

# Microscopic details of asphaltenes aggregation onset during waterflooding

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## Abstract

We report detailed microscopic studies of asphaltenes aggregation onset during waterflooding of petroleum reservoirs. To achieve this objective, a series of simulations are performed on asphaltene-oil miscibilized with water at high pressure and temperature through molecular dynamics. Our simulation results illustrate that the aggregation onset in waterflooding generally follows three sequential steps: (i). Asphaltene-water interaction; (ii). Water bridging; (iii). Face-to-face stacking. Then, asphaltene-water and water-water hydrogen-bonding network surround every aggregate boosting the intensity of aggregation onset. We intend to utilize such understanding of these details in our predictive and preventive measures of arterial blockage in oil reservoirs during waterflooding.

**Keywords:** Aggregation; Asphaltene; heteroatoms; Hydrogen-bonds; Molecular dynamics simulation; Onset of aggregation;  $\pi$ - $\pi$  interaction; Radial distribution function; Waterflooding; Water-bridge.

## 1. Introduction

To practicing engineers, the importance of knowledge about the behavior of asphaltenes in petroleum is similar to the knowledge needed by cardiologists regarding cholesterol in the arteries of patients (Leontaritis et al., 1986). Asphaltenes, if present in a petroleum fluid, tend to aggregate and deposit in flow paths causing plugging in the reservoir porous media and transmission pipelines (Branco et al., 2001; Escobedo and Mansoori, 1997; Hu et al., 2004; Mansoori, 2009; Vazquez and Mansoori, 2000).

Recently, we reported a series of molecular dynamics (MD) studies on the onset of asphaltenes aggregation during a waterflooding process (Yaseen and Mansoori, 2017; 2018a; 2018b). According to our studies, asphaltenes became poorly soluble when water was miscibilized in the oil phase at high pressures and temperatures. Face-to-face contact was the predominant stacking of the onset of asphaltenes aggregation. Additionally, we showed that

using high-salinity brines (25 wt.%), instead of pure-water, significantly reduced the intensity of asphaltenes aggregation at the onset.

The microscopic details of asphaltenes aggregation onset in waterflooding of reservoirs remained uncertain. Motivated by our previous studies, considerable attention is given to understanding the reasons behind asphaltenes aggregation onset due to waterflooding. Specifically, we study the role of various segments of seven different asphaltene molecules in this research. For this purpose, we perform an MD study on asphaltenic-oil/pure-water systems under a reservoir condition. We choose ortho-xylene as the oil medium because it is the best hydrocarbon solvent for asphaltenes. The onset data produced in this study is also valid for the real asphaltenic crude oils. This study will provide, from a molecular level, an advanced insight into the relation between water-injection and asphaltenes aggregation onset at reservoir conditions.

## 2. Molecular asphaltenes

Seven different asphaltene molecules labeled as  $A_1$ ,  $A_2$ , ...  $A_7$ , are used in this study as shown in Figure 1. These molecules were also used in our previous studies (Yaseen and Mansoori, 2017; 2018a; 2018b). Their molecular weights are ranged between 543 ( $A_1$ ) and 1197 ( $A_4$ ). Their molecular architectures are classified into the island ( $A_1$ ,  $A_3$ ,  $A_4$ ,  $A_5$ ,  $A_7$ ) and archipelago ( $A_2$ ,  $A_6$ ). Their elemental compositions are mainly composed of carbon and hydrogen atoms. However, their structures also contain heteroatoms, including nitrogen (N), oxygen (O), and sulfur (S).

Presence of N- and O-segments in asphaltenes structures are responsible for possible hydrogen-bonding. Such segments include amide, amine, carboxyl, hydroxyl, and pyridyl. On the other hand, S-segments, such as sulfide, thioanisole, and thiophene, could not form hydrogen-bonds.

To investigate the role of heteroatom-segments on the onset of asphaltenes aggregation, two other “hypothetical” groups of seven molecules are considered in our study. The first “hypothetical” group of molecules (Group B) are assumed to have the same structures as the asphaltenes in Figure 1, but their S-segments are removed and replaced with carbon and hydrogen atoms (see Figure 2). The second “hypothetical” group of molecules (Group C) are assumed to have the same structures as the asphaltenes in Figure 1, but their N and O atoms are removed and replaced with carbon and hydrogen atoms as shown in Figure 2.

In what follows through MD simulation of asphaltene molecules and the two hypothetical sets of molecules we report the microscopic reasons for the onset of asphaltenes aggregation during petroleum reservoir waterflooding.

## 3. MD simulation method used in this study

MD simulation is a powerful tool to gain insight into the microscopic (atomic level) characteristics of materials. The trajectories of atoms are determined by solving Newton's equation of motion. MD simulation has been found to be quite useful for investigating the

aggregation onset of asphaltenes in various model petroleum fluids (Khalaf and Mansoori, 2018a; 2018b; Mohammed and Mansoori 2018). In the current study, GROMACS 5.1.2 software package ([www.gromacs.org](http://www.gromacs.org)) is employed to perform MD simulations. The bonding and non-bonding interactions between the neighboring atoms are calculated by force fields. In this report, water is modeled by the SPC/E potential (Berendsen et al., 1987). On the other hand, asphaltenes and ortho-xylene are represented by OPLS-AA potential (Jorgensen et al., 1996).

During a typical MD simulation, the simulation box is constructed such that it is composed of two phases: the oil phase and the aqueous phase. The oil phase is selected to be composed of ortho-xylene and asphaltenes. Twenty-four asphaltene molecules (10 wt%) are packed into the oil phase, and the simulation box is then expanded in the Y-direction and packed with pure-water.

Once the simulation box is constructed, it undergoes an energy minimization step to relax the system towards equilibrium. MD simulations are performed with periodic boundary conditions in X-, Y-, and Z-directions. They are performed for 20 ns duration in the NPT ensemble at constant temperature (550 K) and constant pressure (200 bar). The detailed description of system preparation and the MD method are reported in our previous publication (Yaseen and Mansoori, 2017).

## 4. Observations resulting from MD simulations

**4.1. Effect of heteroatom-segments on aggregation intensity:** We calculate radial distribution functions (RDFs) of asphaltenes and the two sets of hypothetical molecules (see Figure 3). The intensity of aggregation onsets is proportional to heights of RDF first peaks. According to Figure 3, asphaltenes and hypothetical B molecules have similar first peak heights. However, RDFs of hypothetical C molecules possess little or no peaks, indicating a lack of aggregation. Accordingly, N- and O-segments are the only causes of asphaltenes aggregation onsets in waterflooding.

According to RDFs in Figure 3, separation distances of peaks are ranged between 0.38 and 0.50 nm, which are within the face-to-face cut-off range (Yaseen and Mansoori, 2018a).

**4.2. Distribution of water near heteroatom-segments:** According to RDFs in Figure 4, S-segments possess little or no peaks. They illustrate that water does not tend to concentrate near these segments. On the contrary, every N- and O-segment possess at least one remarkable peak. They reveal that water highly occupies spaces near these segments.

## 4.3. Hydrogen-Bonding of asphaltenes

We calculate average numbers of hydrogen-bonds of asphaltenes ( $HB_{Ai-Ai}$ ,  $HB_{Ai-W}$ ) and hypothetical molecules ( $HB_{Bi-Bi}$ ,  $HB_{Bi-W}$ ,  $HB_{Ci-Ci}$ ,  $HB_{Ci-W}$ ), using the *gmx hbond* analysis tool ([www.gromacs.org](http://www.gromacs.org)). According to Table 1, the numbers of  $HB_{Ai-Ai}$  and  $HB_{Bi-Bi}$  are rather small as compared with  $HB_{Ai-W}$  and  $HB_{Bi-W}$ , respectively. In the case of hypothetical C molecules, both  $HB_{Ci-Ci}$  and  $HB_{Ci-W}$  are zero.

## 4.4. Distribution of N & O heteroatoms at the onset of asphaltene aggregation:

According to Figure 5, RDFs of asphaltenes and hypothetical B molecules have apparent peaks in such a separation distance ranging between 0.33 nm and 0.38 nm. These peaks reveal that the

N- and O-segments are close to each other in the stacked asphaltenes and hypothetical B molecules.

**5. Discussion and conclusions:** Depending on the MD results that reported in Section 4, we could find out why and how asphaltenes aggregation onset occurs. We propose that the aggregation onset of asphaltenes follow three consecutive stages, including asphaltene-water interaction via  $HB_{Ai-W}$ , the formation of water-bridges via  $HB_{W-W}$ , and face-to-face stacking of asphaltenes via  $\pi$ - $\pi$  interaction.

- Stage I: Once water molecules diffuse into the oil phase, some of them migrate toward the N- and O-segments of asphaltenes, displace ortho-xylene, and form  $HB_{Ai-W}$  (see Figure 6-I). At this stage, all N- and O-segments are bounded by clusters of water molecules.
- Stage II: Then,  $HB_{W-W}$  is formed between water clusters that surrounds different asphaltene monomers (see Figure 6-II). In this case, water clusters serve as bridges between every pair of neighboring asphaltenes monomers.
- Stage III: Once two asphaltenes monomers are close enough to each other due to water-bridges,  $\pi$ - $\pi$  interaction occurs between aromatic moieties, and a face-to-face asphaltenes dimer is formed (see Figure 6-III). As a result,  $\pi$ - $\pi$  interaction, as well as the hydrogen-bonds network ( $HB_{Ai-W}$  and  $HB_{W-W}$ ), altogether, maintain the stability of asphaltenes aggregates.

In conclusion, there is a lack of a fundamental understanding of the microscopic details underlying asphaltenes instability during waterflooding. Understanding reasons behind molecular asphaltenes aggregation onset are highly required. In this report, a series of MD simulations are performed to understand why and how the onset of asphaltenes aggregation happens. We employ simulations on asphaltenic-oil/pure-water systems under 550 K-200 bar. MD results illustrate that the association of asphaltenes is due to the presence of the N- and O-segments in their structures. We demonstrate the fact that S-segments have little or no roles in asphaltenes aggregation onset due to waterflooding. We suggest a three-step mechanism for asphaltenes aggregation onset. These steps include asphaltene-water interaction, water bridging, and face-to-face stacking of asphaltenes.

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## 6. Nomenclature, Abbreviations, Formulas

$A_i$	Notation for asphaltenes, where $i=1, 2, \dots, 7$ .
Amide	$-C^{alkyl}-ONH_2$
Amine	$-C^{alkyl}-NH-C^{alkyl}-$
bar	A unit of pressure measurement, which is equal to 14.5 pounds per square inch (psi).
$B_i$	Notation for hypothetical B molecules, where $i=1, 2, \dots, 7$ .
Carboxyl	$-C^{alkyl}-OOH$
$C_i$	Notation for hypothetical C molecules, where $i=1, 2, \dots, 7$ .
$HB_{Ai-Ai}$	Hydrogen-bonds among asphaltenes.
$HB_{Ai-W}$	Hydrogen-bonds between asphaltenes and water.
$HB_{Bi-Bi}$	Hydrogen-bonds among hypothetical B molecules.
$HB_{Bi-W}$	Hydrogen-bonds between hypothetical B molecules and water.
$HB_{Ci-Ci}$	Hydrogen-bonds among hypothetical C molecules.

HB <sub>Ci-W</sub>	Hydrogen-bonds between hypothetical C molecules and water.
HB <sub>W-W</sub>	Hydrogen-bonds among water.
Heteroatom	Term is used to describe non-hydrocarbon atoms, such as nitrogen (N), oxygen (O), sulfur (S)
Hydroxyl	-C <sup>aromatic</sup> -OH
K	Degree Kelvin is a unit of temperature measurement.
MD	Molecular dynamics
N-segment	Nitrogen-containing segment
O-segment	Oxygen-containing segment
OPLS_AA	Optimized Potential for Liquid Simulations - All Atom force field
Pyridyl	-C <sup>aromatic</sup> -N-C <sup>aromatic</sup> -
RDF	Radial distribution function
S-segment	Sulfur-containing segment
SPC/E	Simple Point Charge/Extended force field
Sulfide	-C <sup>alkyl</sup> -S-C <sup>alkyl</sup> -
Thioanisole	-C <sup>aromatic</sup> -S-C <sup>alkyl</sup> -
Thiophene	-C <sup>aromatic</sup> -S-C <sup>aromatic</sup> -
$\pi$ - $\pi$	A type of non-covalent interaction that involves aromatic/benzene rings.

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**Table 1.** The average number of hydrogen-bonds of asphaltenes (Ai) and hypothetical molecules (Bi and Ci) at 550 K and 200 bar.

Hydrogen-bonds	i=1	i=2	i=3	i=4	i=5	i=6	i=7
HB <sub>Ai-Ai</sub>	1.1	1.0	2.9	5.0	0	0.9	0
HB <sub>Ai-W</sub>	28.7	29.2	47.1	81.8	0	17.8	4.9
HB <sub>Bi-Bi</sub>	0.8	0.9	3.2	5.0	0	1.1	0
HB <sub>Bi-W</sub>	29.0	29.2	46.5	81.2	0	18.0	4.8
HB <sub>Ci-Ci</sub>	0	0	0	0	0	0	0
HB <sub>Ci-W</sub>	0	0	0	0	0	0	0

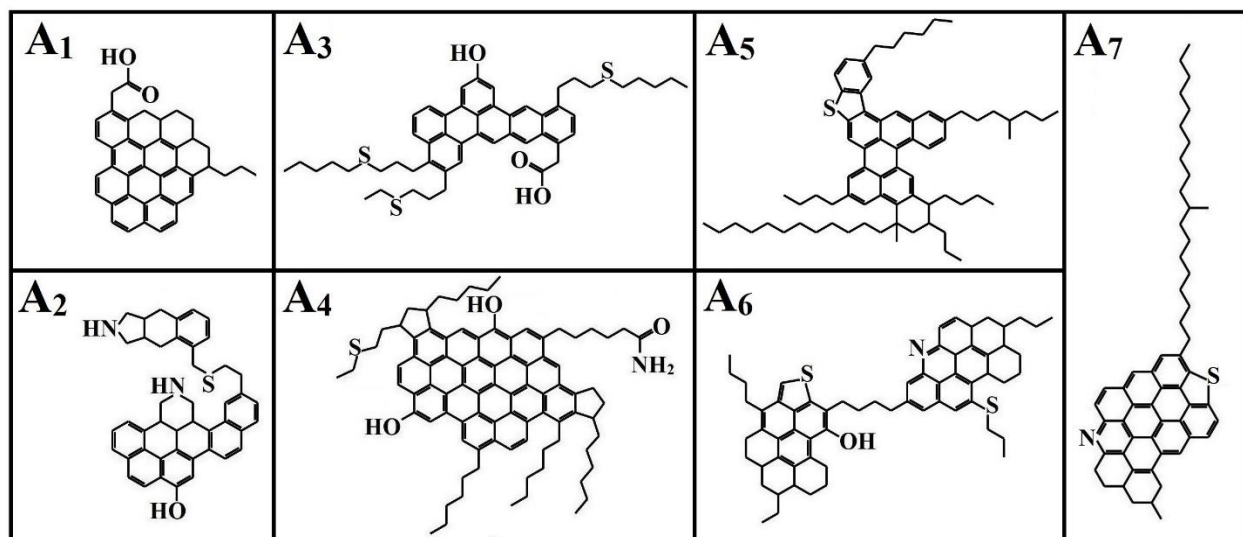
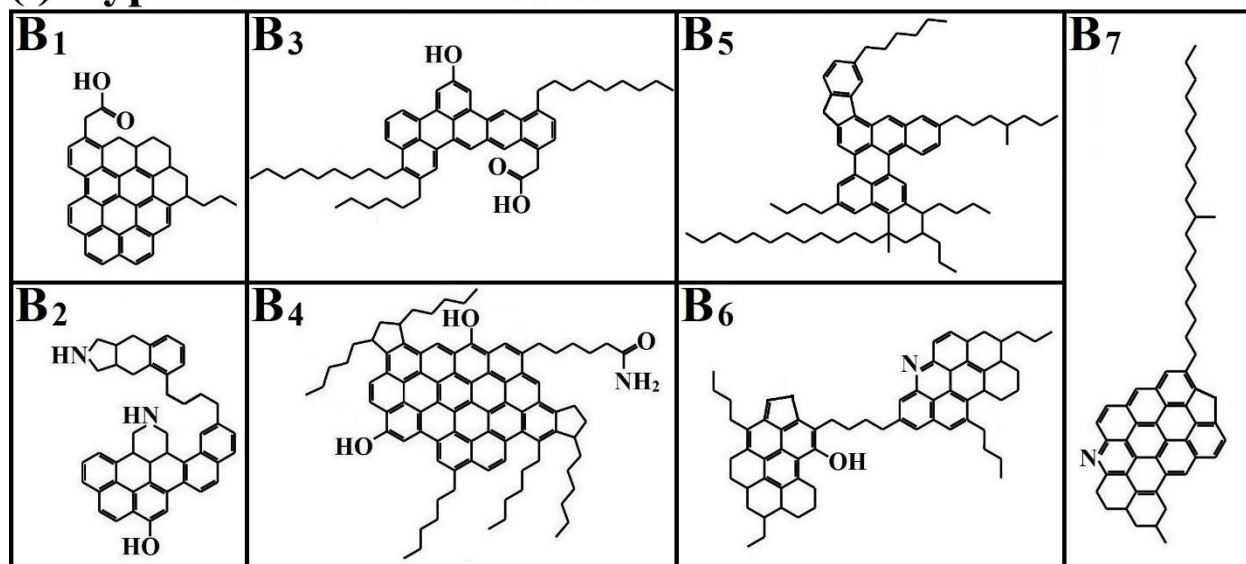


Figure 1: Molecular structures of asphaltene molecules used in this study.

### (i) Hypothetical B Molecules



### (ii) Hypothetical C Molecules

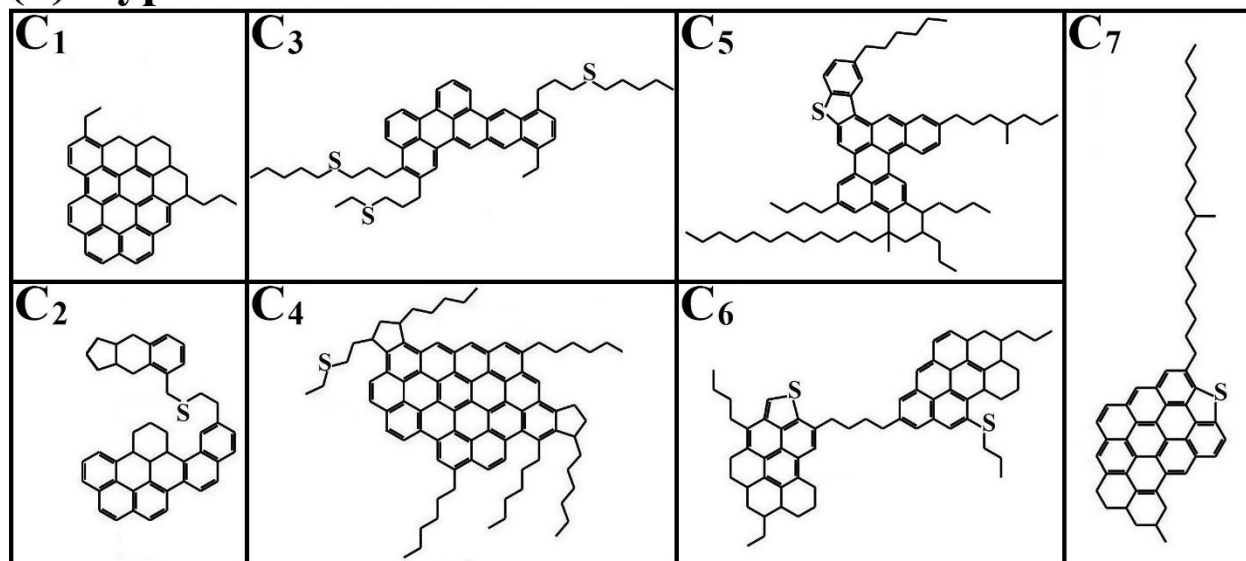


Figure 2: (i) Hypothetical B molecules, having the same structures as asphaltenes in Figure 1, but lacking sulfur in their structure. (ii) Hypothetical C molecules, having the same structures as asphaltenes in Figure 1, but lacking nitrogen and oxygen in their structures.



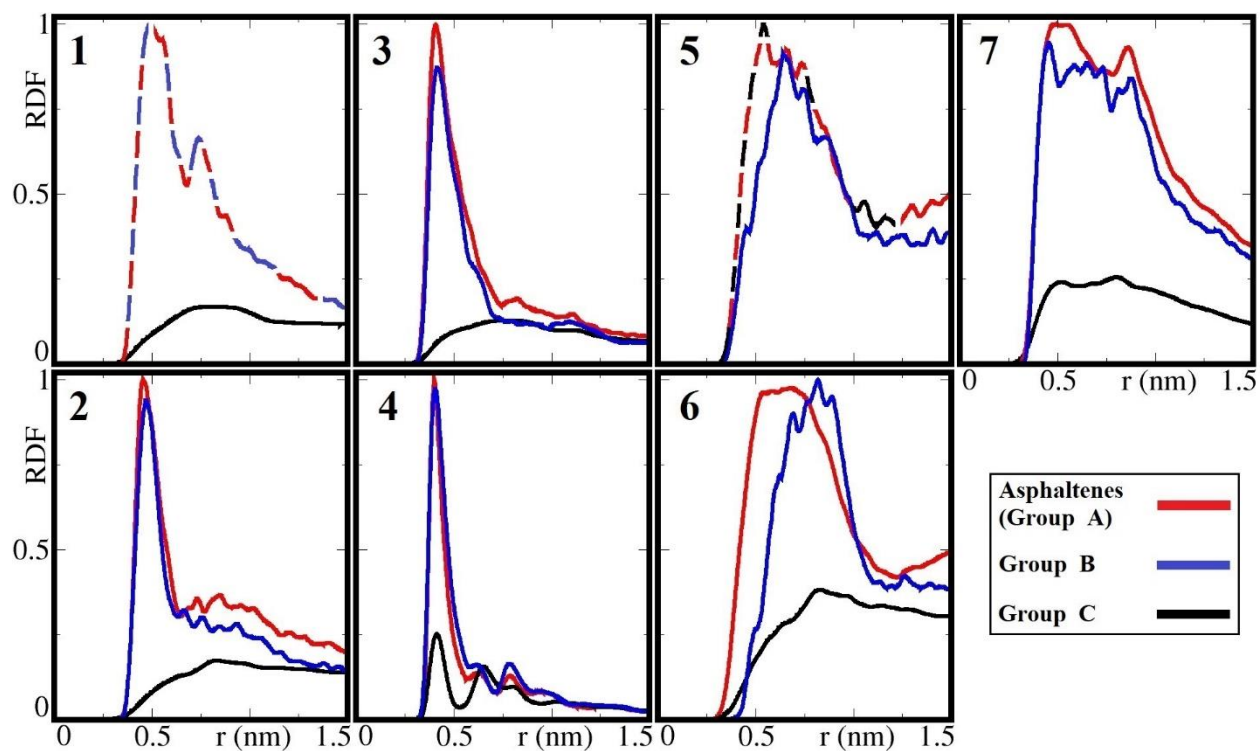


Figure 3. RDFs of asphaltene-asphaltene stacking as compared with RDFs of hypothetical molecules (B and C). Differences of RDFs of asphaltene with hypothetical molecules, B & C, are indications of the roles of heteroatoms (N, O, S) in asphaltene aggregation. All the calculations are for the centers of mass interactions. The two-colored graphs in Figures 3-1 and 3-5 indicate the similarity of results for asphaltene with B and C molecules, respectively.

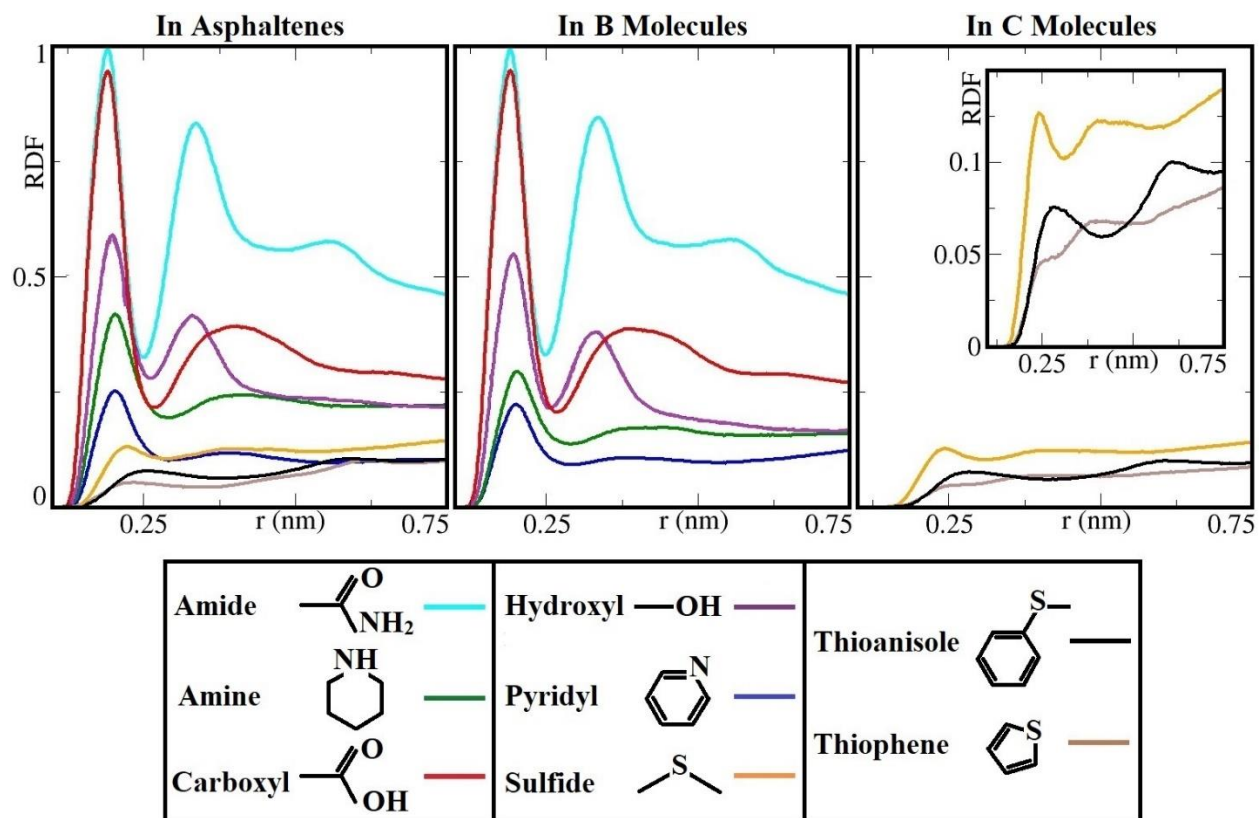


Figure 4. Relative distributions of water around various segments listed above (represented by RDFs) appearing in asphaltenes, B and C molecules.

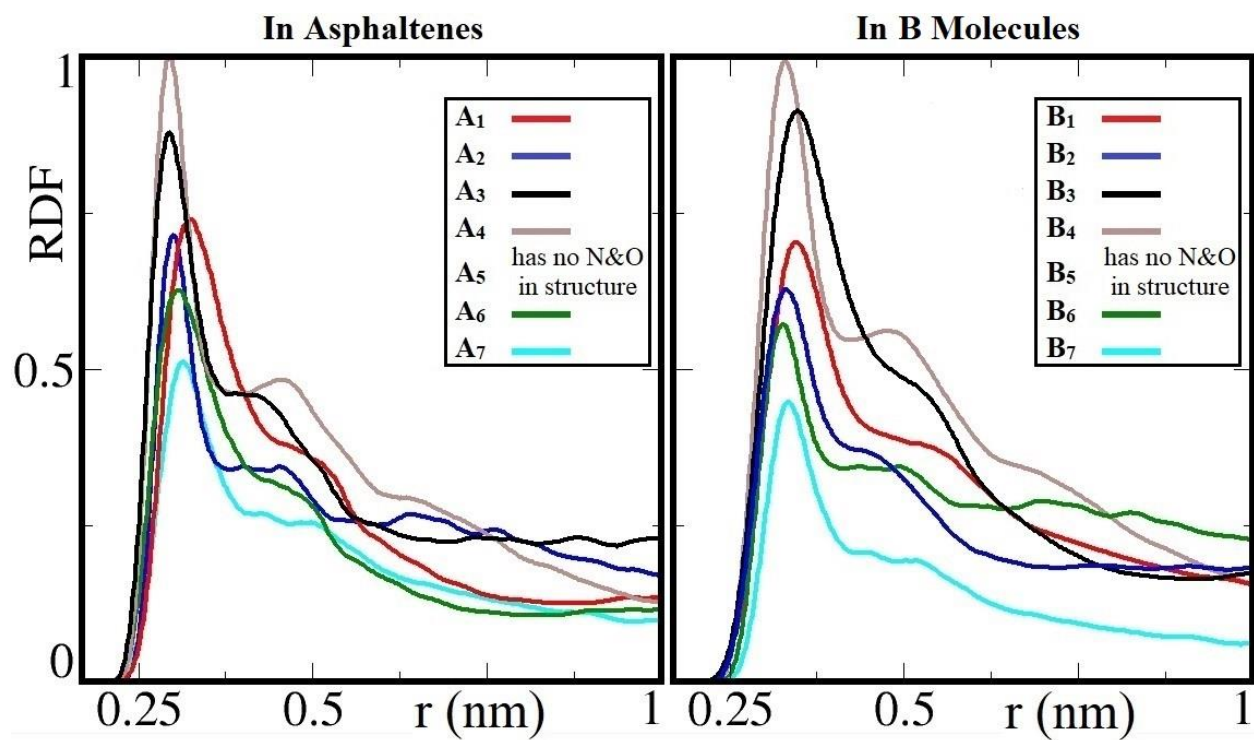


Figure 5. Relative distributions of N- and O-segments in the stacked asphaltenes and hypothetical B molecules at their onset of aggregation. The distribution is represented by segment-segment RDFs of one molecule with respect to another.

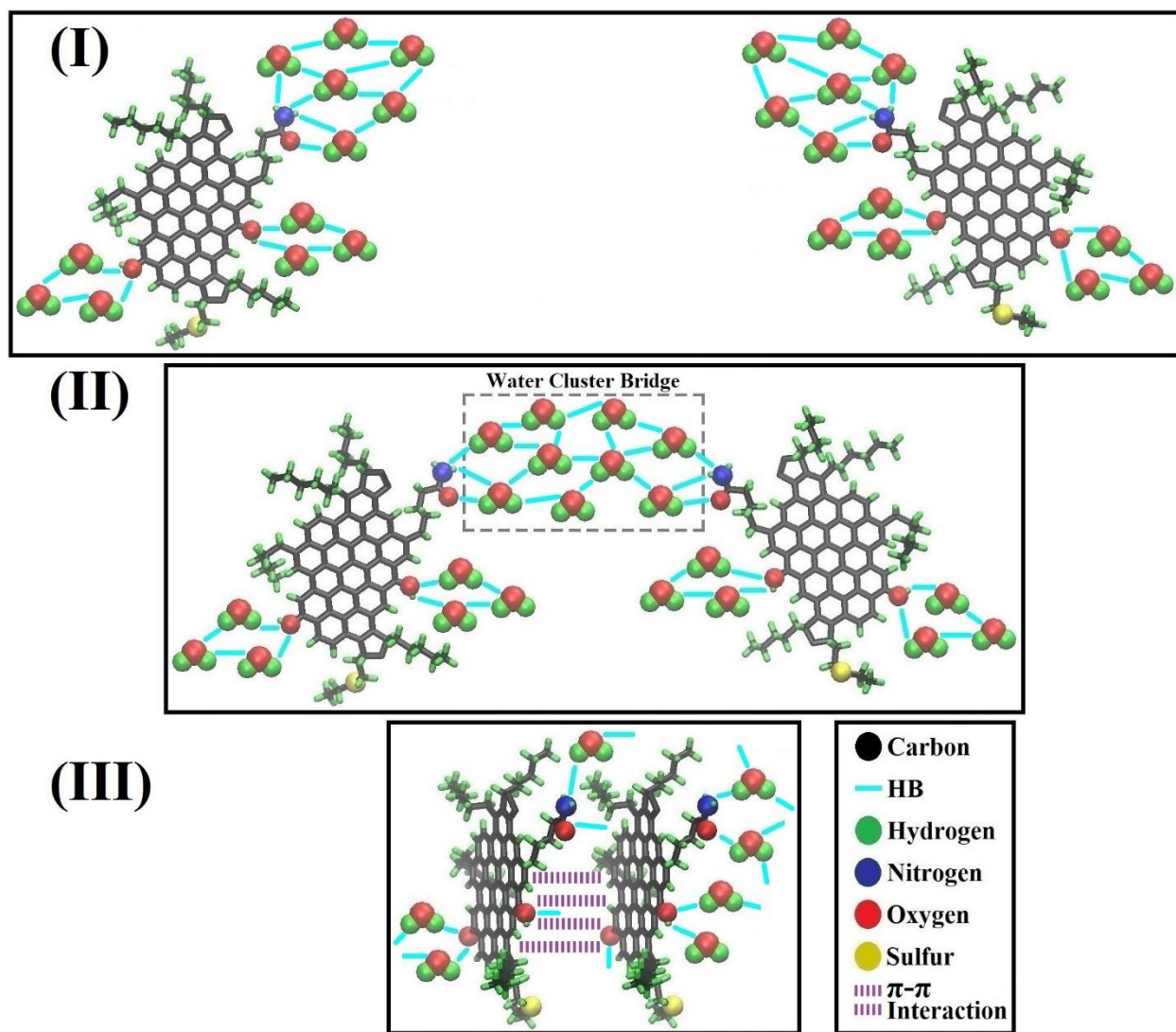


Figure 6. Schematic representation of sequential steps involved in asphaltenes aggregation due to waterflooding. In these figures, oil is omitted for clarity. Stage I: Asphaltene-water interaction via  $\text{HB}_{\text{Ai-w}}$ . Stage II: Formation of water bridges by  $\text{HB}_{\text{w-w}}$ . Stage III: Face-to-face stacking configuration of asphaltenes via  $\pi$ - $\pi$  interaction.