



Full Length Article

The role of metalloporphyrins on the physical-chemical properties of petroleum fluids



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ABSTRACT

The presence of metalloporphyrins in crude oil has been known by many years now but their role on the physical-chemical properties of petroleum fluids, such as the aggregation of the high-molecular weight phases, remains unknown. In this paper, these properties are studied using different molecular modeling techniques (Molecular Dynamics, Semi-empirical PM7 and Density Functional Theory). This combined methodology allowed us characterizing the nature of these interactions, how it dominates the electronic structure of the stacked molecules and what is their participation on the formation of the nano-, micro- and macro-aggregates.

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1. Introduction

Processing heavy crude oil has become of uppermost importance in oil industry. Refining these fractions allows one obtaining low-molecular weight distillates by catalytic and non-catalytic conversion [1–4]. The presence of metals in these fractions is known since the early '50s [5–9]. These metallic centers are found complexed in tetrapyrrolic macrocycles (porphyrin derivatives) [10] and have a major negative impact during the phases of oil processing, since they can contaminate and deactivate the catalysts used in the refinery [11,12]. Moreover and very recently, it has been pointed out that these metalloporphyrins might play a major role on the asphaltene aggregation, being somehow trapped by these high-molecular weight oil's fractions [13]. This physico-chemical process is of remarkable interest in oil industry since, if not controlled, it can induce problems in several fields of petroleum utilization, from oil recovery and transportation to refining [14]. These complications arise from their tendency to aggregate out

of solution, increasing oil viscosity, adsorption on solid surfaces, precipitation, etc. [15,16].

The asphaltene molecules consist of a complex mixture of polycyclic aromatic hydrocarbons substituted with alkyl side chains and the presence of heteroatoms, like nitrogen, sulfur and oxygen is common in the conjugated core [17–22]. Porphyrins also make part of this crude oil's polar fraction. Fourier transform ion cyclotron resonance mass spectroscopy (FT-ICR-MS) results indicate that they can bear either nickel, vanadium or iron as metallic centers [9,12,13,23–30]. Besides the fact that the asphaltene composition changes for different oil sources, the relative porphyrin contents are not constant across different oil sources [31–35]. Some crudes are richer in metals, namely nickel or vanadium, and up to our knowledge, no clear clue on their role on the aggregation has been proposed [16,36].

Size exclusion microchromatography with high-resolution inductively coupled plasma mass spectrometric detection technique (ICP-MS) has demonstrated the trapping of metalloporphyrins (MP) by asphaltene nanoaggregates [16]. Caumette et al. [37] and Barbier et al. [38] have shown using the same technique that nickel and vanadium can be found trapped in asphaltene aggregates with a mass range between 200 and 40,000 Da, in dif-

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ferent fractions with proportions that depends on the geographical or geochemical origin of the crude oil under study. More particularly, electron-spin resonance (ESR) quantitatively measured levels of the paramagnetic vanadyl ions VO^{2+} and organic radicals trapped in crude oils with and without asphaltene [16]. Moreover, pulsed ESR spectroscopy has identified a porphyrinic structure of the vanadium (IV) in the asphaltene for several crude oils through the coupling with the four neighboring nitrogens [39]. Both ESR and high-resolution mass spectroscopy have shown that around 2/3 of the VO^{2+} is trapped in MP embedded within asphaltene nanoaggregates while 1/3 stays in the bulk [16]. Recent experiments of nuclear magnetic relaxation dispersion (NMRD) in crude oils with asphaltenes have proven useful for characterizing the translational diffusion of maltenes at proximity of asphaltene nanoaggregates including trapped VO^{2+} paramagnetic sources of relaxation [16,40,41].

Basically, in NMRD techniques, the proton Larmor frequency ω_1 is varied allowing an exploration of the time scales of the magnetic fluctuations (noise) to which the longitudinal proton spin relaxation $1/T_1$ is sensitive [16,40]. Further, the magnetic field dependence of $1/T_1$ provides a good test of the theories that relate the measurement to the microdynamical behavior of the fluid. This is still true in complex fluids, such as crude oil, where the effect of reduced dimensionality may force more frequent reencounters of proton-spins bearing hydrocarbons with either paramagnetic species or proton-surface groups on asphaltene nanoaggregates. The remarkable observed features of the nuclear magnetic relaxation dispersion (NMRD) profiles of proton $1/T_1$ for bulk and confined crude oils with and without asphaltene have been interpreted with an original relaxation model of intermittent surface dynamics of proton species at the surface of asphaltene nanoaggregates and bulk dynamics in between the slowly rotating clusters of these nanoaggregates [40,41]. This allows probing the 2D translational diffusion correlation time as well as the time of residence of the hydrocarbons at the surface of the asphaltene nanoaggregates. The latter time gives an average radius of exploration, $r_{2D} \approx 3.5$ nm, for the 2D diffusion of hydrocarbons (maltenes) at proximity of the surface of asphaltene nanoaggregates that agrees with the sizes found previously by SAXS and SANS studies [42]. These NMRD experiments results are thus important for understanding the role of asphaltenes in the dynamics and hydrodynamics of crude oils confined in rocks. An immediate consequence of this experimentally observed 2D diffusion of hydrocarbons (maltenes) at proximity of the surface of asphaltene nanoaggregates is the existence of an attractive potential interaction between the maltene and asphaltene nanoaggregates. One of our aims here is to find from our MD simulations the origin of such an attractive interaction for the vanadyl-containing porphyrins.

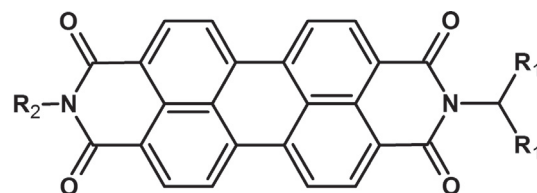
In silico, and up to our knowledge, no study has yet addressed the effect of these metallic centers on the asphaltene aggregating process and on other physical-chemical effects. Most of this is due to the need of using Classical Molecular Dynamics Simulations (CMDS) to study this phenomenon, but the parameters for metal centers are rare in number, quality and variety. Moreover, the structure of these porphyrinic and asphaltenic compounds is weakly resolved and a big effort has been done in our group in this sense [41,43,44]. Experimentally, a recent study has proposed the synthesis of nickel porphyrins having $-\text{COOH}$ functions grafted to it in order to study the aggregation mechanism with asphaltenes but only intermediated by this polar function [45].

Iron and nickel molecular dynamics parameters are known and have already been published in several reports, being able of reproducing very well experimental data [46,47]. The former has been an intense object of study because of its presence in hemoglobin and several force fields present parameters for it [48]. Nickel parameters are rarer but can be found in late '90s reports, although

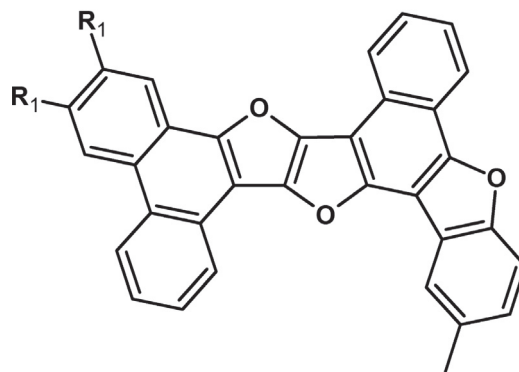
they are only a few [49]. However, for the case of vanadium, as it is found as the vanadyl radical cation, no classical molecular dynamics parameter set can be found for it or can be either produced because of its radical character. Although this limitation, we pursue our wish to acquire more information on their role in the aggregation process and we propose a simple way to introduce classical molecular dynamics parameters for the vanadyl group. To circumvent this weakness of CMDS, we use Density Functional Theory (DFT) and the semi-empirical PM7 hamiltonian (PM7) calculations to validate the results obtained by the former. Moreover, for the case of vanadyl radical cation, the use of DFT and PM7 allowed us to explicitly take into account any possible effect due to the unpaired electron for which CMDS cannot account. This multi-scale approach herein presented proved then to be essential for studying the aggregation of asphaltene in the presence of metals.

2. Methodology

The computational details behind the classical molecular dynamics simulations (CMDS) are fully exposed in the ESI. We used two molecular models to study asphaltene's behavior, both of them of the "island"-type [50]. The first, called C5Pe (Fig. 1) is a N-(1-Hexylheptyl)-N'-(5-carboxy-licpentyl)-perylene-3,4,9,10-tetracarboxylicbis-imide derivative and was chosen since it has already proved to be a good model for asphaltenes besides the possibility of theory-experience confrontation due to its synthetic availability [51,52]. The second, called A13, is derived from the experimental work of molecular cartography done by Schueler et al. [53] which isolated and identified it using Atomic Force Microscopy (AFM). The behavior in solution and the aggregation of these molecules were studied and published recently by our group [43,44]. We took a simple porphyrin model bearing a metallic center to model the metalloporphyrins that can be found in crude oil. As the experimental molecular structure of these metallic compounds is weakly determined, we preferred not to introduce long alkyl lateral chains grafted on the conjugated core in order to study the effect on the



(a) C5Pe molecule



(b) A13 molecule

Fig. 1. Molecular structure of (a) C5Pe and (b) A13 molecules studied in this paper. R_1 is a $n\text{-C}_6\text{H}_{13}$ chain and R_2 is a $n\text{-(CH}_2)_5\text{COOH}$ one.

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