Fuel 236 (2019) 468–479

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Preferential adsorption of nickel porphyrin to resin to increase asphaltene precipitation

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ARTICLE INFO

Keywords:
Metalloporphyrin
Asphaltene
Peptizing
Nanoaggregates
Precipitation
Polydispersity

ABSTRACT

This paper incorporates a multi-scale approach to evaluate the contribution of nickel porphyrin to the aggregation and precipitation of asphaltenes in a medium of solvent/precipitator. This study provides an in-depth understanding of the role of metalloporphyrins in the complex matrix of petroleum/bitumen. Density functional theory (DFT) calculations and laboratory experiments were performed to examine the changes in physicochemical and rheological properties of a selected bituminous structure when doped with Ni octaethylporphyrin (NiOEP). Based on the DFT results, light and small assemblies of asphaltene-resin (in the limit of a single asphaltene molecule) are easily attracted to NiOEP. This in turn may help establish the role of a metal center as a nucleating agent promoting formation of small nanoaggregates in solution. Our experiment results using size-exclusion chromatography and rheological analysis of bitumen doped with NiOEP indicate an increased number of small-size nanoaggregates, as evidenced by a reduction in large molecular size (LMS) and a reduction in the polydispersity index. The latter is indicative of the formation of uniform particle size within the matrix after being doped with NiOEP. The modeling results further show that in larger nanoaggregates, asphaltene-asphaltene intermolecular interactions are too strong to allow an asphaltene core to be affected by NiOEP. In such cases, small resin molecules surrounding asphaltenes show preferential adsorption to NiOEP and take distance from the original nanoaggregates, reducing nanoaggregates' overall size. This was in line with UV–Vis absorption spectroscopy of a NiOEP-doped solution of bitumen showing that at least 95% of the added NiOEP remained in the maltenes portion containing resin, while only a trace amount of NiOEP was found in the asphaltenes. Considering the role of resins in stabilizing asphaltene aggregates, their departure can promote precipitation of asphaltene nanoaggregates. The latter was also evidenced by TLC-FID chromatography measurement, showing a substantial increase in asphaltene extracts in NiOEP-doped specimens compared to a control sample.

1. Introduction

Many aspects of the refining and upgrading processes in the natural gas and petroleum industries are affected by the significant detrimental impact of metal compounds. In natural gas and oil power plants, trace metals, particularly V, cause ash deposits on power-generating turbines, disturbing their functions. Trace metals deactivate catalysts and also increase gas and coke formation, leading to reduced gasoline yields [1]. The metals' effects become more pronounced when light compounds are volatized in the distillation process and metallic compounds concentrate in heavy petroleum residues. Many attempts have been made to remove trace metals from the matrix of heavy oil or to develop strategies to increase resistance against the deteriorating effects of trace metals [2].

Although there is no a clear molecular picture of the metal compounds in petroleum, based on a wide variety of analytical analyses, a main fraction (but not all) of the Ni and V metals in petroleum residues are chelated with porphyrins [3]. Another category of metal compounds containing Zn, Ti, Na, Ca and Mg are mainly found in the form of metal soaps/salts of naphthenic acids [4,5]. Of all trace metals present in heavy oils or bitumen, just two metals, Ni and V, have been proven to exist in significant amounts.

It has been well-documented that metalloporphyrins are concentrated in the most polar-aromatic components of petroleum residues; asphaltenes and resins [6–9]. SARA (saturate, aromatic, resin, and asphaltene) fractionation of seven atmospheric residues, performed by Reynolds using modified ASTM 2007 separation, verified that a great majority of metals are found in polar fractions, with a further majority

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https://doi.org/10.1016/j.fuel.2018.09.034
Received 25 April 2018; Received in revised form 25 August 2018; Accepted 7 September 2018

in asphaltenes [10]. Petroleum asphaltenes are among the low-solubility class of crude oil/ bitumen that accumulate in vacuum residues [11]. They are operationally defined as the toluene-soluble, and n-alkane (mostly n-heptane and n-pentane)-insoluble entities. This definition, which considers a solubility class for asphaltenes, implies that the precipitated material in an n-alkane medium are a heterogeneous aggregation of coagulated asphaltenes in combination with components that are inherently insoluble [12,13]. Gray uses the term of "coagulation" to describe the attractive interactions between a broad spectrum of asphaltene colloidal aggregates with different sizes in an n-heptane medium [13].

The inherent potential of asphaltenes to form aggregates allows them to have a wide range of aggregate stability in low concentrations, high temperatures, and in almost all strong solvents for asphaltenes, such as *o*-dichlorobenzene, nitrobenzene, chloroform, THF, and toluene [14–16]. The persistence of relatively stable aggregates even at favorable conditions for their solubility suggests that occlusion of metalloporphyrins within asphaltene aggregates could be started at early stages before precipitation. Occlusion/ trapping into the void spaces of asphaltene aggregates is not limited to the metalloporphyrins, indeed, precipitation of asphaltenes is always accompanied by the entrapment of species that are basically soluble in n-heptane/pentane [17–22,14]. The void volumes of asphaltene nanoaggregates are thought to be spacious enough to encompass the rather large molecules of metalloporphyrins in such a way that Acevedo et al. [17] believe that no specific interaction is required for entrapment of metalloporphyrins within asphaltene aggregates.

Beyond Acevedo's belief, the nature of predominant interactions in the formation of asphaltene- metalloporphyrin associates/aggregates is a matter of controversy. Π-stacking and non-covalent interactions are the oldest conceptual models to describe these interactions. Dickie-Yen [23], Sakanishi et al. [24], and Ancheyta et al. [25] are among the first groups who magnified the role of non-covalent interactions in the occlusion of porphyrins within asphaltene aggregates. In recent years, however, the dominant arrangement of π-stacking in asphaltene-metalloporphyrin associations and also even in asphaltene-asphaltene associations has been challenged by researchers who believe that the physicomechanical properties of asphaltene aggregates are not consistent with an architecture dominated just by electrostatic and/or van der Waals forces [13]. Instead, they provide evidence that the preferred aggregation modes of metalloporphyrins with asphaltene molecules are orientations leading to the strong covalent interactions, such as metal coordination, Brønsted acid-base interactions, H-bonding, etc. [26–28]. However, our studies on this topic show that strong donor-acceptor interactions are not necessarily achieved through covalent chemical bonding. Although non-covalent forces are the main stabilizing factors in a π-stacking arrangement, this orientation still takes advantage of strong orbital interactions arising from the formation of donor-acceptor hybrids between monomers (asphaltene and metalloporphyrin).

The fact that a main portion of metalloporphyrins are contained within the asphaltene nanoaggregates poses a serious hurdle to their selective removal. The association/aggregation of asphaltene-metalloporphyrin has been a source of inspiration for many research studies to interpret this phenomenon and find specific strategies to extract metaloporphyrins from the asphaltene fraction. Despite a general consensus on the co-precipitation of asphaltene-metalloporphyrin, there is disagreement about the fashion of inclusion of metalloporphyrins within asphaltene aggregates, and disagreement on the nature of predominant interactions ruling these two interacting species (asphaltene and metalloporphyrin); thus, there is still no clear picture regarding the promotion or demotion effect of metaloporphyrins on the aggregation behavior of asphaltenes. The questions posed are whether the entrapment/inclusion of metalloporphyrins into the void spaces of the flocculated asphaltenes leads to an increase in the asphaltene tendency to aggregate out of the solutions, and how the interplay between metal centers and fused ring aromatic centers (asphaltene or resin) changes the aggregation behavior of asphaltenes.

Detection and justified description of the aggregation behavior of asphaltenes in the presence of metalloporphyrins require a systematic study at both macroscopic and microscopic levels. This study starts with a series of quantum-mechanics-based calculations, using a dispersion-corrected density functional theory (DFT-D) approach, on model systems that capture the molecular response of asphaltene and resin molecules to the presence of one Ni-porphyrin molecule trapped between two asphaltene nanoaggregates in a colloidal state. In the next step, we try to extend our molecular-level knowledge to laboratory findings conducted by SARA (saturate, aromatic, resin, and asphaltene) fractionation using thin-layer chromatography with flame ionization detection (TLC-FID). Size-exclusion chromatography (SEC) analysis is conducted using gel permeation chromatography (GPC) to study the molecular size distribution of bitumen with and without inclusion of Ni-porphyrin. The rheology of the prepared samples is evaluated with a dynamic shear rheometer (DSR) to understand the effect of aggregation on the macrostructure level. UV–Vis absorption spectroscopy analysis is also carried out to estimate the concentration of Ni-porphyrin in each fraction of asphaltene and maltene.

2. Methods and materials

2.1. Materials

Bitumen was acquired through Associated Asphalt in Greensboro, NC and was graded as PG64-22. Elemental analysis of the bitumen by inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using an Agilent 5100 ICP-OES, although no trace metal could be detected above the 1 ppm detection limit (data not shown). The physical properties of the binder are listed in Table 1.

Nickel octaethylporphyrin, NiOEP, was purchased from Sigma-Aldrich. It has the chemical structure similar to Ni etioporphyrin with the molecular weight of 591.45 Da and empirical formula of $C_{36}H_{44}N_4Ni$. The solvent for asphaltene extraction was *n*-Heptane, purchased from Sigma-Aldrich.

2.2. Doping procedure of Ni-porphyrin

NiOEP was dissolved in chloroform to a concentration of 2 mg/mL. Roughly 1.5 mL of solution was then added to each gram of neat bitumen so that the composition of solids in the mix was 0.26–0.3 wt% NiOEP, corresponding to 260–300 ppm of elemental nickel. Others have reported finding ~100 ppm of trace nickel in native bitumen [17], so this 300 ppm initial doping concentration was selected to hopefully be large enough to overwhelm any native concentration of nickel porphyrin but not so large as to lead to separation of pure porphyrin from the mixture or other anomalous effects. The bitumen was dissolved fully in the mixture, then the chloroform was evaporated by setting the mixture on a hot plate at 80 °C overnight. The mix was heated to 100 °C for 1 h in a convection oven to dry off trace solvent. For a control "undoped" sample, an equivalent volume of pure chloroform was mixed with neat bitumen and evaporated by the same procedure in order to account for possible effects of solvent evaporation.

Table 1
Physical properties of the PG 64-22 bitumen sample.

Product Name	PG 64-22
Boiling Point	> 900 °F
Specific Gravity	1.0–1.10
Melting Point	110–130 °F
Solubility in water	Negligible
Vapor Density (air = 10)	Not Determined
pH	Neutral
Flash Point and Method	> 550 °F