

## Asphaltene structural models simulated by molecular dynamics

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Asphaltenes are complex mixtures containing mainly organic compounds of high molecular mass, formed by polyaromatic systems with aliphatic side chains and few heteroatoms. Asphaltene definition is based in solubility criteria, being soluble in aromatic solvents (e.g., toluene) and insoluble in aliphatic ones (e.g., n-heptane).

Asphaltenes lead to serious problems of precipitation during the production and poisoning of catalyst during the refine. The problem takes bigger proportions in countries like Brazil, whose mainly reserves are founded in high depth in the sea.

The chemical complexity of some petroleum fractions makes hard to elucidate the asphaltene molecular structure. Several analytical methods (e.g., NMR, XRD, etc) have been applied to asphaltene fractions from different petroleum samples, in order to help in this issue. In fact, models that represent an average of the asphaltene fractions are used to study its properties, since its molecular structure is not known.

The current project has the objective to validate the methodology that will be used with representative models of asphaltenes, derived from NMR data, using as reference models similar asphaltene structures, which have experimental data of association behavior.

The reference models used to study the association behavior are: hexabenzocoronene (HBC), 4,4'-bis-(2-pyren-1-yl-ethyl)-[2,2']bipyridinyl (PBP), pyrenol (P-OH), hydroxymethyl-pyrene (P-CH<sub>2</sub>OH), pyrene (P) and methylpyrene (CH<sub>3</sub>-P) [1,2]. It is expected to obtain the energy of dimerization that could be used as an association parameter and serve as basis to propose more complex models.

Each asphaltene model was simulated in vacuum (Table 1) and in pure n-heptane and toluene (Table 2), by 50 ps, at 298 K, using NVT and periodic boundary conditions. MD simulations were carried out with the *Compass* force field, using the *Discover* (in vacuum) and *Amorphous Cell* (in solution) modules of *Materials Studio* v.4.4 [3].

Table 1 shows the dimerization energy in vacuum from the MD simulation. Table 2 shows also internal energies ( $E_{inter}$ ) and non-bonded energies ( $vdW$ , van der Waals;  $elect$ , electrostatic; and  $Hb$ , hydrogen bonding) for simulation in solution.

Table 1. Dimerization energies in vacuum (Kcal/mol).

Structure	$E_{monomer}$	$E_{dimer}$	$\Delta E_{dimeriz}$
HBC	1152.1	2165.4	-138.8
PBP	690.4	1321.3	-59.5
P-OH	313.4	597.9	-28.8
P	318.0	619.8	-16.3

Table 2. Dimerization energies in solution (Kcal/mol).

Structure	Solvent	$\Delta E_{dimeriz}$
HBC	n-heptane	-137.2
	toluene	-127.8
PBP	n-heptane	-27.2
	toluene	836,3
P-OH	n-heptane	-3.6
	toluene	-1.9
P	n-heptane	-18.3
	toluene	-3.8

Experimental data [1,2] indicate that structures such as HBC and PBP associate even in polar solutions and structures of 3 to 4 aromatic rings, as pyrene (P), do not associate. However, some polar groups, when added to pyrene-like structures, such as pyrenol (P-OH) can slightly raise its association.

This behavior is evident in the results from vacuum (Table 1). However, when the solvent is included, this observation become more complex. We may impose an arbitrary limit to predict the dimerization occurrence analyzing the results when the solvent is present. Structures with dimerization energy lower than c.a. -20 Kcal/mol are more associated. In the other hand, values higher than c.a. -20 Kcal/mol indicates weak or no association.

It was possible to predict the association of representative structures of asphaltenes in the vacuum and in solution (n-heptano and toluene), using the dimerization energy as a parameter. In future works, it is expected to predict if proposed structures by RMN are associated or not in these solvents.

### References

- [1] Akbarzadeh K. et al. (2005) *Energy & Fuels* 19, 1268-1271.
- [2] Tan X. et al. (2008) *Energy & Fuels* 22, 715-720
- [3] Accelrys 2007 *Materials Studio 4.4*, Accelrys Software Inc., San Diego, CA 92121, USA. Biddle, J.F., et al. (2006) *Proc. Natl. Acad. Sci. USA* 103, 3846-3851.