Sorption and distribution of asphaltene, resin, aromatic and saturate fractions of heavy crude oil on quartz surface: Molecular dynamic simulation

Guozhong Wu [a], Lin He [b], Daoyi Chen [a,*]

[a] Division of Ocean Science and Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China
[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

- Quartz–oil and oil–oil interactions calculated by molecular dynamic (MD) simulation.
- MD simulating sorption, diffusion & distribution of oil fractions on quartz surface.
- Van der Wall energy contributed to >90% of molecular interactions.
- Aromatics and saturates fate randomly through asphaltene–resin complex.
- Oil distribution on quartz surface could be rearranged by increasing temperature.

ARTICLE INFO

ABSTRACT

The molecular scale sorption, diffusion and distribution of asphaltene, resin, aromatic and saturate fractions of heavy crude oil on quartz surface were studied using molecular dynamic simulation. Sorption of saturates on quartz decreased by 31% when temperature increased from 298 to 398 K while opposite trend was observed for resins, but insignificant changes were found in asphaltenes and aromatics. Despite of this variety, the main contribution of interactions was van der Waals energy (>90%) irrespective of molecular components and temperatures. The diffusion coefficient of saturates was predicted as 10.8×10^{-10} m^2 s^{-1} while that of the remaining fractions was about 4×10^{-10} m^2 s^{-1} at 298 K. The most likely oil distribution on quartz surface was that aromatics and saturates transported randomly into and out of the complex consisting of asphaltenes surrounded by resins, which was influenced by temperature. Overall, the knowledge on quartz–oil and oil–oil interactions gained in this study is essential for future risk assessment and remediation activities as previous studies on soil remediation either limited to light oil fractions with <40 carbons or treated the heavy crude oil as a single pseudo entity ignoring the interactions between oil fractions.

1. Introduction

Oil spills or leaks from storage during oil exploitation and discharge operations present as one of the principal sources of organic contaminants, which drive risk assessment and remedial actions at the land or marine environment. Considerable research efforts have focused on integrating petroleum fate and transport, microbiology and environmental diagnostics into site management regulatory and human health assessment frameworks (Brassington, 2008). Consequently, substantial technologies have been developed to remove petroleum pollutants from soils and sediments (Reddy et al., 1999; Khan et al., 2004; Gan et al., 2009).

For practical purposes, petroleum oil is generally divided into four fractions including asphaltenes, resins, aromatics and saturated hydrocarbons (Speight, 2007). Majority of previous work regarding oil clean-up concentrated on the removal of aromatic and saturate fractions with less than 40 carbon atoms while limited information is available for heavy crude oil removal from soil and sediment (Li et al., 2012a). Although it is well known that the bioavailability significance of light fractions are more obvious than heavy fractions, the toxicity and carcinogenicity of heavy fractions such as asphaltenes have also been recognized (Wess et al., 2004). The heavy crude oil adsorbed onto the soil surface was capable of altering the surface from water-wet (hydrophilic) to oil-wet (hydrophobic) and increasing the potential risks to human health and environment (Amro, 2004). However, previous studies often considered the complex crude oil as one pseudo material without

* Corresponding author. Tel.: +86 0755 2603 0544; fax: +86 0755 2603 6290.
  E-mail address: chen.daoyi@sz.tsinghua.edu.cn (D. Chen).

taking into account the varied molecular sorption behaviour of different oil fractions (Li et al., 2012b). Studies are needed to improve knowledge on the molecular scale sorption, diffusion and distribution of different fractions of crude oil on soil surface, which is of great benefit to determine the relative contribution of each fraction to the overall potential risks and increase the reliability of decision making for risks control.

More importantly, the presence of heavy crude oil as non-aqueous phase liquid (NAPL) would significantly limit the application of more sustainable site remediation technologies such as bioremediation (Wu et al., 2013). It would become one of the most significant compartments for distribution of hydrocarbons, which results in the infinite degradation half-lives because of the toxicity to microorganisms, lack of water, nutrients and oxygen to support degradation (Coulon et al., 2010). However, previous studies often focused on the oil–soil interactions while the interaction between specific oil fractions and their host oil matrix was less reported (Pollard et al., 2008). For example, Hogshead et al. (2011) investigated the interaction forces and adhesion energy between oil and silica surface using atomic force microscopy technique, but the oil fractionation and the interactions among oil fractions were not reported. Although Murgich et al. (1998) and Yu et al. (2012) calculated the adsorption energy of asphaltene and/or resin on silica surface, only one single molecule was loaded in the system, which warrants future works to gain insights into the sorption behaviour of asphaltenes with coexistence of NAPL containing other crude oil fractions.

Additionally, when obvious NAPL exists, solvent extraction is a promising method for oil removal (Wu et al., 2011). Most recently, Li et al. (2012a) demonstrated the efficiency of hexane–acetone mixture to extract four fractions of heavy crude oil from soil. However, it remains unclear about the distribution of oil fractions on soil and the influences of solvent extraction conditions such as temperature on oil distribution are less understood. Drawing on a detailed mechanism understanding of the molecular distribution of different oil fractions on soil surface is expected to support the optimization of solvent extraction, because chemical extraction efficiency was influenced by the molecular forces and binding energies of oil associated with soil (Dumitran et al., 2009).

The four fractions of crude oil may (i) gradually distribute from inner to outer soil mineral surface or (ii) homogeneously distribute in the form of colloid system where the central located asphaltenes are surrounded by the remaining fractions. To the best of our knowledge, there is not yet theory evidence or experimental validation for these hypothesises so far. In order to bridge the gaps between our knowledge on the micro scale distribution of oil fractions and the implementation of heavy crude oil removal, we turned to molecular dynamic (MD) simulation method. Widely applied as alternative to experimental approaches, MD is a versatile toolbox for modelling isotherm or thermodynamic processes of diffusion and sorption. Generally, it generates information at the microscopic level including atomic positions and velocities and then use statistical mechanics to covert this information to macroscopic properties such as pressure, energy and heat capacity. This study aims to employ MD simulation method to mimic the equilibrium sorption and partitioning of different oil fractions on quartz surface which is one of the most important constituent of sandy soil. Although there is no unique molecular morphology that is currently thought to exactly represent heavy fractions of crude oil due to its complex nature, this limitation should not be taken as a barrier preventing doing any molecular simulation involving heavy crude oils. Information of qualitative value can be obtained from the model molecules if proper precautions are taken in the analysis of the results (Murgich, 2003).

The specific objectives of this study were to (i) quantify the quartz–oil and oil–oil interactions by calculating the corresponding sorption energies, and (ii) determine the equilibrium diffusion and distribution of different oil fractions on quartz surface.

2. Methods

2.1. Force field

Material Studio software package was used to perform molecular simulation on a computer consisted of Intel Core i5-3450 CPU (3.1 GHz) and 8G RAM. The condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field, a widely used all-atom force field based on ab initio and optimization by experimental data (Sun, 1998) was used to describe all the atoms in this study. COMPASS field includes bonded potential (quartic bond stretch, angle-bend contributions, torsion, out-of-plane angle, and cross-coupling terms) and non-bonded potential (van der Waals interactions represented by Lennard–Jones function and electrostatic interaction represented by Coulombic equation). This force field has been validated to be capable of accurately predicting structural, vibrational, and thermophysical properties for a broad range of organic and inorganic substances including asphaltene, crude oil and quartz surface. Although hydrogen bonding energy was not exactly calculated in COMPASS, we believed this force field was suitable for the present study because Murgich et al. (1998) showed that the contribution of hydrogen bonding to the overall adsorption energy of asphaltene and resin on neutral silica surface was negligible (<1%).

2.2. Model construction

Despite of the fact that asphaltenes cannot be treated as simple homogeneous entities and thus be represented using an "average" asphaltene molecule, there is a certain consensus that asphaltenes could be structurally classified into "continental" and "archipelago" types (Aguilera-Mercado et al., 2006; Kuznicki et al., 2008). Both types might coexist in real asphaltenes at various degrees. In order to reduce the computational cost, only continental type model ($C_{54}H_{65}NO_2S$, MW: 792) was used in this study, because it allows the formation of aggregates by stacking of their aromatic regions and has been widely used as a basis for molecular and phenomenological models (Murgich et al., 1996; Rogel, 2002). This simplification was feasible as a recent study demonstrated that a single well defined compound could be successfully used for modeling the asphaltene aggregation process (Breure et al., 2013). Briefly, the model asphaltenes were described as aromatic cores composed of stacked aromatic sheets and surrounded by aliphatic chains (Fig. SM-1a in Supplementary Material (SM). The model resin ($C_{50}H_{80}S$, MW: 713) from an Athabasca oil sands bitumen (Murgich et al., 1996) and the sulphur containing molecules of aromatic fraction ($C_{46}H_{50}S$, MW: 635) (Verstraete et al., 2010) were used in this study, both of which had been previously validated by means of different techniques such as average molecular weight, elemental analysis (EA), ^1H nuclear magnetic resonance (NMR) and Fourier-transformed infrared (IR) spectroscopy. Eicosane ($C_{20}H_{42}$, MW: 282) was chosen as a representative compound of saturate fraction.

Energy minimization was performed for each molecular using smart minimizer approach, which altered from steepest-descent to conjugated gradient and then to the Newton method as the energy derivatives declined to accelerate the computation (Ling et al., 2012). Iterations were assigned cascade convergence levels of 1000, 10 and 0.1 kJ $(mol\,Å)^{-1}$ for these three methods, respectively. An oil mixture layer was built by setting up an amorphous cell containing 2 asphaltene molecules, 4 resin molecules, 6 aromatic molecules and 7 saturate molecules, which corresponded to a mass ratio of 15:30:35:20 roughly (Li et al., 2012b). Five different