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CHROMATOGRAPHIC ANALYSIS OF PARAFFINIC WAXES

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SUMMARY

Gel permeation and gas chromatographic analyses of crude paraffinic waxes are reported. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular-weight distributions of crude paraffinic waxes containing different amounts of oil have been determined using a gel permeation chromatographic calibration curve for n-paraffins. A fraction consisting mostly of n-C_{18}–C_{30} yields a distribution curve that peaks at 27.6 counts with a $\bar{M}_w/\bar{M}_n$ ratio of 1.02 using four 4 ft. × 3/8 in. Styragel columns having pore volumes of 500, 500, 100 and 100 Å. A fraction consisting of mostly oil (m.p. <23°) yields a distribution curve that peaks at 27.9 counts, with a $\bar{M}_w/\bar{M}_n$ ratio of 1.09. It is shown that gel permeation chromatography gives reliable $\bar{M}_n$ and $\bar{M}_w$ values for crude paraffins having $\bar{M}_w/\bar{M}_n$ <1.05 or containing <30 wt. % oil, using a calibration curve for n-paraffins. Gas and gel permeation chromatograms of the fractions are presented and are found to complement each other well.

INTRODUCTION

Paraffinic waxes having a low oil content (<1 %, w/w) are useful materials in the coatings and plastic-processing industries and as starting materials for chlorinated paraffins and other products. These waxes are obtained from a petroleum fraction by various techniques and are n-alkanes with chain lengths ranging from 16 to 50 carbon atoms.

It is known that crude oils from eastern Venezuela[1] such as Guere and Anaco have a wax content that may be as high as 20% by weight. In this paper we report our attempts to characterize paraffinic waxes obtained locally by gas–liquid and gel-permeation chromatography. Our interest lies mainly in analyzing crude paraffinic waxes in order to select sources capable of yielding n-paraffins suitable for given applications. We were especially interested in identifying a source having a high content of n-paraffins in the C_{16}–C_{26} range, since this fraction is a useful starting material for chlorinated paraffins, as was shown by Rotenberg[2].

Crude paraffinic waxes are usually characterized by their oil content and their

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melting point range. A typical sample from a refinery may contain 30% (w/w) oil and a melting-point range as wide as 10°. The crude waxes form a two-phase system upon standing and often the melting-point ranges depend on the sampling techniques used. If the crude waxes are fractionated, the molecular weights of the fractions can be estimated from their melting points. Molecular-weight distributions, however, must be obtained either by gas or gel chromatography.

In our laboratory, gas chromatography (GC) is used routinely to analyze *n*-paraffins up to a chain length of 40 carbon atoms; however, we sought a method that would give us more information on all of our crude samples as well as the chlorinated products. The temperatures required to analyze *n*-paraffins having chain lengths above C_{40} are almost at the upper useful limit of routine GC. Gel permeation chromatography (GPC), on the other hand, has been used extensively to characterize small and large molecules[3–5]. The elution characteristics of solvents, as well as asphalts and crude oils, have also been studied[6]. In GPC, the large molecules exit from the columns first and the small molecules exit last. Thus, GPC permits the routine analysis of high-molecular-weight materials. The analysis of temperature-sensitive compounds is also facilitated by GPC.

EXPERIMENTAL

Four wax samples (A, B, C and D) containing 30% (w/w) oil were obtained from an eastern Venezuelan refinery for analysis. The waxes were melted and stirred well before obtaining the samples used in the analyses. Solutions containing 0.5 g of wax per 100 ml of tetrahydrofuran were used for GPC analyses. Benzene was used as the solvent for GC analyses. Sample D was fractionated by the sweating technique using a 500-ml büchner funnel and a procedure resembling the industrial process. A 200-g sample of the wax was placed in the funnel, which was then placed in an oven at $50 \pm 1°$ for 2 days. The material that did not melt at this temperature was labelled fraction 1 and the material that did melt was cooled, placed in the filter and kept in the oven at $40 \pm 1°$ for 2 days. This procedure was repeated and fractions 2, 3 and 4 were collected at 40, 30 and 23°, respectively. The fifth fraction consisted of the oil that had seeped through the filter at 23°.

GC analyses were carried out in a Packard–Becker Model 420 gas chromatograph equipped with a thermal conductivity detector and a 5 ft. × 1/8 in. column packed with 6% (w/w) SE-30 on Ultraport at 240°. Retention times of *n*-paraffins were determined using analytical standards purchased from PolyScience Corp. (Evanston, Ill., U.S.A.; Kit 26 A). A plot of log retention time of the peaks *versus* carbon number gave a straight line. Peak areas were obtained by triangulation and planimetry.

GPC analyses were carried out using a Waters Model 200 instrument equipped with four 4 ft. × 3/8 in. columns having pore volumes of 500, 500, 100 and 100 Å. Using tetrahydrofuran as a solvent, the columns yielded 640 plates per ft. for dodecane at 30°. A typical gel permeation chromatogram for a four-component mixture is shown in Fig. 1. In this and in all the gel permeation chromatograms, the abscissa gives the elution volume in counts (1 count = 4.69 ml) and the ordinate gives the response of the differential refractometer. A calibration curve was obtained by determining the elution volumes of six *n*-paraffins purchased from Humphrey Chemical Co. (Chicago, Ill., U.S.A.). The best plot gave the following relation which was used
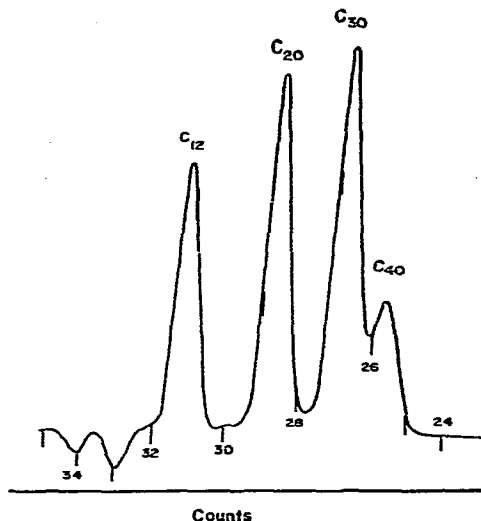
Fig. 1. GPC trace for a mixture of *n*-alkanes, showing the response of the differential refractometer. One count is equal to 4.69 ml.

in all the calculations: $\log \bar{M} = -0.0971(\text{counts}) + 5.215$. Good agreement was obtained between $\bar{M}_n$ and $\bar{M}_w$ values obtained by GPC using the procedure outlined in the Water's GPC Manual and the theoretical values of known mixtures. Utilization of Polyscience calibration mixtures consisting of 10% (w/w) C_{18}, 25% (w/w) C_{19}, 30% (w/w) C_{21} and 35% (w/w) C_{22} ($\bar{M}_n = 288$) yielded an average $\bar{M}_n$ of 298, which is within 3.5% of the theoretical value.

TABLE I

GPC ANALYSIS OF CRUDE PARAFFINIC WAXES (30 WT.% OIL)

$\bar{M}_n$ and $\bar{M}_w$ values were calculated using the calibration curve for *n*-paraffins.

Sample	Counts at GPC peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Av. chain length
A	24.2	664	685	1.03	C_{47}
B	26.2	490	508	1.04	C_{35}
C	26.8	417	242	1.02	C_{30}
D	27.6	353	359	1.02	C_{25}

TABLE II

GPC ANALYSIS OF THE FRACTIONS OBTAINED FROM SAMPLE D

The oil content was estimated from the gas chromatogram.

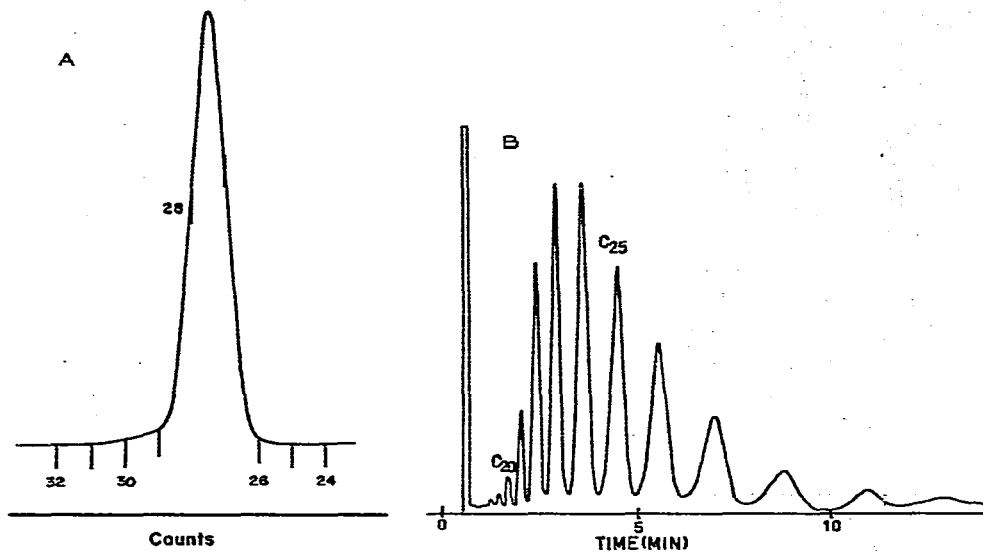| Fraction	M.p. range (°C)	Oil content (%, w/w)	GPC peak	Av. chain length	Yield (%, w/w)
1	51–52	10	27.6	C_{25}	55
2	41–43	31	27.6	C_{25}	22
3	31–33	54	27.6	C_{25}	10
4	23–27	66	27.6	C_{25}	4
5	<23	87	27.9	C_{23}	8

Fig. 2. Gel permeation (A) and gas (B) chromatograms for fraction 1. See Table II.
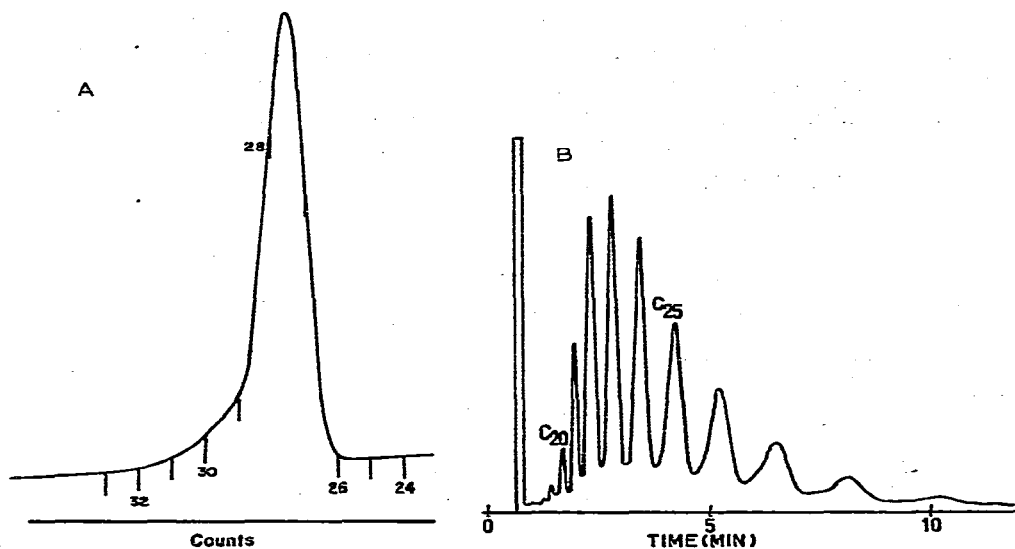
Fig. 3. Gel permeation (A) and gas (B) chromatograms for fraction 2.

RESULTS AND DISCUSSION

All of the samples obtained were analyzed by GPC, but only samples C and D yielded useful GC chromatograms. Table I shows the results of the GPC analyses. The calibration curve obtained with the n-paraffins was used to estimate the molecular-weight averages of these samples, although it was known that the waxes contained 30% (w/w) oil according to refinery specifications.

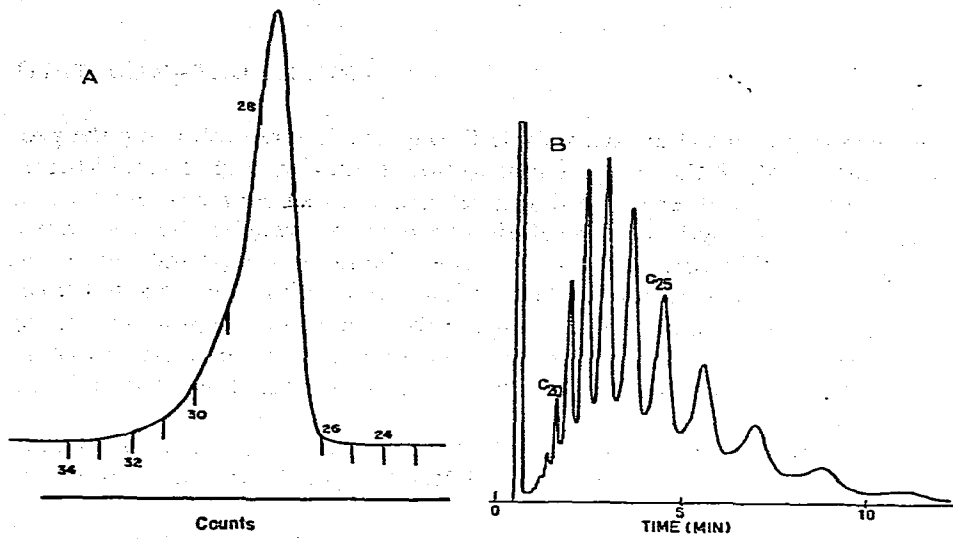In order to evaluate the effect the oil had on our estimates of molecular weights

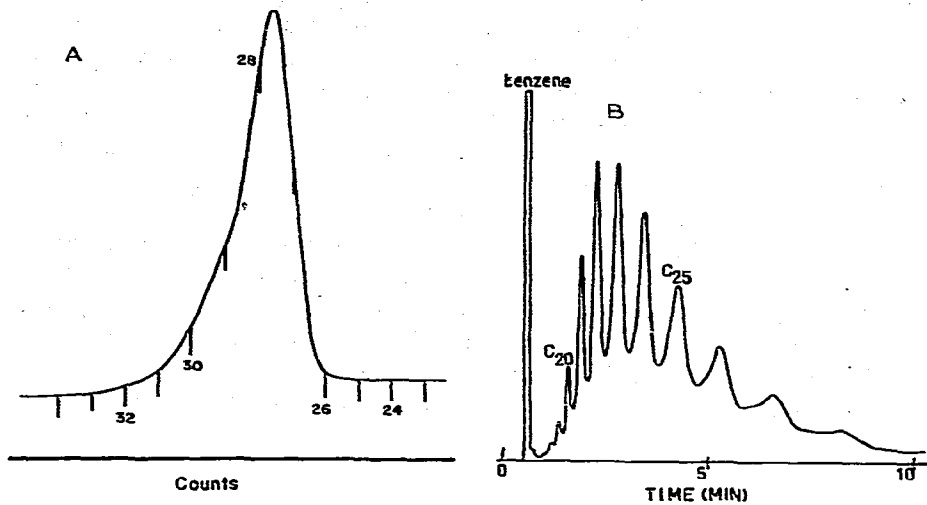Fig. 4. Gel permeation (A) and gas (B) chromatograms for fraction 3.

Fig. 5. Gel permeation (A) and gas (B) chromatograms for fraction 4.
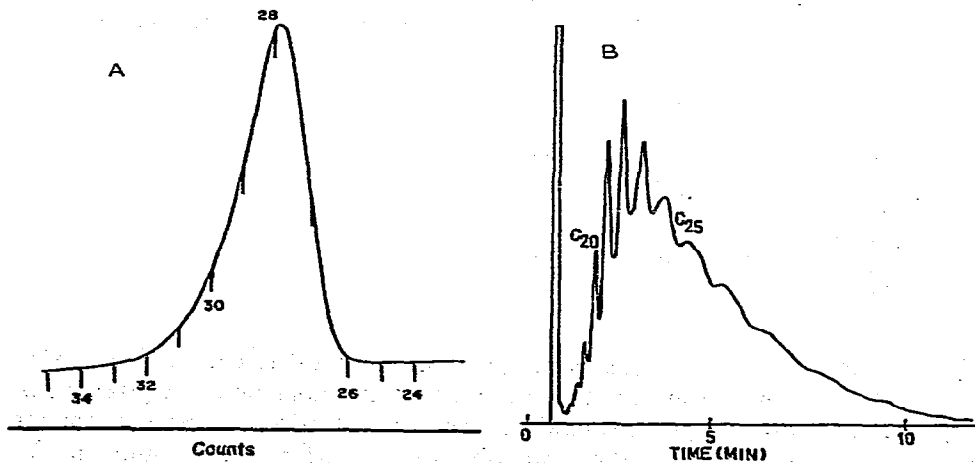

Fig. 6. Gel permeation (A) and gas (B) chromatograms for fraction 5.

and on molecular-weight distributions, sample D was fractionated following the procedure outlined previously in the experimental section. Both Hendrickson and Moore[7] and Schulz[8] have shown that there is no simple relation between molar volume and/or an effective carbon chain length with the elution volume for branched hydrocarbons. Schulz measured the elution volumes of 32 branched alkanes (C_7–C_{11}) and found that the elution behaviour of these compounds correlates well with a function that takes into account both molar volume and carbon number for a homologous series, for example the 5-methylalkanes. Since paraffinic waxes are complex mixtures of n-alkanes and branched alkanes (oil), the best that could be expected was approximate $\bar{M}_n$ and $\bar{M}_w$ values.

Table II summarizes the data obtained for the fractionated samples. Figs. 2A–6A show the gel permeation chromatograms and 2B–6B show the gas chromatograms for the five fractions.

An inspection of Figs. 2A–6A reveals that as the oil content increases the base of the gel permeation chromatogram increases, while the peak remains at the same elution volume up to an oil content of ca. 66%. Fig. 6A shows that the elution volume measured at the GPC peak changes for the fraction that is mostly oil (m.p. <23°). Figs. 2B–6B show that as the oil content increases in a fraction a broad peak appears, underneath the peaks representing the n-paraffins, and grows until the n-paraffin peaks almost disappear. The oil content of each fraction was estimated by outlining the broad peak and dividing its area by the total area. A sample with <1% oil gives a gas chromatogram with a very straight baseline[9].

Table III summarizes the GPC data. Perhaps the most important information obtained is the $\bar{M}_w/\bar{M}_n$ value which gives an idea of the broadness of the distribution. The fraction containing the most oil has the highest M_w/M_n value. As the melting point of the fraction decreases, both the GPC and GC data show that the distribution of n-alkanes is shifted to lower carbon numbers, as expected. If the $\bar{M}_n$ and $\bar{M}_w$ values of sample D, fraction 1 and fraction 2 are compared, the $\bar{M}_n$ values differ by at most 8%, although the fractions contain 10–30 wt. % oil.

TABLE III

MOLECULAR-WEIGHT DISTRIBUTION OF THE FRACTIONS

$\bar{M}_n$ and $\bar{M}_w$ were estimated using the calibration curve for n-paraffins. The oil content was estimated from the gas chromatogram.

Fraction	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Oil content (%, w/w)
1	340	346	1.02	10
2	329	346	1.05	31
3	293	314	1.07	54
4	293	319	1.09	66
5	266	290	1.09	87
Sample D	353	359	1.02	30

An $\bar{M}_n$ value for the fraction containing the least oil (fraction 1) was also obtained by GC. This was done by considering that the area under a given peak divided by the total area is proportional to the concentration of the component responsible for the peak. Peak areas were obtained by triangulation and an $\bar{M}_n$

value of 346 was obtained for fraction 1. This value is in good agreement with the $\bar{M}_n$ value obtained from GPC data calculated using the calibration curve for n-paraffins.

CONCLUSIONS

The results of this study show that GPC values of $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ of crude paraffinic waxes are useful in characterizing these samples although calibration curves for the complex mixtures may not be available. Crude paraffinic waxes containing $>30\%$ (w/w) oil show $\bar{M}_w/\bar{M}_n$ values of >1.05. A sample having a melting point below 23° and an estimated oil content of 87% shows a $\bar{M}_w/\bar{M}_n$ ratio of 1.09. As the melting point of the fraction decreased both GPC and GC show that the distribution changes to lower carbon numbers. Apparently, the oil sample has a distribution curve with a peak at 27.9 counts and an $\bar{M}_w/\bar{M}_n$ value of 1.09, while the main n-paraffinic fraction is a distribution of C_{18}–C_{30} with a peak at 27.6 counts and an $\bar{M}_w/\bar{M}_n$ ratio of 1.02. The distribution curve of the n-paraffins is apparently affected only slightly when the oil is present in amounts up to 30%. GC data complement very nicely the information obtained by GPC for paraffinic waxes having an average chain length of C_{25}, and one would expect the same for fractions having greater chain lengths.

ACKNOWLEDGEMENT

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