Study of Asphaltene Nanoaggregation and Effect of Additives by Molecular Dynamics

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Abstract

The study of asphaltene nanoaggregation using additives has become an important new area of research because it may be useful to obtain insight on the mechanism of asphaltene precipitation and redispersion. Furthermore, these additives may find application in processes such as deasphaltation, in which asphaltic material is removed from petroleum residues as part of some petroleum derivates, such as wax or lubricating oils. Another potential application of these compounds may be heavy-oil upgrade, in which a partial reduction of the asphaltic fraction would improve the crude oil market price.

In this work, the nanoaggregation of asphaltene dispersions and the effect of additives was studied by Molecular Dynamics simulations. The systems under study were chosen to mimic as closely as possible real systems experimentally studied at the UFRJ in Brasil. In particular, the effect of cardanol (a liquid fraction extracted from the shell of a cashewnut obtained from *Anacardium occidentale*) and polycardanol, were investigated. Both simulations and the systems studied in UFRJ, were performed in the presence of toluene and heptane. The lifetime of dimers of asphaltenes were analysed in this work and compared between the systems.

Keywords – Asphaltenes, Additives, Cardanol, Nanoagreggation, Molecular Dynamics

1. Introduction

Oil is a major source of today's energy with high economic value and therefore it is necessary to implement measures and techniques to improvise their maintenance and extraction allowing greater yield.

One of the problems that arises in the oil industry is the presence of compounds, which have a tendency to form agglomerates and clog the pipes. These compounds are the asphaltenes and the study to monitor their precipitation and solubilization is of extreme importance since it is a multi-million dollar industry. The control of asphaltenes' behavior with the use of additives can also have an important application in processes in which asphaltic fractions are removed.

1.1 Oil Composition

Oil can be defined as a complex mixture of organic compounds. The main compound present in crude oil are hydrocarbons (paraffins, naphthenes and aromatics) and also non- hydrocarbons. The non-hydrocarbons contain other elements than carbon and hydrogen, such as nitrogen, oxygen, sulfur, and some metals.

The primary process that permits the separation of different oil fractions is distillation, in which products are obtained with different volatilities and boiling points. However, there are compounds with a very low volatility becoming not distillable compounds, like asphaltenes and resins. These compounds may be separated by an alternative method that use solvents. The SARA method consists in the separation of compounds in four fractions: saturates, aromatics, resins and asphaltenes. (Figure 1)
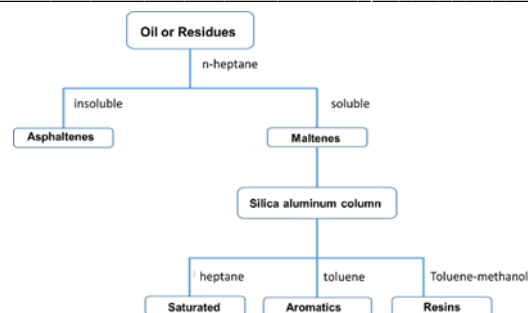

Figure 1 - SARA method. Adapted from[1]

Resins and asphaltenes are the most complex fractions of oil. These compounds are structurally similar and each molecule consists of aromatic rings with aliphatic chains and also by heteroatoms (O, N, S), having a high boiling point. However, resins and asphaltenes are different, while the resins are soluble in aliphatic hydrocarbons such as heptane, the asphaltenes are only soluble in aromatic hydrocarbons such as toluene.

Asphaltenes are the more polar and non-volatile components present in the oil with a high molecular weight. Due to their polar and aromatic character, the asphaltene molecules have a high tendency to form agglomerates, which may precipitate during transportation leading to the blockage of pipes. Therefore, the need to study methods that allow the stabilization of this fraction as a way of minimizing the problem.

One strategy to try to keep asphaltenes in solution is to use synthetic additives or from other origin with a chemical structure similar to the resins. The intention is that these additives should be capable of promoting the stabilization of asphaltenes.

1.2 Molecular Simulation [8]

Molecular simulation is a process that allows to describe complex chemical systems in a molecular

level. Through this method, we can see macroscopic physical properties that can be distinguished in:

(1) Properties of equilibrium statistics such as the potential energy of a system, density and the radial distribution function;

(2) Dynamic properties or non-equilibrium, as the viscosity of a liquid or diffusion process.

The choice of technique to use depends on the questions that we intend to in order to obtain reliable results. Monte Carlo and Molecular Dynamics: Two methods can be used.

1.2.1 Molecular Dynamics

Molecular dynamics is a computer simulation method that allows to study the physical movements of atoms and molecules over a given time and enables the explanation of macroscopic properties of systems using realistic models.

In this study method, the particles are placed in a simulation box where each one has a coordinate. Given that the systems are normally small (less than one million atoms), due to computational constraints, a cluster of particles would have undesired bonds with the surrounding environment (vacuum) if the simulation was conducted with real phase boundaries. To avoid this problem, the simulation box is surrounded by replicas of itself.

The movement of the particles is governed by Newton's equation of motion (Equation 1) for a system of N atoms, which have interaction:

$$m_i \frac{\partial^2 r_i}{\partial t^2} = F_i, i = 1 \dots N \quad (1)$$

Where m_i is the mass of the particle, $\frac{\partial^2 r_i}{\partial t^2}$ is the acceleration and F_i the resultant force.

The particle interactions are divided into:

-Interactions of non-bonded atoms: all pairs of interactions between a particle and other particles of the system;

-Intramolecular interactions: Energy angles, energy of dihedral and bond energy.

The energy of interaction between non-bonded atoms are described by the terms of van der Waals and electrostatic, represented by Lennard-Jones potential and Coulomb, respectively. For both, a cut-off is used allowing to establish a distance from which the interactions between the atoms are ignored. For distances above the cut-off, methods like Ewald sum are applied.

For the intramolecular components, the energy of the bonds and angles are usually treated as harmonic oscillator around the equilibrium values. The energy of the dihedral is associated with the torsion of dihedral angles and is represented by a Fourier series.

The simulations in molecular dynamics can be performed on different approaches including the NVE, NPT and NVT ensembles. In NVE, the volume is constant, pressure and temperature are unregulated and no exchanges of energy with the environment occur. The NVT and NPT systems are similar, however, in NPT additionally to a thermostat regulating the temperature, a barostat is also used for pressure control. The system temperature control is achieved by small adjustments of the speed of the particles while maintaining the total energy constant and control of pressure is done through small variations in the box size.

The system is followed for some time and the coordinates are written to an output file in regular intervals. The coordinates versus time trajectory represents the system. After some initial changes, the system reaches an equilibrium state. From the output file the macroscopic properties can be extracted, by averaging over this equilibrium trajectory.

1.3 State of Art

One possibility to promote asphaltenes nanoaggregation was studied through the use of amphiphilic dispersants, particularly those derived from alkylbenzenes which are the most important for this work. These compounds have usually a polar group which links to the surface of asphaltene molecule. In addition, they contain an aliphatic chain, which prevents the approach of another asphaltene molecule. This characteristic allows the dispersant to be soluble in aliphatic solvent.[3]

Chang and Fogler used derivates of amphiphilic alkylbenzenes and concluded that the stabilization of asphaltenes was mainly controlled by the polarity of this group in the amphiphilic molecule and also by the length of the aliphatic chain. These authors found that the increase of acidity of the polar group can promote the amphiphilic molecules a greater ability to stabilize the asphaltenes, possibly increasing the acid-base interaction. On the other hand, also observed that the higher the aliphatic chain, more stable the asphaltenes would be. [4]

In order to understand if it was possible to prevent the deposition of asphaltenes in pipes, keeping them stable, the group Macromolecules Institute of the Federal University of Rio de Janeiro, with which the Center of Structural Chemistry research group maintains contact, studied experimentally their behavior in the presence of an additive. The additive in study was the cardanol, present in the liquid extracted from the the shell of a cashew nut (CNSL) obtained from *Anacardium occidentale*, or *Anacardium anum* that are native trees of northern Brazil. This has the advantage of being a phenolic compound obtained naturally and with large production in Brazil. However, only a fraction has an industrial application and it is necessary to develop new applications.

The cardanol is a dark viscous liquid comprising a mixture of compounds of various isomers. These isomers are mainly phenolic compounds with an aliphatic chain containing 15 carbon atoms, which is substituted in the meta position of the aromatic ring, but may have multiple unsaturation or unsaturation on different locations of the aliphatic chain. [5] [6] It is believed that the cardanol have a similar behavior to natural resins present in crude oil and when these are added to the asphaltene particles, they form a stabilizing layer, holding asphaltenes molecules in solution. [7]

By way of comparison in the same laboratory was already studied, the behavior of asphaltenes in the presence of polycardanol. This polymer can be obtained by polycondensation and polyaddition. The molar masses obtained by condensation are considerably higher compared to those obtained by addition [6]. The concentration of polycardanol by addition with different molecular weights cause different effects, which appears to stabilize the asphaltenes to a certain concentration, but also cause destabilization at high concentrations in the presence of toluene as solvent, as seen in Figure 3. [8]
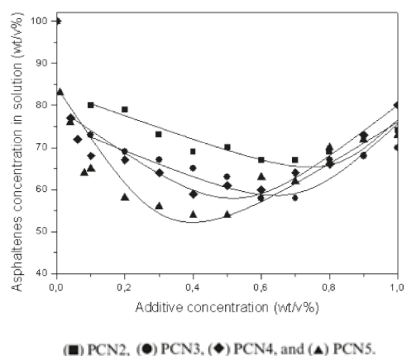

(■) PCN2, (●) PCN3, (♦) PCN4, and (▲) PCN5.

Figure 3 - Asphaltene precipitation by various polycardanol samples in the absence of heptane. [8]

Through Figure 2 we can see the effect of polycardanol monomer and the precipitation of asphaltenes in heptane / toluene mixture.
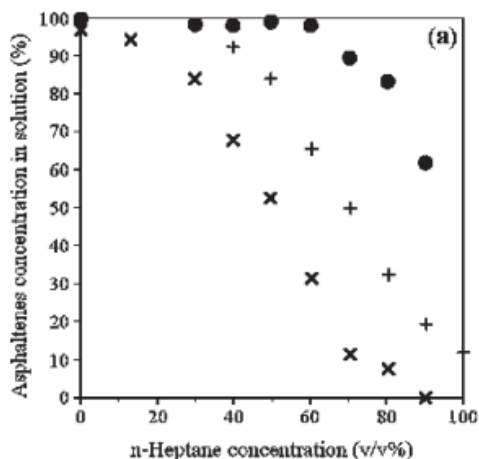

Figure 2 - Asphaltene precipitation diagrams in toluene/heptane mixtures in solutions with or without polycardanol. Initial asphaltene concentration separated from asphaltic residue= 100 mg/L. (+) No additives, (●) 1 wt% cardanol, (x) 1 wt% polycardanol PCN1 (MM=2300 Da). [8]

While cardanol appears to be a good dispersant with the increase of heptane/toluene ratio, polycardanol induces precipitation at low concentrations of heptane and the amount of precipitate increases for all the solvent ratios.

With a molecular approach, Cuiying Jia et al simulated aggregation of asphaltene in toluene. [9] They verified that the aggregates formed in toluene appear smaller and less stable compared to the aggregates formed in

water in which the asphaltenes are insoluble. The interaction between toluene and polyaromatic cores asphaltene could be a justification for this behavior (π-π interaction). This type of interaction is more important compared to interactions between asphaltenes side chains.

Thomas F.Headen et al used Molecular Dynamics to understand the nanoaggregation of asphaltenes in toluene and heptane. [10] They concluded that, in general, the asphaltene molecules formed dimers and trimers in both solvents. However, once formed, these seem to persist longer (some almost total time of 20ns simulation) compared to heptane where dimers and trimers only lasted a few nanoseconds.

The group of Chemistry Department of Petroleum Engineering at the University of Wyoming also studied the aggregation of asphaltenes and the impact of alkylphenols. [3] The group used Molecular Dynamics to understand the mechanism of interaction between the asphaltene model and octylphenol in mixtures of heptane and toluene. Through simulations, they verified that the octylphenol molecules tend to form hydrogen bonds with asphaltenes. These linkages occur at the periphery of the asphaltenes and, as a result, agglomerates and nanoaggregates would be prevented to form due to repulsion between aliphatic chains of octylphenol. Furthermore, octylphenol molecules seem to saturate the binding centers of the hydrogens atoms of asphaltenes molecules, decreasing the likelihood of interactions between asphaltenes. The effectiveness of octylphenol was impaired due to its self-association and the fact that they interact with the asphaltenes in periphery, leaving the aromatic cores exposed.

Roger and Lénon simulated amphiphilic alkylbenzenes at high and low concentrations in asphaltenes surfaces in order to study the interactions therebetween, the orientation of the additives on the surface of the asphaltenes and the structure of the additive layers. [11] They concluded that at high concentrations on the surface, the adsorption would be more favorable. The polar additive zone seemed to be parallel to the surface of the asphaltene and the formation of hydrogen bonds between additives adsorbed molecules indicates the beginning of micelle formation. Depending of the increases of polar group size, the better the barrier, and consequently, the better the additive activity as asphaltene stabilizer.

Asphaltenes structure also has high importance in the aggregation effect. [12] The presence of heteroatoms in the structure as well as the number of aromatic rings and the presence of aliphatic chains are relevant factors. The position of heteroatoms in asphaltenes also have an influence in aromatic interaction between asphaltenes. These can be linked to the aromatic nuclei or to the aliphatic chain. The size and number of aliphatic chains have a major impact on the asphaltene aggregation; they appear to cause a repulsion hindering the association of molecules.

Nowadays carbon dioxide effect on asphaltenes is very studied due to the low solubility. Experimental studies show that asphaltenes become more stable as the temperature decreases, in the presence of carbon

dioxide. [13] Thomas F. S. Headen and Edo Boek studied asphaltenes aggregation in the presence of CO2 as well as the effect of limonene by Molecular Dynamics. They concluded that the number of molecules per aggregate was greater in the presence of CO2, with up to six molecules compared to toluene and heptane where only trimers were observed. [14]

Michael L. Greenfield made a review on studies of asphaltene molecules by simulation. [15]

In this work the aim was to try to elucidate at a molecular level the behavior of systems with asphaltenes and additives such as cardanol and polycardanol. To achieve this we used Molecular Dynamics and systems were carried out in order to mimic experimental systems made on Macromolecules Institute of Federal University of Rio de Janeiro with which we maintained a connection during the process. [8]

2. Molecular Modules and Simulation Details

2.1. Molecular Models

In Molecular Dynamics a model of molecules is established, being atomistic in this case, which means that each atom corresponds to an interactive center. The whole study was based on the OPLS- AA model - developed by Jorgensen *et al.* [17]

The choice of the molecular model parameters was a crucial step to the work, since they define the model used in the simulations, conditioning the results. In this work were also applied improper dihedrals in the force field allowing the restriction of the molecular geometry.

The solvents, toluene and heptane, were first to be built. For these models were used the parameters from Jorgensen *et al.* [17] However, in the case of toluene it is similar to the original, but the charges used were re-parameterized by Udier-Blagovic *et a*l.[18] For both models of solvents, simulations were performed in order to check the density (ρ) and the self-diffusion coefficients (D), comparing them with real values. (Table1) The density values obtained by simulation are very close to the experimental values with errors of less than 2%. The diffusion coefficients deviate significantly from the experimental values (58% and 24%, respectively), but it is considered that acceptable since the models used were not optimized to reproduce this property, and it is not intended in this work to make quantitative analysis of diffusion in the studied systems.

Table 1 – Solvents densities and diffusion coefficients of models e experimental systems.

	ρ_{Model} (g cm^{-1})	$\rho_{Experimental}$ (g cm^{-1})	D_{Model} (m$^2 s^{-1}$)	$D_{Experimental}$ (m$^2 s^{-1}$)
Toluene	0,8820	0,8623 [19]	$1,03 \times 10^{-9}$	$2,18 \times 10^{-9}$ [20]
Heptane	0,6711	0,6799 [21]	$2,38 \times 10^{-9}$	$3,12 \times 10^{-9}$ [22]

It was necessary to choose an asphaltene model because exists a wide range of different molecules. This was chosen in order to respect some characteristics obtained from experimental data of Macromolecules Institute of the Federal University of Rio de Janeiro. The structure were also based in some proposals from a PhD thesis. [1] The main features to

take into account were the percentages of aromatics and aliphatic hydrogens, heteroatoms and molecular weight. (Table 2)

Table 2 – Asphaltenes models characteristics used in MD and experimentally studied.

	Model	Experimental [23]
MM (g/mol)	449,7	445
% $H_{aliphatic}$	77	78
% $H_{aromatic}$	23	22
% N	3,11	1,14

The asphaltene was built based on the pyridine model proposed by Caleman *et al.* [24] The charges of the central rings were based on the benzene model, however, the charges of the central carbons were adjusted in order to maintain the molecule neutral. [17] The charges of aliphatic chains atoms were based on alkanes models. [17] The asphaltene model has the particularity of not being able to make hydrogen bonds between them.

In the construction of cardanol model, the base was the phenol model reparametrized by Caleman *et al*. [24] The charge of the first carbon of aliphatic chains was applied in order to compensate the charges of phenol hydrogens thereby maintaining the neutral molecule. For the rest of the aliphatic chain were used charges of alkanes and alkenes. [17] The chosen model matches the most abundant isomer, representing about 52% of the existing isomers in the mixture. [5]

The polycardanol, as mentioned above, can be polymerized by radical addition through the double bond (polyaddition) or through benzene ring using formaldehyde (polycondensation). In this work were built both models. For polycardanol model by addtion was built a trimer polymer that have a high steric hindrance. For these models were used the same parameters used in monomer.

The model of the CO2 molecule used in the simulations was the EPM2 where angles and bonds are considered rigid. [25] For this model the density was also calculated and compared with the experimental value shown in Table 3.

Table 3- Experimental and MD densities of CO_2.

	ρ_{Model} (g cm^{-1})	$\rho_{Experimental}$ (g cm^{-1})
CO_2	1,022	1,036 [26]

2.2. Simulation Details

The molecular dynamics simulations were performed in the program DL_POLY Classic [16] The solvent systems ratio is 70:30 toluene/heptane (v/v%), thereby causing to be approximately 200 molecules of toluene to heptane 100 the simulated systems. In systems were applied periodic boundary conditions in all directions in order to eliminate the effects of surface. The sizes of the boxes were estimated in order to adjust the number and size of the simulation molecules.

For each system, the following method was applied: initial relaxation of molecules and minimization of energy in NVT, equilibration in NPT for 3 ns followed by a simulation production time of 50 ns NPT. The simulations were performed at a temperature of 298.15 K and 1 atm. In simulations with carbon dioxide, the pressure used was 100 atm and the temperature was the same. The Nose-Hoover thermostat with a relaxation constant of 0.5 ps was used for NVT and NPT simulations wherein the system is coupled to a heat bath, which keeps the temperature in the value required. The barostat of Nose-Hoover is also used in the simulations NpT to maintain the desired pressure by adjusting the volume of the simulation box with a constant of 0.2 ps.

All simulations were performed with a time step of 2fs except for the simulation with CO_2 where a time step of 1fs was used. The vibrations of bonds with hydrogen atoms were restricted to their equilibrium value using a vibration tolerance algorithm (SHAKE algorithm). For both Lennard-Jones and electrostatic potential was established a range of cut-off of 12 Å. For long-distance interactions, then the distance established by the cut-off was used Ewald summation method. [27]

The trajectories were visualized with Visual Molecular Dynamics program (VMD). [28] Nanoaggregation analysis and some radial distributions functions were performed with Travis. [29]

In order to confirm the system steady state, the variations of energy were observed. Typically, the energies have a variation of less than 0.4% relative to the average.

3.   Results and discussion

3.1. Definition of systems

To elucidate the behaviour of the additives in both solvents when they are isolated and their effect on nanoaggregation, various systems were made. The typical composition of the compounds in real systems in case of additives is between 0.05 and 1 m / vol% and in case of asphaltenes is 1% w / v. However, as these are not accessible from the viewpoint of the size of the systems and required time, we used higher concentrations also used in other simulation works. In the system with carbon dioxide, the number of molecules of CO_2 used was determined in order to maintain the same volume proportion 70/30 (v / v%) used in other systems.

3.2. Behaviour of Additives in Solvents

Before studying the behaviour of asphaltenes it was necessary to understand the behaviour of additives in the solvent mixture. For that, simulations were performed with different concentrations of monomers and compared between themselves and with polymers.

The radial distribution function, g(r), represents the probability to find a particle at a distance r from another particle. The short distances (less than the atomic radius), the radial distribution function is zero due to the strong repulsive forces. When we integrate these functions using equation 2, we can obtain the number of atoms that surround a given reference atom, N (r).

$$N(r) = \int_0^r \rho 4\pi g(r) r^2 dr \qquad (2)$$

Where r is the radius of coordination shell and ρ the segment bulk density.

By this integration, it is possible to quantify the hydrogen bonds between oxygen and hydrogen of cardanol and represent the results obtained as a function of concentration, using a distance criterion of 2.68 Å. (Figure 4)
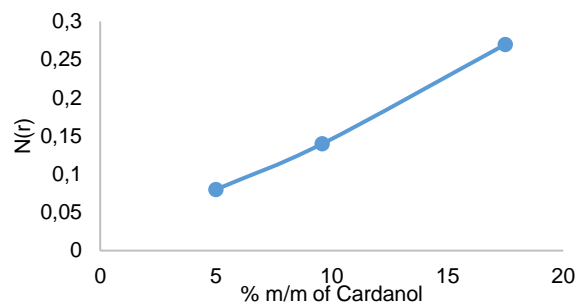

Figure 4 – Number of H around O of cardanol molecule in function of concentration.

By the analysis of the graph above it can be seen that the higher the concentration of cardanol in the solvent mixture, the greater the number of hydrogen bonds formed, indicating that the interaction between monomers increases with concentration.

Representing g(r) between C4C cardanol carbons (Figure 5) and compare with g (r) between oxygens (OHC) and hydrogen (COH) of cardanol (Figure 6), we can take some conclusions about the preferred position when they interact.
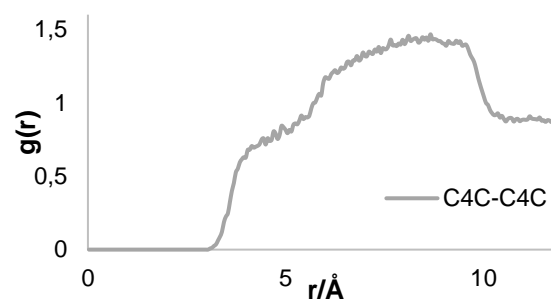

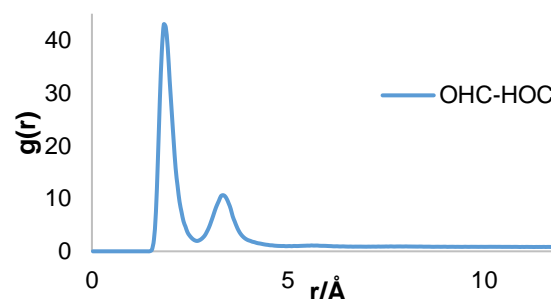Figure 5 – Radial distribution function between C4C carbons of cardanol.

Figure 6 – Radial distribution function between oxygen and hydrogen of cardanol.

For cardanol in the mixture of solvents, are represented in the figures above only the g(r) for one

5

system wherein the behaviour for different concentration of the remaining systems is similar.

The peaks of both radial distribution functions are not in the same distance, suggesting that the monomers do not tend to approach via aromatic rings, being in a linear conformation. This suggests that the primary interaction between cardanol molecules occurs by hydrogen bonding. The peak of interaction between carbons occurs only at longer distances ~ 8Å and may be influenced by atoms that are making hydrogen bonds.

In addition to monomer was also studied the behaviour of polymers in the solvent mixture in which the hydrogen bonds were quantified in the systems in question (**Erro! A origem da referência não foi encontrada.**). For these molecules were taken in account both intermolecular and intramolecular hydrogen bonds as well as associated uncertainties

Table 4 – Polycardanol Hydrogen Bonds.

	Concentração de aditivo %(m/m)	% Pontes de Hidrogénio OHP-HOP		
		Total	Intra-molecular	Inter-molecular
Policarda nol por adição	8,7	14±2	5,2±0,9	8±1
Policarda nol por condensa ção	7	77±3	77±3	-

By table values, we verify that the capacity of polycardanol by condensation to make hydrogen bonds is higher compared to polycardanol obtained by addition and to the monomers for similar concentrations. In polycardanol by condensation, the OH groups of the polymers are very close together, which leads to an increased formation of hydrogen bonds suggesting that the molecule adopts a conformation that allows curling on itself.

3.3. Behaviour of Asphaltenes in Solvents

Through a simulation with a mixture of solvents and asphaltene molecules with a production time of 10ns, it was possible to understand the efficacy of the toluene solvation and heptane using the analysis of the radial distribution function (Figure 7) and respective integral (Figure 8).
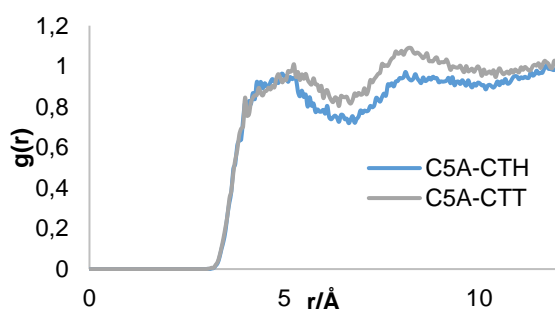

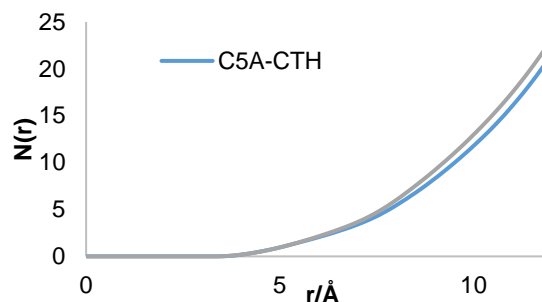Figure 7 – Radial Distribution Functions between C5A-CTH and C5A-CTT.

Figure 8 – Number of atoms CTT and CTH around C5A as function of distance.

From analysis of the figures above, it appears that the aromatic cores of asphaltenes are preferentially solvated by toluene molecules, which was expected due to π-π interactions between the two molecules. The aliphatic chains of asphaltenes are preferentially solvated by heptane, as can be seen in Figure 9 and Figure 10 since there are a greater number of CTT heptane atoms around the asphaltene CTA atoms.
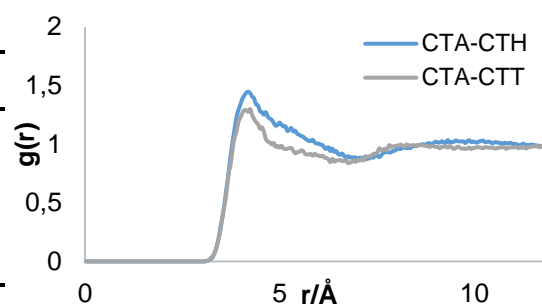

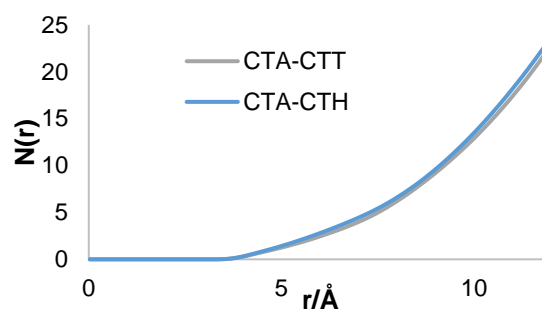Figure 9 - Radial Distribution Function between CTA-CTH.

Figure 10 - Number of atoms CTT and CTH around CTA as function of distance.

As mentioned above, asphaltene is soluble in toluene and insoluble in heptane and the aggregation when they are solvated by heptane is higher. In order to verify this behaviour with the asphaltene model chosen for this work, we performed two simulations with ten asphaltene molecules in toluene and heptane, respectively, and analysed the nanoaggregation tendency.

To proceed to the nanoaggregation analysis it was necessary to establish a criteria which is analogous to the criteria proposed by Lamia Goual et al.[3] We represented the distance between two asphaltene atoms as function of simulated time and considered that the molecules would be aggregated when the distance between these two atoms was less than 8.5 Å

and not aggregated to a distance greater than 10Å. Among these values, the aggregation would be accepted or not, according to the distances of the following frames. The temporal analyses were performed to the central carbon (CDA). Figure 12 shows the analysis for only two pairs of molecules of a system with asphaltene in heptane, to illustrate the established criteria. Figure 11 represents two pairs of asphaltene molecules at different distances with different conformations.
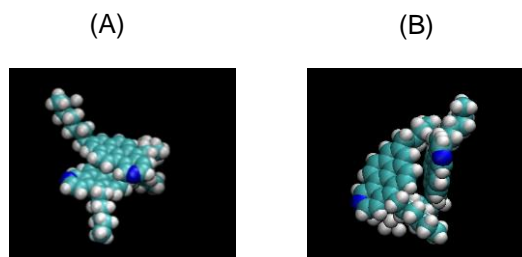
Figure 11 - Snapshot of two asphaltene moleculares with (A) d=4,35Å e (B) d=7Å.

Through the histogram, we see that the number of nanoaggregates formed in a system solvated only by heptane is superior for both short and long nanoaggregates lifetime, which agrees with experimental results.
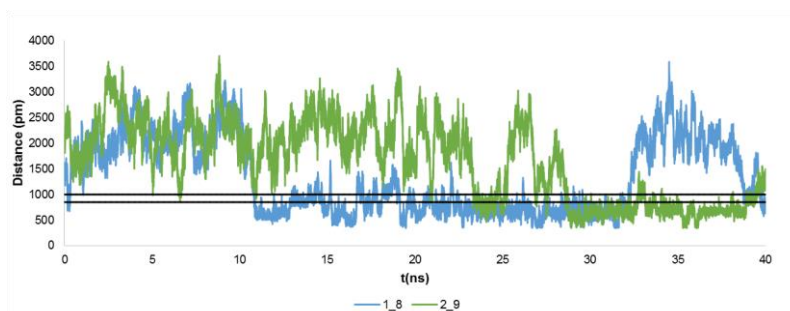

Figure 12 – Distance between asphaltene molecules as function of simulation time.

We counted the frequency of asphaltenes dimers formation and represented the respective duration obtaining the following histogram. (Figure 13)
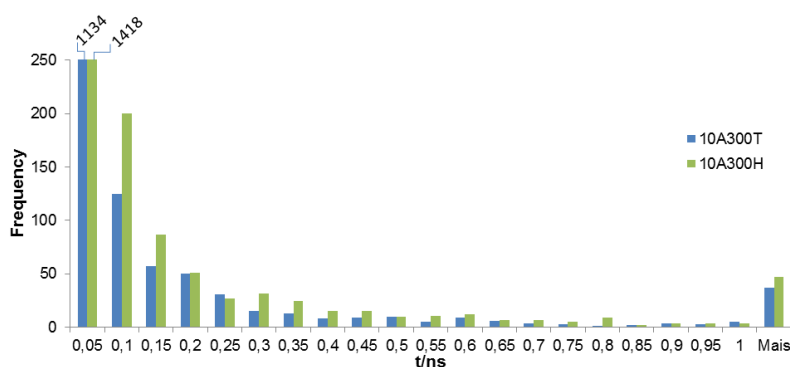

Figure 13- Asphaltene dimers lifetime in systems with 10 molecules of asphaltenes in toluene and heptane, respectively.

The result of the radial distribution functions between C5A carbons of asphaltenes of both systems (Figure 14) are in agreement with results where it can be seen that in a system only solvated with toluene, the highest peak in g(r) corresponds to a value close to 8Å. This indicate that the distance between asphaltene molecules in toluene is higher than a system solvated by heptane where the peak is set to a value of 4Å, typical of a close proximity between two carbons.
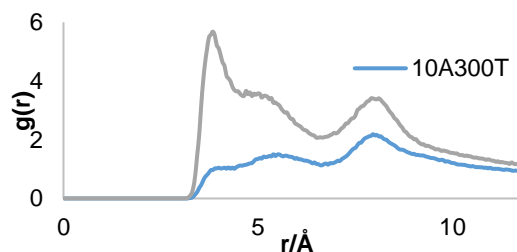

Figure 14-Radial distribution functions between C5A-C5A for systems in toluene and heptane, respectively.

It is also possible to understand that asphaltene molecules have higher tendency to aggregate in the presence of heptane. Through the Figure 15 we can

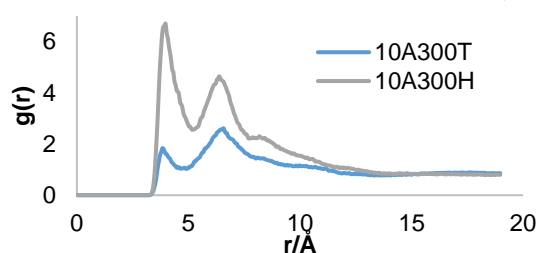possibly identify the most probable position of asphaltene molecules in both systems.

Figure 15 - Radial distribution functions between CDA-CDA for systems in toluene and heptane, respectively.

The g(r) indicates that the most probable peak between two CDA asphaltene atoms in a system solvated by heptane occurs at~ 4Å. In the presence of toluene the peak occurs at a distance of ~ 6.5 Å. When the asphaltenes are solvated only by heptane, they can have a configuration in which aromatic cores are closer, in a parallel conformation (Figure 11 (A)), however, in toluene, the most common configuration is the one that aromatic cores are almost perpendicular

Table 5 - OHC-HOC and OHC-NAA hydrogen bonds.

	Concentração de Asfalteno %(m/m)	Concentração de Cardanol %(m/m)	% Pontes de Hidrogénio OHC-HOC	% Pontes de Hidrogénio NAA-HOC
Cardanol emTolueno	1,4	9,7	11±4	8±5
	6,8	9,2	7±1	16±6
Cardanol na Mistura	6,7	9	15±2	17±3

Table 6 - OHP-OHP e NAA-HOP hydrogen bonds.

	Concentração de Asfalteno %(m/m)	Concentração do Aditivo %(m/m)	%Pontes de Hidrogénio OHP-HOPErro! Marcador não definido.			% Pontes de Hidrogénio NAA-HOP
			Total	Intra-molecular	Inter-molecular	
Policardanol por condensação	1,4	7	73±2	73±2	-	0
Policardanol por adição	1,4	8,6	18±6	8±3	10±4	14±8
	6,7	8,1	21±4	6±3	15±3	15±2

From the values shown in the table, it appears that on average each cardanol makes hydrogen bonds for about 10% of the time. This means that cardanol is quite dissociated. Although the monomer have a tendency to form hydrogen bonds, it is often free with approximately 90% of the time available.

As can be seen the cardanol appears to form more hydrogen bonds in the mixture of solvents that only in toluene. The toluene molecule is more polar and due to this fact, solvate better the OH group of cardanol. In the presence of heptane, each time these groups met they tend to remain together because the solvation is not as effective.

Moreover, for the same concentration of asphaltenes, the interaction between cardanol and asphaltene, appears to be equivalent to the solvent mixture and toluene. In an environment with only toluene to the same concentration of cardanol, but increasing the concentration of asphaltenes, there seems to be a

(Figure 11 (B)). This also allows to understand that, in a system solvated by heptane, we observe nanoaggregates formation with a greater number of molecules (Figure 23). In heptane the most likely conformation corresponds to π-π asphaltenes interactions and they can be more compressed and not feel so much the effect of the side chains that disturbs the nanoaggregation.

3.4. Behaviour of Additives in the Presence of Asphaltenes

The presence of asphaltene molecules in the systems influences the behaviour of additives. This influence was studied for the three additives in which the hydrogen bonds were verified among OH groups and also between them and the nitrogen of asphaltene molecule in order to understand their interactions. Table 5 shows concentrations and calculated hydrogen bonds for cardanol. In these results, we can see that
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greater percentage of asphaltene-cardanol hydrogen bonds.

3.5. Effect of Additives in Nanoaggregation

Through the count of asphaltenes dimers and reperctive lifetime, it was possible to understand the effect of additives in asphaltene nanoaggregation. In histogram shown in Figure 16 we can see the number of asphaltene nanoaggregates formed in a mixture of solvents as well as its duration in different simulations in the presence of polycardanol by addition or cardanol.
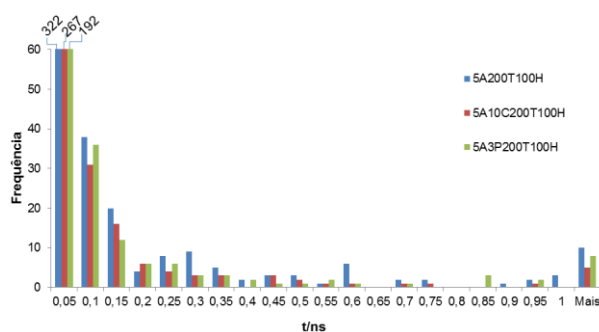
Figure 16 – Asphaltene dimers lifetime in systems with 5 asphaltene molecules in solvent mixutes in the presence or not of additives.

Both cardanol and polycardanol seem to prevent the formation of nanoaggregates. For the simulation where there is only asphaltene in the solvent mixture (5A200T100H), the formation of nanoaggregates is higher compared to systems where cardanol (5A10C200T100H) and polycardanol by adding (5A3P200T100H) is present. This occurs for short and long dimers lifetimes of asphaltene.

The difference in nanoaggregation systems can be explained by the fact that asphaltenes have relatively long aliphatic chains and few aromatic rings. The asphaltenes of this work are not able to establish hydrogen bonds with each other, and the main interaction between them occurs by aromatic cores. However, as stated above, the aliphatic chains of the asphaltenes hinder aggregation owing to repulsion, reducing the possibility of the aromatic rings interactions. In the presence of cardanol, the heteroatom asphaltene is capable to form a hydrogen bond with the H of the additive. This will also prevent aggregation while the bridge remains, with the same effect as an aliphatic chain.

3.6 Effect of Carbon Dioxide in Nanoaggregation

Due to the importance of the effect of carbon dioxide on the asphaltene molecules we made up only a preliminary study in which a simulation was performed with a 10 ns time of production. It Is possible to compare systems with carbon dioxide and toluene and systems which the solvent mixture is toluene and heptane. For these systems were made nanoaggregation analysis with the same criteria cited earlier. According to the analysis performed, the nanoaggregation is bigger for both short and long lifetimes in the presence of CO2. As stated above, the asphaltenes have a low solubility in the presence of carbon dioxide thus the association of these molecules will be significantly higher.

4. Conclusions and Future Remarks

Molecular dynamics allows us to understand the behaviour of systems by analysing the radial distribution functions and nanoaggregations. The cardanol have tendency to aggregate with the increase of concentration in a particular position. The fact that polycardanol is a polymer allows these to form intramolecular bridges in addition to the interaction with other molecules.

The behaviour of asphaltenes in toluene and heptane solvents agrees with other work already carried out, where the nanoaggregation is higher in heptane. In addition, the interaction between asphaltene molecules is not random. The interaction between rings is more probable in systems solvated by heptane.

When we introduce asphaltene molecules in systems with solvent and additives, it is found that the fact that the additive and asphaltene can make hydrogen bonds, results in a reduced availability for additives to form hydrogen bonds among themselves. The additives prevent the formation of nanoaggregates for both short and long lifetimes.

The characteristics of the system and how the modelling was performed may, for future works, be varied in order to understand if these results are only representative. This will provide a better comprehension about aggregation time.

The asphaltene model can also be changed allowing to understand the effects of aliphatic chains present as well as the heteroatoms.

For future plans new systems could be realized with a larger simulation time as well as larger systems. This could lead to more specific conclusions on the aggregation of asphaltenes because, in systems with only five molecules is not possible to observe the formation of large aggregates, only nanoggregates. Done with these variations we could have a greater sensitivity about the fluctuation of systems.

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