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π - π Stacking Interactions between Asphaltene and Aggregation Inhibitors: A Study by Density Functional Theory.

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Solid deposition is one of the most serious problems that arise in oil production. The tendency of certain oils to flocculate and form deposits is attributed to asphaltenes and their respective molecular interactions. One of the most effective methods of preventing the precipitation and deposition of these compounds is the use of inhibitors and since understanding the mechanism of inhibition is of great practical relevance, numerous studies have been performed to investigate the factors that affect the efficiency of inhibitors. It is known that π - π stacking interactions are responsible for the aggregation of asphaltenes and resins [1]. Molecular modeling can play an important role in the investigation of association phenomena of asphaltenes but most of the standard semiempirical, density functional theory (DFT) and ab initio methods do not properly account for the dispersion term. π - π stacking interactions have proven to be sensitive to the methodology that is employed and are very dependent on the size of the basis set used in calculations being subject to large basis-set superposition errors (BSSE). The goal of this study is investigate π - π interactions between asphaltene and aggregation inhibitors using selected exchange-correlation functionals to overcome the well-known problems related to the use of DFT to correctly describe the dispersion interactions which constitute one of the main components of π - π stacking interactions [2].

An average structure of an asphaltene and three potential inhibitor molecules, p-nonylphenol, p-nonylaniline and cardanol were used for computational simulations by standard methods adopted by our group: Conformational analysis was done by molecular dynamics using the COMPASS force field for both asphaltene and inhibitor structures. Docking between the most stable structures of the asphaltene molecule and each inhibitor molecule was adjusted manually and conformational analysis of asphaltene-inhibitor structures was carried out by molecular dynamics using the same force field. Then only the structure involved in the interaction between the asphaltene and p-nonylaniline was used to test some functionals with a 6-31G(d,p). basis set. Results for the energies that were calculated are given in Table 1:



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Table 1 – Interaction energies calculated by MPW91, PW91 and B3LYP functionals

Functional 6-31G(d,p)	pnonylaniline	Asphaltene	Asphaltene-pnonylaniline	ΔE (hartree)	ΔE (kcal/mol)
MPW91	-641,431805	-2053,01985	-2694,434391	0,017263	10,83
PW91	-641,257690	-2052,49620	-2693,750908	0,002983	1,87
B3LYP	-641,562238	-2053,34581	-2694,888824	0,019222	12,06

Only the interaction energy calculated by the SVWN functional, shown in Table 2, gave a negative value. Thus calculations for the other asphaltene-inhibitor systems were carried out with the SVWN functional and the 6-31G(d,p) basis set adjusted for BSSE – Basis-Set Superposition Error.

Table 2 - Interaction energies (kcal.mol^{-1}) (ΔE , corrected for BSSE) for Inhibitor-asphaltene systems calculated by SVWN functional and the 6-31G(d,p) basis set.

Inhibitor	Energy	Asphaltene	Inhibitor - asphaltene	ΔE	$\Delta E_{\text{corrected}}$
p-nonylaniline	-637,88	-2041,47	-2679,38	-23,21	-20,72
p-nonylphenol	-657,66	-2041,47	-2699,17	-24,53	-22,04
cardanol	-888,52	-2041,47	-2930,04	-35,34	-29,11

Calculations with the ω B97X-D functional that has atom-atom dispersion corrections are being run with 6-31G(d,p), 6-31+G(d,p) e 6-31++G(d,p) basis sets.

Key-words: π - π stacking, asphaltenes, inhibitors, DFT

Support: CNPq and PCI/CETEM.

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