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Note

Gas chromatography of alkenes in water vapour as carrier gas on a solid support impregnated with silver nitrate

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The determination of alkenes is an important analytical task in petrochemistry. After the pioneering work of Bradford *et al.*[1], many chromatographers solved this problem by gas–liquid chromatography using silver nitrate in organic solvents[2–4] and water[5]. Because of the low column temperature, only the lower alkenes C_2–C_5 were separated in those studies. With organic solvents the column temperature must not be higher than 65°C[2] owing to the reduction of silver ions. Wasik and Tsang[5] showed that in aqueous solutions of silver nitrate the silver ions are primarily responsible for the selectivity. However in this case the temperature used was only 20°C; owing to possible volatilization of the water. Furthermore, the carrier gas was saturated with water in order to prolong the column life.

It was of interest to investigate the selectivity of separation of the higher alkenes, *i.e.*, C_{10} on a sorbent containing silver nitrate and using only water vapour as the carrier gas. For this "steam" chromatography, it is necessary to study the physical state of the silver nitrate. The use of incompletely saturated water vapour leads either to a solid salt modified with water[6] or to an aqueous solution on the solid salt[7].

EXPERIMENTAL

The gas chromatographic system providing the water vapour mobile phase was as described earlier[8]. The initial sorbent was Celite C-22, 60–80 mesh (Ferak, Berlin), with 20% (w/w) of silver nitrate, contained in a stainless-steel column (2 m × 3 mm I.D.). The oven temperature was varied from 105 to 120°C to ensure an inlet pressure of 1.2–1.3 atm. The linear velocity of the mobile phase was 3 cm/s. The chromatographed compounds were C_{12}–C_{16} *n*-alkenes and decenes.

For visual investigation of the physical state of the silver nitrate, two glass U-tubes were connected in parallel with the steam source: the first contained silver nitrate, the second was empty.

RESULTS AND DISCUSSION

Visual observation has shown that at 105–120°C when water vapour is passed

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TABLE I

RETENTION INDICES OF SOME DECENES ON DIFFERENT STATIONARY PHASES

n-Alkene	*Squalane 115°C*[9]	*Apiezon L 130°C*[10]	*Dibutyl tetrachloro-phthalate 80°C*[11]	*Silver nitrate in water 108°C*
Decene-1	983	990	1011	1428
cis-5-Decene	982	989	1005	1434
trans-5-Decene	985	988	1000	1358

over solid silver nitrate the salt is transformed into a solution the volume of which became constant. Obviously the saturation vapour pressure above the equilibrated solution is equal to the pressure of the steam mobile phase. No vapours were condensed in the check tube.

The retention indices of some decenes on the studied phase and on ordinary stationary liquid phases are shown in Table I. It follows that the stationary phase investigated is highly selective towards alkenes in comparison with non-polar hydrocarbons (retention indices of decenes: 1358–1434). Secondly, the difference in the retention indices for the decene isomers is 76 units, *i.e.*, selectivity towards these

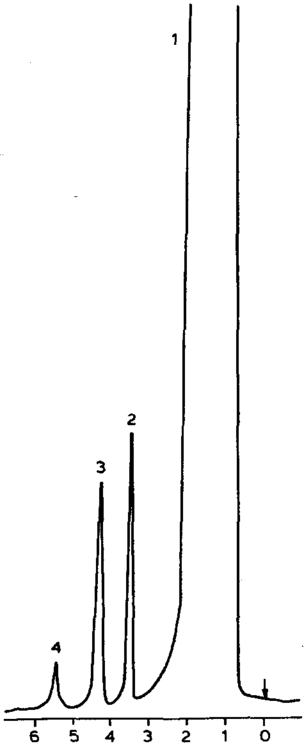

Fig. 1. Separation of a mixture of decenes in hexane solution by elution with water vapour at 108°C Peaks: 1 = hexane; 2 = *trans*-5-decene; 3 = 1-decene; 4 = *cis*-5-decene.

isomers is essentially higher than in the case of known polar or non-polar liquid phases. The retention indices of decenes changed insignificantly during 3 days, even at 120°C. In 2 weeks, there was a noticeable change; however, the values were still much higher than on other stationary liquid phases. As seen from Fig. 1, decenes are separated completely in a short time. With use of a mixture of water vapour and nitrogen (1:1) as carrier gas the retention time increased to 8 min and the peaks resolution worsened. The passage of dry carrier gas (nitrogen) through the column led to complete retention of the decenes.

Thus, it was shown that with water vapour as carrier gas at temperatures higher than 100°C, silver nitrate forms an aqueous solution. The resulting solid support and solution of silver nitrate displays selectivity towards unsaturated hydrocarbons and can be used for the separation of higher alkenes.

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