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Separation and Characterization of High-Molecular-Weight Saturate Fractions by Gel Permeation Chromatography*

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Summary

Gel permeation chromatography was applied to the saturate portion of a 450–475°C cut of Wilmington crude oil prepared by American Petroleum Institute Research Project 60. Selected fractions were analyzed by mass spectrometry, which demonstrated that a separation based on the number of rings was achieved. An early fraction contained 95.5 wt% no-, one-, and two-ring compounds; and a late fraction contained 95.9% wt% three-, four-, five-, and six-ring compounds. The relationship of the experimental results to those predicted from calibration curves relating carbon number to both distillation and GPC is discussed.

INTRODUCTION

The characterization of selected petroleum oils boiling above 400°C is an objective of American Petroleum Institute Research Project 60. To achieve this objective, the specimen oil must be divided into subfractions which are amenable to suitable analyses. Any separation scheme must be selective and chemically nondestructive. One such

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technique is gel permeation chromatography (GPC). This technique has been used previously on petroleum fractions (*1–6*). We report here preliminary results from the GPC of a saturate concentrate isolated from a distillate fraction of a Wilmington crude oil.

The separation of the high-boiling saturates into types is important not only for the characterization of the particular oil but to provide standards for the calibration of analytical techniques which may be applied in this molecular-weight range. A satisfactory method for dividing the saturates into types has not been available. Adsorption chromatography has not been useful because the saturate molecules do not possess the varying polar characteristics that are prerequisite for adsorption chromatography. Although thermal diffusion has been successfully applied (*7*, *8*), this technique is not always practical because it requires a large sample and long separation periods. The lengthy exposure to elevated temperatures may alter the composition of some heat-sensitive samples. GPC minimizes these difficulties; it is thermally gentle to the sample, and the separation may be completed in a few hours on samples of less than 1 g.

EXPERIMENTAL PROCEDURES

A cut equivalent to 450–475°C at 760 torr was prepared by molecular distillation of a Wilmington crude oil and was separated into saturate and aromatic fractions by adsorption chromatography on alumina. The saturate fraction thus prepared (33% of the cut) was further separated by GPC, using Poragel A-1 preswollen in methylene chloride. A jacketed glass column 5 ft × 0.5 in. i.d. was filled with the preswollen gel, and the column was sealed with plugs of porous glass wool. The upward flow of the solvent, methylene chloride, through the column was maintained from a pressure reservoir (15 psig N_2) and held to a constant flow of 0.8 ml/min by a needle valve at the discharge side of the column. Samples were injected from a syringe into a valve connected directly with the lower end of the column. By means of a siphon, constant volume fractions (3.4 ml) were collected. Solvent was stripped from these fractions under nitrogen, and the weights of the fractions were determined. The refractive indices were determined on selected fractions, and molecular weights were measured for these fractions by vapor pressure osmometry in benzene. Mass spectra were obtained on a CEC 103 mass spectrometer and the data processed by Hood and O'Neal's saturate method (*9*).

RESULTS AND DISCUSSION

Separation of materials by GPC is a function of several variables; however, one may hold many of these variables constant within a given experiment so that the elution volume for a compound will depend primarily on its molecular volume. The sorption effects noted for many types of compounds should be negligible for the saturate compounds.

In Fig. 1 a correlation diagram is presented which relates boiling point, carbon number, and relative elution volume. The solid lines relate carbon number with literature values for normal boiling points. Curve $\mathrm{I}n_{\mathrm{T}}$ represents the relationship between boiling point and carbon number for the normal paraffins. Curve $\mathrm{I}i_{\mathrm{T}}$ represents the lowest boiling branched paraffins of each carbon number, and II_{T} approximates

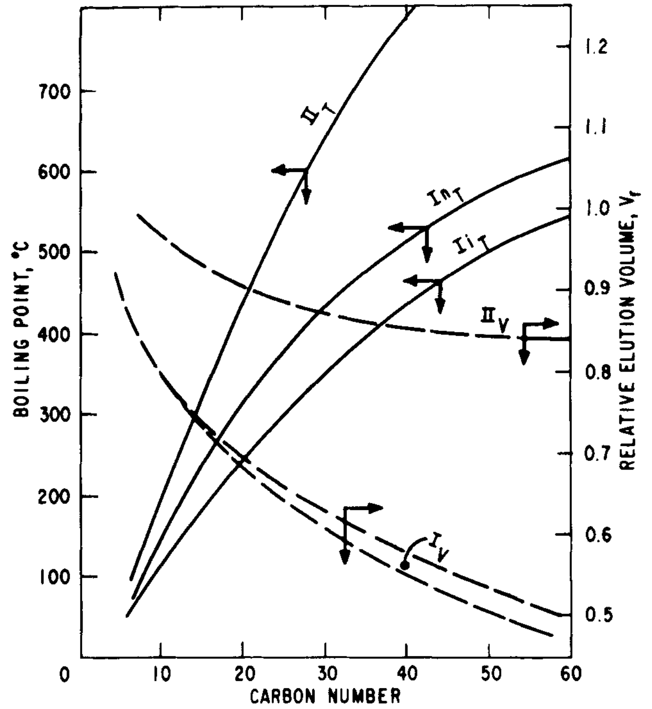

FIG. 1. Correlation of boiling point, relative elution volume, and carbon number for petroleum compounds. (——) Boiling point; (- -) GPC (Poragel/methylene chloride. I*i* = branched paraffins; I*n* = *n*-paraffins; II = condensed rings.

the most highly condensed compounds. Thus, Curves Ii_T and II_T define the carbon-number limits for a given distillation cut. Between Curves In_T and II_T a family of curves should exist which define the limits for saturates with one ring, two condensed rings, etc. The band of one-ring compounds lies immediately above the In_T line with its lower limits extending somewhat below this line. The two-ring band lies above the one-ring, etc. The dashed lines represent similar limits for the GPC that we have established for our system, using model compounds. The relative elution volume, V_r, is plotted against carbon number. The V_r is the ratio of the elution volume of the material to the elution volume of benzene. The curve for the *n*-hydrocarbons, shown at the bottom of the Fig. 1, has been well established by calibration compounds for our system. Based on a few points, we believe the branched paraffins will be included in the band labelled I_V. The II_V curve is an estimated limiting curve for the most condensed paraffins; it is based on only a few points. Between Curve I_V and Curve II_V a family of curves should exist that describe limits for saturates with one ring, two rings, etc. These should lie successively above the I_V curve and approach the II_V curve as condensation increases.

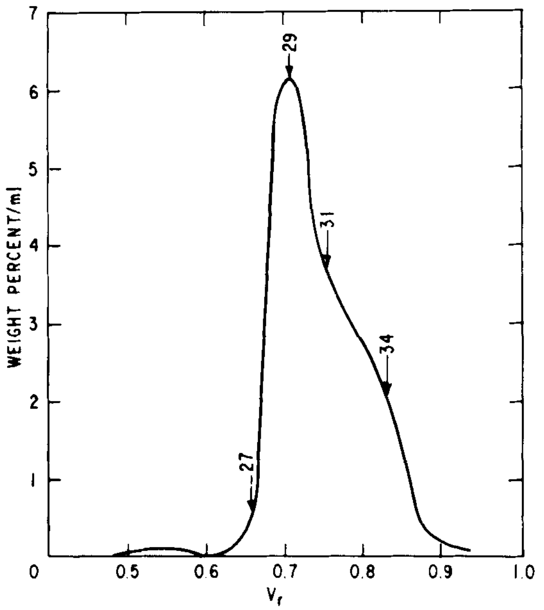

FIG. 2. Amount of material as a function of V_r 450–475°C saturate.

According to Fig. 1 the 450–475°C cut, if ideal, should contain normal and branched paraffins (no-ring compounds) between lines In_T and Ii_T or those with carbon numbers of 32 to 46. The ring compounds should have carbon numbers somewhat lower, ranging from about 20 to 35. Moving these limits to the GPC curve suggests that the GPC separation of this cut could be represented by a line from the intersection of the C_{46} line and the I_V line and moving upward and to the left. Thus the highest molecular weight no-ring compounds should emerge first, followed by lower molecular weight no-rings which would be followed by, and undoubtedly mixed with, the highest molecular weight one-ring compounds. These in turn would give way successively to condensed two-ring, three-ring, and four-ring compounds. Thus, in successive fractions the number of rings should increase while the molecular weight decreases. These data suggest that GPC, when applied to a narrow-boiling saturate cut, will effect a separation according to number of rings.

Data from GPC of the saturate cut are shown in Fig. 2. The weight per cent of material per milliliter of eluent is plotted as a function of the V_r. Most of the material emerges between the V_r's of .65 and .90 as predicted from Fig. 1. The compositional changes across this curve were checked by a detailed examination of four fractions noted by arrows. Data on these fractions are shown in Table 1. The increasing refractive index strongly suggests increasing condensation. Mass spectral analyses confirm this suggestion. The no-ring compounds predominate in Fraction 27, one-ring compounds in Fraction 29, two-ring compounds in Fraction 31, and finally four-ring compounds in Fraction 34. (The skipping of the three-ring compounds is probably due to fraction selection—two fractions intervened—and to the predominance of four-ring compounds in the saturate cut.) The change in composition from the first to the last fraction is striking. The early Fraction, 27, contains 95.5 wt% no-, one-, and two-ring compounds; and a late Fraction, 34, contains 95.9 wt% three-, four-, five-, and six-ring compounds.

Inspection of Fig. 1 predicts a decrease in molecular weight in successive fractions. The average molecular weights of Fractions 29, 31, and 34 suggest carbon numbers of 38, 36, and 29, respectively, which are consistent with the increasing condensation and complexity predicted. The low molecular weight of Fraction 27 appears to be anomalous. More detailed examination of Fig. 1 suggests that the no-ring compounds that emerge at the V_r corresponding to Fraction 27 should have carbon numbers between 20 and 30. Although most of

TABLE 1

GPC-MS Data on 450–475°C Saturates

	Mass spectral analyses, wt%									
	No-ring	One-ring	Two-ring	Three-ring	Four-ring	Five-ring	Six-ring	Mono-aromatics	Mol wt	Refractive index
Charge	12.3	9.5	19.3	20.3	27.6	7.4	3.0	0.6		
Fraction 27	67.6	20.1	7.8	3.1	0	0	0	1.4	427	1.451
Fraction 29	18.5	40.6	22.6	10.4	6.3	0	0	1.6	535	1.460
Fraction 31	1.0	18.9	27.2	17.6	17.2	9.2	3.7	5.1	510	1.481
Fraction 34	1.5	0	2.8	23.7	51.6	13.0	7.6	0	400	1.503

these compounds would not be present in an idealized 450–475°C cut, they are inevitable in a real cut; thus these low-molecular-weight no-ring compounds appear with the higher-molecular-weight one-ring compounds and lower the average molecular weight of this fraction. We have observed this same phenomenon in other cuts from this oil.

The data from this separation suggest the positions of the families of GPC curves that might be added to Fig. 1. Similar data on additional fractions from this and other crude oils should provide sufficient information to estimate the elution parameters for various condensed systems. Such data will aid in the design of the separation system and in the interpretation of the results.

CONCLUSIONS

Gel permeation chromatography is a thermally gentle, rapid, and effective method for separating the saturates from high-boiling distillate fractions according to number of rings. The technique provides concentrates of condensed ring compounds that are needed as calibration standards for other methods of separation and of analysis.

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Mention of specific models of equipment or brand names of materials is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

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