Asphaltenes Aggregation during Petroleum Reservoir Air and Nitrogen Flooding

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Abstract
Aggregation onsets of seven different asphaltenes dissolved in model oils, due to the effects of misciblized compressed air or nitrogen injections, were studied through molecular dynamics simulation. Natures of aggregations, cumulative coordination numbers and interaction energies were investigated. Aggregation processes were highly affected by injected gas concentration. In more cases little differences were observed between using air and pure nitrogen. However, asphaltene aggregation was highly affected by its molecular architecture. Asphaltenes with long aliphatic chains and archipelago structure showed low aggregation affinities.

Keywords: Asphaltene, Compressed Gases, Enhanced Oil Recovery, Interaction Energies, Molecular Dynamics, Onset of Aggregation.

1. Introduction
Crude-oil is a complex mixture of hydrocarbons in a wide range of molecular weights. It also includes other polydispersed organic compounds such as resins, asphaltenes, and organometallic compounds which are composed of carbon, hydrogen, metals, nitrogen, oxygen, and sulfur in their structures; inorganic oxides; salts; and metals (Escobedo and Mansoori, 2010; Kim et al., 1990).

Asphaltene constituents are the polar and heaviest part of the crude-oil. While they are not soluble in paraffins, they are soluble in aromatic and polar hydrocarbons like toluene and o-xylene. Asphaltenes are composed of polycyclic clusters, alkyl groups, nitrogen, oxygen, and sulfur, in addition to carbon and hydrogen. The asphaltene fraction of petroleum fluids may also contain some iron, nickel, and vanadium metals (and/or their oxides). Asphaltenes present in petroleum fluids are polydispersed and contain a large molecular weight distribution similar to polymers. Asphaltenes are known to have a high tendency to be associated together and form large aggregates that eventually flocculate causing asphaltene deposition which leads to several problems in the oil industry (Kawanaka et al., 1991; Pacheco and Mansoori, 1997).

In producing petroleum from underground reservoirs, there are primary, secondary and tertiary oil recovery techniques. In primary oil recovery, the location of the producing well is carefully chosen, as petroleum would flow out as a result of the reservoir gas-cap pressure. To maintain the gas-cap amount and pressure it is recommended to reinject the separated-gas from the produced petroleum. When, for various reasons that is not achieved, in order to maintain the gas-cap amount and pressure one may inject air/nitrogen in the reservoir. There is the question whether the asphaltene content of the oil will aggregate, grow in size and plug the porous media and production facilities as a result of the gas-cap’s air/nitrogen dissolution in the oil (Dehghani et al., 2007).
The secondary oil recovery process (Water-Injection) is used after the gas-cap pressure is reduced to such low levels where it cannot be maintained to force the oil out of the reservoir. Forced water-injection forces the oil out of the reservoir.

Upon completion of primary and secondary recovery stages, a substantial fraction of the oil (60-70%) remains in the reservoir, primarily in the form of being adsorbed in the porous media of the reservoir formation. That is when the tertiary or enhanced oil recovery (EOR) process would be used to get the oil out of the reservoir (Mansoori and Jiang, 1985; Kawanaka et al., 1988). One of these EOR methods is by injecting dense (supercritical) gases (e.g., natural gas, separated gas, flue gas/carbon dioxide, air/nitrogen). Supercritical fluids (sc-fluids) have densities near that of a liquid and low viscosity, since it is a gas. In addition, a sc-fluid has solvent potential, the same as hydrocarbon solvents, so it could dissolve even solids (Park et al., 1987). Therefore, sc-fluids are used in EOR to reduce the viscosity and improve the mobility of the oil due to its swelling by being miscibilized with the injected sc-fluids toward the wells. The sc-fluids and the bulk (crude-oil) are considered miscible when there is no interface between them and the pressure at this point is known as minimum miscibility pressure (MMP) (Benmekki and Mansoori, 1988). To ensure that sc-fluids are totally dissolved in the bulk, the injected pressure should be higher than MMP. Natural gas has become less favorable for gas injection because it is highly sought as transportation clean fuel and residential and commercial use for heating. Carbon dioxide is another good option, but it has several drawbacks which include its lack of purity, unavailability in large volumes, causing unnecessary oil/water emulsions, and the corrosion it may cause in the well-surface facilities (Mohammed and Mansoori, 2018b; Mungan, 2003).

One of the economically promising methods of EOR for underground petroleum reservoirs is an injection of high pressure (supercritical) air. Literature is rich in discussing nitrogen injection. However, purification of nitrogen for huge underground reservoirs is economically prohibitive. Accordingly, we are comparing the use of pure nitrogen and air (which contains ~79% nitrogen) in this report. This process is particularly attractive for off-shore reservoirs and other remote locations where separated-gas, natural gas, and other more proper gases, which would miscibilize with oil at lower pressure, are not available and/or economically not attractive (Mungan, 2003).

In the process of compressed air or nitrogen injection, when miscibility is reached, there is always the question whether the asphaltene content of the oil will aggregate, grow in size and plug the porous media and production facilities as a result of its interaction with compressed air or nitrogen (Jamaluddin et al., 2002). This is a problem which requires much research to understand the conditions under which asphaltenes may start to aggregate due to compressed air or nitrogen flooding and the factors which may contribute to its aggregation. One of the promising methods to study the onset of such aggregations is the use of molecular dynamics (MD) simulation.

MD is a computer simulation method for studying the dynamics of atoms or molecules. It could provide details about the behavior and structure of the system and helps in interpreting experimental data. MD simulation solves Newton’s equation of motion for a system of “N” interacting particles (atoms). It is used to investigate the structure, dynamics, and thermodynamics of chemical, physical, and biological systems at a molecular level. MD simulation can correct experiments and it is a bridge between microscopic (molecular level) and macroscopic (bulk) properties. In the recent years, MD simulation has become prevalent and successfully used to describe asphaltene behavior (Headen and Boek, 2011; Khalaf and Mansoori, 2018; Mohammed and Gadikota, 2019; Mohammed and Mansoori, 2018b; Sedghi and Goual, 2016; Yaseen and Mansoori, 2017, 2018).

MD simulation of the sc-fluids injection and its interaction with the live oil (oil in the reservoir) is computationally challenging at the present time due to the tremendous number of components in the oil and requirement of huge computational resources. For these reasons, we chose our system as asphaltenes dissolved in ortho-xylene (their best hydrocarbon solvent) and then pressurized it with compressed air or nitrogen to study the onset of asphaltenes aggregation. Considering that asphaltenes are completely dissolved in o-xylene, we are confident their onset of aggregation is exactly the same as their onset in live oil.
The instability of asphaltene during compressed gas flooding is attributed to the changes in the solubility of asphaltene and heavy fractions, where the injected fluids modify the composition and conditions of the reservoir fluids. Experimental investigations showed that nitrogen injection influences the aggregation and deposition of asphaltenes and the problem is more severe for heavy oils. Thus, understanding the behavior of asphaltene during the high-pressure gas flooding is required to reduce the possibility of asphaltene precipitation during such EOR.

Due to the importance of the asphaltene aggregation during EOR using miscible gas injection, several studies have focused on asphaltene aggregation during the process. Most of the experimental investigations focused on asphaltene aggregation during hydrocarbon gas and CO₂ injection (Mohammed and Mansoori, 2018a, 2018b). To our knowledge, there is little or no MD simulation of asphaltene aggregation during air or nitrogen flooding. Only two MD simulations of sc-CO₂ flooding were found in the literature on the asphaltene aggregation in the presence of dispersants [d-limonene and polyvinyl acetate (PVAc)] (Sedghi and Goual, 2016). Considering the use of any such dispersants in large underground reservoirs is economically prohibitive we avoided studying their role during air/nitrogen injections reported here.

This study aims to use the MD simulation technique to investigate the onset of asphaltene aggregation during air or nitrogen flooding since we are using ortho-xylene to represent oil phase, of which asphaltenes are completely miscible. We intend to examine the impact of sc-fluids concentration on the process and find the difference between the use of compressed air and pure nitrogen.

2. Asphaltene Structures

We conducted this study to understand the effect of the molecular structure of the asphaltenes and the presence of different heteroatoms on the aggregation during air and nitrogen injection. In the present study, seven different well-known asphaltenes were chosen. Figure 1 shows seven different asphaltenes named A1-A7. A1-A3 are reported in (Boek et al., 2009), A4 and A5 are reported in (Pacheco-Sánchez et al., 2004), A6 is reported in (Zhang and Greendfield, 2007) and A7 is reported in (Takanohashi et al., 2003). The asphaltenes in this study were extracted from Athabasca (A1-A3), Venezuelan (A4), Mayan (A5), Kuwait (A6), and Khafji (A7).

Figure 1. The seven asphaltenes (A1- A7) used in the present study.
3. Simulation Methodology

3.1 Initial Configurations

Twenty-four molecules of each asphaltene model were used in this study. Asphaltene molecules were randomly distributed in the simulation box to study the onset of asphaltene aggregation. In each simulation, the dimensions of simulation box were varied depending on the asphaltene and compressed gas concentration. To a better representation of asphaltene in real systems, these asphaltenes were placed in o-xylene at a constant concentration (7 wt%). Four different concentrations 20, 40, 60, and 80 wt% of compressed air or nitrogen were added to the system to better visualize the effect of compressed air or nitrogen on the onsets of asphaltenes aggregation. The ingredients of air are based on 79% nitrogen and 21% oxygen only (neglecting the effects of small concentrations of other gases). The minimum miscibility of nitrogen in crude oil system is about 360 bar, thus in all the simulations 400 bar of injection pressure was chosen. Simulations temperature of 350 K was chosen based on reservoir’s conditions (Dehghani et al., 2007).

3.2 Force Fields

Lennard-Jones parameters and partial atomic charges of nitrogen and oxygen were used as described in (Vujić and Lyubartsev, 2016) and reported in Error! Reference source not found.. For other molecules (asphaltenes and o-xylene), OPLS-AA force field had been employed. The total energy was calculated based on the summation of bonded (bending, stretching, and torsion) energies and nonbonded (van der Waals represented by Lennard-Jones and electrostatic represented by coulomb) energies. In addition, OPLS-AA works well in calculating and producing hydrogen bonds between all possible donors and acceptors interactions. OPLS-AA is shown to work well for organic liquids in reproducing experimental data and therefore used successfully for asphaltene aggregation simulations (Khalaf and Mansoori, 2018; Yaseen and Mansoori, 2017).

Table 1. Partial atomic charges and Lennard-Jones parameters for Nitrogen and Oxygen.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charges</th>
<th>( \varepsilon ) (kJ/mol)</th>
<th>( \sigma ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-0.482</td>
<td>0.3026</td>
<td>0.332</td>
</tr>
<tr>
<td>M-N(^a)</td>
<td>0.964</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>-0.112</td>
<td>0.4217</td>
<td>0.305</td>
</tr>
<tr>
<td>M-O(^b)</td>
<td>0.224</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\( a \): massless charge point in nitrogen. \( b \): massless charge point in oxygen.

3.3 Simulation Details and Algorithm

A series of classical MD simulations were carried out using GROMACS 5.1.2 simulation package. After preparing the simulation box in the desired concentrations, energy minimizations were conducted using “steepest descent” method to eliminate any high-energy structures. Energy minimization was followed by 100 ps NVT and 500 ps NPT ensemble simulations to bring the system to equilibrium temperature and pressure. In all the simulations, leapfrog algorithm was used to integrate the equation of motion. The periodic boundary conditions were applied to represent the bulk in a small box, two-femtosecond time steps were applied. The Particle Mesh Ewald (PME) method was applied to calculate long range Coulomb interaction forces. In all nonbonded interactions, the cutoff was set to 1 nm. The simulations were performed at constant temperature and pressure (350 K and 400 bar). To constrain the bond lengths in the simulations, the LINCS algorithm was utilized. To keep the temperature and pressure constant, V-rescale thermostat and Parrinello-Rahman pressure coupling were used. Over the course of the simulation (50 ns of NPT), the atomic positions were recorded every 10 ps, which allowed the tracking of the position of the molecules.
4. Results and Discussions

In EOR processes, compressed air or nitrogen is injected in different quantities depending on the reservoir conditions. To simulate real systems, we used different air and nitrogen concentrations to investigate the impact of injected fluids on asphaltene aggregation. Twenty-four asphaltene molecules of each structure were used in the simulation box with periodic conditions. The effect of injected fluids concentrations on the asphaltene aggregation process at 350 K and 400 bar were analyzed through: (i). cumulative coordination number, $N$, (Equation 1), (ii). the van der Waals (vdW) interaction energies, (iii). The electrostatic interaction energies (ES), and (iv). The hydrogen bond (H-b) interaction energies.

In section 4.1 we report the use of cumulative coordination number and the average size of aggregates to quantify the effect of misciblized compressed air and nitrogen on asphaltene aggregation. In section 4.2 we report the roles of compressed air and nitrogen on asphaltenes interaction energies during aggregation.

4.1. Effect of Misciblized Compressed Air and Nitrogen on Asphaltene Aggregation

The effect of injected sc-fluids concentration on asphaltene aggregation was analyzed through the use of asphaltene cumulative coordination number $N(r)$, defined by the following equation (Headen and Boek, 2011).

$$N(r) = \int_0^T \rho g(r)4\pi r^2 dr$$

$N(r)$ represents the number of asphaltene molecules in a sphere of radius $r$. Where $\rho$ is the local density of asphaltene molecules and $g(r)$ is the asphaltene radial distribution function.

Figures 2 and 3 show the $N(r)$ of asphaltene molecules (A1-A7) in oil at four different misciblized nitrogen and air concentrations (20, 40, 60, and 80 wt%). In both compressed gasses, the onset of all 7 asphaltene aggregation remains almost the same when the injected gases concentration is below 60%. At 20% misciblized gases concentration, dissolved A1 becomes unstable and shows a high aggregation affinity in comparison with other asphaltenes.

Increasing the concentration of misciblized gases to 40 wt% enhanced the aggregation of all 7 asphaltenes. A1 showed higher aggregation onset than other asphaltenes. Aggregation onsets of A2-A7 were slightly increased from the 20% concentration. This clarifies that A2-A7 have lower aggregation affinity than A1 due to their molecular structure and molecular size. According to the results of misciblized gas flooding, injection of 40% misciblized gas is applicable for A2-A7 asphaltenes and is not preferred for A1 asphaltene.

Stability of asphaltenes was highly affected when the injected sc-fluids concentration reached 60%. Similarly to the previous case, A1 showed higher aggregation onset and other asphaltenes started alternating. A5-A7 asphaltenes showed big changes in their aggregation onset and their aggregation affinities were higher than A2-A4 asphaltenes.

When the misciblized gas was 80%, the aggregation onset was high: A1 and A6 showed higher aggregation onsets, while the others stayed in between. A2 and A3 did not show high aggregation affinity, due to their molecular structures. A2 asphaltene has archipelago structure which gives it the ability to interact with itself through its aromatic and hydrogen bonds. A3 has long aliphatic chains in comparison with its aromatic core size, where they participate in steric repulsion.

In addition to cumulative coordination number, average size of aggregate (average number of asphaltene molecules in the aggregates) was analyzed and reported in Figures 4 and 5. The reported results are in both compressed gasses for the last 10 ns of the simulations. At 20% of compressed gases, A1 was unstable and reached clustering point (more than 8 molecules in the aggregate). A2-A7 were in nanoaggregate ranges (less than 8 molecules in the aggregate). Increasing the concentration of injected gases to 40% enhanced the affinity of aggregation of other asphaltenes such as A4. When the concentration became 60%, the asphaltenes were unstable except for A2 and A3 due to their structures. A2 and A3 showed stable behavior in all the cases and even at 80% injected gases.
Figure 2. Cumulative coordination number of different asphaltenes in different misciblized air concentrations.

Figure 3. Cumulative coordination number of different asphaltenes in different misciblized air concentrations.
In addition to cumulative coordination number, average size of aggregate (average number of asphaltene molecules in the aggregates) was analyzed and reported in Figures 4 and 5. The reported results are in both compressed gases for the last 10 ns of the simulations. At 20% of compressed gases, A1 was unstable and reached clustering point (more than 8 molecules in the aggregate). A2-A7 were in nanoaggregate ranges (less than 8 molecules in the aggregate). Increasing the concentration of injected gases to 40% enhanced the affinity of aggregation of other asphaltenes such as A4. When the concentration became 60%, the asphaltenes were unstable except for A2 and A3 due to their structures. A2 and A3 showed stable behavior in all the cases and even at 80% injected gases.

The results show that the general trends of the onsets are the same in both injected compressed gases. This means there are no differences between the use of compressed air or compressed nitrogen. Out of all the concentrations, trajectory visualization and N(r) calculations showed that A1 affinity to aggregate was higher than other asphaltenes. When the injected high-pressure gas was 40% A1 showed very high aggregation onsets. For A2-A7, the aggregation onset increased with the increase of the misciblized gas concentration. A4 had almost constant behavior, where the onset aggregation was slightly affected by increasing the concentration. For A1 and A4-A7, when the concentration of misciblized gas was high (80%), the aggregation was severe and happened immediately. This is because of misciblized gas changes the solubility of A4-A7 asphaltenes in the system which finally lead to phase separation. We can conclude that an asphaltene with a chemical structure similar to A1 will have a higher tendency to aggregate than the other asphaltenes at low and moderate nitrogen and air concentrations. Figure 6 shows snapshots of seven model asphaltene placed in 20% misciblized nitrogen. According to the snapshots, A1 had the highest aggregation affinity. Our detailed analysis of trajectories, which are not reported here, and the calculated results, we conclude that the aggregation affinities of the seven model asphaltene with respect to each other is as follows:

\[A1 > A7 > A6 > A4 > A5 > A2 > A3\]

4.2. Interaction Energies

Reported in the literature, the driving force for asphaltene aggregation is the core-core attraction which is represented by vdW energies. In our previous study(Khalaf and Mansoori, 2018), we showed that the energies were affected by the medium and asphaltene’s molecular structure. To understand the effect of compressed gases on electrostatic (ES), van der Waals (vdW), and the average number of hydrogen bonds (H-bs) interaction energies, we report the interaction energies between asphaltenes at different compressed gas concentrations. The results are reported in Figures 7 and 8 for the last 10 ns of simulations.

The interaction energies reported in Figure 7 are the vdW and ES interaction energies between the asphaltenes at different concentrations of misciblized air and nitrogen. In both compressed gases, the results showed that increasing misciblized gas concentration leads to increase in the vdW interactions (increase the attraction energy) between the asphaltene molecules in all 7 cases. This is due to the reduction in the aromatic-aromatic interactions between asphaltene and \(\pi\)-xylene. For example, in both gases, the vdW attractions of A2 and A3 doubled when the concentration of compressed gases increased from 20% to 80%. Basically, vdW interactions are related to the size and geometry of the aromatic core of asphaltenes. Thus, the aggregation affinity of A1 was the highest in comparison with other 6 asphaltenes. On the other hand, ES interactions are affected by the presence of heteroatoms attached to the aromatic core, which contribute to reduction of \(\pi\) electron clouds. Due to that, the ES interactions of A2, A4, A5, A6 and A7 were attraction while A1 and A3 were repulsion. From the interactions results and the aggregations trends, the ES interactions have low effects on the aggregation process in comparison with the effects of vdW interactions. The interaction energies are almost the same in compressed nitrogen and compressed air. Of course, this is because of the injected air has 79% nitrogen which dominates on the interactions.
Figure 4. Average size of aggregates of different asphaltenes in different misciblized nitrogen concentrations.

Figure 5. Average size of aggregates of different asphaltenes in different misciblized air concentrations.
Figure 6. Snapshots of seven model asphaltene in 20% misciblized nitrogen. O-xylene and nitrogen molecules were removed for clarity.
In Figure 8 we report the average number of H-bs between asphaltenes with increasing the concentrations of misciblized gases. According to this figure, the average number of H-bs between A2 molecules was higher than other asphaltenes. A1, A2, A3 were almost the same in misciblized nitrogen and air. In the case of A4, there was a difference between misciblized nitrogen and air flooding. A5 has only an accepter position with no donor positionm and A6 has no sites for H-bs, thus they do not have potential to participate in H-b interactions. It is reported that H-b interactions play a minor role in asphaltene aggregation, which is mainly due to vDW interactions ($\pi$-$\pi$ interactions) (Sedghi et al., 2013). In addition, H-bs may affect the shape of aggregated asphaltene (Yaseen and Mansoori, 2018). Overall, there were slight differences in the average number of H-bs of some asphaltenes. However, even with these differences, the general trends of aggregation of these asphaltene in misciblized air and nitrogen were the same. Due to this we can conclude that H-bs had small effects on the aggregation process in comparison with vDW interactions.

According to the results, the general trend of aggregation affinity was almost the same in both nitrogen and air flooding when the concentration was below 60%. The simulation results suggested that injection of air is applicable at low concentrations. Air injection is economically preferred and is applicable everywhere due to its availability and purity.

![Figure 7](image)

**Figure 7.** vDW and ES interaction energies for 7 different asphaltenes at different misciblized gas concentrations.
Figure 8. Average number of H-bs for 7 different asphaltenes and different misciblized gas concentrations.

5. Conclusions

Molecular dynamics simulations of different asphaltenes in different concentrations of misciblized nitrogen and air were conducted. The effect of injected misciblized gas concentrations and the role of interaction energies were investigated. The asphaltene aggregation process is highly affected by the concentration of injected gases due to the solubility effects. Asphaltenes with long aliphatic chains and archipelago architecture showed low association affinity than other flat asphaltenes. Overall, there are no appreciable differences between the use of misciblized nitrogen and air on asphaltene aggregation during enhanced oil recovery. Additionally, the architecture of asphaltene plays an important role in the aggregation process.

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