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GPC Separation and Integrated Structural Analysis of Petroleum Heavy Ends*

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Summary

Three hundred grams of a Venezuelan asphalt was separated on a 70-liter GPC column in one run. The 30 cuts collected were consolidated to 7 fractions. After separating the insoluble asphaltenes from the soluble maltenes by *n*-pentane extraction, the maltenes were chromatographed on deactivated alumina into oil and three different resin fractions. Selected fractions were analyzed by NMR, IR, density, and elemental analysis. The experimental results were evaluated by a novel method making use of an extensive scheme of structure relations. Percentages of aromatic, naphthenic, and paraffinic carbon; number of ring systems per molecule, their average size, compactness, composition, and substitution are given explicitly or implicitly.

The structural analysis of crude oil residua, coal, and similar complex organic mixtures has been the target of research for many years. The main difficulties of this endeavor are the great variety of chemical structures and the large range of molecular weights encountered in these materials. Because of this variety, any measurements on the whole mixture will generally give insufficient information. More detailed data are often needed for optimizing processing conditions, for blending specifications, etc. It is then mandatory to separate the mixtures into distinct subgroups and to analyze these.

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Ordinary fractionation methods such as distillation, precipitation, extraction, distribution, and adsorption techniques separate by both chemical structure and molecular weight. The only specific separation technique is GPC which segregates by molecular size. The fact that proper GPC conditions are sometimes difficult to meet in practice and that other properties may have an effect on the fractionation is only of secondary importance. At least, *there is* a principle that allows us to separate by one property, molecular size, alone. Once we have achieved a separation by size, we can then proceed to fractionate by chemical nature, selecting from the other techniques the one best suited to a specific material.

It is not necessary to do the size separation by GPC first and then follow it by structural separation. The order of techniques will be determined by several considerations: the range of molecular weights, the types and varieties of chemical structure, and the capacity of the selected separation systems. In complex organic mixtures there are various kinds of interactions that may interfere with separations. Frequently it may be necessary to start with GPC and thereafter subfractionate by alumina chromatography; in other mixtures, the reverse sequence may yield better separation. Indeed, the reverse sequence will generally be preferred because an alumina column can separate much greater quantities of material than a GPC column of equal size. In certain applications we may start with a general separation, follow with GPC, and then use alumina or silica gel chromatography.

Proper fractionation is very important; however, it is only part of the task. The other part is an adequate analysis of the fractions. Among the most useful analytical methods for heavy petroleum fractions are elemental analysis, NMR, IR spectroscopy, and molecular weight and density determination. Mass spectroscopy, though a powerful tool for volatile samples, is difficult to interpret on samples containing involatile or unstable components.

In this paper we wish to report a preparative fractionation of an asphalt and a novel evaluation of analytical data (*1*) obtained on some of its fractions.

Experimental

Three hundred grams of a Venezuelan asphalt was dissolved in 1.5 liters of benzene containing 10% methanol and fractionated on a GPC column 10 ft long and 6 in. in diameter. This is a high loading ratio

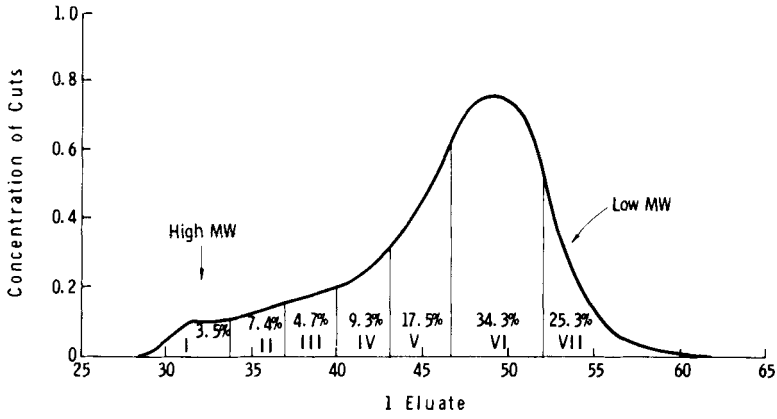

FIG. 1. Elution curve of Venezuelan asphalt obtained on large column.

of 430 mg sample/100 ml column volume (*1*). The column was packed with a polystyrene gel of 100,000 molecular weight exclusion limit.* A flow rate of 15 liters/hr was maintained. Thirty cuts were collected and reconstituted in such a way as to yield the 7 fractions shown in Fig. 1. After evaporation under a nitrogen stream on a hot plate and later under vacuum at 50°C, the fractions were extracted with 30 times their volume of *n*-pentane to separate the soluble "maltenes" from the insoluble "asphaltenes."

Ten-gram amounts of the maltenes were further fractionated on 3-ft × 1-in. columns packed with Fisher alumina, A-540, which had been deactivated with 10% water. The samples were eluted with *n*-pentane followed by cyclohexane, benzene, and, finally, benzene plus 20% methanol. The resulting 30–40 fractions were reconstituted by criteria based on IR, UV, and fluorescence spectra to render an oil and 3 distinct resin fractions. In some minor cases, cuts were left out if they could not be assigned to either the previous or the next fraction because they contained too much from both.

The total fractionation is presented schematically in Table 1, which also includes the number-average molecular weights of pertinent cuts. The molecular weights were obtained by vapor pressure osmometry as described earlier (*2*).

Selected fractions were subjected to elemental analysis, NMR, IR, molecular weight determination, etc. Heteroatom content, C/H ratio,

* Column design and gel preparation were carried out by Dr. O. L. Harle.

TABLE 1

Fractionation Scheme with Per Cent of Asphalt Sample and Molecular Weights

GPC fraction	Extraction chromatography on alumina plus 10% water				
	n-Pentane			Cyclohexane, Resin 2	Benzene plus 10% MeOH, Resin 3
	Asphaltene[a]	Oil	Resin 1		
I	3.5% 25,000	—	—	—	—
II	4.4% 20,000	—	—	—	—
III	4.1% 15,000	←———	0.6%[b]	———→	
IV	5.5% 8,000	1.0% 5,500	0.6% 2,500	0.4% —	0.6% 2,000
V	1.0% 5,000	5.7% 740	3.6% 950	1.0% 750	1.6% 800
VI	2.6% 1,900	←———	13.6%[b] 700	———→	
VII	2.1% 960	15.0% 550	0.6% 550	1.1% 560	1.4% 650

[a] In each case, the first entry is the wt% of the fraction relative to the total amount of asphalt; the second entry is the number-average molecular weight of that fraction.
[b] These maltene fractions were not subfractionated.

and per cent of functional or structural groups can be plotted versus molecular weight for the different groups, such as oils, resins, and asphaltenes. The plots are not always very enlightening, as demonstrated by the examples given in Figs. 2 and 3. A more detailed structural breakdown is desirable because it provides additional information and also removes much of the scatter of the primary data.

PRINCIPLES OF INTEGRATED STRUCTURAL ANALYSIS

We developed a scheme (*3*) which combines the results from NMR, IR, elemental analysis, molecular weight, and density determinations to calculate the percentages of aromatic, naphthenic, and paraffinic carbon; number of ring systems per molecule, their size, compactness, composition, and substitution; and the number, length, and branching of paraffinic chains.

The analysis is limited by three approximations:

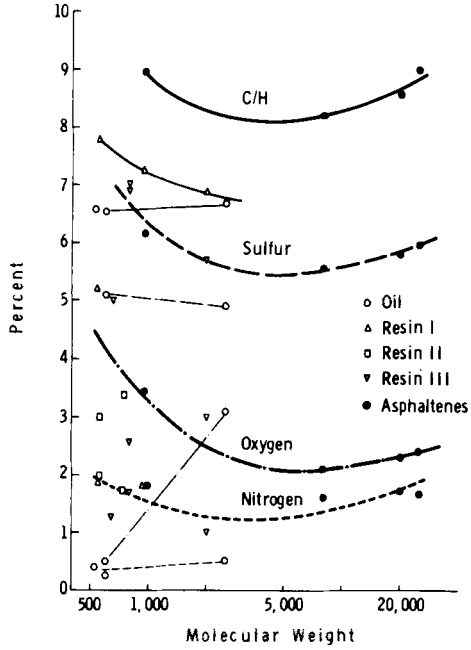

FIG. 2. Per cent O, N, S, and C/H ratio in asphalt fractions as a function of molecular weight.

(a) The calculated results are based on an averaging concept both for fused ring structures within a molecule and for molecules within a sample.

(b) Functionality of heteroatoms is approximated from IR data. Heteroatoms must be replaced by appropriate hydrocarbon groups, and proper adjustments must be made in carbon and hydrogen content as well as in molecular volume. The latter correction is based on relations given by van Krevelen (*4*).

(c) The model considers only six-membered rings. We cannot rigorously account for five-membered ring systems. The error introduced by their presence in petroleum fractions is generally quite small and can be further reduced by use of a high estimate for a compactness factor (to be defined later).

Despite these approximations, the results obtainable through "integrated structural analysis" are much more detailed than previously thought feasible. Our scheme was made possible by the intro-

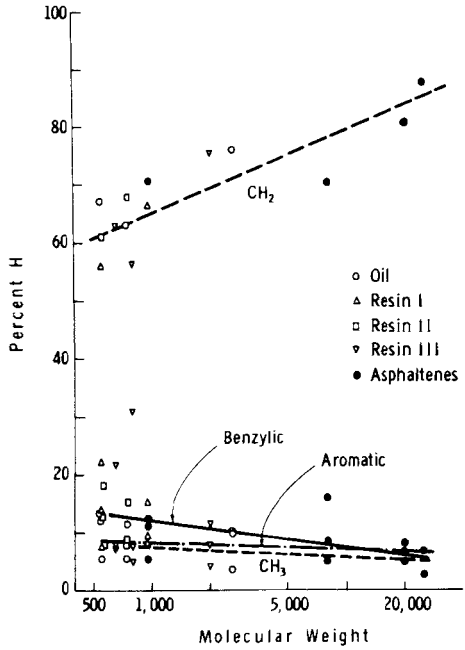

FIG. 3. Per cent H in CH_3, CH_2, aromatic, and benzylic configuration as measured by NMR in asphalt fractions as function of molecular weight.

duction of an improved set of relations between chemical structure and density (*5*), a complete analytical compilation of relations between structure variables, and by the use of "floating parameters."

The new density relations are based on 455 hydrocarbons spanning a molecular weight range from 70–619.

The inclusion of four "floating parameters" was necessitated by the fact that the number of structural variables considered exceeded the number of independent structural relations by 4. The floating parameters themselves are structural variables whose values must be estimated. They were selected in such a way that their numeric values fall into narrow ranges and that inaccurate assignments do not significantly affect the structural results.

An important consideration in our scheme is the number, size, and shape of fused ring systems. The definition of a "compactness factor" relating linearly actual, maximal, and minimal numbers of peripheral

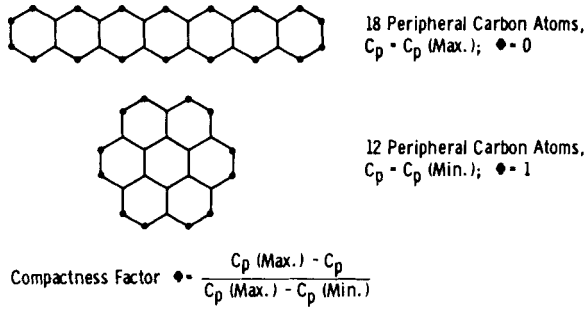

FIG. 4. Illustration of the ring compactness factor which holds for any six-membered ring system: aromatic, naphthenic, and mixed.

ring carbons greatly simplified the analysis. Figure 4 illustrates this relation and also shows that open (catacondensed) ring systems have more peripheral ring carbons than compact (pericondensed) ones.

The large number of structure relations were reduced to 3 simultaneous equations in 3 unknowns which can be numerically solved by digital computer using the Newton-Raphson method (*5*).

Our scheme was tested on a model molecule. Calculated values of structural variables were very close to the actual values provided by the structure. The test also revealed a high sensitivity of the analysis to the accuracy of experimental data. On the other hand, the results were not much affected by improved estimates in the floating parameters.

RESULTS

We applied our method to three fractions of the Venzuelan asphalt, viz., VII Oil, VII Asphaltene, and II Asphaltene. According to the data listed in Table 2, the high and the low molecular weight asphaltenes are distinctly different in their structure. The high molecular weight asphaltenes have larger ring systems with higher compactness in their aromatic and lower compactness in their naphthenic parts, and they have a greater proportion of paraffinic chains. The asphalt oil is different from the asphaltenes only in degree, not in basic nature. It is quite aromatic with smaller, but still considerable, fused ring systems having an average of five rings. Predictably, it is much more naphthenic and has twice as many paraffinic chains per size, though not longer ones than the asphaltenes.

These data present only a brief example of the kind of information

TABLE 2

Comparison of Selected Structural Parameters of an Oil and Two Asphaltene Fractions

Fraction	Ring systems per molecule	Aromatic rings	Naphthenic rings	Aromatic carbons	Benzylic carbons	Naphthenic carbons	Paraffinic carbons
		Per ring system		Per 100 carbon atoms			
VII O	1.09	2.0	3.1	24.4	9.8	25.4	40.4
VII A	0.78	10.2	6.8	48.1	12.5	11.1	28.3
II A	25	8.0	4.4	37.7	5.2	12.9	44.2
Range (%)	±5	±5	±13	±1.2	±6	±7	±2

that can be obtained by our integrated structural analysis. More details and various tests to show the accuracy and the limits of the method are to be published elsewhere (*3*).

This paper demonstrates how GPC in combination with other fractionation methods can yield distinct and large enough fractions for extensive analysis. A novel "integrated structural analysis" applied to such fractions affords new insight into the structural details of the heavy ends of petroleum and similar materials.

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