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Insights from atomistic and molecular simulations

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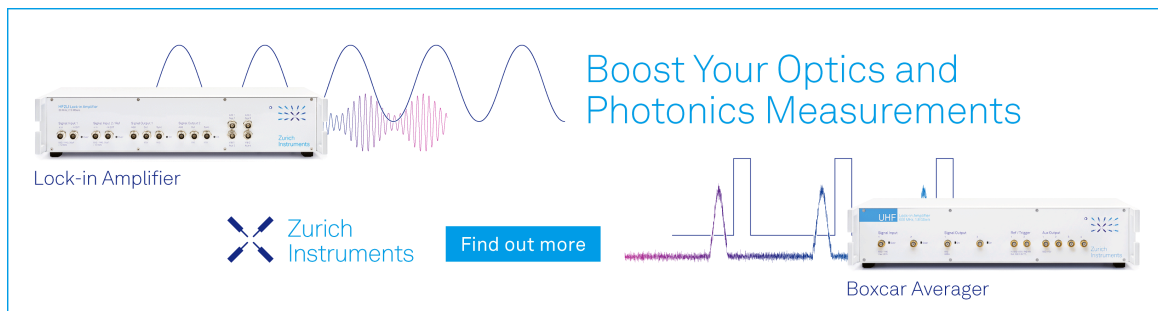Anoop Kishore Vatti ; Srikanth Divi ; Poulumi Dey ✉

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Effectiveness of inhibitors to prevent asphaltene aggregation: Insights from atomistic and molecular simulations Ⓕ

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ABSTRACT

The technological landscape for industrial processes handling asphaltene is evolving at a rapid pace due to the increase in the extraction of heavy crude oil. The main underlying challenges in this regard are the flow assurance, the recovery of the spent solvent, and the sophisticated extractor setup required to develop the process to an industrial scale. The number of studies focused on the handling of the asphaltene at the atomic and molecular scales is growing enormously in order to identify new sustainable solvents for the effective extraction of asphaltene from heavy crude oil or oil-bearing sands. This Perspective focuses on the importance of density functional theory and molecular dynamics simulations to explore the broader range of asphaltene inhibitors, e.g., nanoparticles, ionic liquids, and deep eutectic solvents, to prevent asphaltene precipitation. We provide a concise overview of the major accomplishments, analyze the aspects that require attention, and high-light the path-breaking studies having a significant impact on the process of chemical enhanced oil recovery from heavy crude oil reservoirs primarily based on atomistic and molecular simulations.

I. INTRODUCTION

Asphaltenes are a class of compounds constituting the heaviest and most polar components present in crude oil and are differentiated from the rest of its constituents (i.e., saturates, aromatics, and resins) by their solubility in aromatic solvents, such as toluene, and insolubility in aliphatic organics, such as n-hexane or n-heptane.[1] This classification arises from conventional treatment methods that result in asphaltenes remaining as low-value residues after vacuum distillation of heavier crude oil fractions.[2] An ambiguity in the structural classification of asphaltenes makes it very challenging to study and define their exact properties and identify the interactions, primarily when the yield, composition, and quality of asphaltene fractions are determined by the crude oil source, the precipitation method, and solvents employed to isolate the asphaltenes.[3] Asphaltenes tend to self-associate, forming aggregates under specific

environmental conditions. These aggregates deposit in wellbores and pipelines, causing flow assurance and transportation issues. These flow assurance issues in transportation refer to the problems that arise primarily from the presence of multiphase fluids in pipes. The primary issues arise from the precipitation and deposition of asphaltenes, which have an adverse impact on the rate of production of crude oil. The highly polar nature of asphaltenes results in the formation of stable emulsions with water.[4] Asphaltene molecules combine to form a thin layer that consists of asphaltene aggregates, which are sandwiched between oil (heptane) and water. Moreover, the interfacial tension (IFT) of the heptane–water system with a small amount of asphaltene molecules is similar to that of a pure heptane–water system. However, the interfacial tension of the system decreases as the number of asphaltene molecules increases.[5] Exposure of asphaltenes to higher temperatures, variations in crude oil composition, or injection of gases, such as CO_2, triggers

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destabilization and a decrease in solubility, leading to the formation of sediments. In addition to reducing the production capacity of oil, this could poison or deactivate catalysts, clog, or corrode filters or pipelines.[3] Furthermore, the release of asphaltenes into the environment is undesirable due to their non-biodegradability and high viscosity, as they could contaminate water and soil.[6] Hence, the investigation of asphaltenes (e.g., their properties, formation of aggregates, and their behavior under various conditions) is required to understand the underlying issues.[7–11] Furthermore, the depletion of existing oil reserves has shifted the focus toward chemical enhanced oil recovery (CEOR) technologies for effectively recovering heavy crude oil and altering properties, such as viscosity, interfacial tension, and wettability,[12] steering further research into solvent, surfactant, or polymer additives and their interactions with asphaltenes.[13–15]

Early studies on asphaltenes focused on the development of experimental protocols to isolate asphaltene fractions from crude oil and the determination of important properties, such as molecular mass, representative structure and aromaticity, H/C ratio, the number of fused polyaromatic rings, type of heteroatoms and functional groups present, and critical micelle concentrations, using various spectroscopic, chromatographic, and scattering techniques, a detailed account of which is already available in the literature.[2,3] The reported range for continental model type asphaltene molecular weight is 750 ± 200 atomic mass units (amu).[16] Furthermore, the most prevalent polycyclic aromatic hydrocarbons in asphaltenes are those with 6–8 rings.[17] It is noteworthy that the range of the molecular weights associated with the archipelago model is much larger than the continental model.[18] These experimentally determined properties were then utilized to computationally generate a set of peri-condensed and archipelago asphaltene structures from a predetermined set of aromatic and aliphatic building blocks. Nonlinear optimization was used to screen those quantitative molecular representations, which approximately simulated experimental results.[19] This and subsequent studies[13] have paved the way for generating asphaltene-like structures for computationally simulating their behavior. A series of experiments and theoretical investigations were also conducted to identify and model the existence of asphaltenes in crude oil and their interactions with other asphaltene molecules, resins, and other constituents.[9,20] Two prominent models, solubility and colloidal, were proposed, the former indicating that asphaltenes exist as a dispersed polar fluid (a homogeneous system). In contrast, the colloidal model presented an alternative perspective of asphaltenes present in the form of micelles in crude oil, further stabilized, or peptized by resins, a detailed account of which is documented by Porto et al.[11] While π–π stacking interactions between asphaltene molecules were proposed to be the primary reason for the formation of aggregates in a hierarchical manner,[9] other modes of aggregate formation, such as the rosary chain arrangement[21] and sol-gel model,[22] have also been put forward.

Advances in computational methods, such as molecular mechanics (MM) calculations, density functional theory (DFT), and molecular dynamics (MD) simulations, have provided new perspectives of understanding asphaltene structure and mechanisms of aggregation at the atomistic and molecular levels covering different length and time scales. While earlier MM studies by Murgrich focused on understanding asphaltene–resin interactions in various

oil samples,[20,23,24] subsequent studies by Carauta et al.[25] explored various conformations of asphaltene structures and their effect on aggregation. Li and Greenfield[26] used force field, Hartree–Fock, and DFT calculations to critically analyze various asphaltene structures proposed in the literature and pointed out the importance of these predicted conformations with high energies that limit the probability of their natural occurrence.

Classical MD simulations that predicted a decrease in solubility parameters with asphaltene aggregation were investigated by Rogel.[27] Subsequent MD studies provided useful insights into the influence of operating conditions, such as pressure and temperature, on asphaltene aggregation.[28–30] Various factors, such as asphaltene side chain length, solvent environment, presence of resins in system, and partial charge parameterization, have been found to affect the aggregation of asphaltenes.[13,26,31–36]

Simulations at a mesoscale level help in bridging the knowledge of interactions at a molecular level to experimental observations at a macroscopic level. Computational techniques beyond classical MD simulations, such as dissipative particle dynamics (DPD),[37,38] Brownian dynamics (BD),[39] and coarse-grained MD simulations, have aided in capturing several mesoscopic effects, such as the formation of larger flocs or aggregates described by the Yen model over larger time scales,[39,40] and sol-gel colloidal transitions triggered by asphaltene aggregation[38] under various operating conditions and solvent environments.

Immense knowledge gained over the years on the behavior of asphaltenes paved the way for application-oriented research on their handling and utilization. Studies in the literature are mainly centered on the identification or development of solvents and additives that could either inhibit the precipitation of asphaltenes or aid in separating asphaltenes from crude oil via a solvent extraction route. Several experimental methods, such as scattering, spectroscopic, and microscopic techniques; computational screening of suitable solvent additives using methods such as Conductor-like Screening Model for Real Solvents (COSMO-RS); mathematical models deriving aggregation kinetics; and extensive simulation studies involving the interactions of asphaltenes with light aromatics and straight chain alkanes,[13,41–44] amphiphilic surfactants,[14,15,45–49] and commercial inhibitors,[14,15] have been developed and are well documented in the literature. Headen and Boek[50] performed MD simulations to investigate the aggregation of asphaltene in supercritical carbon dioxide, both with and without the presence of an aggregation inhibitor, specifically limonene. In the absence of limonene, asphaltenes in supercritical carbon dioxide showed a strong propensity to aggregate; however, a reduction in asphaltene aggregation was noted when 50% limonene was present. Furthermore, the authors probed the effect of pressure and temperature on asphaltene aggregation. Asphaltene aggregation in the mixture exhibited a complex relationship with temperature and pressure, with the minimum amount of aggregation observed at 150 bar and 350 K. New classes of solvents, such as ionic liquids (ILs),[51–62] and deep eutectic solvents (DESs)[63–68] have been highly pursued as potential asphaltene aggregation inhibitors or separation agents due to their unique properties, such as high thermal and chemical stability, relatively non-toxic nature, non-flammability, and non-volatility, compared to conventional additives.[12] Boukherissa et al.[51] investigated the potential of 1-propyl boronic acid-3-alkylimidazolium bromide and 1-propenyl-3-alkylimidazolium bromide ILs as inhibitors of asphaltene

aggregation. A lateral chain, which included the propenyl group, was used as a substitute for the 1-methyl-3-alkylimidazolium bromide. The study found that the inclusion of the boronic acid group improves the interaction between asphaltenes and ILs, resulting in a significant reduction in asphaltene aggregation. El-hoshoudy *et al.*[57] utilized three ILs to study asphaltene precipitation. The IL [(−C$_4$H$_9$-IL) FeCl$_4$−] [1-butyl-3-hexadecyl-1H-imidazol-3-ium tetrachloroferrate(III)] is found to have the highest dispersion efficiency in asphaltene based on both experimental and computational studies. It is the most effective IL (out of the three ILs) as the long alkyl chain acts as a resin that disperses asphaltenes. For conventional applications, such as road asphalts, the high asphaltene contents in heavy oil reserves demand innovations that could upgrade these substances to high-value products. Recent studies have employed asphaltenes as fillers in polymer composites to improve thermal or mechanical properties, adsorbents for volatile organic compounds (VOCs), and precursors in the synthesis of carbonaceous materials, such as activated carbon and graphene,[69] and in supercapacitors, all of which have been documented in a detailed review by Kamkar and Natale.[70] Catalytic and thermal (non-catalytic) upgrading of asphaltenes using hydrogen donor solvents, such as tetralin,[71] ethylene glycol-based DESs,[72] and other solvents,[73] are other potential attempts at asphaltene valorization, which could significantly increase market value and aid in the production of valuable products. Several recent reviews have dealt with various aspects of asphaltenes.[11,12,74–76] Alimohammadi *et al.*[74] provided a comprehensive account of the solubility model of asphaltenes and reviewed various mathematical models developed to analyze the kinetics of asphaltene precipitation. In addition, MD simulation based studies describe factors affecting asphaltene precipitation and support developing various techniques for inhibition of asphaltene precipitation and valorization. Porto *et al.*[11] put forward a detailed review on the evolution of various models pertaining to bitumen microstructure and aggregation, emphasizing the colloidal mode, supported by numerous experimental and theoretical results. A detailed account of spectroscopic, chromatographic, microscopic, diffractometric, osmometric, and other experimental approaches along with MD and Monte Carlo (MC) methods for the analysis of asphaltene aggregation was put forth by Hassanzadeh and Abdouss.[76] Ali *et al.*[75] elucidated various experimental procedures, such as precipitation, aggregation, and deposition tests, involving the testing of dead and live oils and described the performance of various chemical additives and the effect of operating conditions, such as additive pH, dosage, temperature, aging time, and the presence of impurities, on the precipitation onset, alteration of asphaltene morphology or asphaltene–surface interactions, aggregate size, and reduction in asphaltene deposition. This study also recommended dead oil testing for the preliminary analysis of chemical additives and careful consideration of solvent availability, cost, and environmental impact before field use. Sanati *et al.*[12] reviewed the utility of novel solvents, such as ILs and DESs, in enhanced oil recovery operations.

Lun *et al.*[77] studied the effect of six inhibitors [(S1) 4-dodecyl benzene sulfonic acid, (S2) 2-dodecyl benzene sulfonic acid, (S3) 4-dodecyl aniline, (S4) 4-dodecyl phenol, (S5) polyisobutylene succinic imide base benzene boric acid, and (S6) polyisobutylene succinic imide base benzene sulfonic acid] on asphaltene aggregation. This study illustrated the impact of acidity and the relative arrangement of polar and non-polar groups of the inhibitor on the

process of asphaltene aggregation. It is observed that the boric acid group in S5 interacts strongly with the asphaltenes (and encapsulates an asphaltene molecule) in comparison with the sulfonic acid group in S6.

The goal of this Perspective is to provide readers with a thorough understanding of current research progress on asphaltene handling mainly using atomistic and molecular simulations. This study presents a comprehensive analysis of asphaltene structure and aggregation, as well as a thorough examination of asphaltene–solvent interactions, including those involving ILs and DESs. This Perspective also summarizes several works based on DFT and MD based simulation techniques that have been utilized to gain a deeper understanding of asphaltene–solvent interactions. This Perspective is organized as follows: in Sec. II, we explain the process of asphaltene aggregation. In Sec. III, we explore the challenges and limitations associated with the usage of the simulation techniques, namely DFT and classical MD simulations, to study asphaltene systems. In Sec. III A, we focus on DFT-based studies with an emphasis on electronic structure calculations, hydrogen bonding, π–π interactions between aromatic rings, and dispersion forces. In Sec. III B, we present an elaborate discussion on the existing classical MD-based studies and important aspects related to it, e.g., limitations of force fields, the interaction of asphaltenes with various solvents and surfactants, and the effectiveness of ILs as asphaltene aggregation inhibitors. In Sec. IV, we present our perspective and summarize major outcomes of the comprehensive atomistic and molecular studies on asphaltenes, solvents, and inhibitors.

II. ASPHALTENE AGGREGATION

Asphaltenes are complex organic molecules in crude oil and can cause significant problems during crude oil extraction and processing. Asphaltenes cause precipitation and surface deposition, disrupting the transportation of crude oil. Two conflicting explanations have been proposed in the literature to explain asphaltene structures, and this discussion is ongoing: (1) the Yen–Mullins continental model and (2) the archipelago model. The predominant asphaltene molecular architecture transformation from single molecules to nanoaggregates and nanoaggregates to clusters of nanoaggregates are shown in Fig. 1 based on the continental model. According to the Yen–Mullins continental model, asphaltene molecules can form

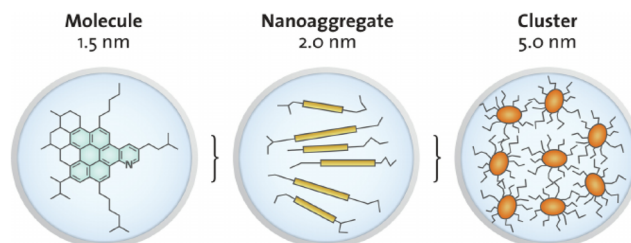**FIG. 1.** (Left) Single asphaltene molecular structure. (Center) Formation of asphaltene nanoaggregates with the aggregation number of 6. (Right) Cluster of asphaltene nanoaggregates. Reproduced with permission from O. C. Mullins, Energy Fuels **24**, 2179 (2010). Copyright 2010 American Chemical Society and Mullins *et al.*, Energy Fuels **26**, 3986 (2012). Copyright 2012 American Chemical Society.

asphaltene nanoaggregates with a single, disordered stack of polycyclic aromatic hydrocarbons and with the aggregation number of 6.[9,78] In contrast, the archipelago model suggests a supramolecular structure for understanding the aggregation of asphaltenes. According to this model, a typical asphaltene component is composed of multiple smaller interconnected polycyclic aromatic or heteroaromatic islands linked together by saturated alkyl bridges. These islands are also adorned with heteroatom functionality and short alkyl side chains.[79,80] Headen *et al.*[81] probed asphaltene aggregates of the two crude oil samples using small angle neutron scattering experiments. It is observed that with increasing temperature, the radius of the gyration decreased. The size of asphaltene aggregates in both the crude oil samples was comparable to that of asphaltene aggregates in aromatic solvents. Seifried *et al.*[82] investigated the process of asphaltene aggregation in crude oil by employing confocal laser-scanning microscopy. An interesting aspect of this study is investigating the kinetics of asphaltene aggregation in relation to various precipitants, solvents, and the Hildebrand solubility parameter. An in-depth investigation is conducted on the two mechanisms of asphaltene aggregation kinetics, namely diffusion-limited aggregation and reaction-limited aggregation, at the onset of precipitation.

Besides the molecule structure, the solvent type also influences aggregation, since asphaltene show different behaviors in different solvents. Side chains can either inhibit the core π–π interactions in toluene due to steric repulsion or support the aggregation in aqueous solutions based on the hydrophobic behavior of the chains.[33,83] At lower salt concentrations, the hydrophobic interactions are enhanced facilitating aggregation, while the hydrophobic interactions are suppressed at higher salt concentrations hindering aggregation. Numerous investigations have been performed mainly to explore the asphaltene aggregation inhibitors.[84,85] These inhibitor molecules migrate, adsorb asphaltenes, and strongly interact with the asphaltenes. Thus, they inhibit the interactions existing between the asphaltene molecules, thereby mitigating the formation of asphaltene aggregates.

Headen *et al.*[42] reported that aggregation is an extremely complex process. Aggregated structure formations are stimulated by decreasing pressure and temperature and/or amalgamated with incompatible oils and/or in the presence of CO_2 gas. They studied five hypothetical structures as shown in Fig. 2, which were consistent with the literature data and employed MD simulations for quantitative molecular representation analysis. Asphaltene "A" is an archipelago-type structure connected by an aliphatic chain and condensed with two aromatic cores. Resin "B" structure has a resin end of the asphaltene spectrum. Asphaltene "C" is an island-type structure formed with a large aromatic core, asphaltene "D" is a large continental asphaltene structure with a single aromatic core, and asphaltene "E" is an archipelago structure with three aromatic cores. Simulations have ascertained the asphaltene cluster properties from radius of gyration, cluster density, aggregation number, and shape anisotropy. MD simulations were performed for a mixture of two different molecules asphaltene "A" (archipelago-type) and asphaltene "C" (island-type) in solvents (toluene and heptane). Studies indicated that the properties for the asphaltene mixture (asphaltene A + asphaltene C + solvent) were bounded by the pure asphaltene A mixture (asphaltene A + solvent) and pure asphaltene C mixture (asphaltene C + solvent). The asphaltene mixture
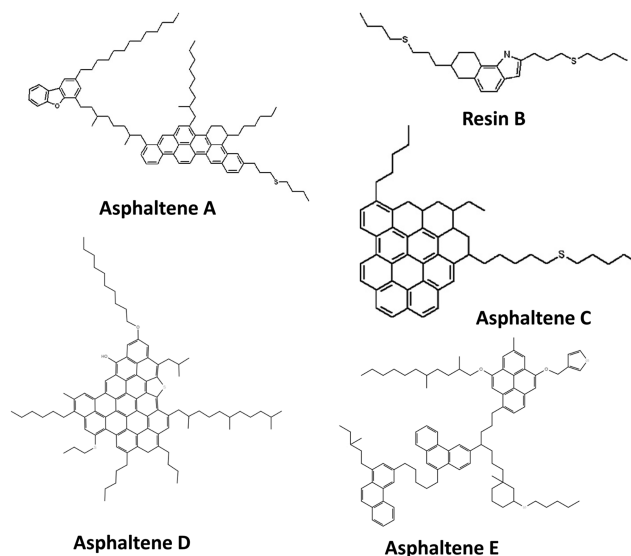

FIG. 2. Molecular structures of asphaltenes. Reproduced with permission from Headen *et al.*, Energy Fuels **23**, 1220 (2009). Copyright 2009 American Chemical Society and Ungerer *et al.*, Mol. Simul. **40**, 115 (2014). Copyright 2014 Taylor and Francis.[86]

properties, cluster radius of gyration and cluster density, are positioned in between pure systems, asphaltene "C" and asphaltene "A," for both solvents (toluene and heptane). An analogous result is depicted for the simulations of a mixture with two archipelago-type asphaltenes "A" and "E." These findings revealed that there is no reduction in asphaltene cluster size when two different asphaltenes are mixed in solvents. This study has stressed on the importance of building accurate coarse grain models with careful benchmarking against the experiments or molecular simulations for large system size and longer time scales.

III. ATOMISTIC AND MOLECULAR SIMULATIONS

DFT and MD simulations have emerged as powerful tools for investigating the molecular interactions of asphaltenes, inhibitors, and asphaltene in solvent removal processes. This section explores the advantages and limitations of these techniques for understanding the molecular interactions of asphaltenes and preventing their aggregation and deposition. Industries are working toward newer, more efficient practices to prevent precipitation and deposition, including inhibitors such as toluene and nanoparticles. The molecular interactions between inhibitors and asphaltenes were investigated with DFT calculations and MD simulations.[87] These atomistic and molecular investigations provide insights into various aspects/parameters associated with asphaltene adsorption at atomistic and molecular scales.[88] Most theoretical studies and experimental methods have provided a reliable understanding but fail to reveal mechanisms prevalent at an atomic level. Atomistic and molecular simulations, on the other hand, can provide atomic and molecular level insights to design effective agents/inhibitors/solvents to reduce asphaltene precipitation/aggregation/deposition in petroleum refineries and crude oil transportation.[27] Thus, atomistic and molecular based simulations

have enhanced our understanding of asphaltene aggregation and deposition. However, many unanswered fundamental questions remain, for instance how surfactants interact with bitumen under high pressure and temperature conditions and how oil emulsification behaves at high temperatures. These challenges must be adequately addressed before applying surfactants/inhibitors/solvents as an effective additive to handle asphaltenes.

A. Density functional theory based studies

DFT is a quantum mechanical method for calculating the ground state of condensed matter systems and is widely used in materials science.[89] Quantum chemistry calculations are used to calculate core-level spectra, total energies, and atomization energies.[90] DFT is also used to calculate the ground state electron density and corresponding activation energies. However, there can be systematic errors in theoretical calculations based on accuracy of exchange–correlation functionals, which must be assessed. Therefore, it is important to compare density exchange–correlation functionals when using DFT to investigate molecular interactions of asphaltenes. The primary application of electronic structure calculations was to model the nanoaggregation of asphaltenes. The complexity of the structure and intra-/intermolecular interactions of asphaltenes make it extremely challenging to achieve a strong correlation between computational and experimental results. It is a known fact that DFT includes electron correlation effects in an approximate manner. Moreover, most of the gradient-corrected density functionals are unable to describe dispersive interactions. It is important to note that in stacked aromatic systems like asphaltenes, aggregation mechanisms involving dispersion interactions are considered crucial to describe the system. To address this, the dispersion term in the interaction energy (DFT-D) can be added in the form of empirical Grimme corrections.[91]

Nanoparticles are seen as promising substitutes of conventional chemical enhanced oil recovery (CEOR) materials. These nanoparticles have demonstrated promising outcomes in terms of enhancing oil recovery through the reduction of interfacial tension between oil and water. They are attracting significant interest because of their promising characteristics, including exceptional thermal stability, high specific surface area, good solubility in polar environments, and enhanced mobility in porous media. DFT calculations are also performed to probe the nanoparticles and asphaltenes interactions. Carbon nanoparticles (CNPs) are utilized to prevent asphaltene precipitation and aggregation in unstable crude oil.[92] The effect of CNPs on asphaltene precipitation and aggregation is evaluated through experiments and DFT. Furthermore, the mechanisms of asphaltene adsorption onto CNPs surfaces are investigated in this study. The CNPs are attributed to the high specific surface area, due to which the onset of asphaltene precipitation is delayed. DFT studies showed a strong hydrogen interaction between the asphaltene active sites and the CNPs functional groups. One highlighting finding is that these interactions comprise π–π interactions present between the electronic cloud of aromatic rings in asphaltenes and CNPs. An asphaltene complex is quite strong and most stable with the chemisorption of asphaltene on the CNPs with the adsorption energy of −91.22 kJ/mol (gas phase) and −107.64 kJ/mol (solvent phase) as shown in Fig. 3. CNPs are synthesized with
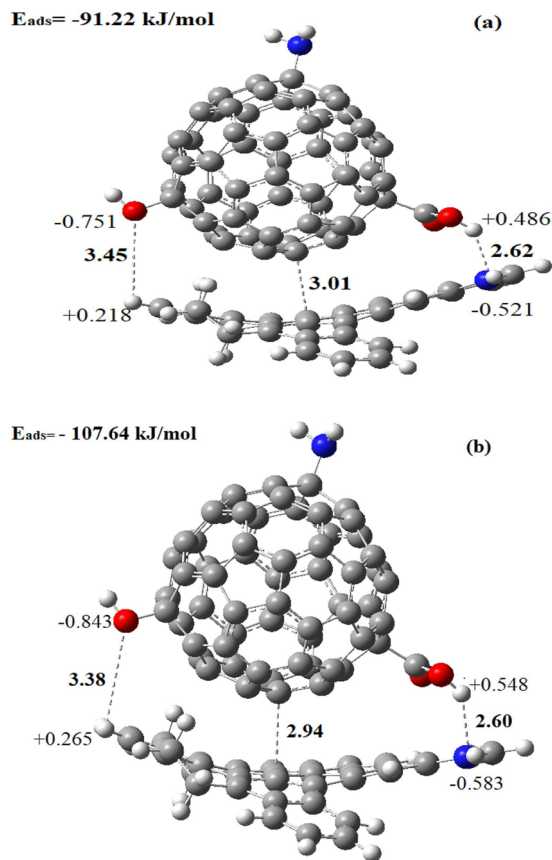

FIG. 3. Most thermodynamically stable complexes of asphaltenes with CNPs were studied under two conditions: (a) in vacuum and (b) in a solvent (toluene). The calculations were performed at the M06-2X-D3/6–31(d) computational level. The interaction distances (Å) and the charges on the interacting atoms involved in each hydrogen bonding were determined. Reproduced with permission from Alemi *et al.*, Chem. Eng. J. **422**, 130030 (2021). Copyright 2021 Elsevier Ltd.

desired features, such as low toxicity, high surface area, economical and environmentally friendly properties to behave as ideal inhibitors/dispersants to handle asphaltenes. The formation of powerful hydrogen bonds between the functional groups of the CNPs and the active sites of the asphaltene, along with the π–π interactions that occur between the electron cloud of the aromatic rings in the asphaltene and the CNPs, are the primary factors responsible for hindering asphaltene precipitation and enhancing the stability of asphaltene aggregates.

Bian *et al.*[93] investigated the experimental and quantum chemical calculations employing DFT to propose the mechanism by which asphaltene aggregates disintegrate through mild H_2 treatment. The degree of hydrogenation influenced the process of disaggregation, and there is a correlation between the stability of asphaltene dimers and the extent of hydrogenation. Five distinct asphaltene molecular series, varying in their degree of hydrogenation, were investigated. The optimized asphaltene dimer structures with varying degrees of hydrogenation, using the B97-3c density functional, are shown
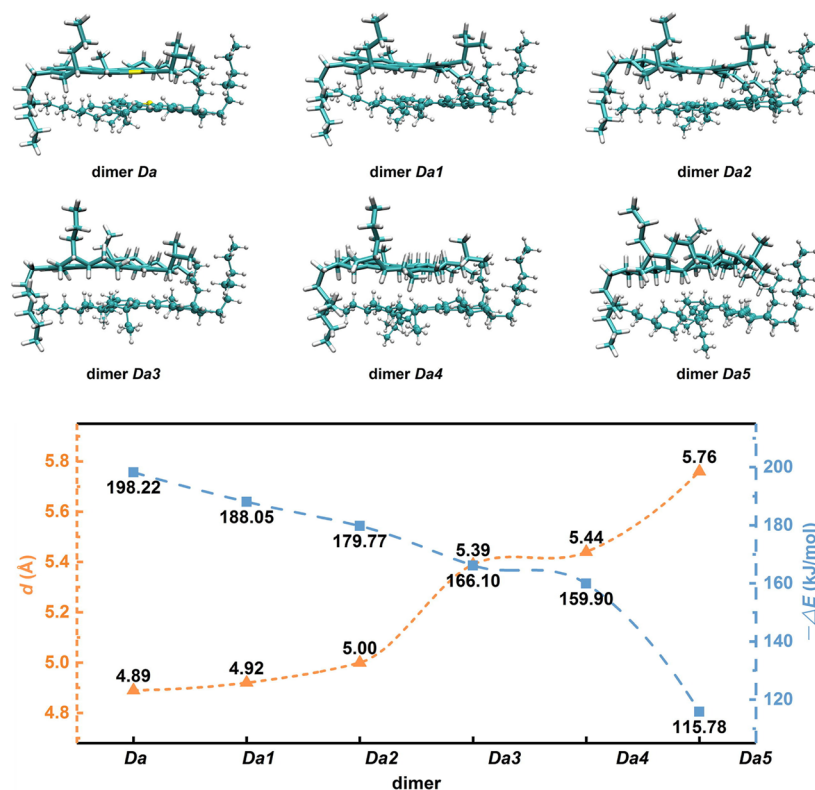
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FIG. 4. The molecular structures of asphaltenes, along with the centroid distances "d" and binding energies (ΔE) of asphaltene dimers with varying degrees of hydrogenation, were optimized in vacuum using the B97-3 level of calculation. Reproduced with permission from Bian *et al.*, Chem. Eng. Sci. **264**, 118106 (2022). Copyright 2022 Elsevier Ltd.

in Fig. 4. In addition, Fig. 4 presents the associated binding energies (ΔE) and distances. The raw asphaltene dimer "Da" results in a strong π–stacking interaction between two neighboring parallel fused aromatic centers. As the degree of hydrogenation increases, the magnitude of ΔE reduces considerably from −198.22 kJ/mol for "Da" to −115.78 kJ/mol for "Da5."

Alvim *et al.*[94] investigated asphaltene, resin, and asphaltene–resin adsorption on the $CaCO_3$ surface in the presence of the water–toluene environment using DFT calculations along with van der Waals dispersion corrections. In their work, the solvent is represented using dielectric continuum. It is observed that there is a minor steric hindrance in the interaction between aromatic parts of the asphaltene on the calcite surface. The presence of high electronic states, which are induced by charge rearrangement, is observed to have a significant role in π–π stacking interactions and is thus an important factor to consider in asphaltene adsorption. Another computational study was performed to model the interaction between alpha-quartz (silica) and a variety of asphaltenes.[95] A DFT periodic calculation was performed with the inclusion of long-range dispersion forces for obtaining the interaction energy between the surface and the aromatic molecule. A ring carbon in asphaltene was functionalized by substitution with heteroatoms (nitrogen, oxygen, and sulfur) to study the effects of interaction energy. Parallel adsorption of the asphaltene to the surface of the rock was most preferred due to extensive long-range

interactions between the aromatic π clouds and the surface as shown in Fig. 5.

In another study, the contributions from π–π stacking and hydrogen-bonding interactions in asphaltene model compounds
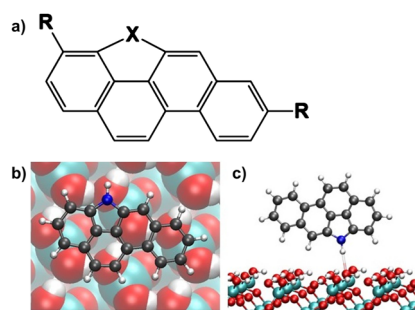
FIG. 5. Adsorption configurations for asphaltene "CA21" with X = NH and R = H. (a) Asphaltene molecular structure. (b) Top view of the parallel arrangement and (c) lateral perspective of the vertical arrangement. The colors assigned to atoms are as follows: Silicon (Si) is represented by the color cyan, oxygen (O) is represented by red, hydrogen (H) is represented by white, carbon (C) is represented by black, and nitrogen (N) is represented by blue. Reproduced with permission from Torres *et al.*, J. Phys. Chem. B **122**, 618 (2018). Copyright 2018 American Chemical Society.

were taken into account by employing the DFT-D method (including WB97Xd density functional with a dispersion correction term in the interaction energy).[96] In petroleum asphaltenes, it is essential to understand the association behavior of pendant aromatic and cycloalkyl groups. The aggregation strength of interactions was evaluated in terms of Gibbs free energy, interaction enthalpy, and the π–π interaction distances. Enthalpy and Gibbs free energy results suggested that hydrogen bonding is an important parameter similar to π–π interactions for understanding the asphaltene aggregation behavior.

Celia-Silva et al.[58] performed MD simulations to investigate the pre-aggregation of asphaltene in the absence and presence of ILs belonging to the 1-alkyl-3-methylimidazolium family. The impact of the alkyl chain length of the cation in ILs and the size of the anion (namely chloride and bromide) on the asphaltene aggregation has been investigated. DFT was employed to determine the stability of asphaltene–IL dimers, as well as to evaluate the energy, shape, and spatial distribution of frontier orbitals. The chosen ILs had a dispersing impact on asphaltene clusters in simulated solvents, with the exception of toluene-rich mixtures.

The aggregation of asphaltene model compounds has been also explored using DFT combined with an extended tight-binding method (GFN2-xtb).[97] Archipelago asphaltene model compounds with pyridine as the central island and pyrene for the outer islands were investigated within this study. Four possible complex formations were identified and explored further. Hydrogen bonding and π–π stacking were found to be crucial for the aggregation of asphaltenes.

B. Classical molecular dynamics based studies

MD simulation uncovers the fundamental mechanisms involved around the asphaltene behavior and interactions with solvents, ionic liquids, and nanoparticles. These simulations have successfully demonstrated the flow behavior of asphaltenes for a wide range of asphaltene systems. These studies have addressed the uncertainties regarding the asphaltene behavior and interactions with solvents, ILs, and nanoparticles. MD studies have also provided an understanding of the bonding and interaction between asphaltenes, for instance the hydrogen bonds reduction in asphaltenes with the increase in copolymer concentration.

It is crucial to comprehend the limitations of force fields employed in MD based studies. Partial charges in most force fields are derived from *ab initio* calculations performed on the specific molecule. Conversely, the optimized potentials for liquid simulations all-atom (OPLS-AA) force field determines the partial charges for a particular moiety through empirical estimation. This is done to precisely replicate the conformational and thermodynamic characteristics of the corresponding organic liquid.[98] In the case of hydrocarbons, empirical partial charges are employed to counterbalance the exaggerated charge localization in interaction-site models, with these charges being slightly lower than the computed ones.[99]

Asphaltene-based crude oils with copolymers were found to have a considerably low viscosity, reducing the chance of aggregation.[100] In another set of MD simulations, the interactions of asphaltene molecules at the interface between water and toluene were studied.[101] At the interface of water–toluene, asphaltene solute molecules exhibit a surfactant-like behavior. The simulations were performed

in the presence of an anionic surfactant, sodium dodecyl sulfate, with a mixture of asphaltene and resin. These studies reported that with the facilitation of surfactants, the heavy oil's viscosity reduced as the interaction between resins and asphaltene molecules weakened.[102] Investigations for archipelago and island architectures of asphaltenes with anionic surfactants showed stronger interactions than any other surfactant type.[103] Solubility parameter profiles were found to characterize the distribution of asphaltenes in water/oil interfaces.[104] In immiscible systems, the water/toluene system was found to have a higher affinity than water/n-heptane for A1 and A2 asphaltene models, as found from the total solubility and density profiles. Asphaltenes were also found to desorb efficiently from the iron matrix with TiO_2 nanoparticles and toluene solvent.[105]

A polyaromatic compound, N-(1-hexylheptyl)-N'-(5-carboxylicpentyl) perylene-3,4,9,10-tetracarboxylic bisimide (C5Pe),[106] was modeled as an asphaltene compound in heptane solvent on silica surfaces using MD simulations. The study revealed that C5Pe morphology is in contact with the silica surface. Molecular-level interactions of the asphaltene adsorption process on oil/solid surfaces are complicated to obtain from experimental technologies. MD studies revealed that the C5Pe molecular configuration aggregates and the protruded carboxylic groups adsorb to the silica surface. It was further found that the hydrophilic and hydrophobic interactions caused surface adsorption.[106]

Vatti et al.[107] employed the Green–Kubo formalism to compute the shear viscosity of asphaltenes in water. The results indicated that the simple point charge (SPC) water model significantly underestimates the viscosity, which is measured to be 0.39 cP. While the viscosity value for the TIP5P water model is enhanced (i.e., 0.71 cP), a superior value of 1.21 cP is obtained with the TIP4P-D water model as shown in Fig. 6. This study emphasizes that the improved dispersion interactions enhance the characterization of the interactions between asphaltenes and water.

ILs and DESs have recently been utilized in chemical enhanced oil recovery and asphaltene treatment. These solvents offer two effective ways for improving oil recovery: inhibiting asphaltene precipitation and separating asphaltenes from the oil fractions. Hernandez-Bravo et al.[108] conducted an experimental analysis and MD to study the interaction between ILs and asphaltene molecules. Their findings revealed that the dominant molecular interactions
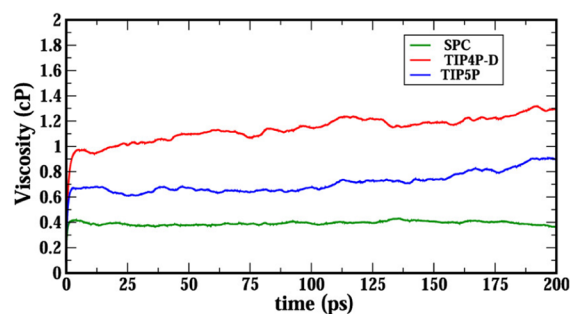
FIG. 6. The viscosity of the aqueous solution containing six asphaltene molecules at 300 K was determined using the SPC, TIP4P-D, and TIP5P water models. The viscosity values are plotted as a function of simulation time. Reproduced with permission from Vatti et al., ACS Omega **5**, 16530 (2020). Copyright 2020 American Chemical Society.

were between the IL-cation and the asphaltene-π ligand. This was attributed to the high aromaticity index of ILs, which led to a strong interaction with the aromatic core of asphaltenes and IL. As a result, the properties of crude oils, such as viscosity and interfacial tension, were modified.

In our earlier work,[60] dissolution studies were conducted for asphaltenes in organic solvents (hexane and toluene) with an IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]). Experimental data through optical microscopy, nuclear magnetic resonance (NMR), and Fourier transform infrared (FTIR) spectroscopy exemplify that asphaltenes distinctly separate out from organic solvent (toluene and hexane) to IL mixture. These findings indicated that the IL has stronger interactions with asphaltenes and

spontaneously form aggregates within IL. It was found that a higher degree of asphaltene separation can be obtained through minimal IL concentrations. Figure 7 illustrates the trajectory density contour of multiple asphaltene aggregates formed in the hexane + IL mixture. It was observed that the hexane + IL mixture have a greater asphaltene separation efficiency in comparison with the toluene + IL mixture.

Sanati *et al.*[109] investigated the performance of two chemical enhanced oil recovery agents, namely 1-dodecyl-3-methylimidazolium chloride as an IL and choline chloride:citric acid (1:1) as a DES, thorough experimental and theoretical studies. The experimental studies included chemical and thermal stability, adsorption, interfacial tension (IFT), wettability alteration, and
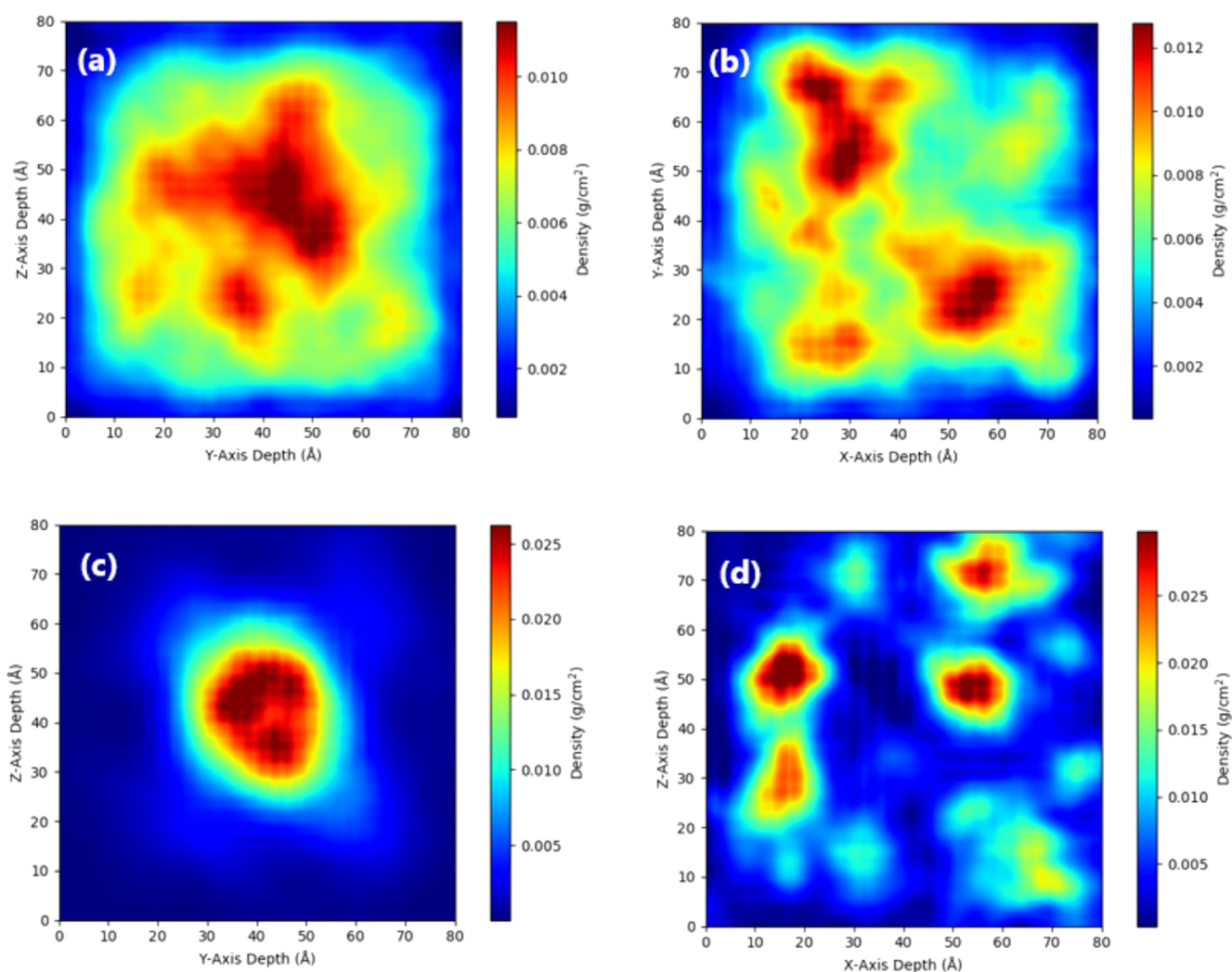

FIG. 7. The asphaltene density contours of the trajectory are shown for four different scenarios: (a) asphaltene dissolved in pure toluene, (b) asphaltene dissolved in a mixture of toluene and [BMIM][PF6] IL, (c) asphaltene dissolved in pure hexane, and (d) asphaltene dissolved in a mixture of hexane and [BMIM][PF6] IL. The color dark red represents the highest trajectory density (g/cm^2), while the color dark blue represents the lowest trajectory density (g/cm^2). Reproduced with permission from Vatti *et al.*, Energy Fuels **36**, 9111 (2022). Copyright 2022 American Chemical Society.

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core flooding. The extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory was used to get insights into the brine/rock interactions. The results obtained highlight that both chemicals were chemically and thermally stable. The IL proved to be a strong interfacial tension reducer and wettability modifier. The selected DES could also be considered as a strong wettability modifier.

In our recent work,[110] we synthesized and investigated the performance of DESs for separation of pure asphaltene through experiments and MD studies. DES solvents (reline, glyceline, and ethaline) cause asphaltene precipitation, resulting in its separation from organic solvents (toluene and n-heptane). Asphaltene separation from organic solvent phase to DES phase was observed by performing optical microscopy experiments. MD studies further quantified the experimental findings of asphaltene aggregation and separation through end-to-end distance, density contours of asphaltenes, and diffusion coefficients. These simulations were performed with an NVT ensemble for asphaltene with n-heptane and DESs. Figures 8(a)–8(d) show asphaltene in n-heptane only, n-heptane + reline mixture, n-heptane + glyceline mixture, and n-heptane + ethaline mixture. From Fig. 8, it is evident that asphaltene molecules (indicated by green color species) form

aggregates with DESs and separate out from n-heptane. These results corroborate the fact that DES solvents can be used to handle asphaltenes.

Ghamartale and Zendehboudi[111] performed high-throughput pre-screening of asphaltene chemical inhibitors using MD simulations. MD is employed to screen six potential inhibitors, including cetyltrimethylammonium bromide (CTAB), octylphenol (OP), Triton X-100, 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) IL, 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) IL, and 1-octyl-3-methylimidazolium chloride ([OMIM][Cl]) IL in heptane and heptol solvents. The results conclude that CTAB has the highest inhibitory effect followed by OP in the n-heptane solvent. Triton X-100 prevents asphaltene precipitation better than OP in heptol. However, ILs selected within this study have shown weaker inhibitory effects compared to surfactants.

The viscosity of crude oil is considered a critical parameter for its transportation and flow through pipes. The viscosity of crude oil is determined by the asphaltene content, as a greater concentration of asphaltenes leads to the formation of aggregates, resulting in a high viscosity. Crude oil is mixed with solvents (toluene, heptane, etc.) to reduce viscosity. Li et al.[112] studied the effect of asphaltene concentration on viscosity and also temperature
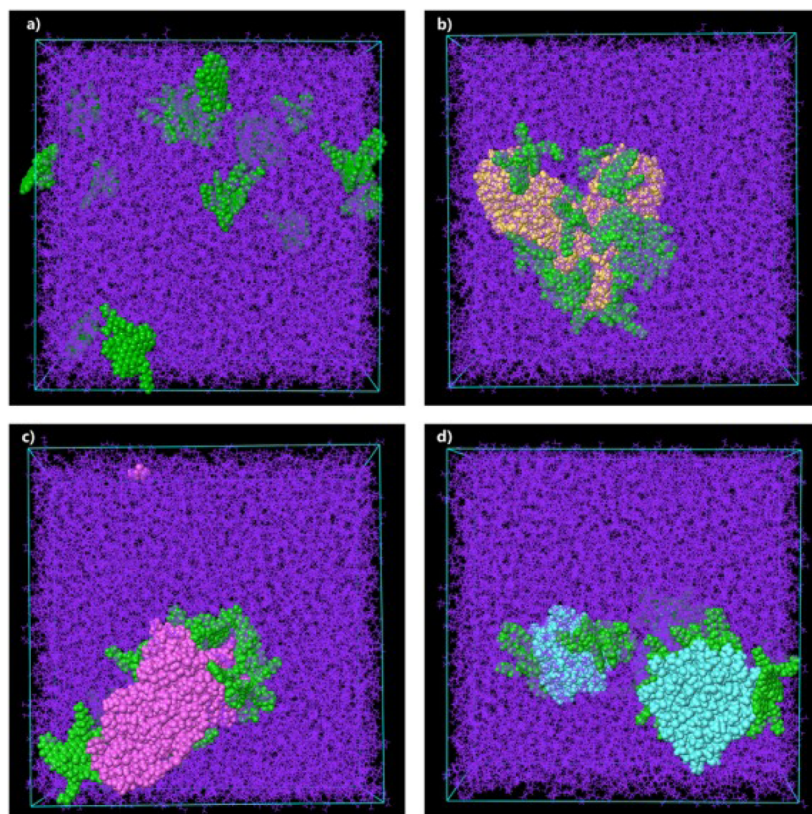

FIG. 8. Snapshots of the MD NVT run displaying asphaltenes in four distinct systems: (a) asphaltene in n-heptane; (b) asphaltene in n-heptane and reline; (c) asphaltene in n-heptane and glyceline; and (d) asphaltene in n-heptane and ethaline. The color scheme is as follows: the color of asphaltene is green, n-heptane is violet, reline is yellow, glyceline is pink, and ethaline is sky blue. Reproduced with permission from Hebbar et al., J. Mol. Liq. **387**, 122627 (2023). Copyright 2023 American Chemical Society.
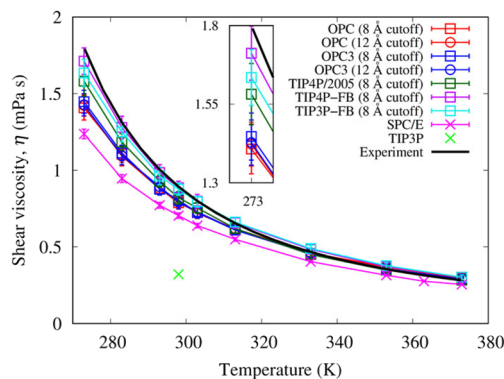
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FIG. 9. Temperature dependence of the shear viscosities of various water models. The results for the OPC, OPC3, TIP4P/2005, TIP4P-FB, and TIP3P-FB water models were obtained in this work, whereas those for the TIP3P and SPC/E were taken from Refs. 121 and 122, respectively. The experimental values are from Ref. 123. The inset shows an enlargement of the region surrounding 273 K. Reproduced from T. Ando, J. Chem. Phys. **159**, 101102 (2023) with the permission of AIP Publishing.

effects on the asphaltene–toluene solutions. They reported that viscosity increases exponentially for the asphaltene–toluene solution with an increase in the concentration of asphaltene. Furthermore, with an increase in temperature, a significant viscosity reduction is seen for asphaltene–toluene solutions. The accuracy of the prediction model depends on the ability to capture the intermolecular interactions affecting the crude oil's viscosity. Bouresli et al.[113] developed a temperature-dependent viscosity model for crude oils [American Petroleum Institute (API) gravity ranging from 11.3 to 26.5]. Their model had the least relative deviation compared to the

other six temperature-dependent viscosity models.[114,115] Sadi and Shahrabadi[116] and Stratiev et al.[117] proposed an artificial neural network (ANN) based approach for achieving a higher accuracy in predicting viscosity for heavy crude oils. The viscosity of mixtures, including various heavy oils and different gas oil diluents, is found to have an exponential relationship with the concentration of the diluent.

Hu et al.[118] conducted viscosity studies on heavy crude oils saturated with CO_2. The measurements were performed at a temperature of 25 °C and pressures of up to 220 bar, while varying the shear rate. A novel rheometer, operating under high pressure conditions, was designed to measure viscosity across a wide range of shear rates using a flow-through Couette geometry. The viscosity of the liquid phase decreases exponentially with increasing pressure in the liquid–vapor region due to dissolved CO_2. In another experimental work of Hu et al.,[119] the non-Newtonian behavior of the Zuata heavy crude oil was gradually reduced as the concentration of dissolved CO_2 increased. Furthermore, the findings from the view cell experiment indicate that the undiluted oil experienced swelling as a result of CO_2 dissolution.

Ando[120] assessed the shear viscosity of water at different temperatures by employing the four-point Optimal Point Charge (OPC) and three-point OPC (OPC3) water models. The Green–Kubo formalism is employed to determine the shear viscosity across a temperature range of 273–373 K. The evaluated viscosities of both models exhibited a high degree of similarity across all analyzed temperatures. The computed shear viscosities showed excellent agreement with the experimental data at temperatures over 310 K as shown in Fig. 9. Nevertheless, at lower temperatures, the water models consistently underestimated the shear viscosity, with the computed values at 273 and 298 K being 20% and 10% lower than the corresponding actual values.
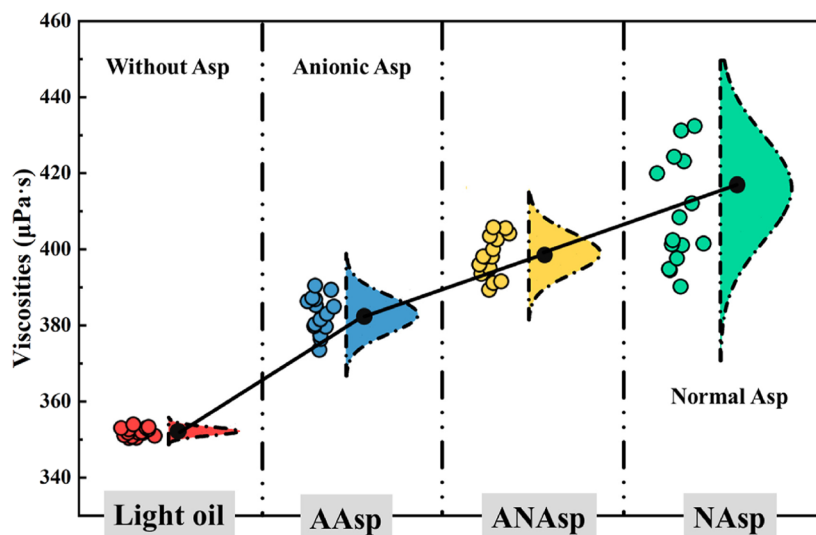

FIG. 10. The viscosities of four systems were determined using the periodic perturbation approach. Reproduced with permission from Cui et al., J. Mol. Graphics Modell. **126**, 108663 (2024). Copyright 2024 Elsevier Ltd.

In a separate study, the viscosity of the asphaltenes was determined for four different systems, i.e., light crude oil, charged asphaltene system Asp1, charged asphaltene system Asp2, and regular asphaltene using the periodic perturbation approach.[124] As depicted in Fig. 10, the viscosity of a light crude oil system without asphaltene is lower compared to a system containing asphaltene. This demonstrates the significant influence of asphaltene molecules in the process of increasing the viscosity of heavy oil.

Chemical enhanced oil recovery (CEOR) has emerged as a significant field in the development of heavy crude oil reservoirs due to the inability of conventional oil recovery methods to meet the growing demand for oil consumption. The primary CEOR techniques encompass polymer flooding, surfactant flooding, wettability alteration, alkaline flooding, and its many combinations, such as surfactant–polymer flooding, alkaline–surfactant flooding, alkaline–polymer flooding, and alkaline–surfactant–polymer flooding. It is important to select sustainable alternatives to heavy crude oil extraction. The development of sustainable heavy oil upgrading technologies is an ongoing process, with many technologies at different stages of development. Additional approaches, such as catalytic deasphalting and solvent-based deasphalting, are currently at the pilot stage. The emerging technologies, including microwave-assisted deasphalting and ionic liquids-based deasphalting, are currently in the preliminary phases of research.[125]

The main outcomes and key learnings from DFT and MD studies are as follows: the variations in the typical morphology of asphaltene clusters can be attributed to the inherent molecular structure as studied using MD simulations. Asphaltene clusters with an archipelago-like structure tend to exhibit elongated prolate shapes, while those with a continental-like structure tend to have oblate shapes.[42] MD simulations have demonstrated that the development of the nanoaggregate is mostly influenced by the size of the conjugated core and the potential existence of polar groups capable of forming hydrogen bonds.[126] DFT calculations have been conducted to examine the relative stability of the asphaltene–IL dimers and interaction energy between the asphaltene and IL. The interaction mechanism between the IL cation and asphaltenes has been elucidated by DFT. The mechanism was primarily influenced by the IL-cation and asphaltene-π ligands, which has a high aromaticity index.[58]

IV. CONCLUSIONS AND OUTLOOK

The oil industry primarily emphasizes investigation of flow assurance by exploring the phase behavior, aggregation, and molecular structures of asphaltenes. Based on decades of rigorous experimental work and theoretical models (including several ingrained models about phase behavior, asphaltenes aggregation, chemical constituents, and molecular structure, i.e., distribution of heteroatoms), numerous disputing claims (continental vs archipelago models) and long-standing discussions have been carried out. Asphaltenes exhibit a multimodal cluster size distribution, and choosing one average molecule as a valid descriptor to represent a multifaceted structural system is very difficult. It is important to consider dispersion interactions for stacked aromatic systems. Viscosity is a crucial parameter in flow assurance applications; therefore, accurate force fields, i.e., TIP4P-D or OPC water models, should be used.

The primary objective of atomistic and molecular simulations of asphaltene-based systems is to predict properties that are not readily observable from experimental methods. Such kinds of simulations also enable us to understand the molecular processes that influence the behavior observed at the macroscopic level.

Significant research contributions from DFT and classical MD based studies have been made to investigate the effectiveness of novel inhibitors to prohibit asphaltene aggregation. Hence, the understanding of the underlying mechanism behind inhibitor–asphaltene interactions is significantly enhanced by atomistic and molecular simulations. Specifically, a complete understanding of the aggregation of asphaltenes can be obtained based on DFT and MD simulations, thereby making it possible to identify prospective green solvents that can be used as inhibitors. The selection of accurate water models is key to reproduce various properties of bulk water (such as density, dielectric constant, heat of vaporization, self-diffusion coefficient, shear viscosity, and surface tension) with a high accuracy. Furthermore, it is crucial to accurately capture the solute–solvent interactions in order to comprehend the underlying mechanism. The identification of these new-age solvents will play a crucial to extract asphaltene from crude oil or in preventing asphaltene precipitation.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Anoop Kishore Vatti: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Srikanth Divi**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Poulumi Dey**: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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