

Molecular Simulation of Asphaltene Aggregation in Crude Oil by Monte Carlo Method

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Abstract

Monte Carlo simulation is adopted to study the aggregation of asphaltene phenomenon in crude oil. Simulation is accomplished by applying two different potential functions to allow for asphaltene-asphaltene, asphaltene-resin and resin-resin interactions to take place. Asphaltene molecule is considered as a flat molecule, consisting of seven spheres. Resin molecule is considered to be a single sphere and the other hydrocarbons molecules contained in crude oil are modeled as a continuum media. The effect of media on intermolecular interactions is described by definition of a parameter that is composed of two dielectric and Hamaker constants. The effects of asphaltene concentration, temperature and solvent type on the aggregation of asphaltene molecules are investigated by applying both of the potential functions. The predicted results are compared.

Keywords: *Asphaltene, Monte Carlo, Simulation, Intermolecular Interaction, Aggregation*

1- Introduction

Asphaltenes are identified as the heaviest and most polar compounds of crude oil. These compounds cause many operational problems by plugging the pipelines during production and transportation stages of crude oil after their molecular aggregation, and consequently precipitation from the oil occur [1-5]. Two main interpretations on the physical state of asphaltenes in crude oil were proposed [6-10]. One considers asphaltenes as a class of compounds that are dissolved in the surrounding medium and they precipitate only if their solubility in oil

falls below a certain threshold. The second interpretation illustrates the specific effect of resin molecules on the stability of asphaltenes. Asphaltenes are considered to be insoluble colloidal solids in crude oil that are peptized by adsorbed resin molecules on their surface. Different thermodynamic models were proposed based on these interpretations [11-13]. Validation of these models is often based on how some parameters of the model are adjusted. Thus, this may be limited for application in a broader set of operational conditions. In order to overcome these limitations, one can

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resort to these interpretations of the recent molecular simulation techniques and statistical thermodynamic theories which provide a way to obtain experimental data on the thermodynamic behavior of complex fluid systems at the colloidal scale in contrast to the macroscopic models [14].

In prediction of the thermodynamic behavior of the system through the molecular simulation technique, the phase stability limit can be determined by taking into consideration the interaction potential between different compounds, the partial structure factor and radial distribution functions [14,15]. The stability limit in colloidal systems depends on the aggregates size distribution. Experimental data is usually used to validate the predicted results of the onset of asphaltene precipitation. These experimental data are strongly affected by asphaltene flocculation process; therefore, a comprehensive thermodynamic model requires taking into account the molecular asphaltene aggregation phenomenon to predict the phase envelope of the asphaltene contained in petroleum mixtures. Molecular theories provide a description for the thermodynamic behavior of a system through microscopic view. Application of these molecular theories for studying the aggregation phenomena and predicting the size distribution of asphaltene aggregates in crude oil require a microscopic description of the given oil. Due to the amazing complexity of the crude oil mixture, with respect to the number and size distribution of the components and the complex interactions involved, obtaining a detailed description of a crude oil type is both an experimental and a theoretical challenge. The difficulty in

modeling the crude oil stems from several linked factors that are currently unresolved. One of these factors is the proper structural characterization of asphaltene molecules. Apparently, simple properties such as the molecular weight of asphaltene are still not clearly obtained from the performed experiments. The large size, the energetic asymmetry and the multiplicity of the components involved are the other factors. The precipitation mechanism of asphaltenes is uncertain [16], therefore, molecular simulation as a powerful alternative for studying these complicated systems is being proposed.

Despite the uncertainties with respect to a generalized shape and molecular structure of asphaltenes, one of possible configurations for these compounds corresponds to a flat disk-like molecule, with a center that has an aromatic core and is surrounded by aliphatic chains [16,17]. This type of model is only one of the possible structures that can describe the overall chemical formula of observed asphaltenes. The actual shape is obviously not unique, although the accepted descriptions involve a core of up to six aromatic rings containing small amounts of sulfur, nitrogen, and oxygen, plus a few saturated ones. These rings are surrounded by alkyl side chains of an average length of 5-6 carbons. As traces of heavy metals such as Ni and V in the ppm level are presented in asphaltenes, only a few of the molecules will have these metals; therefore, due to their very low number they are not considered in this model. This model allows the formation of aggregates from their aromatic regions. Another type of asphaltene model molecules was proposed where the aliphatic chains

interconnected groups of small aromatic regions [16]. This model has a large overall area that gives it very distinct aggregation properties. It is reasonable that real asphaltene fractions might have varying degrees of both types of molecules or a significant amount of intermediate structures. In this article, the aggregation behavior of colloidal asphaltene-resin-solvent systems are described and size distribution of asphaltene aggregates are predicted using Monte Carlo simulation. Asphaltene molecules with resin compounds are considered in crude oil. The basis of this method is minimization of total molecular energies in the crude oil. Two different potential functions are used in studying the intermolecular interactions. The effect of oil media on these interactions is considered by introducing some parameters in the applied potential functions.

2. Theoretical simulation

2-1. System description

This proposed system contains asphaltene and resin molecules in crude medium. In this work, the effect of crude media on intermolecular interactions is also considered. As shown in Fig. 1, asphaltene is modeled as a molecule formed by a central sphere surrounded by six external spheres of the same size, forming a ring of radius L relative to that of the central sphere. The size and energetic properties of the internal (σ_{int} , ϵ_{int}) and external (σ_{ext} , ϵ_{ext}) spheres are different in principle. This fact allows us to describe the center as more aromatic and the external sites as more aliphatic in nature. Resin molecule is taken to be a single sphere

molecule of diameter σ_{resin} and energy of ϵ_{resin} . Except for heavy compounds such as asphaltene and resin, the rest of the oil mixture, with lighter compounds, is modeled as a continuum medium that influences the intermolecular interactions. The values of the molecular model parameters for asphaltene and resin molecules are represented in Table 1. The model used here is the one developed by B. Aguilera, et al. [16]. The parameters values were obtained by fitting Eq. (1) into the molecular mechanics results of the interaction energies between asphaltene-asphaltene, asphaltene-resin and resin-resin already calculated by the authors of Ref 14. Interaction between spheres is described by two potential functions and the predicted results are compared.

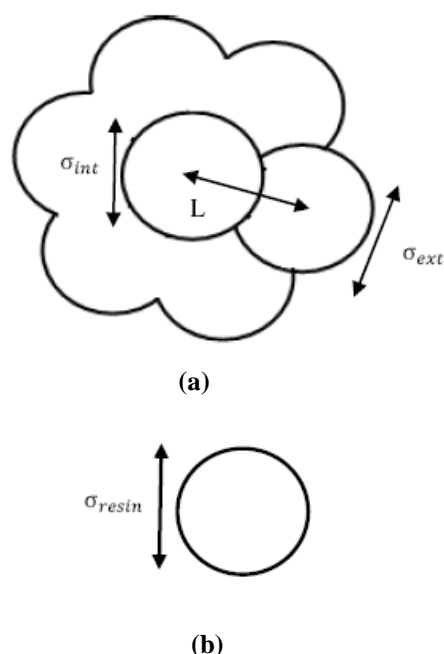


Figure 1. 2D Drawing of the Molecular Model of a) asphaltene b) resin.

Table 1. Molecular model parameters [16].

Model parameter	Value
σ_{ext} (Angstrom)	5.745
σ_{int} (Angstrom)	5.769
σ_{res} (Angstrom)	3.086
L (Angstrom)	5.3714
ϵ_{ext} (KJ/mol)	0.9462
ϵ_{int} (KJ/mol)	82.18
ϵ_{resin} (KJ/mol)	50.74

2-1-1. Lennard Jones potential function

In this section, the Lennard-Jones potential function is applied for evaluating the repulsion and dispersion forces, as follows

$$\phi_{\text{LJ}} = \sum_i \sum_j 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

It is evident that, in the organic molecules solutions the repulsion, dispersion and electrostatic interactions are the main terms that account for the fluid phase behavior. Even in the case of hydrogen bonding presence, the relatively large size of the aromatic regions of asphaltene molecules makes their contribution minor in the stability of the continental asphaltene aggregates. Therefore, for our purposes, this Lennard-Jonesium would seem sufficient to take into account the repulsion, dispersion, and basic anisotropy of the molecules. In general, any simple intermolecular potential may be arbitrarily separated into two major contributions: a short-range repulsion mainly due to the presence of electrostatic forces, and a long-range dispersion force called London or vander Waals forces. In LJ potential, the r^{-12} term corresponds to the repulsion and the r^{-6} term corresponds to the dispersion [16].

The parameter called Hamaker constant, for an appropriate description of the system, can

be used for considering the effect of the media on these interactions. This parameter represents a conventional and convenient manner of assessing the magnitude of the vander waals interactions. The ratio of this parameter value when the molecules are placed in the continuum media m to the same, when placed in vacuum may be written as [16]:

$$H_{i,m,j} = \frac{\phi_{i,m,j}^{\text{Dispersion}}}{\phi_{i,j}^{\text{Dispersion}}} = \frac{A_{i,m,j}}{A_{i,j}} \quad (2)$$

where, $A_{i,j} = \sqrt{A_{i,i}A_{j,j}}$,
 $A_{i,m,j} = (\sqrt{A_{i,i}} - \sqrt{A_{m,m}})(\sqrt{A_{j,j}} - \sqrt{A_{m,m}})$
 and $\phi_{i,m,j}^{\text{Dispersion}}$ refer to the dispersion part of the potential for a pair immersed in a continuum media m . $A_{i,j}$ is the cross Hamaker constant between two species i and j in a vacuum. $A_{m,m}$ is the Hamaker constant of the media. In a vacuum $A_{m,m} = 0$ and $A_{i,m,j}$ become identical to $A_{i,j}$.

Although Hamaker constant can be used for long- range dispersion forces, modeling it is not useful for determining the repulsion force. Thus, using the dielectric constant is the alternative approach, which considers the electrostatic nature of the repulsive interactions. On the other hand, dielectric constant is used for scaling between interactions of two particles within a fluid and in vacuum [16].

$$e_m = \frac{\phi_{i,j}^{\text{Repulsion}}}{\phi_{i,m,j}^{\text{Repulsion}}} \quad (3)$$

where, $\phi_{i,m,j}^{\text{Repulsion}}$ refers to the repulsion part

of the potential for a pair immersed in a continuum media m . In fact, the dielectric constant of the media is explanatory for its ability of breaking the polar dispersion forces between asphaltene molecules. With an increase in the dielectric constant asphaltene aggregates are completely solved in the mixture.

In this work, the Hamaker and dielectric constants represent the effect of the surrounded media on the interactions between i and j particles. These parameters are introduced to account for the variance of intermolecular interactions of the mixture, in comparison with the state that two molecules are placed in a vacuum without fluid. To study these effects on aggregation, parameter f , called the crude screening factor, is identified. It is a combination of two Hamaker and dielectric constants and is expressed as [16]:

$$f_{i,m,j} = H_{i,m,j} \sqrt{e_m} \quad (4)$$

Thus, LJ, the potential function considering the effect of the media is rewritten as:

$$\varphi_{i,m,j} = \sum_i \sum_j 4 \epsilon_{i,j} \left[\frac{1}{e_m} \left(\frac{\sigma_{i,j}}{r_{i,j}} \right)^{12} - H_{i,m,j} \left(\frac{\sigma_{i,j}}{r_{i,j}} \right)^6 \right] \quad (5)$$

Alternatively, in the other form:

$$\begin{aligned} \varphi_{i,m,j} &= \sum_i \sum_j 4 \epsilon_{i,j} (H_{i,m,j})^2 e_m \left[\left(\frac{\sigma_{i,j} (H_{i,m,j} e_m)^{-1/6}}{r_{ij}} \right)^{12} \right. \\ &= \left. \left(\frac{\sigma_{i,j} (H_{i,m,j} e_m)^{-1/6}}{r_{ij}} \right)^6 \right] \quad (6) \end{aligned}$$

and by replacing these terms:

$$\begin{aligned} \sigma_{i,m,j} &= \frac{\sigma_{i,j}}{(H_{i,m,j} e_m)^{1/6}}, \sigma_{i,j} = 0.5(\sigma_{i,i} + \sigma_{j,j}), \\ \epsilon_{i,j} &= \sqrt{\epsilon_{i,i} \epsilon_{j,j}} \text{ and } \epsilon_{i,m,j} = \epsilon_{i,j} (H_{i,m,j})^2 e_m \text{ in} \\ \text{Eq. (6) the LJ potential function is given by} \\ &[16]: \end{aligned}$$

$$\varphi_{i,m,j} = \sum_i \sum_j 4 \epsilon_{i,m,j} \left[\left(\frac{\sigma_{i,m,j}}{r_{ij}} \right)^{12} - H_{i,m,j} \left(\frac{\sigma_{i,m,j}}{r_{ij}} \right)^6 \right] \quad (7)$$

where, the summation, run over all the spheres that make up the model molecules and the Lorentz- Berthelot mixing rules are applied [16,18,19].

In this work, four different substances are considered as a media, where asphaltene and resin molecules float in. These substances are n -pentane, n -heptane, toluene and n -hexadecane, the Hamaker and dielectric constants of which are presented in Table 2. The values of Hamaker constant for asphaltene and resin molecules are considered 17.15×10^{-20} (J) and 13.25×10^{-20} (J) [16] respectively in this work.

Table 2. Dielectric constants, e_i , the main electronic absorption frequency in the uv region, ν_e , refractive index of the medium in the visible spectra, n_i , and Hamaker constants, A , for some solvents at 25 °C [16].

Substance	Dielectric constant (e_i)	Refractive index of the medium in the visible spectra (n_i)	Main electronic absorption frequency in the uv region (ν_e) (s^{-1})	Hamaker constant (A) (J)
n -pentane	1.844	1.349	2.99×10^{15}	3.75×10^{-20}
n -heptane	1.92	1.378	2.98×10^{15}	4.32×10^{-20}
n -hexadecan	2.05	1.423	2.94×10^{15}	5.26×10^{-20}
Toluene	2.4	1.496	3.00×10^{15}	5.4×10^{-20}

For substances that are used in this work the dielectric constant is rather constant. The Hamaker constant of various materials can be estimated by correlating the measurable experimental parameters and temperature as follows:

$$A_{i,i} = \frac{3}{4}kT \left(\frac{e_i - 1}{e_i + 1} \right)^2 + \frac{3hv_e}{16\sqrt{2}} \frac{(n_i^2 - 1)^2}{(n_i^2 - 1)^{3/2}} \quad (8)$$

where, k and h are Boltzmann's and Planck's constants, v_e is the main electronic absorption frequency in the ultra violet region, e_i is the dielectric constant, and n_i is the refractive index of the medium in the visible spectra. Eq. (8) relates the Hamaker constant of the media with experimentally available parameters.

2-1-2. Ortega-Rodriguez potential function

Stability of an asphaltene-resin mixture could be investigated by another effective potential function which is proposed by Ortega-Rodriguez et al. as follows [14,20]:

$$U_{ij}(r) = \frac{Z_1 Z_2}{r} [e^{-\alpha r} + (C_1 \epsilon r e^{-\beta r})] - \frac{C_2}{r^6} e^{-\gamma/r^4} \quad (9)$$

where, r is the distance between the centers of mass of each molecule, and Z_1 and Z_2 are the number of atoms in each asphaltene or resin molecule. The parameters α , β , γ , C_1 , C_2 in Eq. (9) are obtained by fitting the equation into the corresponding molecular mechanics, numerical results as previously predicted from the INSIGHT II and DISCOVER 3.0 suite of programs [21]. In this section, dielectric constant, ϵ_m , is

introduced in potential function, to account for the effect of the media on intermolecular interactions. So by considering the effect of the media, Eq. (9) can be rewritten as:

$$U_{ij}(r) = \frac{Z_1 Z_2}{\epsilon_m r} [e^{-\alpha r} + (C_1 \epsilon r e^{-\beta r})] - \frac{C_2}{\epsilon_m^2 r^6} e^{-\gamma/r^4} \quad (10)$$

The values of the O-R potential parameters for this work are presented in Table 3.

Table 3. Parameters for Ortega-Rodriguez potential function.

Parameter	Asphaltene-Asphaltene	Asphaltene-Resin	Resin-Resin
α	13.7	15	20
β	2.75e8	4.44e6	7.00e4
γ	3.2512	2.9869	2.3531
C_1	5303594	876039	136367.1
C_2	50.1429	113.7438	309.476

2-2. Simulation details

Monte Carlo simulation process begins with a collection of N_A asphaltene molecules and N_R resin molecules, which are randomly disposed in a cubic simulation box of edge length L with periodic boundary conditions. The number density of the molecules in this cubic box is defined as $\rho_i = \frac{N_i}{L^3}$. The number

of molecules, the volume and the temperature are fixed. For a definition of the initial situation of each molecule a random number is generated between 0 and L in X, Y, Z directions and each molecule is placed in its initial situation, having no overlap with each other. In this state, the interaction energies of each molecule related to all other molecules are evaluated in the simulation box. The molecules are then randomly translated and the total interaction energy of the system is

calculated again. Acceptance or rejection of each displacement is recognized by the metropolis algorithm [22]. These steps are repeated until the system reaches equilibrium. In this state, the situation of each molecule is calculated with respect to other molecules. Clusters are identified by recognizing that two molecules form a cluster when any two parts of the molecules are closer than a given distance, namely $2^{1/6}\sigma_{ij}$. In the next step, the mean cluster size, Z , is calculated and the size distribution of clusters is predicted under different conditions as follows:

$$Z = \frac{\sum_M (m_M)M}{\sum_M (m_M)} \quad (12)$$

where, M denotes the cluster size and (m_M) is the mean number of cluster of size M .

2-3. Case study

In this work, a system containing 100 asphaltene and 200 resin molecules is considered. The effects of some parameters such as asphaltene concentration, temperature and crude oil media on the results of simulation are investigated qualitatively. Table 4 presents a summary of the conditions used in these simulated systems. The molecular weight of asphaltene was taken directly from the atomistic models 794 [16].

Table 4. Operation conditions used in simulated systems.

Asphaltene Concentration (gr/ml)	Temperature (K)	Solvent
0.111	298	<i>n</i> -pentane
0.236	333	<i>n</i> -heptane
0.794	353	<i>n</i> -hexadecan
1.54	398	Toluene

3. Results and discussion

In this section, the results of simulation at different values of identified parameters are presented. The effects of asphaltene concentration, temperature, type of interaction potential and crude oil media on aggregation and size distribution of asphaltenic clusters are investigated.

3-1. Effect of interaction potential

The values of the parameters of both interaction potentials used in this work are obtained by fitting these equations in the results of molecular mechanics calculations for asphaltene-resin systems as demonstrated in Fig. 2. In order to confirm these parameters' value, the interactions potential energies are evaluated in different relative distances between each pair of molecules. As indicated in Fig. 3, both L-J and O-R potentials evaluate equal values of interaction energies at the same distances. In addition, the values of interaction energy between asphaltene-asphaltene, asphaltene-resin and resin-resin molecules are calculated by both interaction potentials. Results illustrate that the values of asphaltene-asphaltene interaction energies contribute the most to the total energy within the system.

3-2. Effect of asphaltene concentration and crude media

The effect of asphaltene concentration on aggregation phenomenon and residual asphaltene monomer fraction in the system is illustrated in Fig. 4, using L-J potential. By increasing the asphaltene concentration in the system, the probability of sticking asphaltene molecules is increased and the aggregation

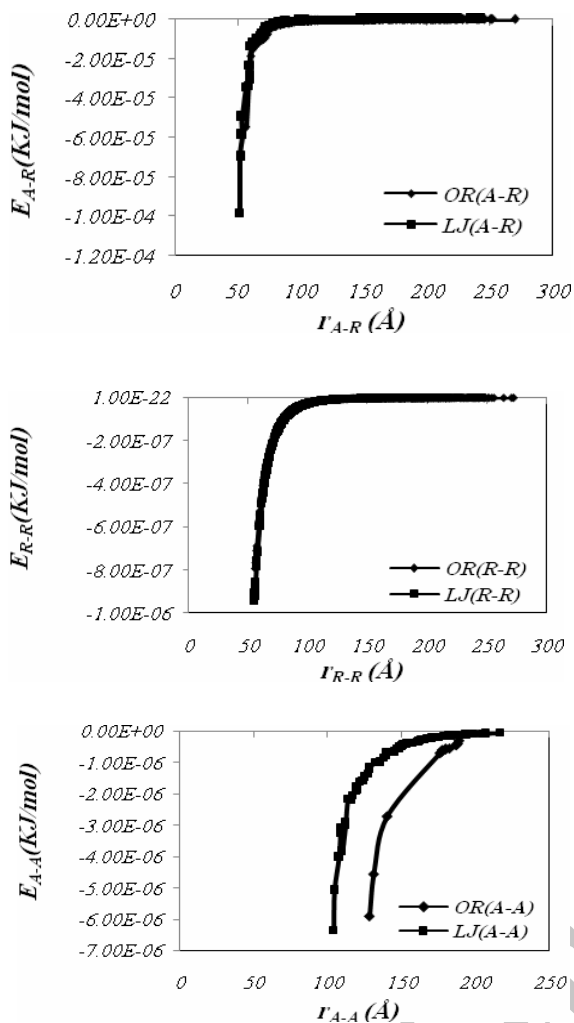


Figure 2. Intermolecular interaction energy for asphaltene-asphaltene, asphaltene-resin and resin-resin molecules calculated by L-J and O-R potential functions.

is improved more. Thus, the mean cluster size of asphaltene is increased and the residual monomer fraction is decreased. These results are obtained by O-R potential function. The obtained values for two interaction potentials at $C=0.111$ (gr/ml) and 0.794 (gr/ml) are compared in Fig. 5. The predicted results are in good agreement. Figure 6 shows the growing mean asphaltene cluster size as the concentration of asphaltene increases. The contribution of the screening

factor, f , which provides a useful measurement of the media nature to the aggregation phenomenon, is an indication of these figures.

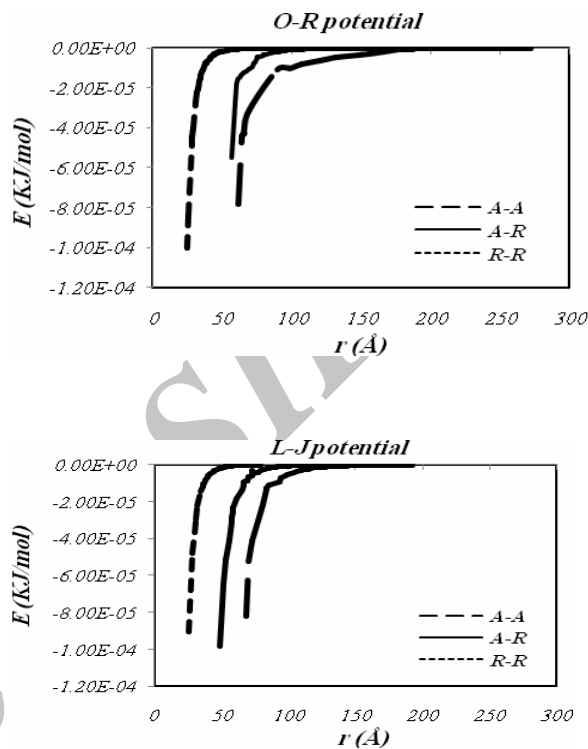


Figure 3. Intermolecular interaction energy for asphaltene-asphaltene, asphaltene-resin and resin-resin molecules calculated by L-J and O-R potential functions.

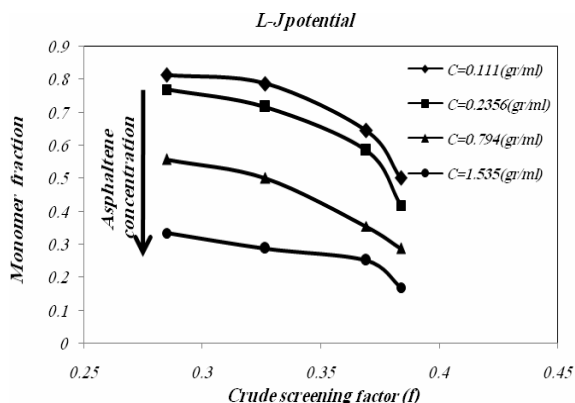


Figure 4. Effect of the media on residual monomer fraction of asphaltene using L-J interaction potential a functions at various concentrations, $T=298K$.

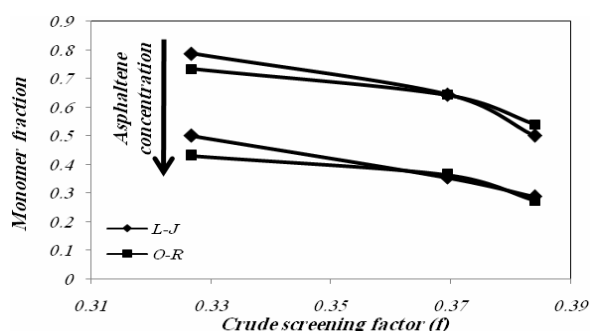


Figure 5. Comparison between L-J and O-R interaction potential functions at $C=0.111$ and 0.794 (gr/ml), $T=298$ K.

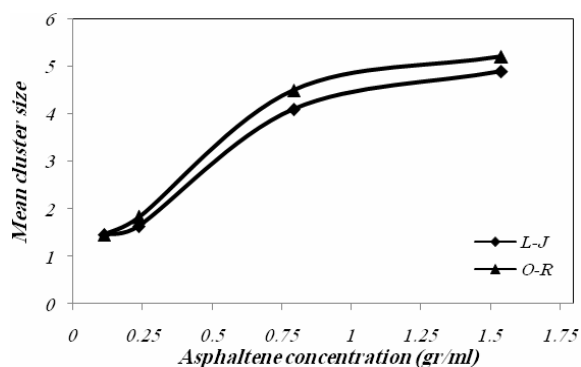


Figure 6. Effect of concentration on mean cluster size using L-J and O-R interaction potential functions at $f=0.3267$, $T=298$ K.

Screening factor is a parameter which contains dielectric and Hamaker constants of media. By evaluating this parameter for substances which are used in this work, it is observed that the aggregation of asphaltene is better improved in *n*-pentane and *n*-heptane with higher f , compared to the state that has lower f (equal to toluene and *n*-hexadecane). It can be observed from Figs. 4 and 5 that a higher media screening factor results in a smaller monomer fraction, consequently, a larger mean cluster size is reached at the end of the simulation.

3-3. Effect of temperature

The residual monomer fraction of asphaltene at the end of simulation, as a function of temperature in different crude media is presented in Fig. 7. As expected, with respect to Eq. (8), by increasing the temperature, Hamaker constant of media is increased, leading to a decrease in parameter f and the mean cluster size of asphaltene. On the other hand, by increasing the temperature in the range under investigation, the aggregation progress of asphaltene is low and the residual monomer fraction is increased.

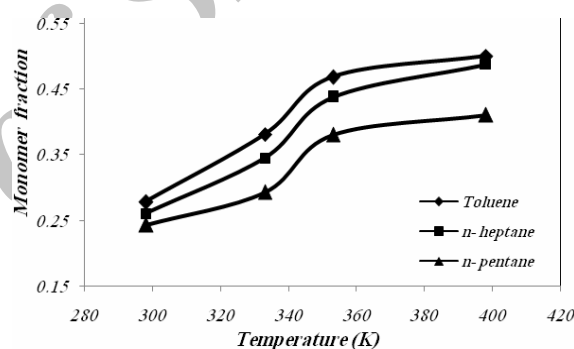


Figure 7. Effect of temperature on the residual monomer fraction of asphaltene, using L-J interaction potential functions at $C=0.111$ (gr/ml).

3-4. Aggregation mechanism

In the simulation, one can consider the aggregation mechanism of asphaltene molecules by using the crude screening factor of the system. As crude media has a higher ability to aggregate asphaltene molecules, their crude screening factor is higher. This state is equal to the media such as *n*-pentane and *n*-heptane. Contrary to the crude screening factor being lower, media's ability to aggregate asphaltene molecules gets lower. In Fig. 8, the residual monomer fraction at the end of the simulation is

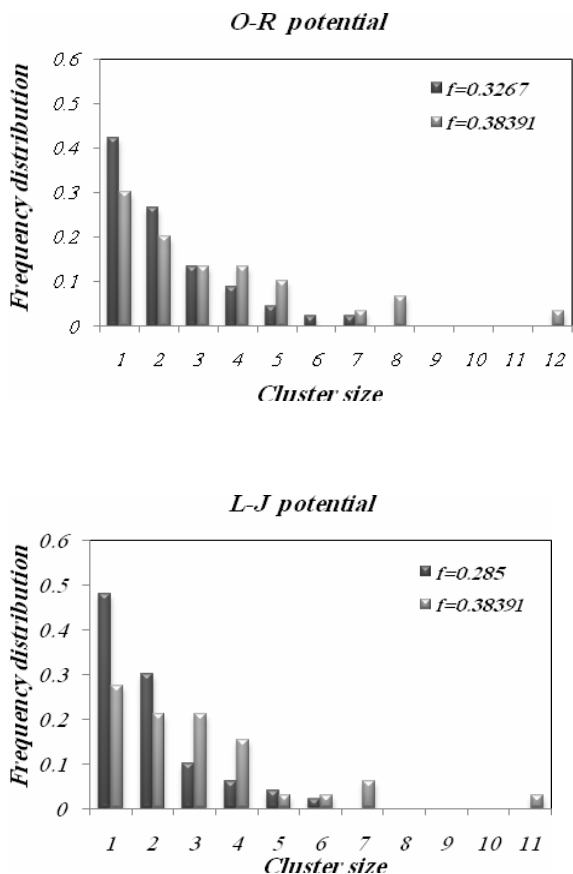


Figure 8. Normalized frequency distribution as a function of cluster size for two crude media, using L-J and O-R interaction potential at $C= 0.111(\text{gr/ml})$, $T=298\text{K}$.

presented as a function of cluster size for two different media using O-R and L-J potential functions. As shown in this figure, in the media with a smaller screening factor (equal to toluene and *n*-hexadecane), half of the asphaltene molecules are presented as the monomer and the distribution is unimodal. In another state where crude media has a higher screening factor (equal to *n*-pentane and *n*-heptane), the aggregation phenomena is significantly improved and nearly one- third of asphaltene molecules present as monomers and the size of the clusters are larger than the previous state. This behavior indicates the

aggregation of clusters and generation of larger clusters. Larger cluster size in the crude media of the higher screening factor is shown with more clarity in Fig. 9. Moreover, in this state, the size distribution of asphaltene is not unimodal. This trend can be related to the type of aggregation mechanism. In other words, both aggregation mechanisms, namely particle- cluster and cluster-cluster aggregation are important at this state. Also, the same results were obtained for a certain crude oil sample by considering the role of aggregation mechanism by Dabir group [24,25].

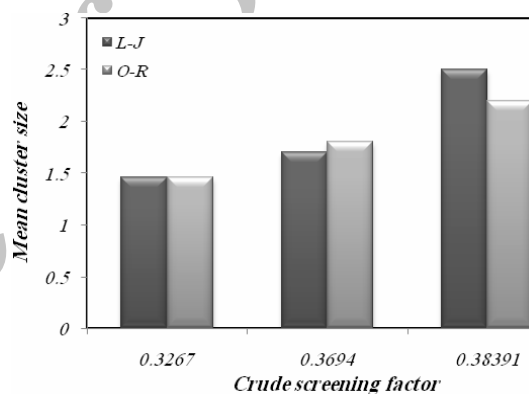


Figure 9. Mean cluster size in various media using L-J and O-R interaction potential functions at $C= 0.111(\text{gr/ml})$, $T=298\text{K}$.

4. Conclusions

In this article, the Monte Carlo simulation is employed to study the aggregation of asphaltene molecules in different media. Intermolecular interactions between asphaltene-asphaltene, asphaltene-resin and resin-resin are calculated using two different L-J and O-R interaction potential functions. The results are then compared against each other. The effect of the media in which asphaltene and resin molecules float on intermolecular interaction is considered by

using the two dielectric and Hamaker constants of the media. The dependence of the cluster size and the residual monomer fraction of asphaltene molecules on the asphaltene concentration, temperature and media are investigated here. An increase in asphaltene concentration and the screening factor and a decrease in temperature result in an increase in the cluster size and a decrease in monomer fraction in the system. Different aggregation mechanisms are expected due to the fact that the asphaltene size distribution is not unimodal in the media, and has a higher screening factor corresponding to the higher ability to aggregate. The predicted results of the simulation using both interaction potentials are in good agreement.

5. Nomenclature

A	Hamaker constant
C	concentration
C_1, C_2	Ortega- Rodriguez Potential parameters
e	dielectric constant
f	screening factor
h	Planck's constant
H	ratio defined in Eq. (2)
k	Boltzmann's constant
L	edge of cubic simulation box
(m_M)	mean number of cluster of size M
M	cluster size
N	refractive index of the medium in the visible spectra
N_A	number of asphaltene molecules
N_R	number of resin molecules
r	distance
T	temperature
U	Ortega- Rodriguez potential function

ν_e	main electronic absorption frequency in the ultra violet region
X, Y, Z	coordinate directions
Z	mean cluster size
Z_1, Z_2	number of atoms in each asphaltene or resin molecule

Greek symbols

α, β, γ	Ortega-Rodriguez potential parameters
ρ	number density of molecules
φ	Lennard Jones potential function
ϵ	intermolecular interaction energy
σ	intermolecular size

Subscripts

i, j	molecules
m	continuum media

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