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

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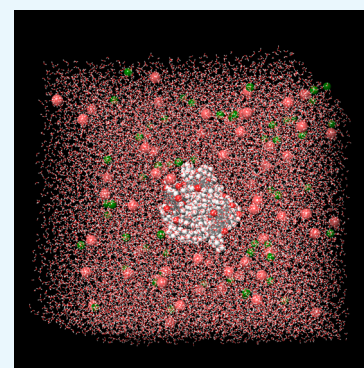
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ABSTRACT: The aggregation behavior of asphaltene in aqueous solution is systematically investigated based on a classical molecular dynamics study. In this work, a novel approach is adopted in order to investigate the structural and dynamical properties 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.¹ The asphaltene molecules present in crude oil hold the highest fraction.² Asphaltenes are dissoluble in aromatic hydrocarbons, for example, toluene, benzene, or pyridine, but insoluble in *n*-alkanes, for example, pentane, heptane, and hexane.^{3,4} They form aggregates in selective organic solvents, water, and oil–water emulsion⁵ and are accountable for the high viscosity of crude oil.^{6,7} It is noteworthy that destabilized asphaltenes can cause serious problems in oil refineries such as coke formation, catalysis deactivation, pipeline blocking, and many more.^{7–9} Furthermore, asphaltenes reduce petroleum productivity because of the high viscosity induced by their presence in crude oil.^{10,11} Also, their release into the environment can have negative impacts on the soil and marine life because of their non-biodegradable nature.^{12,13}

In-depth understanding of the asphaltene chemistry has the potential to increase the efficiency of oil recovery.¹⁴ Many experimental investigations and theoretical simulations have been performed in order to uncover the mechanisms behind asphaltene aggregation and asphaltene–solvent interactions.^{14–17} 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.^{15,18,19} Within the abovementioned model, the aliphatic

side chain surrounds the polyaromatic core and aggregation occurs mainly because of the π – π interactions between the cores.²⁰

Mullins et al.¹⁵ 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 Firoozabadi²¹ 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.²² probed coal-derived asphaltenes' and petroleum asphaltenes' molecular structures using atomic force microscopy (AFM) and scanning tunneling microscopy. Zhang et al.²³ 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

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ratio of toluene to heptane in the heptol mixture. Shi et al.²⁴ performed experimental investigations using AFM to probe the asphaltene interaction in oil–water emulsion. It is observed that the presence of the asphaltene at the oil–water interface induces strong steric repulsion. Li et al.¹⁷ performed experiments on the kinetics of the asphaltene aggregation in microcapillaries. Crude oil samples were analyzed for the aggregate size in various organic solvents at different flocculation times. The diffusion-limited-aggregation and reaction-limited-aggregation models were analyzed in depth at low and high concentrations of the asphaltene. Joonaki et al.¹⁴ also performed experimental investigation of asphaltenes in water. Their work was focused on aqueous asphaltene solutions with different salt concentrations. The study pointed out the importance of the H-bonding network in the solutions and showed that the viscosity increases for stronger H-bonding networks in asphaltene solutions.

Headen et al.¹⁹ investigated the nanoaggregation of asphaltene and resin in toluene and heptane solvents using molecular dynamics (MD) simulations. In their work, the asphaltene model consisting of two aromatic cores was taken into consideration and the structural properties of asphaltene–asphaltene and resin–resin were investigated. Jian et al.²⁵ performed MD simulations to study how the aliphatic side chain affects the aggregation of the asphaltene (Violanthrone-78-based model) in water. The aggregation behavior based on four different lengths of the side chain was discussed. The authors concluded that the long and short side chains can form concentrated aggregates unlike the chains with intermediate length. Headen et al.²⁶ performed classical MD simulations for four different asphaltene models in toluene and heptane solvents under ambient conditions. The study showed that monomers and dimers form the common size of the clusters in a good solvent. Sun et al.²⁷ performed MD simulations on Violanthrone-78-based asphaltene model varying the side chain length in the presence of salt ions in solution. It is noticed that the hydrophobic interactions are enhanced at low salt concentrations facilitating aggregation, while such kinds of interactions are suppressed at higher salt concentrations, thereby hindering aggregation. Yaseen and Mansoori²⁸ investigated the asphaltene aggregation because of the water-flooding using MD simulations. In their study, seven different asphaltene water models were probed. The structural properties mainly radial distribution function and hydrogen bonding within asphaltene–asphaltene and asphaltene–water were analyzed. In the work performed by Santos Silva et al.,²⁹ MD simulations were performed on CA22-based molecular systems in order to investigate the mechanisms behind nano- and macroaggregation of asphaltenes. The study concluded that the size of the aromatic core and the presence of the polar group play an important role in nanoaggregation, whereas the formation of the macroaggregates is governed by the occupancy of polar groups and length of the side chains. Furthermore, the study showed that the heteroatoms enhance the π – π interactions. Recently, Bian et al.³⁰ investigated the disaggregation of asphaltenes using the functional group methylation by performing both experiments and MD simulations. It is observed that the methylated asphaltenes are prone to disaggregation. Tirjoo et al.³¹ investigated asphaltene aggregation using two asphaltene-based models viz. M1 and VI. Within this study, the solubility parameters were calculated using MD simulations.

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)³² in the Desmond³³ MD package within Schrödinger simulation software have been used.³⁴ Violanthrone-78 ($C_{70}H_{84}O_6$) is considered as a model asphaltene compound, as shown in Figure 1. Earlier nanoaggregate investigations were performed

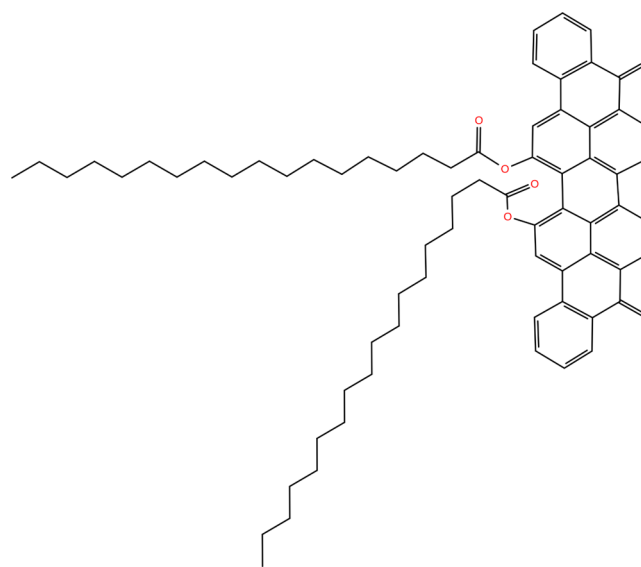


Figure 1. 2D molecular structure of Violanthrone-78. Polycyclic aromatic core, polar heteroatoms, and two side chains are shown.

at an asphaltene concentration of 20 g/L.²⁷ 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,³⁵ TIP4P-D,³⁶ and TIPSP³⁷ water models and the OPLS3e potential for the asphaltenes.

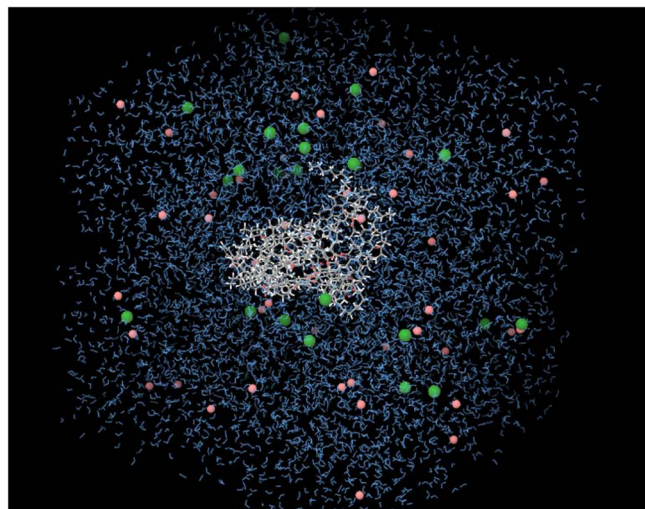


Figure 2. Snapshot of asphaltene aggregates in aqueous NaCl solution is shown in the figure. The following is the color coding: sodium ion (pink), chloride ion (green), asphaltene aggregates (gray), and water molecules (blue).

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 model³⁸ for the semiflexible side chains.³⁹ 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 equation³⁹

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

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

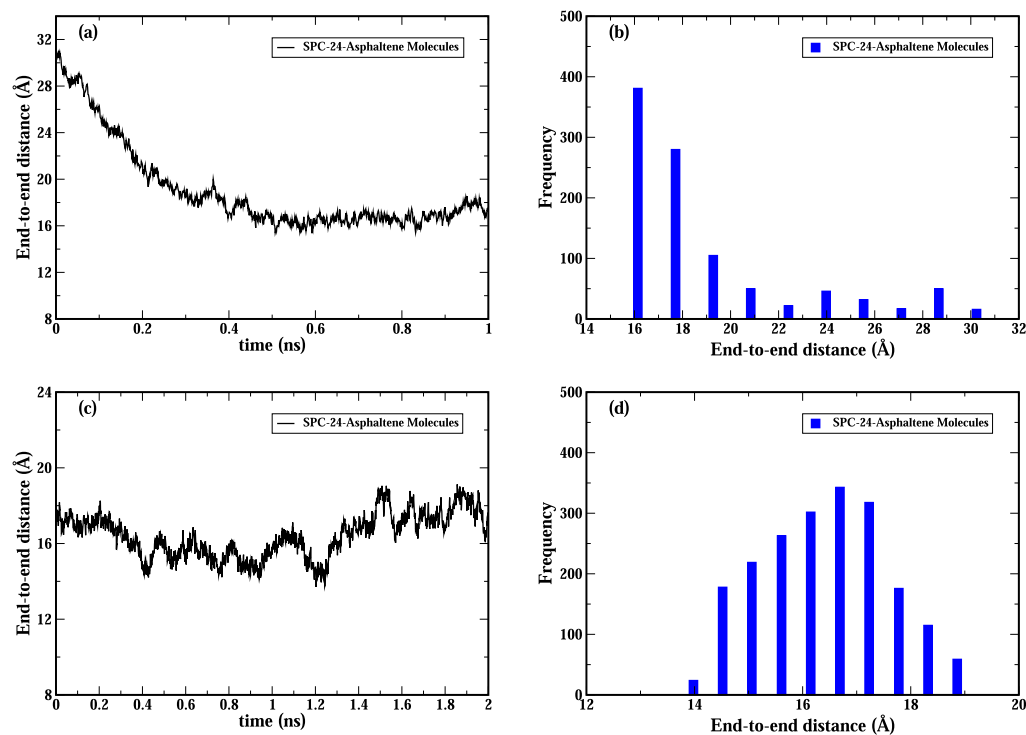


Figure 3. (a) End-to-end distance of asphaltene molecules is shown for the first 1 ns using the SPC water model MD trajectory. (b) Frequency vs end-to-end distance of asphaltene molecules is shown for the first 1 ns using the SPC water model MD trajectory. (c) End-to-end distance of asphaltene molecules 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.

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)
6 Asphaltene Molecules				
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
12 Asphaltene Molecules				
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
24 Asphaltene Molecules				
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 1. The end-to-end distance of the asphaltene molecule changes with respect to the concentration of asphaltene in water. It is evident from our study that the choice of the water model has a significant effect on the persistence length, especially when the TIP4P-D water model is used for the dilute concentration. It is noteworthy that previous studies have shown that the TIP4P-D water model can successfully explain the unfolded protein states in solutions.³⁶ In our study, a persistence length of 4.9 Å is observed for the TIP4P-D water model in the dilute limit. This is due to the fact that frequent aggregation and disaggregation occurs between two aggregate sizes. The persistence length indicates that beyond this distance there will be no correlation, that is, the aliphatic side chains are stiffer 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.⁴⁰ 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 formation of H bonds with water molecules. It was thus concluded that 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 water models than the TIP5P water model.⁴¹ 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

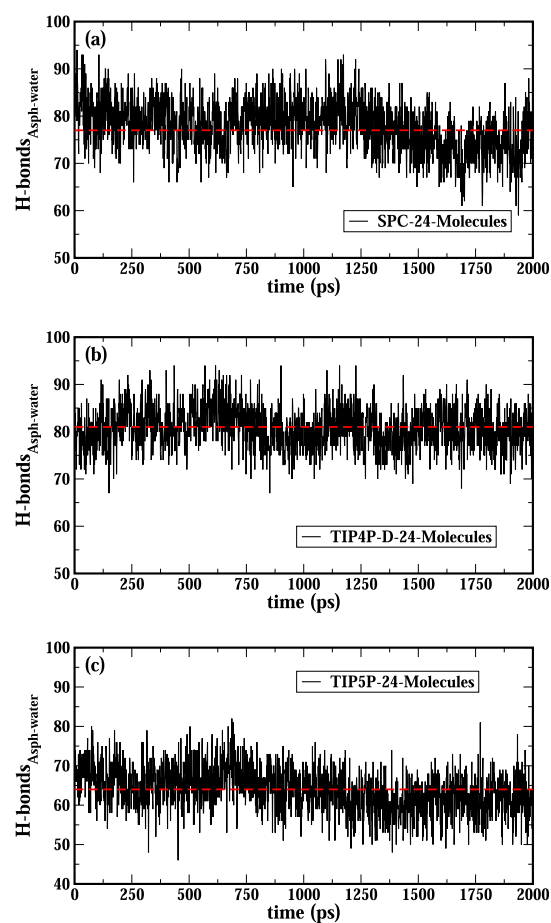


Figure 4. Hydrogen bonds between asphaltene and water molecules are shown for 24 molecule system size for the three water models, namely, (a) SPC, (b) TIP4P-D, and (c) TIP5P. The average number of H bonds is indicated by a red-dashed line in each of the subfigures.

concentrations using the different models in Table 2. TIP4P-D is more effective than the TIP4P/2005 water model because

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

	SPC	TIP4P-D	TIP5P
24 asphaltene molecules	78	81	64
12 asphaltene molecules	47	56	35
6 asphaltene molecules	26	27	18

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, C_6 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.³⁶ 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.

3.3. Diffusion Coefficient. The diffusion coefficient averaged over all the asphaltene molecules is calculated using the following equation⁴²

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \quad (2)$$

$\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$ 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

Table 3. Calculated Diffusion Coefficients (in m^2/s) are Shown for Three Different Asphaltene Concentrations Using Different Water Models

	diffusion coefficient (m^2/s)
6 Asphaltene Molecules	
SPC	7.76×10^{-10}
TIP4P-D	1.93×10^{-10}
TIP5P	2.52×10^{-10}
12 Asphaltene Molecules	
SPC	3.91×10^{-10}
TIP4P-D	3.07×10^{-10}
TIP5P	3.68×10^{-10}
24 Asphaltene Molecules	
SPC	3.78×10^{-10}
TIP4P-D	1.32×10^{-10}
TIP5P	2.19×10^{-10}

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 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 equation⁴³

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \rangle dt \quad (3)$$

where V is the volume of the system, k_B is the Boltzmann constant, T is the temperature, $P_{\alpha\beta}$ 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 Abascal⁴⁴ and Tazi et al.⁴⁵ 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 all three water models are summarized in Table 4. Our results show that the viscosity is severely underpredicted by the SPC water model, that is, 0.39 cP.

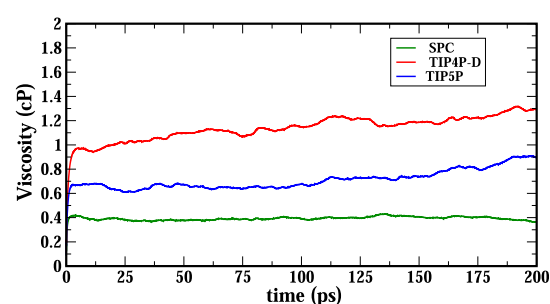


Figure 5. Calculated viscosity using SPC, TIP4P-D, and TIP5P water models is shown as a function of time for 6 asphaltene molecules in aqueous solution at 300 K.

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

	6 asphaltene molecules	
	viscosity (cP)	σ (cP)
SPC	0.39	0.26×10^{-3}
TIP4P-D	1.21	2.73×10^{-3}
TIP5P	0.71	8.03×10^{-3}

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–solute and solute–solvent interactions. The strengthening of the water dispersion interactions results from 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.⁴⁶

4. CONCLUSIONS

In the present work, the aggregation of asphaltene (Violanthrone-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

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 asphaltene 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

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