



Molecular polydispersity improves prediction of asphaltene aggregation

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ABSTRACT

Asphaltene flocculation and deposition from petroleum fluids may cause severe formation damage and flow assurance challenges. Flocculation occurs when asphaltene aggregates are no longer colloidally stable in solution. Although extensive experimental and modeling studies have been performed on asphaltene aggregation, some of the mechanisms and parameters governing this phenomenon (such as molecular structure and polydispersity) are still not fully understood. In this study, a polydisperse mixture of asphaltene molecules varying in size, aromaticity and functionality was studied by atomistic molecular dynamics simulations. Aggregation in systems spanning 105 to 1005 molecules was simulated for approximately one microsecond under ambient conditions and a concentration of 5 wt% in heptane. Simulation trajectories revealed two stages of aggregation: nanoaggregation and clustering, in agreement with the Yen–Mullins hierarchy. Distinctions between nanoaggregates and clusters were observed by various analyses including trajectory visualization, fractal dimension, and cluster size analysis. Different roles for molecules varying in size and aromaticity were observed in the aggregation process: molecules low in molecular weight and/or aromaticity tended to cap larger aggregates, prohibiting further accumulation and limiting nanoaggregate size. Comparisons to simulations of monodisperse systems containing only one type of molecules, either highly hydrogen bonding or non hydrogen bonding, accentuated these findings. This study demonstrates the importance of polydispersity on asphaltene aggregation and provides a lower limit of approximately 375 molecules in such a mixture to represent the two stages of aggregation.

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1. Introduction

Asphaltenes, considered to be the heaviest and most polarizable molecules of crude oils, are of particular interest to the petroleum industry as their precipitation in reservoirs and flow lines complicates and significantly inhibits production. Specifically, changes in field conditions, such as oil mixing and pressure drop, can trigger asphaltene precipitation and lead to formation damage, wellbore or pipeline fouling and plugging, and sedimentation during crude oil storage [1–4]. Furthermore, asphaltene aggregates or flocculates can pollute subsurface aquifers [5]. Their adsorption or deposition on rock surfaces alters wettability and causes the capillary forces to overcome the viscous forces during water flooding, leaving a large portion of residual non-aqueous phase liquids (NAPLs) trapped in the rock. This can limit the success of remediation processes and render aquifers unusable [6]. For the above-mentioned reasons; it is desirable to develop a reliable way to inhibit the aggregation and surface activity of asphaltenes, and this requires intricate knowledge of the aggregation mechanism and structure of asphaltene assemblies.

Asphaltenes are defined as a solubility class of petroleum fluids that are soluble in aromatic solvents such as toluene, but insoluble in normal alkanes such as *n*-heptane [5,7,8]. Based on this broad definition, asphaltenes consist of thousands of species with different molecular structures [7,9]. While the majority of asphaltenes may have a common architectural structure containing a polycyclic aromatic core and peripheral aliphatic chains, their size and aromaticity vary considerably. The average asphaltene molecule is reported to have a molecular weight of ~750 g/mol and an aromaticity in the range of 0.45–0.65 [8,10]. They may also contain any number of different functional groups, heterocycles, alcohols, thiols, acids and bases [1,11]. These groups appear to play a large role in asphaltene aggregation where a number of different processes have been implicated including ion pairing due to acid base interactions, hydrogen bonding, and π – π stacking [1,7,12,13].

Numerous studies have been performed over the past few decades to understand processes by which asphaltenes aggregate and the shapes and structures of asphaltene conglomerates. Lin et al. and Jullien et al. identified two kinetic regimes, dissociative and reactive, in which aggregation is rate limited [14,15]. Dissociative (non-associative) aggregation simply involves individual molecules in solution finding aggregates or other molecules, after which binding through dispersion forces is quick. In the simplest approximation of the dissociative

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model, no orientation factor is needed or it is negligible. This could be because the preferred orientation is highly probable, as might be the case for π - π stacking of two large aromatic molecules in water, or because there is no preferred orientation, when a molecule may associate with an aggregate from any direction with little preference for any one, but having a strong preference for deposition over solvation. The so-called “reactive” mechanism assumes that the rate-limiting step for aggregation is something other than diffusion, a chemical reaction or a physico-chemical process such as a difficult orientation, coordination and/or removal from solvent.

Several studies have implicated a high probability for particular interactions, such as T-shapes formed by small aggregates or association between polar groups in particular conditions, and considering this, a strictly diffusive aggregation mechanism seems unlikely [16,17]. Solvent composition is another factor that can affect asphaltene aggregation and ultimately aggregate structure; indeed, by definition, asphaltenes are soluble to a significant extent in aromatic solvents and not in aliphatic ones. It is conceivable, for example, that a serendipitous solvent mixture could promote π - π stacking to such an extent that long rods are preferred, while another may significantly limit the length of such assemblies. The existence of a range of aggregate structures is evidenced by experimental studies revealing fractal dimensions of asphaltene aggregates varying over a range of 1.3–2.3 depending on temperature and pressure conditions [18,19].

While the asphaltene environment appears to be a critical factor governing aggregate structure, it is still likely that the most important variable is the composition of the asphaltene sample. Certainly, heteroatom content, hydrogen bonding ability, molecular size, and aromaticity are important. However, the polydispersity of these variables may itself be a key factor. This is evidenced by the varying results of some different modeling studies: Jian and Tang using a monodisperse collection of asphaltenes observed the formation of long 1-D assemblies [20], whereas simulations of polydisperse mixtures (in the present work) exhibited much smaller limits in the size of aggregates formed through π - π interactions, in agreement with experimental observations [21].

The categorization of aggregation processes as diffusive or reactive necessarily focuses on one process or one set of experimentally indiscernible processes as the critical, rate determining parameter. Another view, however, known as the modified Yen model or Yen–Mullins model considers different aggregation states with a progression of mechanisms of formation [1,10,22]. In this scheme, asphaltene molecules first self-assemble through π - π interactions to form 2–3 nm size nanoaggregates (NAs) with an aggregation number less than 10 and a characteristic stacking width of \sim 3 nm. In the second stage, nanoaggregates can themselves associate, presumably largely through weak interactions between aliphatic side chains, to form 5–10 nm size clusters of \sim 10 nanoaggregates, which in turn self-assemble, flocculate, and eventually precipitate under specific conditions [10,21,22]. In this process, clusters constitute the building blocks of flocculates [21].

Considering this view, it is the first stage of aggregation that has been most frequently studied and observed. Experiments employing small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS), for example, propose asphaltene nanoaggregates having ellipsoid shapes which suggested formation by parallel stacking of asphaltene polyaromatic cores [13,23–25]. In order to visualize this and gain insight into the driving forces of association, molecular dynamics (MD) simulations have recently been used to probe aggregation behavior in the first stage of assembly in vacuum, organic and inorganic solvents [8,16,20,26–32]. These simulations have generated molecular level information describing energy barriers to asphaltene association in solution, the roles of heteroatoms and polar groups, and at larger scales, possible mechanisms of aggregation and deposition under flow conditions. All-atom simulations reveal fundamental information of early stage aggregation and asphaltene interactions, but examination of later stages and larger clusters are generally restricted by limitations in computational resources. Ultimately, in order to regularly simulate

second and possibly later stages of assembly, which will involve formation and interactions of aggregates consisting of hundreds or thousands of solvated molecules, coarse grained (CG) models are needed. In this work, we take a computationally intense, brute force approach to access large volumes and time scales to provide atomistic information that additionally should be useful in the development of CG models.

The purpose of the present work is to develop an improved understanding of asphaltene aggregation by creating a realistic polydisperse molecular representation of asphaltenes and examining their association in large assemblies over long times using a classical, atomistic force field. We focus on a few different aspects of asphaltene aggregation and also modeling that currently requires more examination. In particular, we seek to address the following questions: (i) How many molecules, or what sizes of simulations are needed in order to simulate aggregation phenomena that can be compared to experimental data? (ii) How does polydispersity affect the aggregation mechanism and aggregate structure? (iii) What are the individual contributions to molecular weight, aromaticity and H-bonding ability on aggregation phenomena? The resulting model is designed to simulate interactions between several different types of asphaltenes with a long-term goal of developing a coarse grained (CG) model that makes use of the interaction data.

2. Methods

All simulations in this work were performed using the GROMACS 5.1.1 simulation package [33]. Many simulations were necessarily large in volume, containing up to 1005 asphaltene molecules at \sim 5 wt % in heptane and as such involved hundreds of thousands of solvent molecules. This low concentration of asphaltene in heptane allows aggregates to grow freely in the solvent without encountering their periodic images. Furthermore, most simulations were run for long times (\sim 1 μ s). In order to minimize computational cost, solvent molecules were represented by the united atom OPLS force field [34] while asphaltenes were modeled using all atom OPLS [35]. All the simulations were performed in NPT ensembles at 300 K and 1 bar using the Nose-Hoover thermostat [36] and the Parrinello-Rahman barostat [37]. Both Lennard-Jones and short range Columbic cutoff radii were set at 1.4 nm. Long-range electrostatic interactions were computed using Ewald summation. A time step of 2 fs was employed in order to access long simulation times and accordingly, all bonds involving hydrogen were constrained to their equilibrium values. To expedite the equilibrium process, we annealed the heptane molecules by increasing their temperature from 300 to 400 K followed by a slow cooling back to 300 K during a total of 20 ns simulation time. The annealing simulation was run in an NVT ensemble. Aggregate sizes were monitored in all simulations until they became constant when equilibrium was reached. We then ran the simulations for another 200 ns for fractal dimension and cluster size analyses.

2.1. Polydisperse asphaltene molecules

In order to generate a realistic and polydisperse pool of asphaltene molecules, we developed an in-house program based on a previous model created by Boek and co-workers [38]. Details of our methodology are listed below:

2.1.1. Part 1: generation of random structures

We first created 34 different asphaltene cores with various molecular weight and aromaticity, similar to experimental structures reported by previous studies [39–41]. These cores contained 5–20 aliphatic and aromatic rings with at least one cycloalkane. We then designed 36 different tail structures with a minimum of one and a maximum of 15 carbon atoms. The tails included both linear and branched alkanes. One of the asphaltene cores was randomly selected and paired with a random number, between 1 and 4, of aliphatic tails to create a carbon skeleton. Heteroatoms (O, N or S) were introduced into the structure by either

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