

SEPARATION FROM EACH OTHER OF COMPLEX MIXTURES OF PARAFFINS AND OLEFINS BY ELUTION ADSORPTION CHROMATOGRAPHY*

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(Received August 27, 1966)

Complex mixtures of paraffins and olefins (from C₉ to C₃₇), such as are found in low temperature coal tars can be separated from each other by elution adsorption chromatography on long columns of activated silica gel, using n-pentane as both solvent and eluant.

Introduction

Mixtures of paraffins and olefins can be separated from each other on the macro-scale by liquid adsorption chromatography on silica gel if the range of molecular weights is not too wide. This forms the basis of the fluorescent adsorption indicator (FIA) method used for lower boiling petroleum distillates, in which the amounts of paraffins, olefins and aromatic hydrocarbons are estimated after separation on the column, but without elution. Here, there seems to be some difference between the results obtained by the IP method (IP156/63 Tentative) and the ASTM method (D1319-61T) resulting from a difference in interpretation at the upper end of the olefin zone.¹ The method, in any case, is not applicable to the higher, solid hydrocarbons.

If elution adsorption chromatography is used to enable recovery of the fractions for further examination, a prior simplification of the wide range of hydrocarbons such as is found in petroleum, shale oils, natural products and low temperature tars, usually by distillation, is resorted to. Thus, Boyer *et al.* distilled the neutral oil of low temperature tars into three fractions, and separated the total olefins from the total paraffins in each of these by the elution method.²

Spence and Vahrman solved the problem of separating such complex mixtures by linking iodine monochloride on to the olefins, thus making possible their clear-cut separation from the paraffins because of the stronger adsorption of the adduct on the silica column. The olefins were regenerated unchanged by refluxing the eluted adduct with sodium iodide in ethanol. An almost quantitative recovery of the two kinds of hydrocarbon was thus made possible.³

Experimental

Two series of experiments were carried out on the total aliphatic hydrocarbons, fraction *a*, of a low temperature tar⁴ obtained by solvent extraction of the neutral portion followed by purification by chromatography.⁵ From previous work, the boiling range of each of the hydrocarbon types (straight-chain, branched-chain and cycloparaffins, and similar series of monoolefins) was known to be from about 175° to 500°C, covering a range of molecules from about C₉ to C₃₇.⁶

(1) Fraction *a* (20 g) was distilled into three sub-fractions, under a progressively increasing vacuum in a Nester-Faust spinning band column (Table 1). Fraction *a* and each distillation frac-

TABLE I.—DISTILLATION OF FRACTION *a*

Fraction	Distillation range °C	Pressure mm Hg	% Yield on fraction <i>a</i>	% Yield cumulative	Appearance of fraction
1.	54-115	2→1	25.8	25.8	Colourless liquid
2.	115-150	1→0.15	34.6	60.4	Pale yellow liquid
3.	Residue, >150	0.15	38.0	98.4 total loss 1.6	Pale yellow wax

tion was separated into alkanes and alkenes by both liquid adsorption chromatography and the iodine monochloride method³ (Table 2). The chromatography was carried out in each case on 4 g of the fraction in 40 ml of n-pentane on a column 150 cm by 1 cm of silica gel (IP standard), the same solvent being used as eluant. The frac-

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tions were recovered by first distilling off the solvent at atmospheric pressure on a water bath, and removing the last traces of it in a vacuum desiccator. The range of the carbon numbers of the straight-chain alkanes and alkenes was determined by gas liquid chromatography on a temperature-programmed (3.12°C per minute was used) Perkin Elmer model 800, using oxygen-free

nitrogen as the carrier gas, a differential flame ionisation detector, and columns of 15% silicone, SE 30 (methyl type silicone elastomer).

(2) Fraction *a*, without prior treatment, was chromatographed by the elution adsorption technique, as above, the eluate collected in small increments, and each fraction examined by infrared absorption spectroscopy for the presence of olefins (bands at 1650–1680 cm⁻¹ and 900–1000 cm⁻¹), which, if present, were estimated by iodine monochloride addition followed by chromatography.³ Fractions 4 and 5, in which both paraffins and olefins were present, were re-chromatographed on silica. The results are given in Table 3.

TABLE 2.—PARAFFINS AND OLEFINS IN FRACTION *a* AND ITS DISTILLATION FRACTIONS.

Fraction	% Paraffins by ICI method	% Paraffins by chromatography	% Paraffins over lapping with olefins	Range of carbon atoms in molecule by g.l.c.
Fraction <i>a</i>	57.1	52.6	4.5	C ₉ —C ₃₇
Dist. fracn. 1	a. 59.0 b. 15.2	a. 59.1 b. 15.2	Nil	C ₉ —C ₁₇
2	a. 55.0 b. 19.0	a. 53.0 b. 18.3	a. 2.0 b. 0.7	C ₁₆ —C ₂₄
3	a. 57.2 b. 21.7	a. 48.0 b. 18.2	a. 9.2 b. 3.5	C ₂₃ —C ₃₇

a. On fraction examined
b. On fraction *a*

Conclusions

1. Complete separation of complex mixtures of paraffins and of olefins from each other can evidently be achieved by liquid adsorption chromatography on silica gel if the column is long enough. If fractions are obtained in which overlap occurs these can be re-chromatographed, or can be treated by the method of iodine monochloride addition.³

2. The distillation experiments showed that the paraffins and olefins were more easily separable in

TABLE 3.—CHROMATOGRAPHY OF FRACTION *a*.

Fraction number	Volume of eluate, ml	% Yield on fraction <i>a</i>	% Yield cumulative	η_{D}^{50}	Appearance of fraction	Olefins from infrared spectrum	Olefins by ICI method (on fraction <i>a</i>)
1	5	22.6	22.6	1.4395	White wax	Absent	Nil
2	5	17.3	39.9	1.4400	White wax	"	Nil
3	5	12.8	52.7	1.4427	White, soft wax	"	Nil
4*	5	6.6	59.3	1.4487	White, very soft wax	Mainly <i>trans</i> -2 olefins	2.3
5*	5	5.5	64.8	1.4605	White, soft wax and colourless liquid	<i>Trans</i> -1 and-2 olefins	4.3
6	5	3.6	68.4	1.4585	White, very soft wax	Mainly 1-olefins	100
7	5	2.3	70.7	1.4549	White, very soft wax and colourless, mobile liquid	"	100
8	5	2.2	72.9	1.4485	"	"	100
9	25	19.4	92.3	1.4465	"	"	100
10	100	3.3	95.6	1.4605	"	"	100

* By chromatography of fractions 4 and 5 combined: % paraffins, 2.8; % olefins, 8.0 (both on fraction *a* basis).

the lower boiling fractions (C_9-C_{17}), but that overlap increased with rise in boiling point (molecular weight), i.e. with degree of "dilution" of the double bond in the olefin molecules, bringing them nearer to the corresponding paraffins in adsorption properties. The hydrocarbons in the residue from distillation ($C_{23}-C_{37}$) thus accounted for most of the overlap found in the chromatography of the whole fraction *a*.

Acknowledgment.—The authors are grateful to the City University, London, for a research fellowship to one of them (M.S.A.A.) and to the National Carbonising Company, Ltd., Mansfield, Notts., for samples of low-temperature tar.

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