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ESTIMATION OF CHAIN BRANCHING IN PARAFFIN WAXES USING PROTON MAGNETIC RESONANCE SPECTROSCOPY AND GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

Two methods using high-resolution proton magnetic resonance spectroscopy (PMR) in conjunction with gas–liquid chromatography (GLC) are described which give a rapid and reliable estimation of the extent of chain branching in paraffin-wax mixtures. Our initial approach has been to compare the area of the methyl resonances of the PMR signal to that of the methylene plus methine protons, having previously calculated an average molecular weight from GLC data. The second method makes use of the slight upfield shift and characteristic splitting of methyl protons attached to methine groups. The contribution of these shifted resonances to the area derived from all the methyl protons is used to estimate directly the degree of branching. The limitations of the techniques and the sources of error are discussed. However, the good numerical agreement between the two methods prompts us to support the postulate that branching in natural paraffin waxes consists to a very large extent of methyl branches only.

INTRODUCTION

The suitability of a paraffin wax for a particular industrial application or product depends on its physical characteristics. For some uses the easily measurable parameters of refractive index, hardness, melting point and viscosity are probably suffcient in deciding the suitability of the material[1]. However, in other instances, such as in the motor-car tyre industry, a knowledge of the degree of branching and the average molecular weight is an important consideration. This is particularly true when a new grade of wax has to be matched with a previously successful product.

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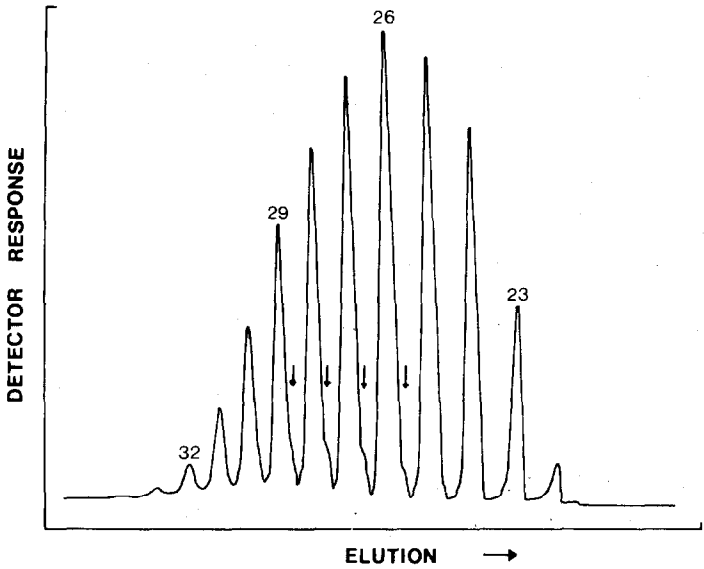

Fig. 1. GLC elution profile of a 130/135 fully refined paraffin wax. Numbers above the peaks refer to the carbon atoms present in the particular straight-chain component. The arrows indicate the peak shoulders which are considered as branched-chain components with the same number of carbon atoms as the more abundant straight-chain molecules.

Recently there has been much discussion concerning the methods available for the determination of the relative proportions of straight- and branched-chain hydrocarbons in commercial waxes. Some industrial concerns use methods based on the urea adduction of straight-chain hydrocarbons[2] while others base their assessment directly on gas–liquid chromatographic (GLC) data.

In the adduction method straight-chain hydrocarbons are precipitated as clathrate-type complexes formed by the urea, while the branched-chain molecules remain in solution. Although the results are usually reproducible for the same mixture, the general applicability of this method to give absolute figures must be questioned.

Brink and Kleynjan[3] show the complexation method is not completely selective. Certain low-molecular-weight isoparaffins, which do not form urea adducts on their own, can be assisted into the adduct in the presence of other straight-chain hydrocarbons such as *n*-decane. Further, if the linear part of the molecule is long, isoparaffins, cycloparaffins and alkyl aromatics can also form direct adducts. Clearly the nature of the whole mixture affects the measured amount of branched chain. Other factors such as the temperature of filtration of the adduct and the amount of solvent used for washing can also lead to variable results.

In the direct GLC analysis approach the branched-chain components are assumed to be the shoulders (see Fig. 1) of the peaks produced by the corresponding straight-chain hydrocarbons. The obvious lack of resolution between the straight- and branched-chain components makes integration of the corresponding peak areas prone to considerable errors.

EXPERIMENTAL

Proton magnetic resonance (PMR) spectra

The wax samples were dissolved in C^2HCl_3 at a concentration of 8–10 mg cm^{-3} and the spectra recorded at 20°C with a Brüker WH 270 MHz spectrometer working in the Fourier transform mode. Integration of the peaks was carried out digitally from spectra generated at low pulse angles (*ca.* 30°). The PMR spectrum of pure tetracontane in C^2HCl_3 was recorded prior to each wax sample as an integration standard.

Gas–liquid chromatography

Analyses were carried out using a Perkin-Elmer F33 GC Instrument with flame ionisation detectors. Integration was performed by computer. The column, 2 m length, was packed with Chromosorb W AS DCS impregnated with 3% Dexsil 300, using nitrogen as the mobile phase. The initial column temperature of 160°C was increased by 5°C/min to a final value of 350°C. Each major elution peak was considered as corresponding to a straight-chain hydrocarbon of a specific chain length and the shoulders, where they occurred, from isoparaffins with the same molecular weight as the main peak. The average chain length was found by calculating the statistical mean after appropriate weighting of the detector response.

Urea adduct analysis

Wax (5 g ± 1 mg) was dissolved in 50 ml carbon tetrachloride and the solution maintained at 50°C for 30 min. Urea (15 g ± 5 mg) was dissolved in 50 ml methanol, the solution kept at 50°C for 30 min, and then added, with stirring, to the wax solution. The mixture was maintained, with stirring, at 50°C for 30 min and then left to cool to ambient temperature before filtration. The precipitate collected was washed with 3 × 50 ml carbon tetrachloride. The combined filtrate and washings (F) was kept. The precipitate was mixed with 250 ml water and heated in a water bath at 80°C for 15 min to decompose the urea adduct. The liberated wax was solidified by cooling in an ice bath and the liquid was removed by filtration. The wax was dissolved in warm carbon tetrachloride (150 ml), the solution allowed to cool to ambient temperature, and then washed with 2 × 30 ml water. The wax solution was evaporated and dried to constant weight (W_1).

The combined filtrate and washing (F) were shaken with 3 × 50 ml water and then these aqueous washings were extracted with 25 ml carbon tetrachloride. The combined carbon tetrachloride fractions were evaporated and dried to constant weight (F_1).

The complete procedure was repeated on the wax fraction W_1 to give fractions W_2 and F_2. W_2 is the straight-chain hydrocarbon portion of the original sample and $F_1 + F_2$ is the branched-chain hydrocarbon fraction; from their respective weights the proportions of straight-chain and branched-chain hydrocarbons can be calculated.

Calculation of the degree of branching from PMR data

(1) From the ratio of the methyl to methylene plus methine protons. If n is the average carbon chain length of the alkanes present in the wax and b the fraction of

the total molecules which are branched (there being t branches in each branched molecule) then the area of resonance peaks corresponding to methylene plus methine protons is proportional to

$$[(1 - b)(n - 2)\,2 + b(n - 2 - 2t)\,2 + bt]$$

and the area generated by the methyl protons is proportional to

$$[3(1 - b)\,2 + 3(2 + t)\,b]$$

Simplification of the above parameters shows that the ratio of the resonances of the methyl to methylene plus methine protons is

$$\frac{6 + 3bt}{2n - 4 - 3bt}$$

and the ratio of methyl to all protons is $\frac{6 + 3bt}{2n + 2}$.

The value of n is obtained from GLC (see previous section) and hence a value for the product bt is readily calculated.

These formulae show that the technique cannot distinguish between the situation where there are three branches on one molecule and that of three molecules each having one branch. However, for convenience of presentation, values could be quoted assuming $t = 1$. This assumption seen in terms of natural product biosynthesis and the low percentage of branching found in the waxes we examined, may not be far from the truth.

(II) From the splitting of the methyl proton signal. In straight-chain alkanes the terminal methyls are always adjacent to methylene groups and the resultant methyl proton spectrum is split into a triplet, of area ratio 1:2:1 (Fig. 2A). However, if the methyl is attached to a methine group, as in a methyl branch, there is a slight upfield chemical shift and the splitting of the methyl protons now becomes a doublet, area ratio 1:1 (Fig. 2B).

Analysis of the recorded spectrum requires an initial computation of the most upfield peak (this is the upfield component of the doublet arising from branched methyls). The area obtained is doubled (see Fig. 3) and this then represents the total area derived from all methyl groups attached to methine groups. Subtraction from the total area in the methyl region of the spectrum gives the area corresponding to all non-branched methyls.

The calculation of the degree of branching is based on the assumption that there is only one branch per molecule and thus two end-group methyls for every branched methyl. Hence, in order to calculate the percentage branching, the area corresponding to the branched methyl group is doubled and is considered as a percentage of the total methyl area less the contribution from the branched methyls.

$$\text{Thus, percentage branching} = \frac{4\,(\text{area of most upfield peak}) \times 100}{(\text{total methyl area}) - 2\,(\text{area of most upfield peak})}$$

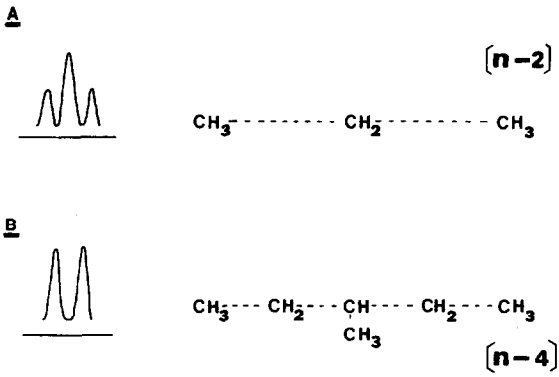

Fig. 2. The number of methylene groups in (A) straight-chain and (B) singly branched chain paraffins with total number of carbon atoms *n*. The appearance of the magnetic resonance spectra of the methyl protons attached to (A) methylene and (B) methine groups is also shown.

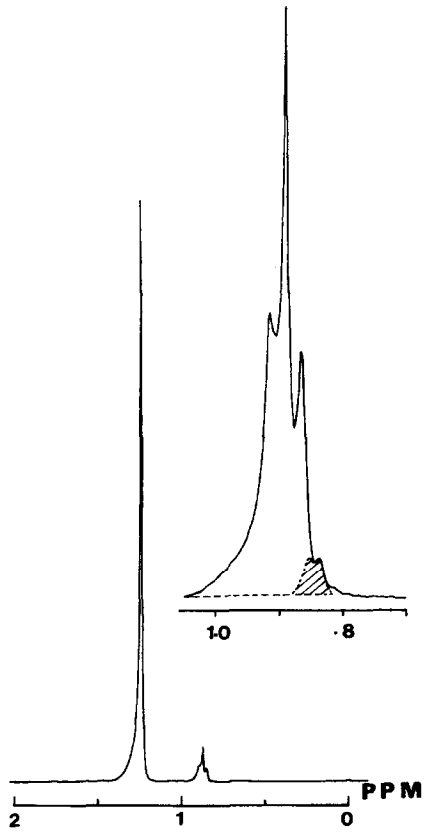

Fig. 3. PMR spectrum of BD 443, a rubber compounding wax. The methyl resonances are in the region of 0.9 ppm (parts per million) with the main methylene peak at approximately 1.3 ppm. The other very small peaks at chemical shifts greater than 1.3 ppm could be from methine or other methylene protons. The reference signal is from tetra methyl silane. The insert shows the methyl resonances in more detail. The most upfield peak is part of the doublet derived from branched methyl groups adjacent to methines. The shaded portion indicates how the total contribution from the branched methyl group is estimated.

This method was tested on a laboratory prepared mixture of *n*-decane and 3-methylnonane (19:1) and was found to give a result within 2% of the expected value.

RESULTS AND DISCUSSION

Reference to Table I shows that the waxes (BD 443, a rubber compounding wax, obtained from VMH Chemical Blenders, and a 130/135 fully refined paraffin wax, obtained from Shell Chemicals, U.K.) used in our investigation had average chain lengths of 26.5 and 26.2 respectively, as measured by GLC. Using this information, in conjunction with the methyl: (methylene plus methine) peak area ratio gives the percentage branching as 6.3% and 5.1%. This is in reasonably close agreement with the values obtained from the analysis of the shifted methyl protons (7.9%, 5.4%). The values obtained from the urea adduct method however are quite different, being approximately triple those from the PMR techniques.

In the PMR techniques we have assumed that there is a maximum of only one branch per molecule, and, therefore, the values quoted are upper limits. The ratio of the PMR signals remains the same whether the total branching occurs in single molecules or as multiples within the same molecule. Therefore the occurrence of a second branch or further branches per molecule will reduce the total calculated number of branched molecules in the mixture.

A reason, excluding the systematic errors of measurement, for the discrepancy between the two PMR methods could lie in the assumption, pertinent to method II, that all branches are assumed to be methyl. Ethyl and larger branches would not give rise to the shifted split methyl resonances and so these would not be detected. However, if there were a large number of long-chain branches, the percentage branching calculated by method II would be expected to be very much smaller than calculated by method I as the latter method is independent of the length of the branched chain. This clearly is not the case. Thus the agreement between the two results leads us to believe that most of the branches are methyl. This observation is in agreement with other general reports[4] which have stated that, although there is an enormous number of possible isomeric forms of high-molecular-weight paraffins, those iso-alkanes found in petroleum are single-chain (methyl) branches.

TABLE I

AVERAGE CARBON CHAIN LENGTH AND ESTIMATED CHAIN BRANCHING IN TWO PARAFFIN-WAX MIXTURES

The values given are averages with the number of data sets considered being given in parenthesis.

Product	*Average carbon chain length*	*Estimated branching (%)*		
		By GLC plus methyl/methylene + methine ratio	*By upfield shifted methyl ratio*	*By urea adduct method*
BD 443, a rubber compounding wax	26.5	6.3 (10)*	7.9 ± 1.0 (7)	21 ± 0.9 (2)
130/135 fully refined paraffin wax	26.2	5.1 (10)*	5.4 ± 1.3 (5)	20 ± 1.4 (2)

* The standard deviation for these measurements was < 0.06.

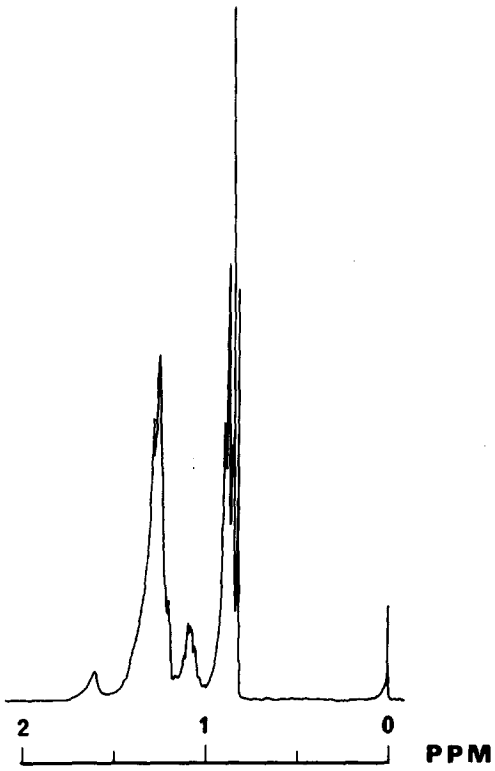

Fig. 4. PMR spectrum of 3-methylnonane. The resonance assignments are: 0.9 ppm methyl groups; 1.1 ppm methylene group adjacent to both a methyl and methine group (C_2); 1.3 ppm methylene groups other than those appearing at 1.1 ppm; 1.6 ppm methine group.

When this investigation was initiated it was hoped to resolve the methylene and methine proton resonances and compare these separately with those from the methyl protons. This would have given a direct read out of the average molecular weight as well as the degree of branching. The results with 3-methylnonane (Fig. 4) show that resolution of all non-equivalent protons is feasible for a single compound but, in our experience, it cannot be extended universally to the industrial waxes. With these latter materials it is not always possible to assign unambiguously the small methine resonances for, in some instances, they become part of the much larger methylene peak. Further, small amounts of unsaturated compounds, when present, could also give chemical shifts in the methine region.

In the techniques we describe for measuring the degree of branching the main source of error is that of estimating peak areas. Spectra of wax samples were therefore recorded under spectrometer conditions which gave acceptable integrated areas for a high-molecular-weight standard. Recording of the spectrum was followed by multiple determinations of the peak area ratios.

In the GLC analysis a flame ionisation detector was used. This means the detector response depends not only on the number of moles of each component present but also on the corresponding chain length. Correction for the variation in

chain length was carried out by assuming the detector response was essentially proportional to the carbon content of the compound being analysed[5]. Failure to correct for chain length can lead to approximately 40% errors in the final calculated degree of branching.

The PMR techniques gave much lower percentage branching values than the urea adduct method. This, according to the work of Brink and Kleynjan[3], can be explained by the non-adduction of a proportion of the normal hydrocarbons. Complete adduction, it is thought, can only be achieved if temperatures of about 25°C are used and there is no washing of the precipitated material.

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