (RTESP, Veeco, Santa Barbara, CA) were used in the AFM experiments. The amplitude set point was set at 95% - 98% of the free amplitude in order to avoid surface damage.

RESULTS AND DISCUSSION

The surface force measurements between two mica surfaces in asphaltene solution using SFA provided information on the adsorption and built-up of asphaltenes on mica. The typical experimental configuration and adsorption process of asphaltenes on mica are shown in Figure 1.
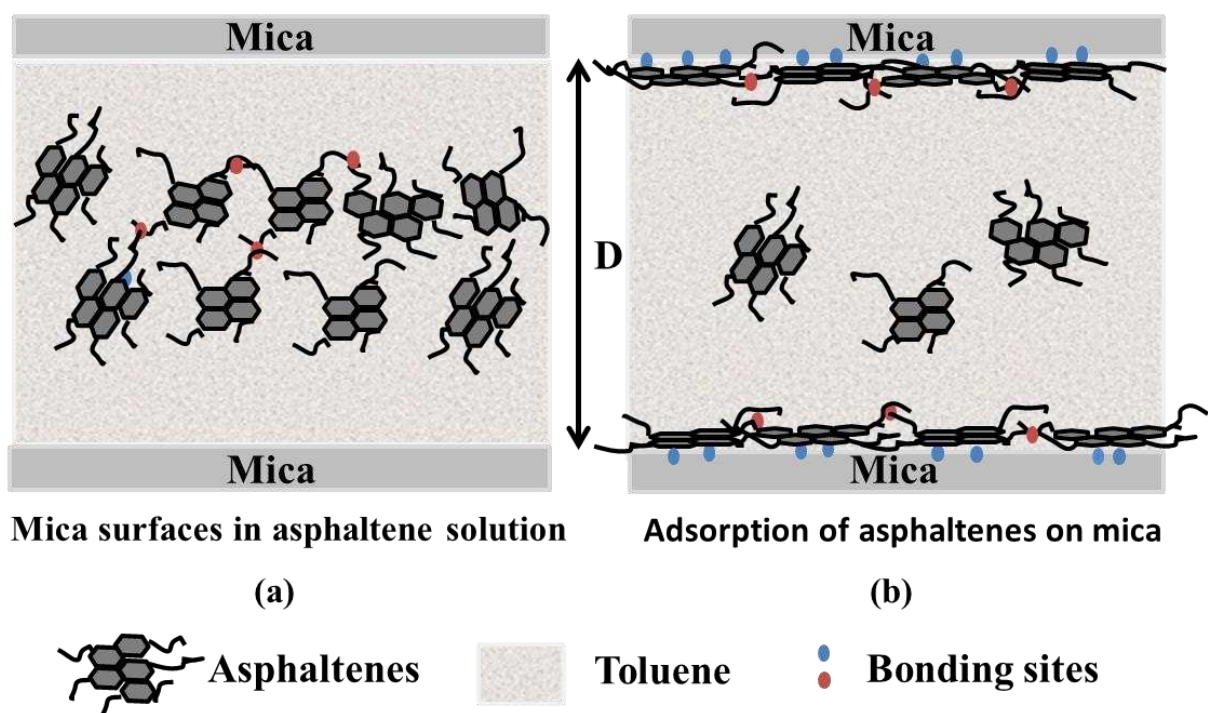

Figure 1. Experimental configuration and illustration of the adsorption process of asphaltenes onto mica in organic solvent: (a) mica surfaces in asphaltene solution, and (b) asphaltene adsorption process indicating the molecular orientation of asphaltene molecules to mica surface at 0.01 wt% asphaltene solution.

Figure 1a shows asphaltene solution confined between two bare mica surfaces. Figure 1b shows the evolution of the adsorption and accumulation of asphaltenes on mica to form a layer. Asphaltenes are known to contain heteroatoms such as O, N and S. Nitrogen atoms are mostly located in the polyaromatic structure of asphaltene while oxygen and Sulfur atoms are either on the alkyl chains or at the corners of the polyaromatic structure. Although the exact conformation of asphaltenes on mica in organic solvent could not be directly determined using the SFA, the asphaltene molecules would most likely have their heteroatom (i.e., N, O and S) containing polyaromatic rings as binding sites to the mica surface, as schematically illustrated in Figure 1b. Such binding configuration has been confirmed by recent studies.[48,49]

Adsorption of Asphaltenes on Mica. Figure 2 shows the typical force-distance curves between two mica surfaces in 0.01 wt% [(a)], 0.1 wt% [(b)] and 1 wt% [(c)] asphaltene solutions at different adsorption time, measured during approach (In) and separation (Out), respectively. The two surfaces were brought closer until the confined layer thickness barely changed with the increased normal load. The thickness of the adsorbed asphaltene layer on mica (T) was determined as half of the confined layer thickness measured between the surfaces, i.e., $T = \frac{1}{2} D$. The thickness of the asphaltene layers at different concentrations and time intervals were determined. Figure 2 (a-In) shows the force-distance profile between two mica surfaces approaching each other in 0.01 wt% asphaltene solution. On approach after 5 min of adsorption, repulsion was observed at ~30 nm separation. With increasing the normal load, the confined layer is compressed to ~12 nm which corresponds to an adsorbed layer thickness of ~6 nm asphaltene layers on each mica surface, and is in good agreement with the previously reported

values.[14,50,51] A slight increase in the thickness of confined asphaltene layer from ~12 nm to ~16 nm was observed as the adsorption time increased from 5 min to ~4 hr.
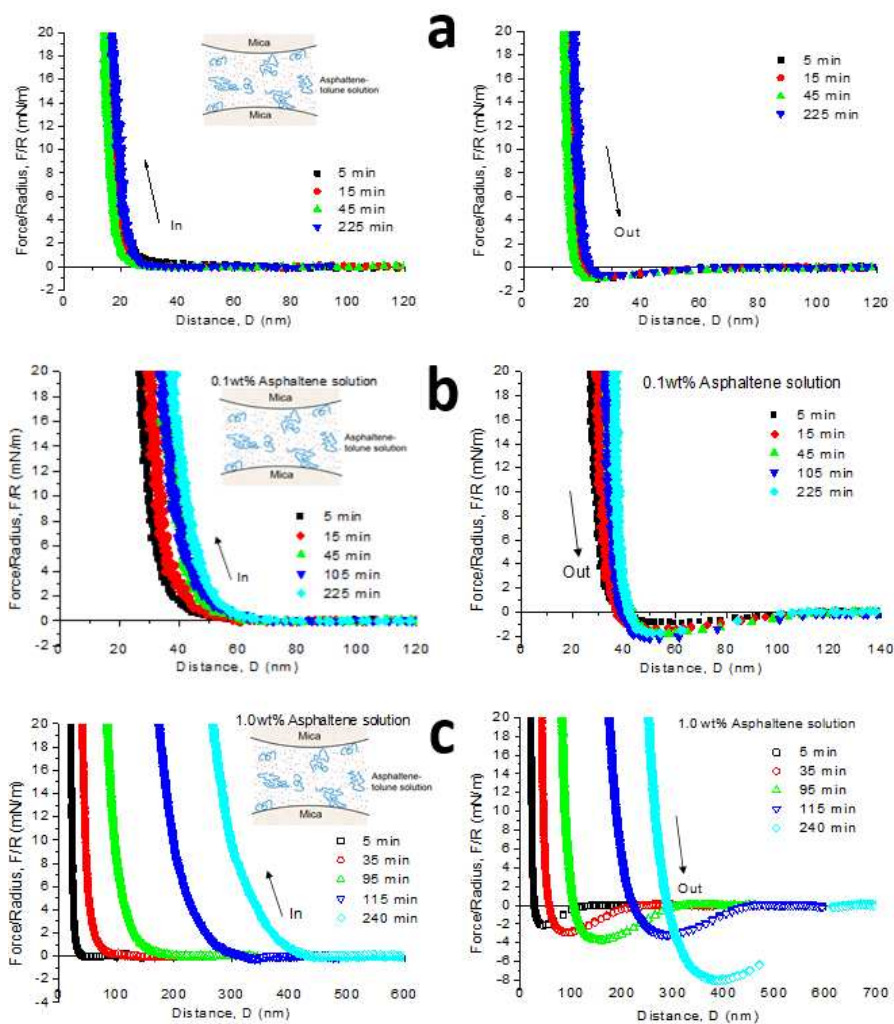

Figure 2. Approach and separation force-distance profiles of two mica surfaces in asphaltene-toluene solutions of different concentrations at different time intervals: (a) 0.01 wt %, (b) 0.1 wt%, and (c) 1.0 wt% asphaltenes in toluene. The reference distance ($D = 0$) was set as the adhesive contact between the two bare mica surfaces in air prior to injecting the asphaltene solution between the surfaces. In this figure, "In" indicates approach of the two surfaces and "Out" indicates separation of the two surfaces.

During separation, an attraction of $F_{ad}/R \sim -0.9 \ mN/m$ ($W_{ad} = 0.19 \ mJ/m^2$), was detected. The adhesion did not vary significantly with increasing adsorption time. The less steep repulsion measured from ~30 nm to ~12 nm during approach is attributed to steric interaction of asphaltenes, which indicates that the adsorbed asphaltene layers were loosely packed and more compressible. The attraction measured during the separation was due to the bridging interaction as a result of interdigitation of the confined asphaltenes between the two mica surfaces. It has been reported that asphaltenes tend to form nano-aggregates, even in a good solvent (e.g., toluene).[52,53] Though the present concentration is very low, under compression, the loosely adsorbed asphaltenes are likely to interdigitate, resulting in bridging attraction.

Increasing the solution concentration to 0.1 wt% and 1.0 wt%, the build-up of asphaltene layers becomes much faster with a significant increase in the confined layer thickness to ~100 nm within ~1.5 hours of adsorption in 1.0 wt% asphaltene in toluene solutions. It is also interesting to note that the repulsive forces become much longer ranged, with a corresponding increase in the confined layer thickness with increasing adsorption time. Such an effect is evident for the 1.0 wt% solution case shown in Figure 2(c), indicating a more compressible adsorbed asphaltene layer. The increase in the confined layer thickness suggests the build-up of 3-D structures of adsorbed asphaltenes on mica surfaces. Although the repulsion is experienced at a much larger separation distance with increasing asphaltene concentration and adsorption time, the decay of the repulsion with decreasing the separation distance appears to be more or less the same, indicating the same nature of the steric repulsion.[14] This repulsive force rises more steeply at smaller separations once the layers become more compressed, indicating the dominate effect of the excluded volume.[43] In addition, during separation, we observe progressively increasing adhesive bridging forces with increasing asphaltene concentration and adsorption time, as well as

at a given asphaltene solution concentration and adsorption time, as shown in Figure 2. All the separation force profiles show that the asphaltene layers were stretched before the two surfaces detached from each other. The above results indicate several aspects of the adsorption mechanism of asphaltenes on mica. First the asphaltenes exhibit a strong affinity to mica as such that the bridging force between two mica surfaces due to interdigitation of the adsorbed asphaltenes could be realized. Second, the adsorption of asphaltenes is a strong function of solution concentration of asphaltenes and adsorption time. Third the adsorbed layers of asphaltenes are soft and compressible under normal load, but with dangling branches to cause long range steric repulsion and high compressibility of the asphaltene layers shown in Figure 2.

Figure 3 shows the typical AFM images of mica and asphaltene films adsorbed on mica from asphaltene in toluene solutions. Freshly cleaved mica was submerged in 0.1 wt% asphaltene in toluene solution for different periods of times and then dried with blowing nitrogen before imaging. The root-mean-square (RMS) roughness of surfaces increased from 0.2 nm to about ~1 nm (Figure 3(a) to 3(f)) in about ~4 hours. The increase in surface roughness with increasing immersion (adsorption) time suggests that the asphaltene film is built up by nanoaggregation of asphaltene molecules. The topography of the adsorbed asphaltene films exhibits heterogeneous nature. Similar heterogeneous patterns were observed for Langmuir-Blodgett deposited asphaltene films by others.[39, 54]
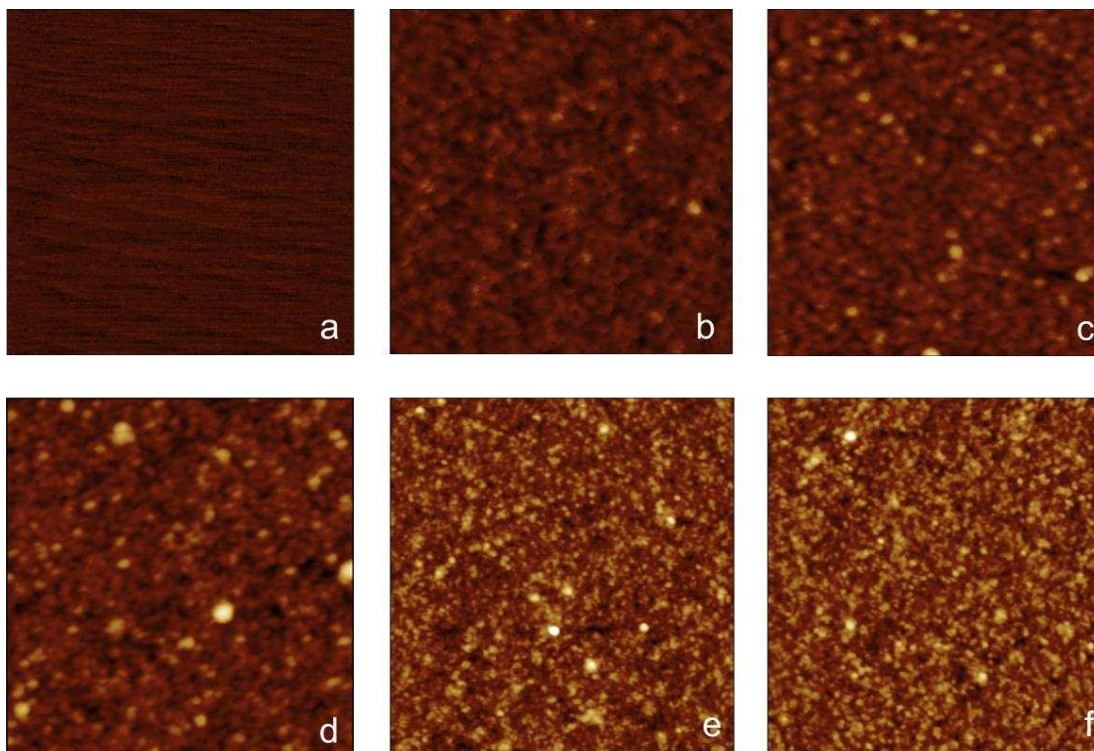
Figure 3. AFM images in air for (a) bare mica surface, and asphaltene layer adsorbed on mica surface for (b) 5 min, (c) 15 min, (d) 45 min, (e) 105 min and (f) 225 min immersion time in 0.1 wt % asphaltene-toluene solution. Note that the surfaces were gently dried with blowing nitrogen before imaging. Image size: $1\mu m \times 1\mu m$.

Our results show that during separation, adhesive bridging forces dominate for all the cases at small distances, exhibiting an adhesive well at 'contact' (seen in Figure 2). The depth of the adhesive well is Fad/R ≈ -1 mN/m (in Figure 2b at 5 min), which corresponds to an adhesion energy in the order of $W_{ad} = F_{ad}/1.5\pi R \approx 0.21$ mJ/m^2. The force curve at 5 min adsorption time at 0.1 wt% concentration has similar values to our previously reported confined layer thickness (~30 nm), repulsion range (~30 to 60 nm), and adhesion energy (0.2 mJ/m^2) of two asphaltenes

films right after immersed in toluene (within ~5 min).[14] This validates the consistency in our measurements.
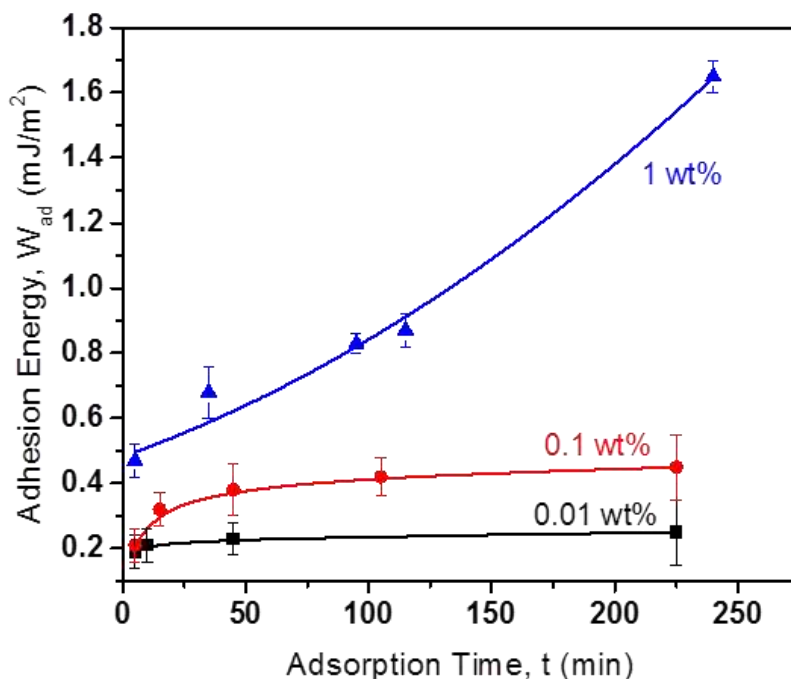

Figure 4. Adhesion energy W_{ad} between mica surfaces in different concentrations of asphaltene in toluene solutions as a function of adsorption time at room temperature.

To determine the controlling mechanism of asphaltene adsorption from their toluene solutions, the thickness of confined asphaltene layers was plotted as a function of square root of time, as shown in Figure 5. The increase in the range of repulsion observed from the force profiles above is mainly attributed to the compressibility of the adsorbed (loosely packed and patchy) asphaltene layers, which is pronounced at higher concentrations. Figures 2 (a-In), (b-In) and (c-In) show that the confined layer thickness increases with increasing adsorption time for all the cases of different asphaltene concentrations and the increment is more pronounced at higher

concentrations. Therefore, we focus our discussions only on the case of lowest asphaltene concentrations (i.e., 0.01 wt%) where the compressibility effect and the aggregation is minimum.
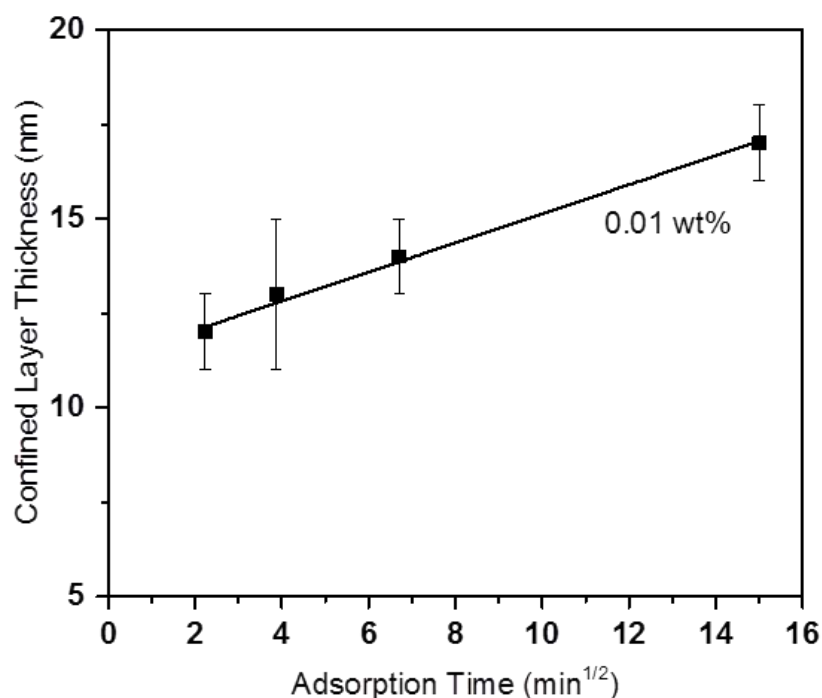
Figure 5. Confined layer thickness (equivalent to two layers) plotted as a function of square root of adsorption time for 0.01 wt% of asphaltene-toluene solution.

The results in Figure 5 show that the confined layer thickness follows a linear relationship with the square root of adsorption time. This result is in good agreement with the result of asphaltene interfacial tension study conducted by Rane et al.[9] For higher concentrations (0.1 wt% and 1 wt%) the confined layer thickness does not follow a linear relationship as well as the case of 0.01 wt%. Thus, for our experimental conditions, asphaltene adsorption from its lowest concentration solution, where layer compressibility was assumed to be negligible, is controlled by the diffusion

of asphaltene molecules from the bulk solution to the substrate. At higher asphaltene concentrations, the deviation of the film thickness increase with increasing inverse square root of adsorption time $(1/\sqrt{t})$ from a linear relationship suggests the transport of asphaltene molecules in the form of aggregates in bulk solutions at high asphaltene concentrations, a well-established phenomenon of CNAC condition measured by Andreatta et al. using ultrasonic method.[52] According to Ward and Tordai,[56] the initial rate change in the adsorbed mass density is a linear function of the inverse of the square root of time, as given by:

$$\frac{d(\Gamma)}{dt} = C \left(\frac{D^*}{\pi t} \right)^{1/2} \tag{3}$$

where C is the concentration of adsorbing species in the bulk solution, Γ is the adsorbed mass density, D^* is the diffusion coefficient, and t is adsorption time. The concentration of the species accumulated at the interface at any time is obtained by integrating the above equation (Eq. 3).

The apparent diffusion coefficient may be calculated from the initial slopes, S, of $\Delta \Gamma / \Delta \Gamma_0$ versus $\sqrt{t}$ curves, according to:[57]

$$S = 2C\left(\frac{D^*}{\pi}\right)^{1/2} \tag{4}$$

The estimated asphaltene diffusion coefficient for 0.01 wt% concentration is on the order of 10^{-10} m^2/s. Ostlund et al.[58] reported diffusion coefficients of asphaltenes in toluene solutions to be on the order of 10^{-10} m^2/s, which is in good agreement with the current study.

Assuming asphaltenes are spherical in shape in toluene, the apparent particle size can be calculated from the Stokes-Einstein equation:[59]

$$D^* = \frac{K_B T}{3\pi\mu d_0} \tag{5}$$

where D* is the diffusion coefficient of the particles, d_0 is the particle diameter, μ is the solvent viscosity, and k_B is the Boltzmann's constant. At 0.01 wt% asphaltene concentration in toluene, the particle diameter is calculated to be ~1 nm (radius ~0.5 nm). Such a small value of asphaltene molecular size suggests that asphaltenes are present at very low concentrations as single molecules or nanoaggregates. Kawashima et al.[53] observed that the aggregation of asphaltenes proceeds stepwise, from monomer to nano aggregates and then cluster of aggregates before forming flocs or precipitates, as asphaltene concentration increases. At very low concentration of 0.1 g/L in chloroform (0.01 wt%), the calculated particle size (diameter) from the Stokes-Einstein equation was ~0.8-1.4 nm. Andrews et al. studied translation diffusion constant of asphaltene molecules using fluorescence correlation spectroscopy.[60] Using simple theoretical models and model-independent comparisons with known chromophores, they obtained a range of molecular diameters of asphaltene molecules between 1-2 nm. The results from both these studies closely match the calculated asphaltene molecule diameter obtained in the present study.

CONCLUSION

The results of this study show that asphaltenes adsorb to toluene-mica basal plane interface quickly and form multilayers. The adsorption of asphaltenes onto mica surfaces strongly depends on the concentration of asphaltenes in the solution, and adsorption time. The adsorption process is controlled by diffusion of asphaltenes from the bulk solution to mica surface with a diffusion coefficient on the order of 10^{-10} m^2/s at room temperature. This diffusion coefficient corresponds to a hydrodynamic radius of approximately 0.5 nm, indicating asphaltene molecules in 0.01 wt% solutions as monomers. The results from this study provide an insight into the basic molecular interactions (e.g. steric interaction, bridging attraction as a function of distance) of asphaltenes and solids in organic media and hence in crude oil and bitumen production.

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