



Full Length Article

The influence of asphaltene-resin molecular interactions on the colloidal stability of crude oil



Masoumeh Mousavi^a, Tahereh Abdollahi^b, Farideh Pahlavan^a, Elham H. Fini^{c,*}

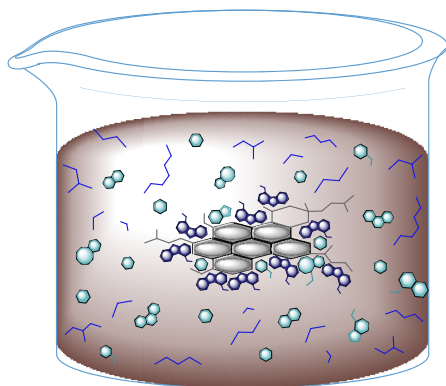
^aCenter for Innovation in Materials, Methods and Management, North Carolina A&T State University, 1601 E. Market St, Greensboro, NC 27411, United States

^bDepartment of Physical Chemistry, University of Mazandaran, Mazandaran, Iran

^cDepartment of Civil Engineering, North Carolina A&T State University, 1601 E. Market St, Greensboro, NC 27411, United States

GRAPHICAL ABSTRACT

Micellar structure of asphaltene in a dispersing medium of lighter resins, aromatics, and saturates.



ARTICLE INFO

Article history:

Received 4 April 2016

Received in revised form 18 June 2016

Accepted 20 June 2016

Available online 25 June 2016

Keywords:

Colloidal state

Asphaltene micelles

Petroleum resin

Density functional theory (DFT)

ABSTRACT

In the colloidal hypothesis of vacuum residua and asphalt, micelles are assumed to have an asphaltenic core with the greatest weight and aromaticity and an outer shell composed of lighter and less aromatic molecules. The true nature of the micelles, and the asphaltenic core in particular, has always been a debatable issue among asphalt researchers. One of the frequently asked questions is whether asphaltenes exist as stacked layers within the micelles or as single molecular units stabilized by resin molecules. In this paper, we investigate the correlation between the number of asphaltene sheets and the final stability of the system in a medium of asphaltene and resin components. Our evaluation is based on rigorous quantum mechanical calculations using a DFT-D approach. Our quantitative findings corroborate the view that the colloidal behavior of crude oil is better described by asphaltene-asphaltene associations. Moreover, our calculations show that if both asphaltene and resin are present, resin-asphaltene interactions are preferred over asphaltene-asphaltene interactions only if the number of resin molecules per micelle is greater than the number of asphaltene molecules per micelle.

© 2016 Elsevier Ltd. All rights reserved.

* Corresponding author.

E-mail addresses: fereshteh_mou@yahoo.ca (M. Mousavi), tahere_abdollahi@yahoo.com (T. Abdollahi), farideh.pahlavan64@gmail.com (F. Pahlavan), efini@ncat.edu (E.H. Fini).

1. Introduction

The bitumen refining process uses a distillation column or fractionation tower to separate lighter petrochemical fractions from the non-boiling components, which are known as an atmospheric residue. The atmospheric residue, a dark and viscous adhesive material, is then introduced to a vacuum distillation unit to be prepared for the solvent de-asphalting process. *Asphaltenes* and *maltenes* are two main fractions of the extracted asphalt. Asphaltene is the wax-free material that precipitates in light paraffinic solvents, while resins along with saturates and aromatics constitute the maltene phase of asphalt [1,2]. Although characterization of asphaltene and resin has been a controversial topic among the research community, there seems to be a commonly accepted view that these components, as the heaviest, most polar, and most aromatic components of crude oil, contain polycyclic aromatic sheets with a variety of functional groups, some traces of transition metal elements, and alkyl chains on the edges.

The matter of asphaltene precipitation and its technical consequences in refinery processing is a serious concern in the petroleum industry. Self-association of the asphaltene sheets is considered as the first step in the formation of precipitated asphaltene particles. The nature of the stacks formed (number, orientation angle, and interlayer spacing between asphaltene monomers) has been frequently investigated in asphaltene studies. Based on high-resolution transmission electron microscopy (HRTEM) and fluorescence depolarization techniques, the size of asphaltene stacks is estimated to be about 1 nm (*width*) \times 1 nm (*height*), mainly comprised of two or three individual asphaltene molecules [3–7]. However, new findings of laboratory centrifugation of a live crude oil indicate that the size of asphaltenes in crude oil is \sim 2 nm, and their aggregation number (in nano-aggregates) is between 3 and 8 [8].

The micellar model is one of the multiple models proposed to describe asphaltene behavior in crude oil. Despite its limitations [9–11], this model has been generally accepted [12–17] and is the most widely used viewpoint in descriptions of the nature of vacuum residua (VR) and bitumen. The idea of colloidal suspension of asphaltenes in bitumen/crude oil goes back to experiments by Nellensteyn [18] in 1924 that were further developed by Pfeiffer and Saal in later years [19,20]. Since then, outstanding contributions have been made to demonstrating the colloidal structure of vacuum residua and the role of petroleum resins in the micellar model [13,14,21–27]. These micelles are molecular aggregates of heavy asphaltene molecules that are peptized by light resin molecules, dispersing in a surrounding medium of lighter resins, aromatics, and saturates [28]. Resin molecules are well known for their stabilizing effect on asphaltene molecules and suspending them in a medium. It should be noted that the micellar model of asphaltene, in its traditional definition of one micelle, has been recently criticized by some research groups [29–31] who believe that resin molecules do not act as “surfactants” and strongly question the stabilizing or peptizing effect of resins on asphaltene aggregates, though they accept the general hypothesis of colloidal dispersion of asphaltene in crude oil/bitumen/organic solvents. In the current study, irrespective of the role of resin molecules, the term of “micelle” is used for a nano-aggregate structure composed of an asphaltenic core surrounded by lighter resins, other aromatic hydrocarbons, and saturates.

There seems to be some evidence that asphaltenes may not form large aggregates in crude oil, rather they exist at a much smaller scale (even a molecular scale) associated with resins in a colloidal structure of crude oil [14,32–34]. This view is further strengthened by the fact that asphaltenes with low aggregation number are well dispersed at very low concentrations [35–37]. Proponents of this view argue on the grounds that asphaltene

aggregates are formed only when the phase separation is occurring and asphaltene flocculation/precipitation is starting.

Against this view, other groups of the asphalt community (with a dominant majority) believe that the micellar behavior of crude oil is better described by “aggregates” [7,21,38]. Indeed, they theorize that the asphaltene-asphaltene association builds graphite-like stacks constituting the center of micelles, at which the shape, size, and number of aggregation are functions of the solvent, the temperature, and other environmental constraints [29]. Advocates of this view point out the asphaltene stacks exist not only in solid phase, but also before reaching the critical micelle concentration (CMC) limit that is considered as the onset of precipitation/flocculation [38].

Creek [39] describes the nature of studies carried out in this fieldwork; at one end of the spectrum are experimental studies that are involved in compositional analysis of the live single-phase reservoir samples, and at the opposite extreme are computational modeling studies that focus on the isolated molecules in a matrix even quite different from the original crude oil. Nevertheless, all of what we know about asphaltene micellization and its peripheral issues are apparently coming from experimental studies, and this approach has shaped our understanding of the issue. Indeed, the contribution of theoretical studies on the complex behavior of the systems like asphaltene under extreme conditions of temperature and pressure is insignificant, and is mostly restricted to classical molecular mechanics/dynamics (MM/MD) [12,40–42].

In the realm of quantum studies, factors like the specific nature of interactions, the complexity, and the massiveness of asphaltene aggregates/micelles have turned the subject of petroleum micelles into a challenge from a computing resource perspective. Additionally, the diversity of interpretations and the lack of consensus on experimental results (structural information, in particular) make asphaltene modeling even more challenging. Accordingly, this challenge and some doubts about the true nature of asphaltene micelles were the main motivation for the present work. In this work, we investigate the interplay between asphaltene and resin molecules in the formation of petroleum micelles. We also try to find a solution for the frequently posed question of whether individual petroleum micelles are stacked aggregates of asphaltene-asphaltene units or single entities of asphaltene (monomers) that are environed, peptized, and consequently stabilized by resin components. This evaluation is based on quantum mechanical calculations through a DFT-D approach, and our emphasis is on refining energy parameters to establish a correlation between the number of asphaltene sheets and final stability of the system in a medium of asphaltene-resin components.

2. Methodology

The geometry of all structures was optimized through a DFT approach implemented in Gaussian 09. All geometry optimizations were performed at 298 K with default convergence criteria for residual forces and energy variations (displacements), without imposing any constraints or extra keyword options. To accurately describe π -stacking interactions, as well as to emphasize the importance of dispersion energy as a key factor in stabilizing the stacked dimers, dispersion-corrected DFT functional, B97-D [43], associated with basis sets 6-31G* and 6-311+G**, was selected as the level of DF calculations to optimize the structures. Recently, B97-D has been widely used to describe macro structures like asphaltene sheets and DNA-base pairs [44–48] Counterpoise (CP) correction [49,50] was performed to limit basis set superposition error (BSSE) while studying intermolecular interactions.

Download English Version:

<https://daneshyari.com/en/article/6633263>

Download Persian Version:

<https://daneshyari.com/article/6633263>

[Daneshyari.com](https://daneshyari.com)