

Phase Separation of Asphaltene Dissolved in Toluene Leads to Nuclei Formation Promoted by the Very Low Solubility of Fraction A1. Soluble Fraction A2 Hinders Nuclei Flocculation

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Short Communication

Sudden aggregation of asphaltenes in toluene at room conditions is the consequence of reaching solubility concentration (close to 90 mg L⁻¹) of the very low soluble asphaltene component A1 [1-3]. Thus at concentrations close to about 90 mg L⁻¹ solid phase separation occurs with formation of nuclei where although type A1 molecules prevail, the nuclei contain enough A2 type molecules to keep them in solution. This view, henceforth called phase separation and dispersion view (PSD view) is consistent with formation in one step of aggregates containing *n* molecules instead of multimers such as dimers, trimers and so on. Indeed it is well known that highly polar molecules, in non polar solvents such as toluene, form multimers after a significant number of steps [4]. For decades the above phase separation was confused with a kind of "inverse micelle" formation because its similarities with the behavior of surfactant in oily media. In this case however, it has been postulated that aggregation of surfactants in oily media occurs by the stepwise formation of multimers [5]. Moreover, using either the molecular aggregation or the micellar views is very hard to understand the start-stop aggregation observed. In the present PSD view phase separation is promoted by A1 as described above and flocculation of

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nuclei is hindered by introduction of the soluble component A2 in the separated nuclei. Thus, nuclei produced could be described as a solid A1-A2 solution with a solubility parameter close enough to the one of toluene so to keep them in solution. Thus the nuclei formed could be defined as a liophilic colloid stabilized by A2.

As reported several times [6-8], using the p-nitrophenol (PNP) method, asphaltenes could be fractionated in the two main components A1 and A2, where solubility (in toluene, laboratory conditions) of A1 is very low (around 90 mg L⁻¹) whereas solubility of A2 is close to the one found for asphaltenes (5-12%, depending on sample). The method has been tested many times and with different samples always affording the two fractions with similar solubility differences. Solubility parameters of asphaltenes, A1 and A2 were consistent with A1 being less soluble than A2 in over 50 different solvents [9].

Compared with A2, the H/C values, obtained from elemental analysis, consistently afford lower values for A1 (see Table 1). However, these fractions share similarities, such as similar content of heteroatoms, similar C-13 NMR spectra and similar LDI MS (Laser desorption Ionization mass spectrometry). For instance, Figure 1, corresponding to Hamaca asphaltenes, shows no significant differences between the C-13 spectra of these fractions.

| Sample | H/C | | | %dif ^d |
|--------------------|-------|-------|-------|-------------------|
| | As | A1 | A2 | |
| Boscan | 1.192 | 1.105 | 1.17 | 5.5 |
| Hamaca | 1.075 | 1.06 | 1.11 | 4.7 |
| Furrial | 0.97 | 0.903 | 0.989 | 8.9 |
| Cerro Negro | 1.138 | 1.023 | 1.102 | 6.9 |
| CNR ^b | 1.115 | 1.084 | 1.185 | 9.1 |
| Model ^c | 1.11 | 1.024 | 1.11 | 7.7 |

Table 1: H/C values ^a of Asphaltenes and Fractions A1 and A2.

^a Experimental values from references (6 to 8).

^b Sample obtained from a Cerro Negro residue.

^c Calculated for the molecular models shown in Figure 2. In this case the H/C value calculated for A2 was used for asphaltenes.

^d $\% \text{dif} = \frac{100((H/C)_{A2} - (H/C)_{A1})}{(H/C)_{Asph}}$; errors in H/C values are usually better than 2%.

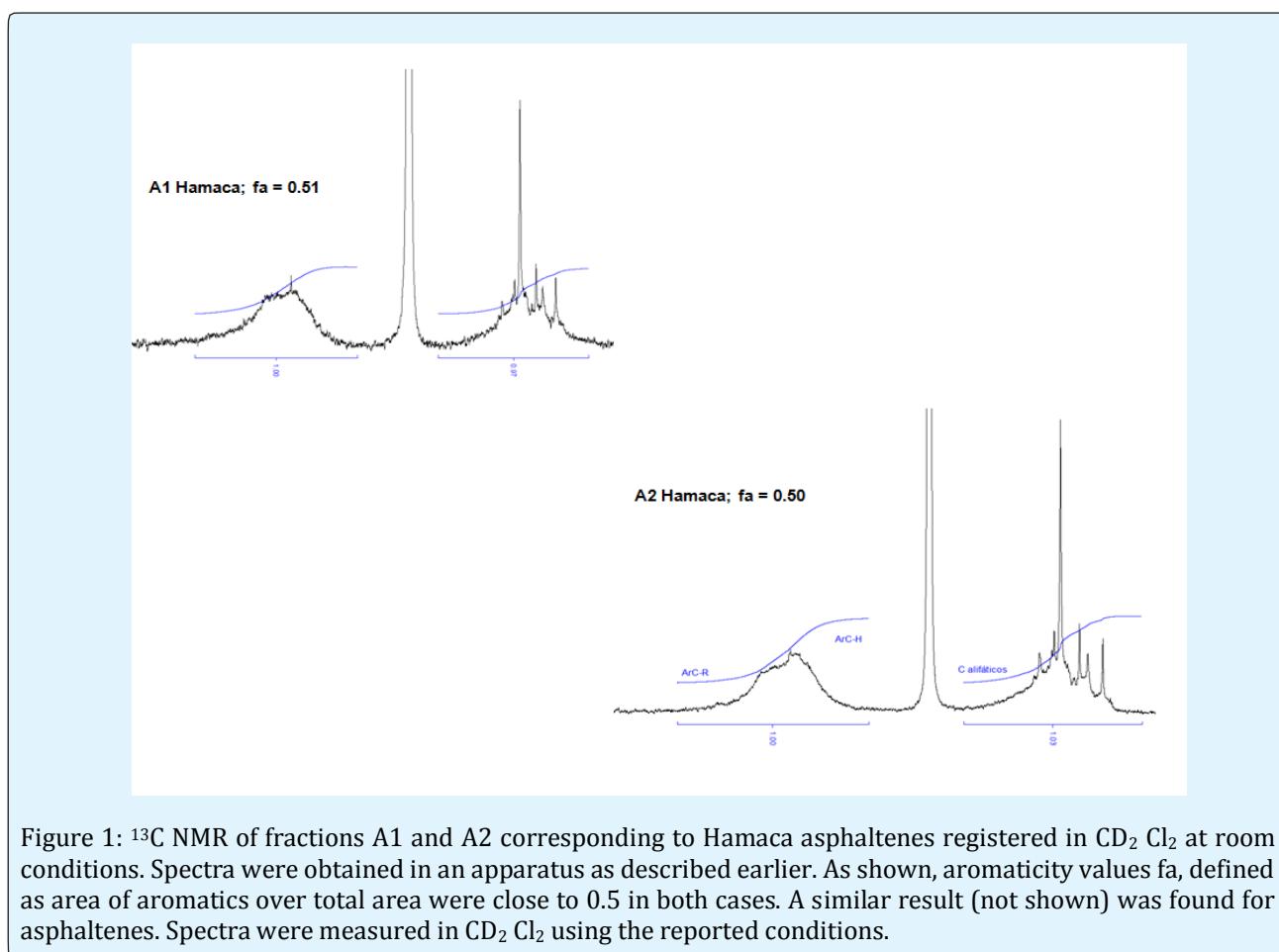
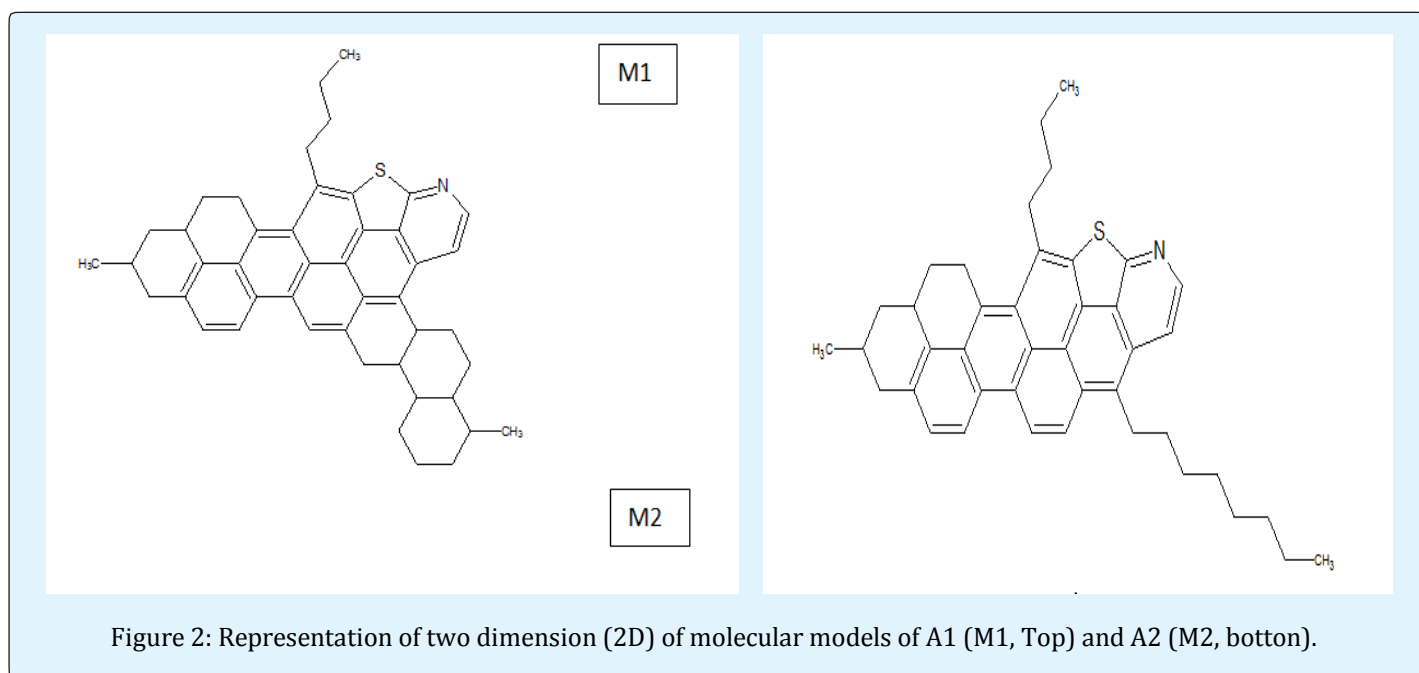


Figure 1: ¹³C NMR of fractions A1 and A2 corresponding to Hamaca asphaltenes registered in CD₂ Cl₂ at room conditions. Spectra were obtained in an apparatus as described earlier. As shown, aromaticity values *fa*, defined as area of aromatics over total area were close to 0.5 in both cases. A similar result (not shown) was found for asphaltenes. Spectra were measured in CD₂ Cl₂ using the reported conditions.



| | M1 | M2 |
|-----|---------|---------|
| C | 42 | 42 |
| H | 43 | 47 |
| N | 1 | 1 |
| S | 1 | 1 |
| H/C | 1.024 | 1.119 |
| DBE | 22 | 20 |
| MM | 593.877 | 597.909 |
| fa | 50 | 50 |

Table 2: Atom content, H/C, DBE and MM of Molecular Models A1 and A2.

a. Double bond equivalent: $DBE = (2C + 2 + N - H) / 2$

Similarities between MM distributions and C NMR, combined with small differences in H/C suggest structural differences such as the one shown in Figure 2 for molecular models M1 and M2 where the two aliphatic rings in M1 were opened to build molecular model M2 [8,12-13]. These structures resemble other recently proposed [3].

It is expected that when the above nuclei are formed in toluene, the long aliphatic open chains of M2 will hamper the approach of these nuclei to each other resulting in its dissolution or dispersion. It is well known that presence of long aliphatic open chains in asphaltene derivatives could increase solubility up to the point of making them soluble in n-heptane. Such is the case of asphaltenes alkylated with n-octyl alkyl groups [13].

Using Diffusion-Ordered Spectroscopy H Nuclear Magnetic Resonance (DOSY), Durand et al observed asphaltene aggregates with radii close to 1.56 nm in toluene at very high dilution (about 100 mg L⁻¹ [10]. Similar values for the smallest particles (about 1.25 nm radii) were reported for asphaltene dissolved in resins (3%) using the combined Transmission Electron Microscopy-Freeze Fracture technique [11]. Figure 3 illustrate an example of an asphaltene nuclei or nanoaggregate built with seven model molecules: four M1 and three M2 type. This was formed using the Molecular Mechanics package of HiperChem after geometrical optimization. As shown, with seven molecules distances between extremes afford values close to radii measure for particles.

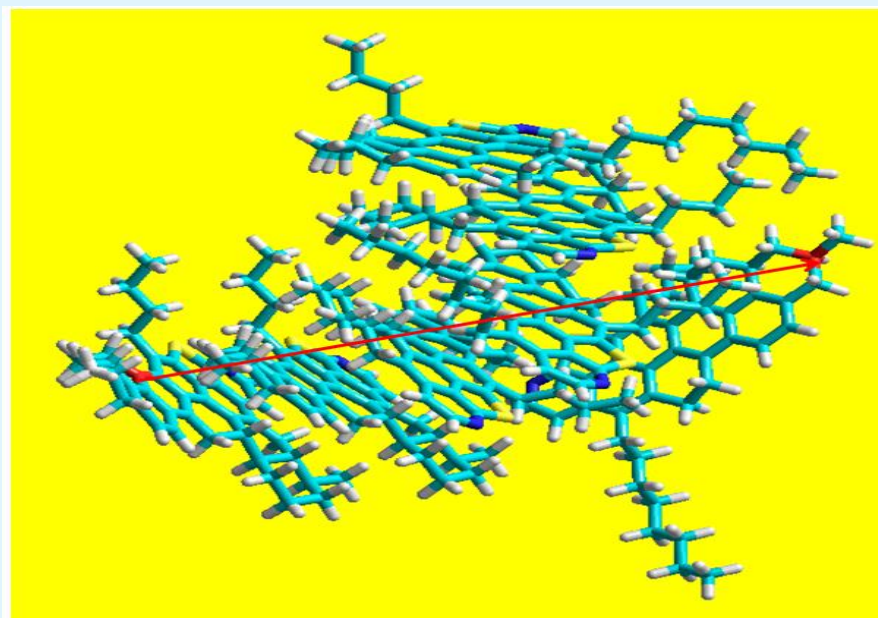


Figure 3: Molecular model used to represent an asphaltene nucleus or nanoaggregate with four M1, and three M2 type molecules. The length of the red arrow is equal to 2.9 nm.

The above nuclei have been called nanoaggregates by Mullins and this was done without any consideration regarding phase separation [3]. I believe that the word

nucleus conveys the idea of phase separation and hence I choose to use it in this work.

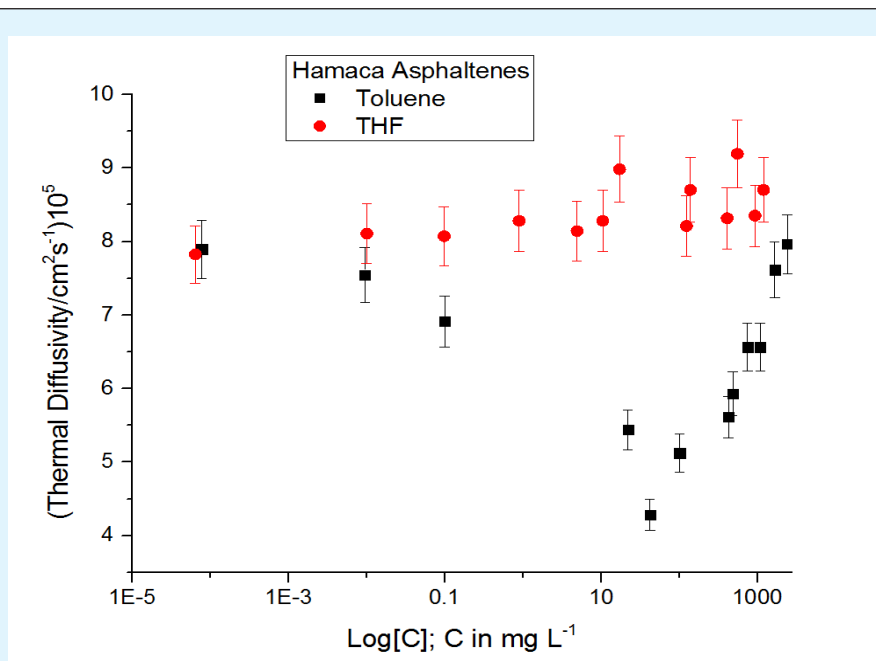


Figure 4: Thermal lens diffusivities for asphaltene solutions measured in toluene and THF under room conditions.

As reported earlier [1], measurements of thermal diffusivity D in toluene at room conditions show a minimum when plotted versus asphaltene concentration. This behavior was consistent with aggregate formation at concentrations close to 100 mg L^{-1} . By contrast, no significant change in D was observed in THF using the same sample concentrations (see Figure 4). It is known that asphaltene form aggregates in THF at room conditions; for instance, number average molecular weight measurement afforded values close to $4000 \text{ g mol}^{-1,12}$, much higher than the now accepted mean around 600 [3]. Thus data in Figure 4 is coherent with the PSD view in toluene and with step-wise aggregation in THF. The reason for this is that A1 fraction is soluble in THF, so no phase separation is expected in these diluted solutions.

From the above it is evident that PSD behavior will occur in solvents where asphaltenes are soluble and A1 is not. Apart from toluene and other monoaromatics like xylene and cumene, the PSD behavior is expected for carbon tetrachloride, 1,2-dichloroethane, among others [9].

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We conclude by underling that nuclei or nanoaggregate formation is a consequence of phase separation promoted by A1 and dispersion promoted by A2.

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