

CHROM. 3880

Separation of naphthenes and paraffins on an alkali-treated molecular sieve

We have described¹ a gas-liquid chromatographic technique in which pelleted type 13X molecular sieve, crushed and screened to 40-60 mesh, is used to separate the saturated hydrocarbons present in petroleum distillates boiling up to 185°. The separation is by carbon number, or by bulk hydrocarbon type within a carbon number and can be used either for analysis or to obtain segregated fractions of naphthenes and paraffins (Fig. 1). It has also been found that within each hydrocarbon type, the order of elution of the individual components is controlled by their geometrical configuration and orientation on the sieve surface and that this order may be altered by prior treatment of the screened sieve with aqueous sodium hydroxide.

In order to understand these facts more fully, we have now obtained and compared data on the relative retentions of a range of C₈ naphthenes and paraffins on both untreated and caustic soda-treated sieves.

The caustic soda-treated sieve was prepared by percolating 2% of aqueous sodium hydroxide through a 12 in. × 1/2 in. I.D. column at the rate of 4 ml/min for 25 min. The sieve was washed, then dried and heated to 450° for 3 h. After packing the adsorption columns, they were further activated by heating to 350° and sweeping with helium for 2 h. The small sample size (0.05 μl per component) that was used, and the high temperatures employed ensured that the peaks obtained were symmetrical and presented no difficulty in measurement. The results obtained are given in Tables I and II.

During adsorption the chemical structure of the surface of type 13X molecular sieve determines the potential energy of the molecular interaction that occurs between the saturated hydrocarbons and the sieve. This interaction, which is non-specific², is due mainly to the dispersive forces between the carbon linkages of the hydrocarbons and the non-uniform distribution of charge on the channel walls of the porous surfaces of the sieve.

For a given saturated hydrocarbon molecule the total energy of non-specific interaction is a function of its overall polarizability and its molecular size and orientation relative to the surface of the sieve. In the distillate boiling range under discussion ≠ C₁₁ the differences in overall polarizability and molecular size that exist between saturated hydrocarbons of different number are such that there is a substantial difference in their energies of interaction and hence in their retention times. Within a carbon number, however, the retention time of an isomer will be determined by its geometrical configuration and orientation, which decide the number of carbon linkages in the molecule that are accommodated on the surface. Most cycloparaffins, because of their ring structure and its relative inflexibility, have fewer linkages in contact with the surface of the sieve than their paraffinic isomers of equivalent carbon number. Thus as a class the retention times of the cycloparaffins are, in general, less than those of the paraffins. However, as the carbon number of the molecules increases the geometrical configurations of both hydrocarbon types are such that overlapping of their retention times can occur (Fig. 1).

Overlapping of the retention times of both hydrocarbon types also occurs when the column is operated at elevated temperatures. At these temperatures the short

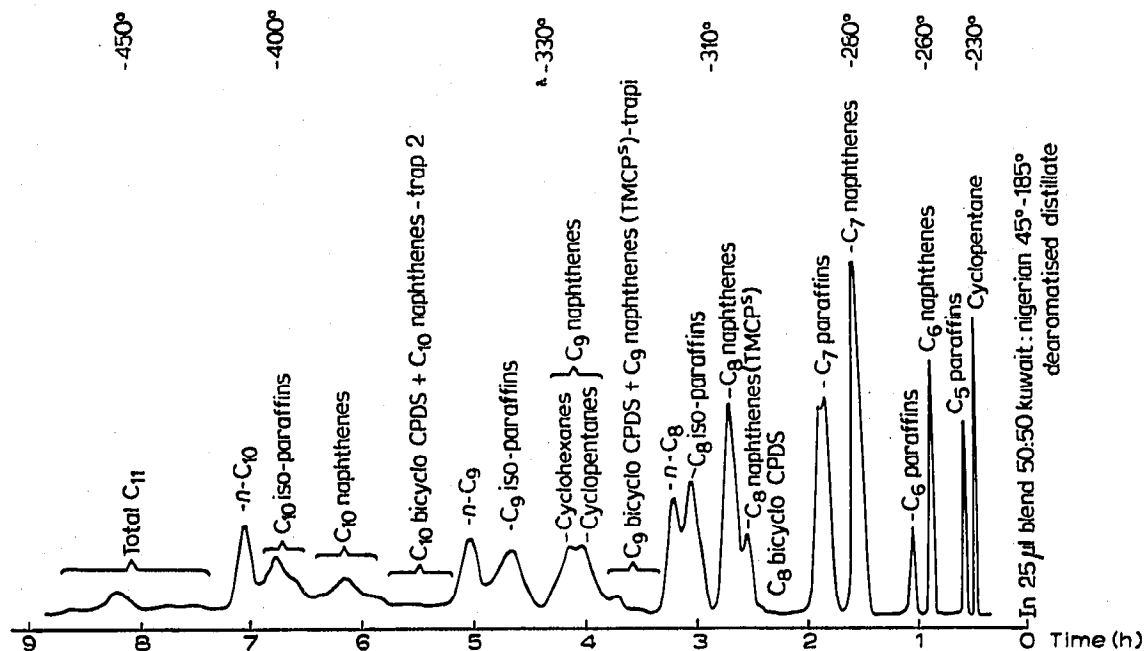


Fig. 1. Typical gas-solid chromatogram obtained with type 13X sieve when used for collection and identification of fractions from a 45–185° dearomatized petroleum distillate. Conditions: column, 3 ft. × 5/32 in. I.D.; packing, 3% NaOH-treated 40–60 mesh type 13X molecular sieve; temperature, programmed; inlet pressure, 11 p.s.i.g. He; flow rate, 80 ml/min; detector, F.I.D.; splitter ratio, 30:1; sample size, 25 µl; chart speed, 2 1/2 in./h.

TABLE I

THE EFFECT OF COLUMN TEMPERATURE ON RELATIVE RETENTION TIMES

The retention times were obtained on a 2 ft. 6 in. × 1/8 in. O.D. stainless steel column containing 40–60 mesh type 13X molecular sieve. Carrier gas: helium; flow rate: 80 ml/min; sample size: 0.05 µl per component; flame ionization detection.

Compound	Boiling point (°C)	Column temperature (°C)					
		275	300	350	400	450	475
<i>cis</i> -Bicyclo[3.3.0]octane	136.5	0.60	0.64	0.71	0.81	0.93	1.00
1,1,3-Trimethylcyclopentane	104.9	0.65	0.69	0.75	0.84	0.89	0.92
Ethylcyclohexane	131.8	0.76	0.79	0.85	0.94	1.00	1.00
2,2,4-Trimethylpentane	99.2	0.91	0.92	0.95	0.94	1.00	1.00
3-Methylheptane	118.9	0.93	0.93	0.94	0.94	1.00	1.00
<i>n</i> -Octane	125.7	1.00	1.00	1.00	1.00	1.00	1.00

residence time leads to a lack of resolution and no overall type separation is obtained. This effect of temperature on retention time for a number of C₈ isomers is illustrated in Table I. Table II shows the differences in the relative retention of the C₈ naphthenes and C₈ paraffins that occur at lower temperatures. In Table II only the retention times of methylcycloheptane and cyclooctane overlap with those of the paraffins. This is because of the larger seven and eight carbon atom rings; these increase the forces of interaction at the aperture to the inner surfaces of the sieve and therefore increase the overall energy of non-specific interaction relative to the other naphthenes. The results also show the influence that *cis* and *trans* isomerization, the chain length,

TABLE II

RELATIVE RETENTION TIMES OF C₈ ISOMERS ($n-C_8 \equiv 1.00 \equiv 32.82$ min)

The retention times were obtained on a 4 ft. \times 1/8 in. O.D. stainless steel column containing; (a) 4.2 g of untreated and (b) 4.32 g of caustic soda-treated 40-60 mesh type 13X molecular sieve. Operating temperature: 320°. carrier gas: helium; sample size: 0.05 μ l per component; flow rate: 80 ml/min; flame ionization detection.

Paraffins		Naphthenes		
Compound	Boiling point (°C)	Untreated sieve	NaOH-treated sieve	Relative difference
2,2,4-Trimethylpentane	99.2	0.94	0.88	1.07
2,2,3-Trimethylpentane	109.8	0.98	0.90	1.09
2,3,4-Trimethylpentane	113.5	0.98	0.90	1.09
2,3,3-Trimethylpentane	114.8	1.00	0.92	1.09
2-Methyl-3-ethylpentane	115.7	0.94	0.87	1.08
3-Methyl-3-ethylpentane	118.3	0.97	0.89	1.09
2,5-Dimethylhexane	109.1	0.93	0.88	1.07
2,4-Dimethylhexane	109.4	0.92	0.88	1.05
3,3-Dimethylhexane	112.0	0.94	0.88	1.07
2,3-Dimethylhexane	115.6	0.95	0.90	1.06
3,4-Dimethylhexane	117.7	0.95	0.90	1.06
3-Ethylhexane	118.5	0.92	0.88	1.05
2-Methylheptane	117.6	0.93	0.94	0.99
4-Methylheptane	117.7	0.91	0.89	1.02
3-Methylheptane	118.9	0.93	0.92	1.01
<i>n</i> -Octane	125.7	1.00	1.00	1.00
1,1,3-Trimethylcyclopentane	104.9	0.71	0.67	1.06
<i>trans</i> -1, <i>cis</i> -2,4-Trimethylcyclopentane	109.3	0.70	0.66	1.06
<i>trans</i> -1, <i>cis</i> -2,3-Trimethylcyclopentane	110.2	0.72	0.67	1.07
1,1,2-Trimethylcyclopentane	113.7	0.75	0.70	1.07
<i>cis</i> -1, <i>trans</i> -2,4-Trimethylcyclopentane	116.7	0.80	0.77	1.04
<i>cis</i> -1, <i>trans</i> -2,3-Trimethylcyclopentane	117.5	0.77	0.71	1.08
<i>cis</i> -1, <i>cis</i> -2,3-Trimethylcyclopentane	123.0	0.83	0.78	1.06
1-Methyl- <i>trans</i> -3-ethylcyclopentane	120.8	0.78	0.75	1.04
1-Methyl- <i>trans</i> -2-ethylcyclopentane	121.2	0.77	0.72	1.07
1-Methyl- <i>cis</i> -3-ethylcyclopentane	121.4	0.76	0.74	1.03
1-Methyl-1-ethylcyclopentane	121.5	0.79	0.74	1.07
1-Methyl- <i>cis</i> -2-ethylcyclopentane	128.1	0.81	0.77	1.05
Isopropylcyclopentane	126.4	0.83	0.79	1.05
<i>n</i> -Propylcyclopentane	130.9	0.81	0.78	1.04
<i>trans</i> -1,4-Dimethylcyclohexane	119.4	0.77	0.74	1.04
1,1-Dimethylcyclohexane	119.5	0.80	0.74	1.08
<i>cis</i> -1,3-Dimethylcyclohexane	120.1	0.78	0.74	1.05
<i>trans</i> -1,2-Dimethylcyclohexane	123.4	0.79	0.75	1.05
<i>cis</i> -1,4-Dimethylcyclohexane	124.3	0.83	0.79	1.05
<i>cis</i> -1,2-Dimethylcyclohexane	129.7	0.82	0.77	1.06
Ethylcyclohexane	131.8	0.82	0.78	1.05
Methylcycloheptane	134.0	0.91	0.85	1.07
Cyclooctane	151.0	1.00	0.90	1.11
<i>exo</i> -2-Methyl-bicyclo[2.2.1]heptane	—	0.62	0.59	1.05
<i>endo</i> -2-Methyl-bicyclo[2.2.1]heptane	—	0.63	0.60	1.05
<i>cis</i> -Bicyclo[3.3.0]octane	136.5	0.68	0.64	1.06

position, and number of the substituent groups have on the sequence of elution of the individual isomers within each hydrocarbon type. From Table II it is also evident that the caustic soda treatment effectively reduces the density and distribution of charge over the surfaces of the sieve. As a consequence there is an overall decrease in the energy of non-specific interaction. This reduction in the average concentration of the force centres of the surface accounts for the relatively large difference in the retention time of cyclooctane, but a study of the results also indicates that the reduction is selective in its effect on different molecules. It would appear that flatter and more elongated molecules, as they are better able to orientate themselves along the sieve surface, have a greater area of contact and hence a smaller decrease in their energy of interaction than more compact molecules. This is borne out by the small relative differences in the retention times of *n*-octane, the methylheptanes and *trans*,4-dimethylcyclohexane compared with those of the trimethylpentanes and 1,1-dimethylcyclohexane. Since this type of selectivity can be increased by controlling the strength of the caustic soda treatment it has important analytical consequences. For, although the overlap between the different series of isomers is considerable, it is possible, by adjusting the chemical treatment and careful control of temperature, to trap and obtain concentrates of a particular group of isomers. For example, a total of sixteen C₉ and forty-three C₁₀ bicyclo compounds were shown to be concentrated in Traps 1 and 2, Fig. 1. This was established by combined GLC-mass spectrometry¹.

Further work may well demonstrate that an extension of the technique to hydrocarbons greater than C₁₁ is possible by a careful choice of sieve parameters and alternative alkali washing procedures.

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¹ J. V. BRUNNOCK AND L. A. LUKE, *Anal. Chem.*, 40 (1968) 2158.

² A. V. KISELEV, in A. GOLDUP (Editor), *Gas Chromatography*, Butterworth, London, 1964, p. 238.

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