Asphaltene Aggregation in Aqueous Solution Using Different Water Models: A Classical Molecular Dynamics Study

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ABSTRACT: The aggregation behavior of asphaltene in aqueous solution is systematically investigated based on a classical molecular dynamics study. In this work, a novel approach is adopted in order to investigate the structural and dynamical properties of the asphaltene nanoaggregates using different water models. The end-to-end distance of the asphaltene molecule is probed in order to understand the aggregation behavior in aqueous solution. The accuracy of different water models, that is, simple point charge, TIP4P-D, and TIP5P, is thoroughly investigated. In order to probe the dynamical properties of the asphaltene nanoaggregates, the transport coefficients, namely, diffusion coefficient and shear viscosity, are computed. The obtained results highlight the importance of using the appropriate water model in order to accurately study the aggregation behavior of asphaltene in aqueous solution.

1. INTRODUCTION

Asphaltenes are the heaviest components of the crude oil. These are complex molecules, consisting of polycyclic aromatic hydrocarbons, aliphatic side chains, and polar heteroatom-containing functional groups. The asphaltene molecules present in crude oil hold the highest fraction. Asphaltenes are dissoluble in aromatic hydrocarbons, for example, toluene, benzene, or pyridine, but insoluble in n-alkanes, for example, pentane, heptane, and hexane. They form aggregates in selective organic solvents, water, and oil–water emulsion and are accountable for the high viscosity of crude oil. It is noteworthy that destabilized asphaltenes can cause serious problems in oil refineries such as coke formation, catalysis deactivation, pipeline blocking, and many more. Furthermore, asphaltenes reduce petroleum productivity because of the high viscosity induced by their presence in crude oil. Also, their release into the environment can have negative impacts on the soil and marine life because of their non-biodegradable nature.

In-depth understanding of the asphaltene chemistry has the potential to increase the efficiency of oil recovery. Many experimental investigations and theoretical simulations have been performed in order to uncover the mechanisms behind asphaltene aggregation and asphaltene–solvent interactions. According to the widely known Yen–Mullins model, the asphaltene molecules tend to nanoaggregate when the number of these molecules is less than 10. The clustered nanoaggregates further combine to form the macroaggregates. Within the abovementioned model, the aliphatic side chain surrounds the polycyclic core and aggregation occurs mainly because of the π−π interactions between the cores.

Mullins et al. performed experimental investigations on asphaltenes in the colloidal form in crude oil. In this study, the equation of state for the asphaltene gradients in oil field reservoirs has been developed. It is concluded that the molecular island architecture is favored, and the most probable molecular weight is approximately 750 g/mol. Aslan and Firoozabadi performed flow-line experiments using differential interference contrast microscopy and dynamic light scattering to investigate the size of the asphaltene aggregates in water. The authors concluded that the deposition of the asphaltenes in water is delayed because of the presence of the hydrogen bonds between the water molecules and asphaltene heteroatoms, that is, oxygen, nitrogen, and sulphur. Schuler et al. probed coal-derived asphaltenes’ and petroleum asphaltenes’ molecular structures using atomic force microscopy (AFM) and scanning tunneling microscopy. Zhang et al. probed the asphaltene molecular interactions in organic solvents using a surface force apparatus. The study showed that the asphaltene interactions strongly depend on the weight...
The existing works on asphaltene nanoaggregation highlight several aspects as elaborated above. However, most of these existing works explain aggregation using the simple point charge (SPC) water model. A systematic analysis of the asphaltene aggregation using different water models is still missing in the literature. The viscosity of the asphaltene molecules in aqueous solution is reported for the first time in the literature through this work. We adopt a novel approach of end-to-end analysis in order to investigate the structural properties of asphaltene nanoaggregates. We report important dynamical properties viz. diffusion coefficient of asphaltene molecules in aqueous solution which has been systematically investigated using three different water models. Furthermore, we provide a detailed analysis of the hydrogen bonds between the asphaltene and water.

2. COMPUTATIONAL DETAILS

Accurate force field parameters are the key to obtain accurate molecular structures. In this work, the latest in-built optimized parameters for liquid simulations (OPLS3e) in the Desmond MD package within Schrödinger simulation software have been used. Violanthrone-78 ($C_{70}H_{46}O_8$) is considered as a model asphaltene compound, as shown in Figure 1. Earlier nanoaggregate investigations were performed at an asphaltene concentration of 20 g/L. In the present work, we have considered three different concentrations, that is, 13.96 g/L (6 asphaltene molecules), 27.91 g/L (12 asphaltene molecules), and 55.82 g/L (24 asphaltene molecules) in order to study asphaltene aggregation. We have used a 90 Å cubic box for the simulations. A snapshot of the aggregation of 6 asphaltene molecules in 0.15 M NaCl aqueous solution is shown in Figure 2. The equilibration runs are performed for 1 ns and the production run of 2 ns is analyzed. A time step of 1 fs is used and the NVT simulations are performed at 300 K. We have used SPC, TIP4P-D, and TIP5P water models and the OPLS3e potential for the asphaltenes.
3. RESULTS AND DISCUSSION

3.1. End-to-End Distance. The end-to-end distance of the asphaltene molecules, that is, the distance between the end of the aliphatic side chain to the other end is an important quantity to probe in order to understand the aggregation behavior of asphaltene in water. The aliphatic side chains are stiff on shorter length scales and the longer length scale side chains bend to participate in the aggregation process. One of the approaches to probe the end-to-end distance is by utilizing the worm-like chain model\(^{38}\) for the semiflexible side chains. In this study, the abovementioned approach is used, that is, the end-to-end distance of the asphaltene molecule averaged over all asphaltene molecules is calculated over the entire MD simulation trajectory using the following equation\(^{39}\)

\[
\langle h^2 \rangle = 2L_pL_0[1 - (L_p/L_0)(1 - \exp(-L_0/L_p))] \quad (1)
\]

where \(\langle h^2 \rangle\) is the mean-squared end-to-end distance, \(L_0\) is the extended chain length, and \(L_p\) is the persistence length. It is evident from Figure 3a for the SPC water model that the end-to-end distance, averaged over 24 asphaltene molecules, is 30.6 Å at the beginning of the first 1 ns of simulation time. This distance gradually decreases to a final value of 16.1 Å, where the aggregation is clearly visible. Figure 3b shows the frequency of the end-to-end distance over a simulation time of 1 ns. Our study shows that the aggregates formed have a minimum end-to-end distance of 16.1 Å and the highest frequency is observed at this particular length. The end-to-end distance oscillates between 13.9 and 18.8 Å during the later 2 ns of the simulation run, as illustrated in Figure 3c. It can be clearly seen in Figure 3d that the maximum frequency is corresponding to 16.6 Å when the SPC water model is used.

Table 1 summarizes the end-to-end distance along with the extended chain length and persistence length for three different water models corresponding to each of the three concentrations under investigation. The aliphatic side chains can adapt to different structures in the solvent, depending on the water models used for the study. This is the main reason for the slight variation in the end-to-end distance obtained corresponding to the different water models, as presented in

Figure 2. Snapshot of asphaltene aggregates in aqueous NaCl solution is shown in the figure. The following is the color coding: sodium ion (pink), chloride ion (green), asphaltene aggregates (gray), and water molecules (blue).

Figure 3. (a) End-to-end distance of asphaltene molecules is shown for the first 1 ns using the SPC water model MD trajectory. (b) Frequency vs end-to-end distance of asphaltene molecules is shown for the first 1 ns using the SPC water model MD trajectory. (c) End-to-end distance of asphaltene molecules is shown for the later 2 ns using the SPC water model MD trajectory. (d) Frequency vs end-to-end distance is shown for the later 2 ns using the SPC water model MD trajectory. Calculations are performed for 24 asphaltene molecules in a cubic box along with 0.15 M NaCl.
The average number of the hydrogen bonds is summarized for the various TIP4P-D water model than the other two water models. The average number of the hydrogen bonds is more for the TIP4P-D in comparison with SPC and TIP5P water models. A similar trend is observed for all the three concentrations of asphaltene in water, that is, the average number of the hydrogen bonds is more for TIP4P-D in comparison with the other two water models. A persistence length indicates that beyond this distance there will be no correlation, that is, the aliphatic side chains are stiff for a large distance. This in turn results in a higher end-to-end distance at lower asphaltene concentrations, that is, in the dilute limit.

### 3.2. Hydrogen Bonds: Asphaltene–Water

The polar heteroatoms of the asphaltene are involved in the formation of the H bonds with water. Murgich et al. performed molecular mechanics calculations and titration calorimetry experiments to investigate the H bonds between asphaltene heteroatoms and water. The study showed that water enhances the association of asphaltene monomers to form dimers because of the hydrogen bonding plays a key role in the aggregation of asphaltenes. Previous investigations on the structural properties of pure water using different water models concluded that the average number of the hydrogen bonds per water molecule is higher for the SPC and TIP4P-D water models than the TIP5P water model. In our study, the hydrogen bonds between asphaltene and water are calculated using three different water models for various concentrations of asphaltene in water. These bonds are analyzed over the production run time of simulation. As illustrated in Figure 4, the average number of the H bonds is more for TIP4P-D in comparison with SPC and TIP5P water models. A similar trend is observed for all the three concentrations of asphaltene in water, that is, the average number of the hydrogen bonds is more for the TIP4P-D water model than the other two water models. The average number of the H bonds is summarized for the various concentrations using the different models in Table 2. TIP4P-D is more effective than the TIP4P/2005 water model because the parametrization of the former includes the excess dispersion interactions on the structure of the TIP4P/2005 water model. The dispersion interactions are incorporated by increasing the dispersion coefficient, that is, C6 by ~50% in comparison with the other water models such as SPC/E, TIP3P, and TIP4P-EW. This enhanced dispersion interaction better describes the water hydrogen-bonding interactions and water–solute interactions. We, thus, conclude that the strong interaction between asphaltene and water molecules is well-captured by the TIP4P-D water model, that is, by the enhanced water dispersion interaction model.

### Table 1. Calculated End-to-End Distance Averaged Over 6, 12, and 24 Molecules Over 2 ns of Simulation Time, Persistence Length, Extended Chain Length (in Å), and Time Series Standard Deviation (σ) Corresponding to the End-to-End Distance Values are Shown for Three Different Asphaltene Concentrations Obtained Using Different Water Models

| water model | end-to-end distance (Å) | persistence length (Å) | extended chain length (Å) | σ (Å) |
|-------------|-------------------------|------------------------|---------------------------|-------|
| SPC         | 15.62                   | 3.11                   | 50.6                      | 2.54  |
| TIP4P-D     | 19.64                   | 4.90                   | 50.6                      | 1.12  |
| TIP5P       | 14.52                   | 2.52                   | 50.4                      | 1.22  |
| SPC         | 14.02                   | 2.32                   | 50.3                      | 1.92  |
| TIP4P-D     | 13.67                   | 2.19                   | 50.7                      | 1.58  |
| TIP5P       | 13.21                   | 2.14                   | 50.6                      | 1.05  |
| SPC         | 16.40                   | 3.32                   | 50.7                      | 1.15  |
| TIP4P-D     | 15.47                   | 2.98                   | 50.6                      | 0.87  |
| TIP5P       | 16.34                   | 3.38                   | 50.8                      | 0.77  |

### Table 2. Calculated Average Number of H Bonds is Presented for Three Different Asphaltene Concentrations Obtained Using Different Water Models

| asphaltene concentration | SPC | TIP4P-D | TIP5P |
|--------------------------|-----|---------|-------|
| 24 asphaltene molecules  | 78  | 81      | 64    |
| 12 asphaltene molecules  | 47  | 56      | 35    |
| 6 asphaltene molecules   | 26  | 27      | 18    |
Using Di reaches a constant value. \( \lim_{t \to \infty} \frac{d}{dt} \langle \vec{r}(t) - \vec{r}(0) \rangle^2 \rangle \) is the mean-square displacement, where the angled brackets indicate an ensemble average, which is an average over all particles and time. The diffusion coefficients obtained within our study are shown in Table 3 for different concentrations of asphaltene using the three different water models. There is a clear signature that the diffusion coefficient decreases with the increase in the concentration of the asphaltene. The lowest diffusion coefficient is obtained using the TIP4P-D water model for all three concentrations pointing toward slow aggregate dynamics. The inclusion of the enhanced dispersion interactions results in the inclusion of the enhanced dispersion forces thus adequately describes asphaltene–water interactions.

3.4. Viscosity. The MD simulations are often used in association with a Green–Kubo formalism to calculate the shear viscosity of liquids. In our work, the viscosity is calculated using the following Green–Kubo equation:

\[
\eta = \frac{V}{k_B T} \int_0^\infty \langle \text{P}_{\text{off}}(t) \cdot \text{P}_{\text{off}}(0) \rangle dt
\]

(3)

where \( V \) is the volume of the system, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \text{P}_{\text{off}} \) denotes the off-diagonal pressure tensor, and the angled bracket denotes the ensemble average. The autocorrelation function of the pressure tensor decays to zero in the long time limit and the integral in eq 3 reaches a constant value.

Earlier investigations by González and Abascal and Tazi et al. concluded based on the Green–Kubo approach that the TIP4P/2005 water model accurately predicts the dynamical properties of pure water, for example, the shear viscosity. In the present study, we performed 10 independent MD runs starting with different atomic velocities in order to calculate the viscosity. The pressure tensor is analyzed for each MD simulation output yielding a viscosity curve with respect to time. The average viscosity at each time is obtained by averaging over multiple viscosity curves, as shown in Figure 5.

An exponential function is used to fit the data of Figure 5 and the asymptote of the fitted functions is considered as the final shear viscosity. The viscosities for the dilute asphaltene concentration for 6 asphaltene molecules are presented along with the standard deviation of the fit (\( \sigma \)) for asphaltene in aqueous solution for the three water models.

Although the viscosity value is improved for the TIP5P water model (0.71 cP), a better value is obtained using the TIP4P-D water model, that is, 1.21 cP. Furthermore, we used the TIP4P-D water model to evaluate the viscosity for 12 asphaltene molecules in aqueous solution which is obtained as 1.31 cP and 24 asphaltene molecules in aqueous solution obtained as 1.46 cP. Our study highlights the fact that the enhanced dispersion interactions improve the description of the asphaltene–water interactions. However, it is noteworthy that the solution behavior is completely dependent on the accurate description of the solute–solvent in solute–solvent interactions. The strengthening of the water dispersion interactions results from the offsetting of inadequate dispersion interactions from the OPLS force field. For the hydrocarbon molecules, it is thus necessary to improve the OPLS force field for better agreement with the experimental results.

4. CONCLUSIONS

In the present work, the aggregation of asphaltene (Viola-nthrene-78) in aqueous NaCl solution is investigated by performing MD simulations using SPC, TIP4P-D, and TIP5P potentials for water–water interaction. It is observed that the end-to-end distance of asphaltene molecules at three different concentrations is approximately the same for the water models under study except the TIP4P-D model (especially in the dilute limit). This discrepancy can be attributed to the frequent aggregation and disaggregation of asphaltene in the dilute limit which is well-captured by the TIP4P-D water model. Our study of hydrogen bonds between asphaltene and water clearly shows that the asphaltene–water interactions are stronger for TIP4P-D than the SPC and TIP5P water models because of the enhanced dispersion interaction in the TIP4P-D water model. Furthermore, we found that the diffusion coefficient of the asphaltene to be higher for the SPC water model than the other two models. In this regard, an interesting observation is that the diffusion coefficient decreases with the increase in the concentration of asphaltene in water. Another highlighting

**Table 3. Calculated Diffusion Coefficients (in m²/s) are Shown for Three Different Asphaltene Concentrations Using Different Water Models**

|       | Diffusion Coefficient (m²/s) |
|-------|-------------------------------|
| SPC   | 7.76 × 10⁻¹⁰                 |
| TIP4P-D | 1.93 × 10⁻¹⁰               |
| TIP5P | 2.52 × 10⁻¹⁰                 |
| SPC   | 3.91 × 10⁻¹⁰                 |
| TIP4P-D | 3.07 × 10⁻¹⁰               |
| TIP5P | 3.68 × 10⁻¹⁰                 |
| SPC   | 3.78 × 10⁻¹⁰                 |
| TIP4P-D | 1.32 × 10⁻¹⁰               |
| TIP5P | 2.19 × 10⁻¹⁰                 |

**Table 4. Calculated Viscosity (in cP) Obtained by the Exponential Fitting is presented along with the Standard Deviation of the Fit (\( \sigma \)) for Asphaltene in Aqueous Solution for the Three Water Models**

|       | viscosity (cP) | \( \sigma \) (cP) |
|-------|----------------|------------------|
| SPC   | 0.39           | 0.26 × 10⁻³      |
| TIP4P-D | 1.21          | 2.73 × 10⁻³      |
| TIP5P | 0.71           | 8.03 × 10⁻³      |
aspect of our study is that the better viscosity predictions can be obtained using the TIP4P-D water model because the errors are large for TIPSP and SPC water models. To summarize, the earlier studies on asphaltene aggregation in water have been primarily performed using the SPC water model. The novelty of the present work lies on the fact that the study highlights the importance of the TIP4P-D-enhanced dispersion water model to better describe the aggregation of asphaltenes in water. It is worthwhile to mention here that apart from improving the atomistic description of the solvent, the improvement in the parametrization of the force field for the hydrocarbon molecules under investigation is necessary for better reproducibility of the experimental results.

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**Notes**

The authors declare no competing financial interest.

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