The Effect of Water on Asphaltene Aggregation and Viscosity of Crude Oil: a MD Simulation Study

Bojin Zhu, Qingyang Hu and Jun Zhang*

College of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, 266000, China

*zhubojinmd@gmail.com

Abstract. A thorough comprehension of the oil-water interactions and their rheological response in the petroleum industry is quite essential. Despite the prior works have demonstrated the significant role of asphaltene in the formation of water in crude oil (W/O) emulsions, the clarification of how the increasing water content affects the aggregation state of asphaltenes, and the molecular mechanism of viscosity alterations in crude oil systems remain obscured, especially in lower water content environments. Therefore, we performed molecular dynamics (MD) simulations to investigate the structural response of asphaltene aggregation and rheological behaviors of crude oil systems under the ever-increasing water conditions. Our research findings indicate that with the continuous introduction of water, the original bulk-phase aggregation of asphaltenes transforms into interfacial adsorption. The hydrogen bonds at the oil-water interface strengthen the asphaltene aggregation behavior. Furthermore, the overall viscosity of the crude oil system consistently decreases with water addition, primarily influenced by the interaction between asphaltenes and the surrounding dispersing medium. The strength of interactions between water and polar oil components also influences the viscosity of crude oil systems to some extent. These microscopic insights contribute to enriching our understanding of the intricate interplay between asphaltenes and water, as well as the stability of W/O emulsions.

Keywords: Asphaltene, Crude Oil Viscosity, MD Simulations.

1 Introduction

In crude oil production and transportation, the presence of varying amounts of formation water, ranging from 1% to over 70% of the total liquid volume [1], can lead to interactions with polar components in petroleum. This interaction may result in the undesired formation of water-in-crude oil (W/O) emulsions, significantly increasing fluid viscosity, elevating operational costs, and reducing overall production efficiency [2]. As the most complicated polar component in petroleum, asphaltenes typically exhibit strong self-aggregation properties according to the Yen-Mullins theoretical model, leading to unfavorable deposition and widely considered to be a major factor

A. E. Abomohra et al. (eds.), *Proceedings of the 2023 9th International Conference on Advances in Energy Resources and Environment Engineering (ICAESEE 2023)*, Atlantis Highlights in Engineering 29,
https://doi.org/10.2991/978-94-6463-415-0_43

for the high viscosity of crude oil. The presence of water in crude oil complicates such microscopic aggregation processes. Numerous studies indicate that asphaltenes play a critical role in the stabilization of W/O emulsions [3], besides, experimental research has demonstrated a decrease in emulsion viscosity with increasing water concentration [4]. However, the underlying molecular mechanisms remain unclear.

Molecular dynamics (MD) simulations have been extensively employed to depict the microscopic evolution of asphaltene aggregation and elucidate oil-water interactions at a molecular level. Especially in characterizing the dynamic aggregation microevolution of asphaltenes, elucidating microscopic driving forces has unique advantages compared to experimental techniques such as dynamic light scattering. Numerous studies have explored interactions among W/O emulsion droplets, providing valuable insights to complement experimental observations. Specifically, the adsorption of asphaltene molecules onto water droplets in heptane and toluene solvents and the droplet coalescence behaviors were investigated by MD simulations by Jian et al [5, 6]. However, these systems are relatively simplistic in representing the true nature of crude oil and lack in-depth investigations into rheological behavior. Thus, In this study, we conducted MD simulations to investigate the influence of low water content environments on asphaltene aggregation and rheological properties, aiming for a deeper understanding of oil-water interaction mechanisms.

2 Methodology

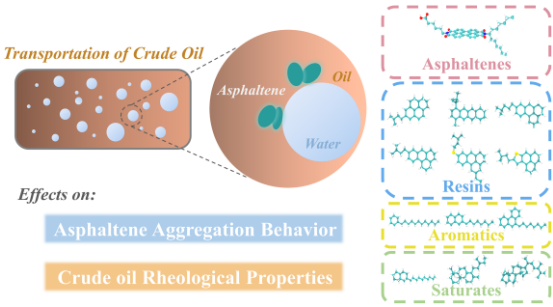

Fig. 1. Schematic illustration of the interplay between asphaltenes and water during crude oil transportation and the molecular topological structures of SARA components (saturates, aromatics, resins, and asphaltenes, respectively).

In the crude oil transportation process, water typically exists as dispersed microdroplets with varying sizes. Polar components like asphaltenes stabilize the oil-water interface, leading to interactions between water molecules and surrounding crude oil components. This study considers seven water-oil mixed systems with mass fractions ranging from 0.25 wt% to 10 wt%. Simultaneously, the SARA four components (saturates, aromatics, resins, and asphaltenes, respectively) represent a real crude oil model, with model oil molecules derived from experimentally characterized structures and commonly used compositions in previous MD simulations. For example, asphaltene molecule C5PE, possessing numerous polar functional groups, is selected due to its

strong aggregation and adsorption characteristics observed in previous MD simulations at oil-water interfaces. The chosen model molecules were randomly placed into a cubic box with dimensions of 12 × 12 × 12 nm³, aligning with predefined mass concentrations (25%, 30%, 38%, and 7 wt%, respectively) while keeping the number of asphaltene molecules constant at 30. Detailed information about SARA molecular structures and model configuration are presented in Fig. 1.

The all-atom MD simulations were conducted with the GROMACS 2019.6 software package [7]. Molecular parameter sets for oils and water molecules were described using the CHARMM General Force Field (CGenFF) [8] and an Extended Simple Point Charge (SPCE) model. The CGenFF force field has been widely employed in previous studies to explore oil-water interface properties, effectively replicating asphaltene aggregation properties [9, 10]. The SPCE water model is known for accurately reproducing structural and thermodynamic transport properties [5]. Visualization and Graphical presentation were achieved by the visual molecular dynamics (VMD) 1.9.3 software package. The initial model underwent energy minimization, followed by a 1 ns pre-equilibrium simulation under the isothermal-isobaric (NPT) ensemble to regulate density. Subsequently, an 80 ns high-temperature annealing simulation (343K-843K) aimed to enable crude oil components to overcome energy barriers and achieve stable aggregate structures. Finally, a 20 ns NPT production simulation was conducted to attain an equilibrium configuration. All simulations were performed at 343 K and 10 MPa to replicate realistic reservoir conditions, utilizing a time step of 1 fs. The V-rescale thermostat [11] and Berendsen barostat [12] were employed as the temperature and pressure coupling methods, respectively.

3 Results and discussion

3.1 Asphaltene aggregation characteristics

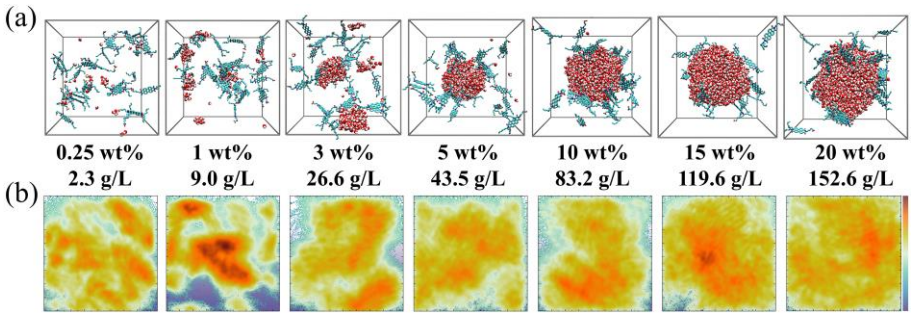

Fig. 2. (a): Final MD simulation snapshots of crude oil systems with increasing water content, only asphaltenes (cyan) and water (red) are depicted for clarity; (b): The 2D-density distribution of asphaltene aggregation configurations along the Z-axis direction for seven systems during the last 10 ns of simulation (The color mapping bar ranging from red-orange to blue-purple represents the variation of asphaltene molecules stacking from strong to weak).

The aggregation characteristics of asphaltenes in crude oil are of vital importance, to compare the influence of water on the aggregation structures of asphaltenes, the final snapshots after 20 ns production simulations are shown in Fig. 2 (a). The mass fractions and mass concentrations of water in the different systems are labeled for clarification. With increasing water content, it is clearly observed that water transitions from dispersed clusters to larger liquid droplets. Meanwhile, asphaltene molecules shift from bulk phase aggregation to polar adsorption on the droplet surfaces. In addition, the presence of water appears to enhance the aggregation of C5PE asphaltene molecules, particularly evident at 1 wt% water content. The enhancement of aggregation tendency can also be vividly viewed from the 2D density profiles of the latter 10 ns asphaltene molecules demonstrated in Fig. 2 (b), including the skeletal features of asphaltene aggregation around water, which is similar to the observation of asphaltene-water interplay reported by Jian et al [6].

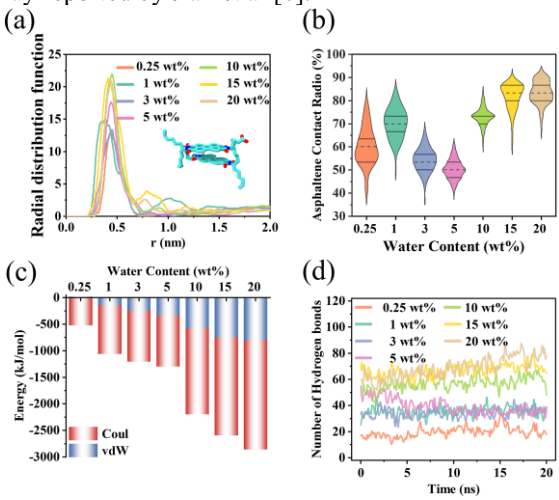

Fig. 3. (a): RDF profiles of the action of the asphaltene core; (b): The Contact ratio of asphaltene molecules around water; (c): Interaction energy between asphaltene and water molecules at different water contents; (d): The number of hydrogen bonds between asphaltene and water molecules. The analytical data are derived from the last 10 ns of trajectories.

The interplay between asphaltene and water is further elucidated through the characterization of several simulation parameters. In Fig. 3(a), the radial distribution function (RDF) among asphaltene molecules is presented to illustrate more association details. The peak height of the RDF reflects the strength of C5PE molecule aggregation. Overall, the addition of water enhances asphaltene aggregation, both in the bulk phase and at the oil-water interface. Fig. 3(b) shows the contact degree between water and surrounding asphaltenes, exhibiting a nonlinear trend that is attributed to the continuous aggregation of dispersed water clusters leading to the gradual formation of W/O emulsions. Fig. 3(c-d) provides an explanation of the increasingly robust interaction between asphaltene and water from the perspectives of interaction energy and hydrogen bonds. In this context, coulombic electrostatic (Coul) interactions in red are identified as the primary driving force compared to van der Waals (vdW) forces.

3.2 Rheological properties of crude oil

The shear viscosities under varying water content for seven oil-water systems were calculated using the improved periodic perturbation method [13] to assess the effect of water on the rheological properties of crude oil. Fig. 4 (a) illustrates the variations in shear viscosity and diffusion coefficients among different aqueous systems. The overall trend indicates a decrease in viscosity with increasing water content, with a certain thickening effect observed under specific trace water conditions (1 wt%).

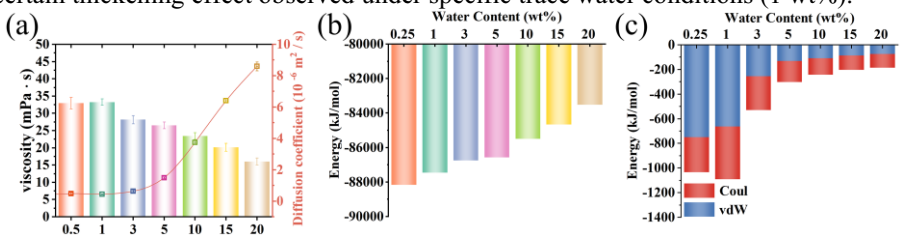

Fig. 4. (a): The shear viscosity and diffusion coefficient of crude oil systems under varying water content; total interaction energy under applied shear force (b): between asphaltene and surrounding oil molecules, and (c): between the crude oil and the water molecules.

We further investigated the interaction energy between asphaltene and surrounding oil molecules, as well as between water and the SARA components of crude oil under shear conditions as depicted in Fig. 4 (b-c). We found a close correlation between these interaction energies and the viscosity values. Considering that viscosity essentially represents intermolecular friction, we conclude that water, through interaction with crude oil, diminishes the friction between asphaltene and the surrounding dispersed medium, thereby influencing the overall viscosity of the system.

4 Conclusion

This study utilizes MD simulation to explore how crude oil systems respond to varying water content, focusing on asphaltene aggregate structures and rheological behavior. The simulation results provide insights into detailed interaction mechanisms and the underlying reasons for viscosity changes. Our research reveals that as water is introduced, asphaltene's original bulk-phase aggregation shifts to interfacial adsorption, strengthened by hydrogen bonds, and driven primarily by Coulombic electrostatic attraction at the oil-water interface. The reduction in crude oil system viscosity is mainly attributed to the diminished frictions between asphaltene and the surrounding dispersing medium. Interactions between water and polar oil components also impact the crude oil system's viscosity. These findings contribute to a deeper understanding of rheological behavior in crude oils with different aggregation states, offering theoretical guidance for efficient crude oil development.

Acknowledgements

The work was supported by the National Key R&D Program of China (2018YFA0702400), and the National Natural Science Foundation of China (51874332).

References

1. J. Czarnecki, P. Tchoukov, T. Dabros.: Possible Role of Asphaltenes in the Stabilization of Water-in-Crude Oil Emulsions. Energy & Fuels 26(9), 5782-5786, (2012).
2. A. Velayati, A. Nouri.: Role of Asphaltene in Stability of Water-in-Oil Model Emulsions: The Effects of Oil Composition and Size of the Aggregates and Droplets, Energy & Fuels. 35(7), 5941-5954, (2021).
3. A.M. Sousa, H.A. Matos, M.J. Pereira.: Properties of Crude Oil-in-Water and Water-in-Crude Oil Emulsions: A Critical Review, Industrial & Engineering Chemistry Research. 61(1), 1-20, (2022).
4. T. Al-Wahaibi, Y. Al-Wahaibi, A.-A.R. Al-Hashmi, F.S. Mjalli, S. Al-Hatmi.: Experimental investigation of the effects of various parameters on viscosity reduction of heavy crude by oil-water emulsion. Petroleum Science 12, 170-176,(2015).
5. W. Li, Y. Nan, X. Wen, W. Wang, Z. Jin.: Effects of Salinity and N-, S-, and O-Bearing Polar Components on Light Oil-Brine Interfacial Properties from Molecular Perspectives. The Journal of Physical Chemistry C 123(38), 23520-23528, (2019).
6. C. Jian, Q. Liu, H. Zeng, T. Tang.: Effect of Model Polycyclic Aromatic Compounds on the Coalescence of Water-in-Oil Emulsion Droplets. The Journal of Physical Chemistry C 121(19), 10382-10391, (2017).
7. M.J. Abraham, T. Murtola, R. Schulz, S. Páll, J.C. Smith, B. Hess, E. Lindahl.: GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. SoftwareX 1-2, 19-25, (2015).
8. K. Vanommeslaeghe, E. Hatcher, C. Acharya, S. Kundu, S. Zhong, J. Shim, E. Darian, O. Guvench, P. Lopes, I. Vorobyov.: CHARMM general force field: A force field for drug-like molecules compatible with the CHARMM all-atom additive biological force fields. Journal of computational chemistry 31(4), 671-690, (2010).
9. J. Jia, J. Li, Y. Liang, B. Peng.: Molecular Dynamics Study on Performance of Olefin Sulfonate at the Decane-Water Interface: Effect of Molecular Architecture. Fuel 308, 122013, (2022).
10. M. Kunieda, K. Nakaoka, Y. Liang, C.R. Miranda, A. Ueda, S. Takahashi, H. Okabe, T. Matsuoka.: Self-Accumulation of Aromatics at the Oil-Water Interface through Weak Hydrogen Bonding. Journal of the American Chemical Society 132(51), 18281-18286, (2010).
11. G. Bussi, D. Donadio, M. Parrinello.: Canonical sampling through velocity rescaling. The Journal of Chemical Physics 126(1), 014101, (2007).
12. H.J. Berendsen, J.v. Postma, W.F. Van Gunsteren, A. DiNola, J.R. Haak.: Molecular dynamics with coupling to an external bath. The Journal of chemical physics 81(8), 3684-3690, (1984).
13. B. Hess.: Determining the shear viscosity of model liquids from molecular dynamics simulations. The Journal of Chemical Physics 116(1), 209-217, (2002).