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## Fractionation of Asphaltene by Complex Formation with *p*-Nitrophenol. A Method for Structural Studies and Stability of Asphaltene Colloids

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Cumene solutions of asphaltenes (8 g/L) were treated with *p*-nitrophenol (PNP) and a precipitated solid was collected after 3 days. For the asphaltene samples examined, between 48 and 70% of the sample could be precipitated by this treatment. PNP, known to form charge-transfer complexes with aromatic compounds, probably forms this type of compounds with asphaltenes, leading to precipitation. The sample precipitated was dissolved in chloroform, and the PNP was removed by extraction with aqueous sodium hydroxide. Although the initial asphaltene sample has the usual high solubility in toluene (higher than 50 g/L, room temperature), the precipitated asphaltene sample obtained in this way (A<sub>1</sub>), has a very low solubility in toluene (≈90 mg/L, room temperature). These results show that asphaltenes are a mixture of compounds with vast differences in solubility and suggest that their solutions in aromatic solvents are constituted by a colloidal phase, formed by the low-soluble fraction A<sub>1</sub> dispersed by a soluble asphaltene fraction A<sub>2</sub>.

### Introduction

The composition of petroleum asphaltenes is a matter of great importance in the study of the physical-chemistry of these materials. In this regard, fractionation of the asphaltene mixture has been attempted many times using several fractionation techniques such as adsorption and ion-exchange chromatography,<sup>1,2</sup> size-exclusion chromatography,<sup>3</sup> differential precipitation,<sup>4</sup> membrane fractionation,<sup>5</sup> and so on.

Besides the usual purpose of characterization of these fractions, there is great interest in gathering knowledge regarding solubility properties; in other words, how the solubility of the asphaltene mixture is related to the solubility of the fractions. This type of information should be very useful in the study of the colloidal behavior of asphaltenes.

In this paper a new and simple procedure for the isolation of two asphaltene fractions is described. As the results below show, the solubility in toluene of these

fractions was very different. The possible relation of these solubility differences to the colloidal behavior of asphaltenes is discussed.

### Experimental Section

**Materials.** Some properties of the Venezuelan crude oils and their asphaltenes used in this work are shown in Table 1. Samples DM-153, DM-22, Boscan, C-148 (west part of the country), and Cerro Negro (Orinoco basin) are stable crude oils without precipitation problems whereas Furrial, from Monagas state (eastern part), has severe flocculation problems. The compound *p*-nitrophenol (PNP) was a commercial sample from Aldrich Chemicals Co., USA. Toluene and cumene were from Riedel de Haën AG, Seelze-Hannover, Germany.

Asphaltenes, free from resins, were obtained from Furrial and DM-153 crude oils by the addition of 40 volumes of *n*-heptane, and the precipitate was treated as described elsewhere.<sup>6</sup> For the highly viscous Cerro Negro and Boscan, the oil was diluted with toluene to a 1:1 mixture before the addition of the alkane as reported earlier.<sup>6</sup> In all cases, resins were thoroughly removed from the precipitate by Soxhlet extraction with boiling *n*-heptane.

**Methods.** *Double-Bond Equivalent (DBE).* A more detailed procedure has been described elsewhere.<sup>7</sup> Briefly, the DBE is obtained from eq 1 where C, H, and N are the number of carbon, hydrogen, and nitrogen atoms, respectively:

$$\text{DBE} = (2C + N - H + 2)/2 \quad (1)$$

Since the number of nitrogen atoms is small, we use eq 2 to

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Table 1. Properties of Crude Asphaltenes and Other Samples Used in This Work

sample	API <sup>a</sup>	% asphaltene <sup>b</sup>	elemental analyses <sup>c</sup>					H/C	DBE <sup>d</sup>
			%C	%H	%O	%N	%S		
Cerro Negro	8.5	13.8	82.29	8.05	1.91	1.85	5.94	1.17	43
DM-153	14.0	10.0	81.05	8.17	2.00	1.64	6.60	1.21	41
Boscán	10.3	17.0	81.10	7.79	1.43	1.11	6.10	1.21	41
Furrial	21.0	7.6	85.50	6.9	2.50	1.70	3.4	0.97	53

<sup>a</sup> Crude oil. <sup>b</sup> Respect to crude oil. <sup>c</sup> Oxygen by difference. <sup>d</sup> Double bond equivalent per 100 carbons.

obtain the number DBE per 100 carbon atoms:

$$\text{DBE} = 101 - 50(\text{H/C}) \quad (2)$$

The DBE is related to the number of aromatic and aliphatic rings in a molecule, being higher as the number of rings grows.

**Solubility and Precipitation Methods.** Toluene or cumene solutions of PNP and asphaltene were prepared in separated flasks and then mixed in 100 mL volumetric flasks to make final concentrations of PNP in the range from 500 to 8000 mg/L and a final constant concentration of 8 g/L in asphaltene. The solutions were allowed to stand at room temperature for 3 days and after this time the contents were filtered, the filtrate was set aside, and the precipitate solid, hereafter called the "PNP complex", was washed with toluene, dried, weighed, and dissolved in chloroform. This solution was washed once with aqueous sodium hydroxide (5%) to extract the PNP, which was then determined as phenolate by UV. The chloroform solution was dried with anhydrous magnesium sulfate, filtered, and the solvent evaporated under vacuum to afford sample A<sub>1</sub>. A similar procedure was used to obtain sample A<sub>2</sub> from the toluene filtrate above. In this case, the toluene was evaporated to dryness, and the solid obtained was then dissolved in chloroform and treated as described above for sample A<sub>1</sub>. The procedure is illustrated in Figure 1.

**Solubility Measurements.** Saturated solutions of sample A<sub>1</sub> in toluene were prepared by placing an excess of sample in toluene at room temperature. For these experiments we used the A<sub>1</sub> fraction obtained from Furrial. In all cases, the sample and the measured amount of solvent were placed in a flask connected to a condenser to avoid evaporation. Sonication was used to ensure that the maximum amount of sample was in solution. The flask content was then stirred magnetically for 8 h. After this time, the flask content was filtered, the filtrate was transferred to a measuring flask, filled to the mark with toluene, and measured by UV. Solubility of asphaltenes, of A<sub>2</sub>, and a 1:1 mixture of A<sub>1</sub> and A<sub>2</sub> at room temperature were too high to be determined by this method. In this case, toluene was mixed with an excess of sample and the solubility was determined by weight difference after weighing the excess of solid. Sonication was used to accelerate the solubility process.

**VPO Measurements.** Number average molecular weight ( $M_n$ ) was measured in nitrobenzene at 130 °C using the equipment from Jupiter Instruments Co., USA, Model 833, calibrated with sucrose octaacetate. Solutions were prepared in the range from 1 to 3.5 g/L, and the  $M_n$  was obtained by extrapolation to zero concentration.

**Thin-Layer Chromatography (TLC).** Using TLC equipment from Iatron TM Co., Japan, equipped with a flame ionization detector, disappearance of asphaltene from cumene solutions (8 g/L) was monitored. The solutions were saturated with PNP. TLC was performed on the silica bars provided by the manufacturer, using ethanol as the mobile phase. Using a microsyringe, the solutions were measured by placing 2  $\mu$ L on the silica bar. Using cumene solutions of asphaltene in the range from 1 to 10 g/L a calibration line was obtained by plotting the chromatographic area against the concentration. At the required times, aliquots were carefully withdrawn from the above asphaltene-cumene-PNP solutions. The asphaltene amount in solution was measured by interpolation of the obtained area in the calibration line.

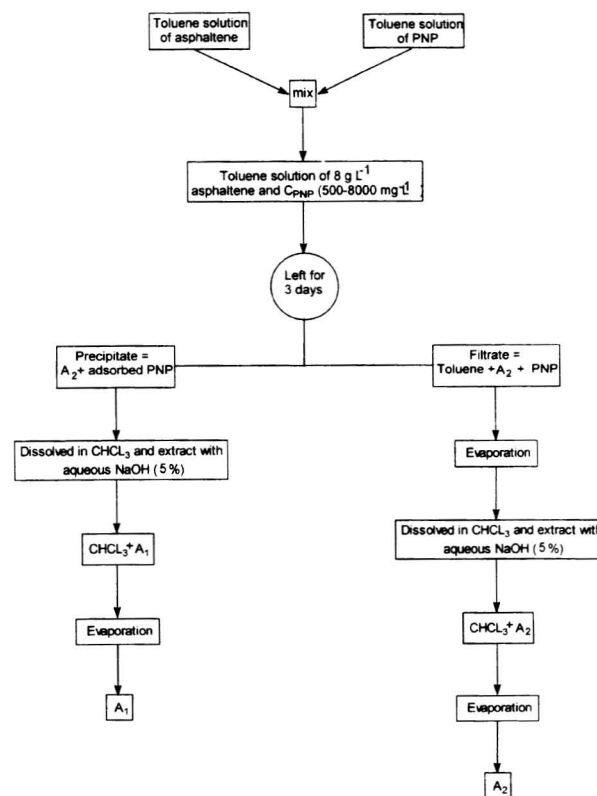
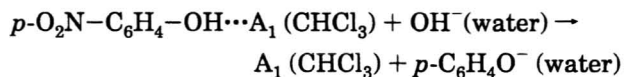


Figure 1. Scheme for asphaltene separation in fractions A<sub>1</sub> and A<sub>2</sub> after treatment with PNP. The very different solubilities of these fractions are shown in Table 3.

<sup>1</sup>H NMR spectra were measured in deuterated chloroform using a JEOL equipment, model Eclipse 270, from JEOL Co., Japan.

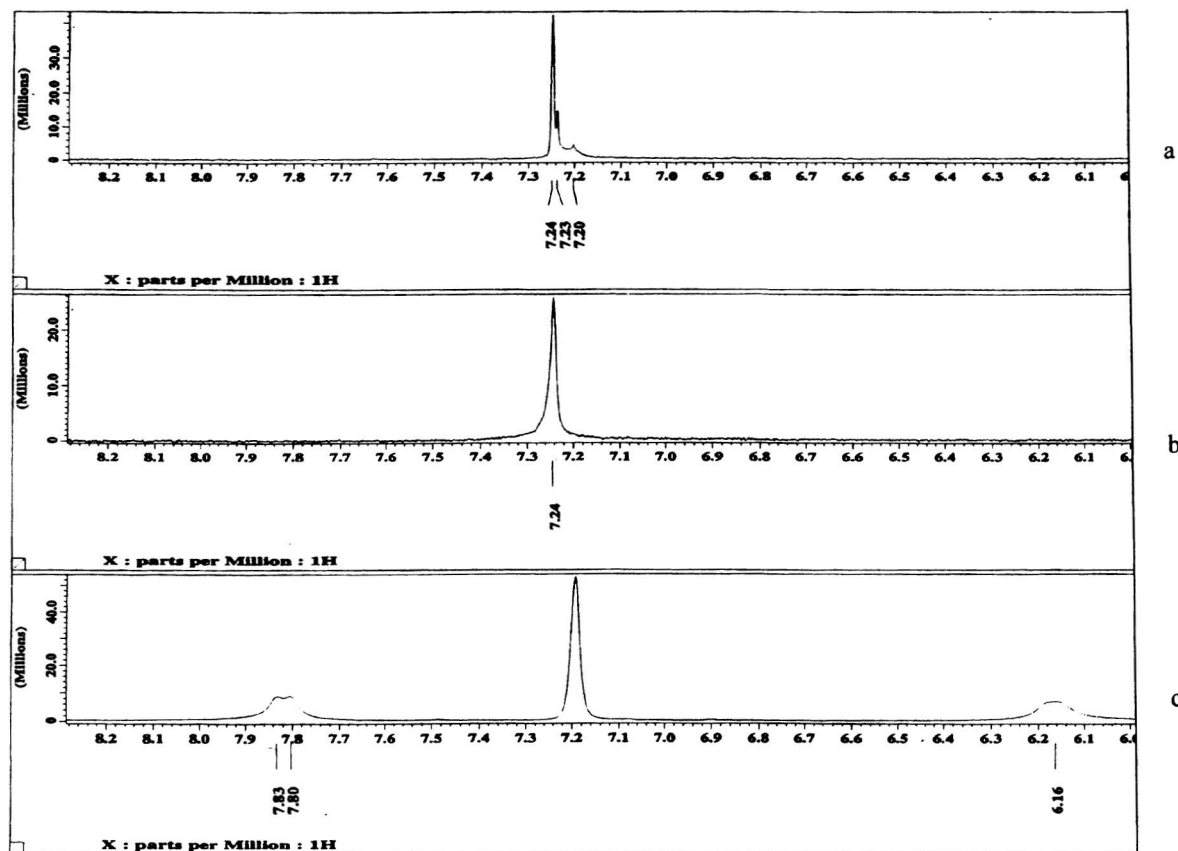
## Results

Recovery of PNP and A<sub>1</sub> after treatment of the chloroform solution with aqueous sodium hydroxide follows the reaction below:



The reaction was very fast and all the PNP was extracted in the first washing. This was determined by the yellow color of the aqueous phase.

Figure 2 shows the results of the <sup>1</sup>H NMR analyses. Under the conditions chosen to measure these spectra, the aromatic protons corresponding to the asphaltene can barely be distinguished from the line base. Figure 2, parts a, b, and c, correspond to the aromatic section of the spectra of the *d*-chloroform solutions of the PNP complex, sample A<sub>1</sub>, and PNP, respectively. Signal



**Figure 2.** Aromatic region of the  $^1\text{H}$  NMR spectra corresponding to several samples in  $d$ -chloroform at room temperature. (a) PNP complex. (b) Sample  $A_1$ . (c) PNP. The strong band located at 7.24 corresponds to the residual chloroform in the solvent. Aromatic proton of asphaltene fraction in spectra a and b are barely distinguished from the line base.

**Table 2. Maximum Amount of PNP ( $v_{\text{PNP}}$ ) and Asphaltene Precipitated<sup>a</sup>**

samples	$v_{\text{PNP}}$ ( $\text{mg g}^{-1}$ ) <sup>a</sup>	$v_{\text{PNP}}$ mol mol <sup>-1</sup> <sup>b</sup>	$A_1$ (%) <sup>c</sup>
Furrial	95	0.68	53
Cerro Negro	120	0.86	72
DM-153	119	0.86	65
Boscan	165	1.19	48

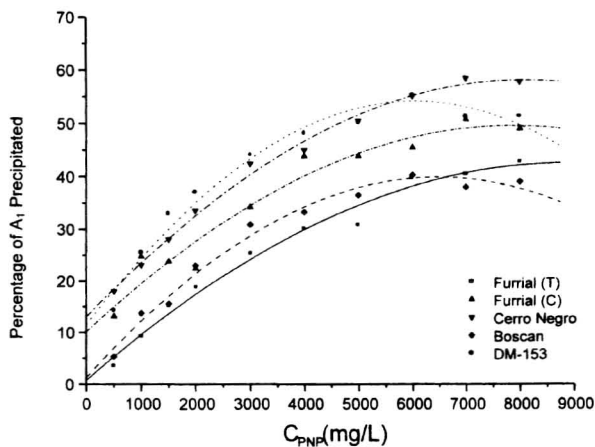
<sup>a</sup> From a solution in cumene containing 8 g/L of asphaltene and saturated solution of PNP (14 g/L of PNP) collected after 3 days.

<sup>b</sup> A molecular weight  $M_A = 1000 \text{ g mol}^{-1}$  was assumed for all asphaltene samples, see eq 3 for definition of mol/mol relationship.

<sup>c</sup> Percentage precipitated from an 8 g/L asphaltene in cumene saturated with PNP.

located at 7.25 corresponds to residual chloroform in the solvent. Figure 2c shows two bands (actually two doublets) separated by about 1.66 ppm corresponding to the PNP solution. This spectrum is of type AA'BB', corresponding to a para-substituted compound. In addition to the solvent band, Figure 2a, corresponding to the PNP complex, shows two bands located at 7.24 and 7.20 ppm. These bands should correspond to the protons of PNP in the complex. It is noteworthy that the chemical displacements of these bands are very different to that corresponding to PNP (Figure 2c). As shown in Figure 2b, no trace of PNP was detected in the spectra corresponding to sample  $A_1$ .

In Figure 3 the percentage of solid precipitated by treatment with PNP ( $A_1$ ) is plotted against  $C_{\text{PNP}}$  or the concentration of PNP in cumene. A similar curve was obtained for Furrial asphaltene in toluene, and is shown



**Figure 3.** Percentage of precipitated solid  $A_1$  as function of PNP concentration ( $C_{\text{PNP}}$ ) in cumene (C) or toluene (T). Initial concentration of asphaltene: 8 g/L. Room temperature.

in the Figure 3 as Furrial (T). The curves in Figure 3 are fittings to a polynomial equation and are drawn only for illustration purposes. Qualitative tests performed in benzene afforded high yields of precipitate when Furrial asphaltene was examined. The other asphaltene samples led to negligible amounts of precipitate in benzene or toluene. However, it should be emphasized that all precipitates (PNP-asphaltene complexes) and  $A_1$  samples collected have very low solubility in toluene and benzene.

Table 3. Solubility in Toluene and Elemental Analysis of Furrial Samples

sample	solubility (g/L)	percentage	% C	% H	% N	H/C	DBE <sup>d</sup>	Mn <sup>e</sup>
asphaltene <sup>a</sup>	56	-	85.5	6.9	1.7	0.97	53	2315
A <sub>1</sub>	0.093 <sup>b,f</sup>	60 <sup>c</sup>	82.15	6.22	1.75	0.903	56	3265
A <sub>2</sub>	59 <sup>b</sup>	40 <sup>c</sup>	80.2	6.66	1.73	0.989	52	1205

<sup>a</sup> See also Table 1. <sup>b</sup> Room temperature. <sup>c</sup> Respect to asphaltenes. <sup>d</sup> Double bond equivalent per 100 carbons (see Text and Table 1). <sup>e</sup> Measured by VPO in nitrobenzene at 130 °C. <sup>f</sup> Other asphaltene A<sub>1</sub> fractions yielded similar low values.

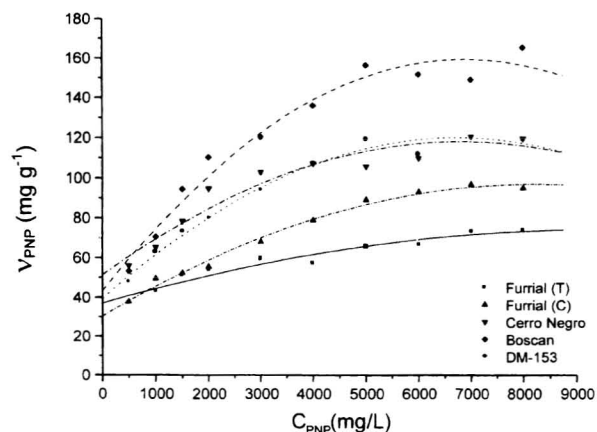


Figure 4. Amount of PNP in asphaltene ( $\nu_{\text{PNP}}$ ) precipitated from cumene (C) or toluene (T) as function of concentration of PNP in solution ( $C_{\text{PNP}}$ ). Initial concentration of asphaltene: 8 g/L. Room temperature.

Preliminary kinetics measurements, using automatic thin-layer chromatography (TLC), and where the amount of asphaltene precipitated was measured against time, showed that more than 90% of A<sub>1</sub> precipitated after 3 days (see Experimental Section). Therefore, percentages in Table 3 were calculated by collecting the precipitate after this time.

Although all PNP complexes and A<sub>1</sub> samples were insoluble in benzene and toluene, in these solvents only Furrial afforded the precipitate in high yield in 72 h. In the other cases (see Table 1) only negligible amounts of precipitate were observed after this or a longer time.

In Figure 4 the amount of PNP extracted from A<sub>1</sub> ( $\nu_{\text{PNP}}$ ) in mg per g of A<sub>1</sub> is plotted against  $C_{\text{PNP}}$ . As in Figure 3, these results correspond to cumene, except the case of Furrial (T) which corresponds to toluene. As was the case for Figure 3, curves in Figure 4 are only for illustration purposes.

In general the  $\nu_{\text{PNP}}$  in Figure 4 were not constant and the general behavior was that of approaching a limiting value as the  $C_{\text{PNP}}$  was increased. In each case, the amount of A<sub>1</sub> collected and the  $\nu_{\text{PNP}}$  determined for  $C_{\text{PNP}} = 8000$  mg/L were practically the same as the corresponding to the saturated solution ( $C_{\text{PNP}} = 14$  g/L). Thus, for the purpose of characterization, the  $\nu_{\text{PNP}}$  values in Table 2 are related to the saturated solution and could be considered as the maximum amount of PNP per gram of asphaltene in the asphaltene-PNP complex. A molecular weight  $M_A = 1000$  g/mol was used for all asphaltene samples for the calculation of the mol (PNP)/mol (A) relationship shown in Table 2. If this

molar relationship is called  $m$ , then

$$m = \nu_{\text{PNP}} M_A / 1000 M_{\text{PNP}} \quad (3)$$

Here  $\nu_{\text{PNP}}$  are the values in Table 2 and  $M_{\text{PNP}}$  is the molecular weight of PNP (123).

In Table 3 the solubility in toluene and other properties of the different samples measured in this work are shown. Solubility of A<sub>1</sub> was very low and this was not improved by sonication and heating. When this sample was remixed with A<sub>2</sub> the usual high solubility of the asphaltene was recovered.  $M_n$  values in this table are only relative and do not intend to show actual average values for these samples. Although nitrobenzene is a very polar organic solvent and the measuring temperature was 130 °C, aggregation cannot be discarded.

## Discussion

As described above, separation of asphaltenes in two fractions of very different solubility could be very easily achieved using the above procedure. The method is of general applicability using cumene as the solvent and is simple, cheap, and clean. It is particularly advantageous for solubility and phase behavior studies. Besides, as suggested by the small differences in elemental analyses (see Table 3), samples A<sub>1</sub> and A<sub>2</sub> should contain negligible amounts of impurities.

Figure 2b shows that all PNP has been removed from sample A<sub>1</sub>. Therefore, solubility and other properties of this sample cannot be attributed to incomplete removal of the phenol. Comparison of Figures 1a and 1c shows that the spectra of PNP complex and PNP are very different. Since some electron transfer between PNP and asphaltene is expected in the complex, this result is not surprising.

As shown in Table 2, percentages of A<sub>1</sub> are very significant in all cases. The result for Cerro Negro is very similar to other reported earlier by our laboratory, where the asphaltene was fractionated by placing it within a membrane and extracted in a Soxhlet with boiling mixtures of tetrahydrofuran (THF) and acetone. Then we found that about 80% of Cerro Negro asphaltene were insoluble in toluene.<sup>5</sup>

Aside from the fact that the present PNP method is superior, these two different methods lead to the same conclusion. That is: A large percentage of the asphaltene solid is actually insoluble in toluene and the high solubility of the complete mixture in this solvent is due to the surfactant or dispersing effect of the rest. In other words, in toluene the insoluble fraction A<sub>1</sub> would be the colloidal phase, which would be dispersed by dispersing components of the soluble fraction A<sub>2</sub>.

PNP is known for its capacity to form charge-transfer complexes with aromatic compounds.<sup>8</sup> Thus, it is quite

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likely that in the above precipitation, formation of very-low-solubility complexes of this type is involved. This argument is supported by the mol/mol ratio of Table 2, which suggests that a chemical reaction could be involved.

The curves in Figure 1, where the amount of A<sub>1</sub> approaches asymptotically a limiting value, are similar to adsorption isotherms. This should be the expected result when the above complex formation is preceded by PNP adsorption on colloid or aggregate surface. Support for this argument comes from the observed solvent effect on precipitate formation.

Whereas in cumene all samples yielded the precipitate, in toluene and benzene only Furril afforded some precipitate (see Experimental Section and Figures 1 and 2). Besides, regardless of the solvent from which they were obtained, all asphaltene-PNP precipitates and all A<sub>1</sub> samples have negligible solubility in toluene and benzene. In other words, once the complex is formed, it will not dissolve in these solvents.

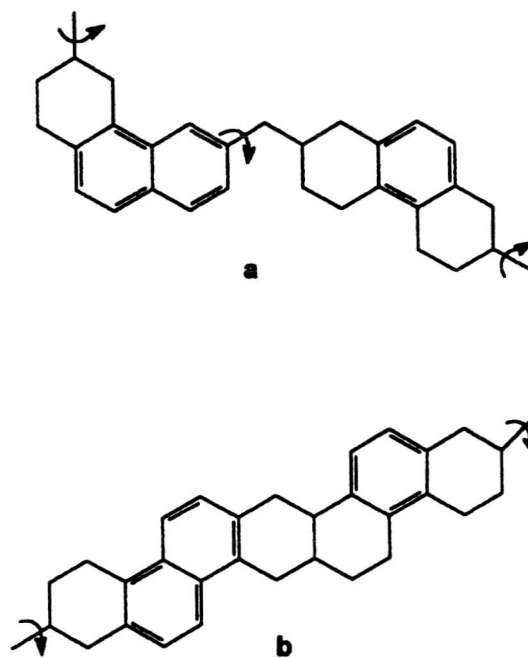
These results suggest that the main reaction leading to precipitate formation should involve asphaltene molecules in the colloid. Since the asphaltene-PNP complex is insoluble in the above aromatic solvents, reaction with "free" A<sub>1</sub> type asphaltenes in solution is unlikely. Such reaction would lead to precipitation in any of the above solvents. In this scenario formation of precipitate would depend on the capacity of the PNP to penetrate the colloid periphery.

It is quite likely that the above difference in solubility would be due to structural differences relevant to the ability of the sample A<sub>1</sub> to pack in a compact way. That is, in a close packing impervious or nearly impervious to solvent penetration. Presumably failure of sample A<sub>2</sub> to pack in the same way accounts for the high solubility of this sample. This is consistent with the difference in DBE which, together with the very large difference in solubility, strongly suggests a more rigid structure for A<sub>1</sub>.

As shown by NMR relaxation times reported earlier, when neighbor molecular sectors are join by alicyclic chains (aliphatic rings), an important impact on molecular mobility should be expected (see Figure 5).<sup>7</sup> Hence, even a small difference in DBE could lead to large differences in molecular mobility and solubility.

The tendency of asphaltenes to form aggregates in solution is well documented.<sup>9</sup> Hence, the  $M_n$  values in Table 3 are probably too high. However, here we are only interested in the trend that shows that the molecular weight of A<sub>1</sub> is the highest. It is unlikely that the enormous difference in solubility between A<sub>1</sub> and A<sub>2</sub> could be due to molecular weight differences. Rather, it is quite reasonable that the  $M_n$  results reflex a higher aggregation tendency of A<sub>1</sub> when compared to the other samples. This would be consistent with the above argument referring to A<sub>1</sub> ability to pack.

Solubility in toluene should not avoid adsorption of sample A<sub>2</sub> on the asphaltene core surface. In fact, adsorption of asphaltenes on an insoluble asphaltene derivative has been reported earlier. When toluene was the solvent a thick asphaltene multilayer was formed at room temperature.<sup>10</sup>



**Figure 5.** Structures to illustrate the differences in mobility in hypothetical asphaltene models. Structure b is more rigid than structure a.

Thus, an appealing model for asphaltene colloids in toluene, cumene, and other aromatic solvents would be constituted by a core of well-packed, and hence insoluble fraction A<sub>1</sub>, surrounded by a periphery constituted by a soluble fraction such as fraction A<sub>2</sub>.

In this model, and under the present conditions of solvent, temperature, and pressure, fraction A<sub>2</sub> could not form compact arrays with A<sub>1</sub> or with itself resulting in a colloidal periphery permeable to solvent molecules. This solvent permeability and the adsorption of A<sub>2</sub> on the colloidal core would be the facts responsible for colloid stability. Thus, in a simple way, both desorption of A<sub>2</sub> and draining of solvent from the colloid periphery would be required for flocculation to occur.

## Conclusions

The simple procedure described above allows for the separation of asphaltenes in two fractions A<sub>1</sub> and A<sub>2</sub> of very different solubility. These fractions were isolated in high yields and characterized by solubility, elemental analysis, and molecular weight. The results were used to propose a model for the colloidal solutions of asphaltenes in aromatic solvents where the low-soluble fraction A<sub>1</sub> would form the colloidal phase, dispersed in the media by the soluble fraction A<sub>2</sub>.

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EF000180Y

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