

PROPERTIES OF HEPTOL SUB-FRACTIONS EXTRACTED FROM BRAZILIAN ASPHALTENES

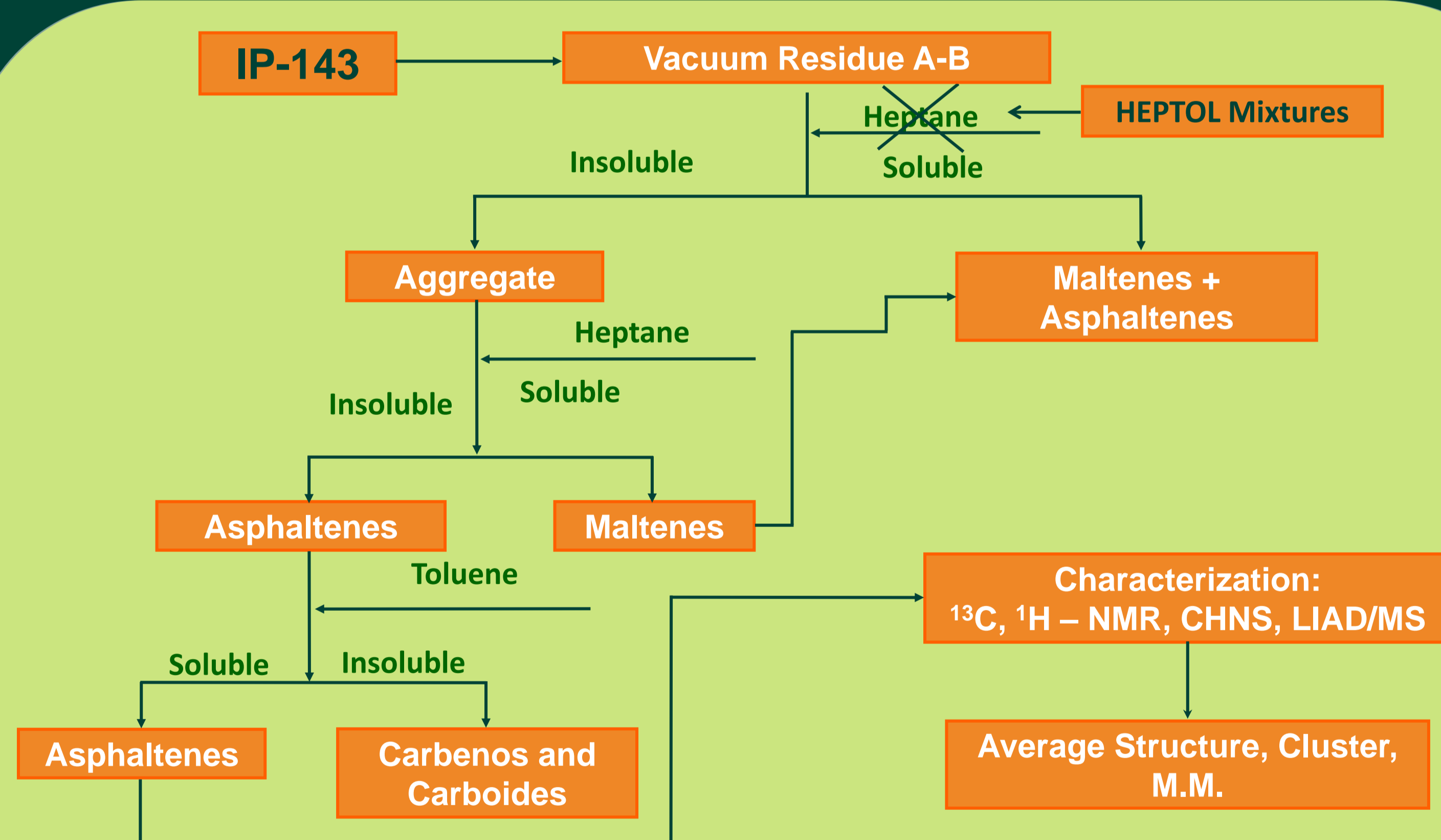
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ABSTRACT

Asphaltenes continue attracting much attention and controversy in spite of the considerable advances in their description and characterization that have appeared in the recent literature [1]. Their tendency to flocculate and precipitate during both oil production and refining is a strong incentive for the development of more efficient processes that can be applied to heavy petroleum fractions. A better knowledge of the chemical structure of this class of substances and their properties under certain conditions may hold the key to understanding their behavior in different stages of petroleum processing. In the present work, a combination of characterization techniques was applied to different asphaltene fractions in order to get new insights into the way they aggregate. Asphaltene fractions were obtained by precipitation of samples A and B, obtained from vacuum residues, and of sample C, from pipeline deposits, using mixtures of heptane and toluene (referred to as Heptol) in different concentrations as a precipitation solvent.

EXPERIMENTAL



¹H NMR
 Varian Inova-300, 705 T
 5 mm Tubes
 5% solutions of a 1:1
 (v/v) CDCl₃ : C₂ : Cl₄
 mixture
 300 MHz, 45° pulses,
 1.0 s intervals, 128
 transients accumulated

RESULTS AND DISCUSSION

Our recent work [2], evidences important differences among asphaltene sub-fractions and reveals that aromatic species with higher content of ring fusion aromatic carbons, can concentrate in specific sub-fractions. It is noteworthy that they are not always in the least soluble fraction, nor in the one with the highest average molecular weight.

The results of sub fractionation indicated that the yield of asphaltenes decreased as the proportion of toluene in Heptol increases, for both vacuum residues. This behavior agrees with solubility principles, but the solubility limit depends on the asphaltene type. Asphaltenes C reveal a completely different solubility behavior. The solubility of asphaltene C doesn't seem to be affected by increasing the amount of toluene in the precipitant mixture up to values in which A and B are practically completely soluble (Table 1).

% Toluene	%Asphaltene A	% Asphaltene B	% Asphaltene C
0	11,3	8,3	48,6
10	7,1	4,6	47,5
20	3,3	1,1	47,9

Table 1. Solubility behavior (weight %)

C asphaltenes show different values for this analysis. Hydrogen NMR (¹H NMR) (Table 2), nevertheless, reveals that the relative proportions of aromatic to aliphatic hydrogens may be used as an indicator for some of these variations. The behaviour of the two vacuum residues is similar, except for small differences for the aromatic carbon in vacuum residue B [2]. For all C asphaltene sub-fractions larger differences are observed, showing a higher proportion of aromatic hydrogens in comparison to A and B asphaltenes for all the sub-fractions. Carbon-13 NMR (¹³C NMR) indicates that these changes may be traced to the fusion of aromatic ring systems. This result helps to validate the importance of sub-fractionating of this specific vacuum residue, once it was found that aromatic species are concentrated in the less soluble asphaltene sub-fraction, and, could serve as an indication that this sub-fraction could have fundamental importance for the association of these complex molecules [2].

Molecular parameter	Chemical Shift (ppm)	Integrated area (%)		
		A - 0%	A - 10%	A - 20%
H Saturated, Hsat	4 - 0	90,4	86,9	92,6
H Aromatic, Har	9 - 6	9,6	13,1	7,4
		B - 0%	B - 10%	B - 20%
H Saturated, Hsat	4 - 0	89,4	89,1	91,5
H Aromatic, Har	9 - 6	10,6	10,9	8,5
		C - 0%	C - 10%	C - 20%
H Saturated, Hsat	4 - 0	86,8	81,3	79,9
H Aromatic, Har	9 - 6	13,2	18,7	20,1

Table 2. ¹H NMR Integrated Area

CONCLUSIONS

The A-10% and all the C asphaltenes sub-fractions reveal high values for Har. This strongly suggests extensive aromatic ring fusion and explains the tendency of the C asphaltene sub-fractions to deposit in pipelines and also consistent with the suggestion that the A-10% sub-fraction can be responsible for the association of asphaltenes in vacuum residue A [2]. The results show that ¹H NMR can be used to make a preliminary evaluation of the behaviour of asphaltenes, from the oil reservoir to the production lines and storage tanks.

REFERENCES

- [1] Wiehe, L.A., Process Chemistry of Petroleum Macromolecules (2008), CRS Press, Boca Raton, 2.
- [2] Navarro, L, Seidl, P; Tasic, L; Leal, K.; Menezes, S. (2008) Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. 53 (1).

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