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THE GAS CHROMATOGRAPHIC SEPARATION OF PAIRS OF ISOTOPIC MOLECULES BY MEANS OF POROUS POLYMER BEADS*

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SUMMARY

The separation of various isotopic molecules with deuterium substitutions is reported.

Columns with porous polymer beads (Porapak Q) are employed. A comparison is made between this packing material and other adsorbents, as graphitized carbon black or silica gel. High separation factors are obtained. The working temperatures are usually higher with respect to the other materials, but the isotopic effects measured with the Porapak are more favourable for many of these separations.

INTRODUCTION

The outstanding properties of porous polymer beads as a fractionation medium, suggested its use as column packing for the separation of isotopic pairs. This investigation deals with the use of Porapak; this material has been used by CZUBRYT *et al.*¹ for the separation of CH₄ and CD₄ in a packed column. Several isotopic systems have been investigated, and it has been found that the separation factor on this material is quite high; separation in several cases could be realized by using classically packed columns.

EXPERIMENTAL

All chromatographic measurements at room temperature or higher have been made on a commercial apparatus (C. Erba, Milano). Measurements below 0°C have been carried out on a home-made gas chromatograph where accurate thermostating was realized by flowing methanol cooled with dry ice and acetone. Measurements at 143° and 113°K have been carried out by replacing methanol with pentane and isopentane cooled with liquid nitrogen.

Porapak Q (60–80 mesh) obtained from Waters Assoc., Framingham, Mass. (U.S.A.) has been used to pack the following columns.

(a) glass (1.5 m, 0.12 cm I.D.);

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- (b) copper (4.3 m, 0.2 cm I.D.);
- (c) copper (1.0 m, 0.15 cm I.D.);
- (d) copper (2.5 m, 0.20 cm I.D.).

The following isotopic pairs have been examined: $\text{CH}_4\text{-CD}_4$, $\text{C}_2\text{H}_2\text{-C}_2\text{D}_2$, $\text{C}_2\text{H}_4\text{-C}_2\text{D}_4$, $\text{C}_2\text{H}_6\text{-C}_2\text{D}_6$, $\text{H}_2\text{S-D}_2\text{S}$, $\text{C}_6\text{H}_6\text{-C}_6\text{D}_6$, $\text{C}_6\text{H}_{12}\text{-C}_6\text{D}_{12}$, $\text{CH}_3\text{Cl-CD}_3\text{Cl}$, $\text{CH}_3\text{-COCH}_3\text{-CD}_3\text{COCD}_3$, $\text{CH}_3\text{OH-CD}_3\text{OH}$.

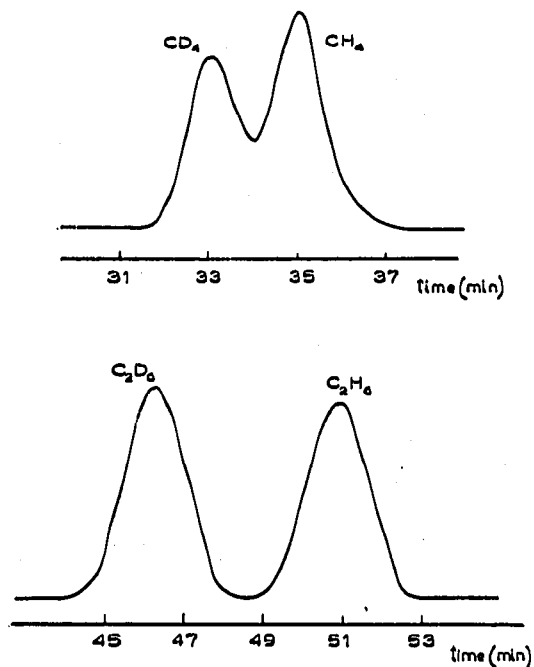
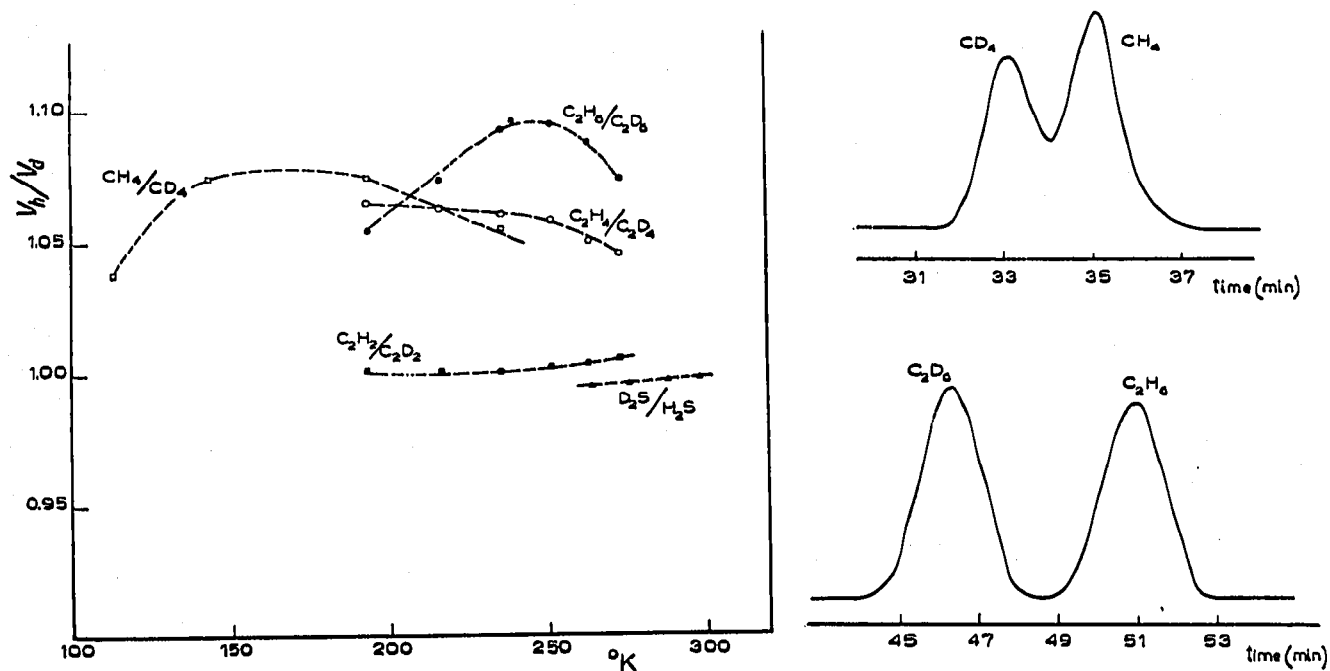


Fig. 1. Plots of the retention volumes ratio (V_h/V_d) vs. temperature for gas isotopic pairs.

Fig. 2. Chromatographic separation of $\text{CH}_4\text{-CD}_4$ and $\text{C}_2\text{H}_6\text{-C}_2\text{D}_6$ on a Porapak Q column (4.3 meter, 0.20 I.D.) $\text{CH}_4\text{-CD}_4$: T_{cal} , 190°K ; P_{N_2} , 1.5 atm; flow, 18.7 ml/min. $\text{C}_2\text{H}_6\text{-C}_2\text{D}_6$: T_{cal} , 250°K ; P_{N_2} , 1.75 atm; flow, 14.5 ml/min.

Nitrogen has been used as elution gas for all systems which were detected by a F.I.D.; hydrogen was used as a carrier gas in the study of $\text{H}_2\text{S-D}_2\text{S}$ for which a microcell conductivity detector was employed.

RESULTS

Separation of gaseous compounds

The elution time of the investigated hydrocarbons on Porapak follows the order: methane, ethylene, acetylene, ethane. All isotopic pairs of hydrocarbons exhibit in the temperature range examined, a reverse isotopic effect, the heavier species being eluted first. To obtain the most favourable operating temperature, the separation factor has been measured in a fairly wide range and the results are plotted in Fig. 1. For the system $\text{CD}_4\text{-CH}_4$, the highest separation factor has been found between 140 and 200°K ; below 140° it decreases much more than above 400°K . Fig. 2 shows the separation $\text{CD}_4\text{-CH}_4$ at 190°K ; it has been obtained with a resolution factor (R) equal to 0.8 on column b which has only 4,500 theoretical plates for CH_4 . A similar

column with 25,000 plates should separate the pair $\text{CH}_4\text{-CH}_3\text{D}$ with the same resolution as the separation factor for this pair at the same temperature is 1.017.

A similar behaviour is exhibited by the pair $\text{C}_2\text{D}_6\text{-C}_2\text{H}_6$, which has been investigated in the temperature range 240–255 °K; the separation factor, as indicated in Fig. 2, is better than for methane, the chromatogram being obtained at 250 °K on the same column.

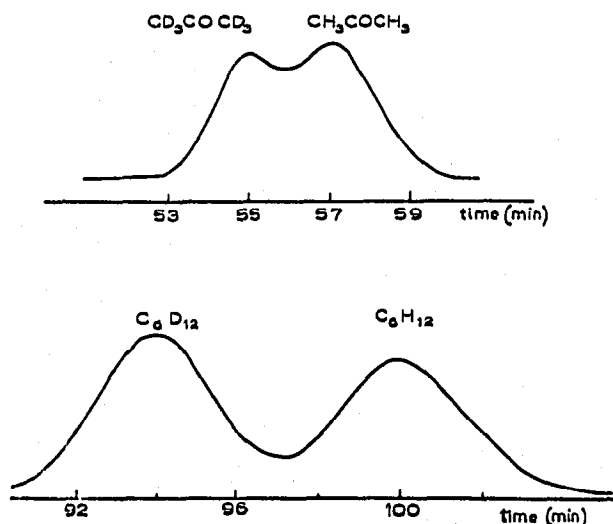


Fig. 3. Chromatographic separation of $\text{CH}_3\text{COCH}_3\text{-CD}_3\text{COCD}_3$ and $\text{C}_6\text{H}_{12}\text{-C}_6\text{D}_{12}$ on a Porapak Q column (2.5 m 0.20 I.D.) $\text{CH}_3\text{COCH}_3\text{-CD}_3\text{COCD}_3$: T_{cal} , 353 °K; P_{N_2} , 0.95 atm; flow, 7.2 ml/min. $\text{C}_6\text{H}_{12}\text{-C}_6\text{D}_{12}$: T_{cal} , 427 °K; P_{N_2} , 0.6 atm; flow, 4.0 ml/min.

The separation of the pair $\text{C}_2\text{D}_4\text{-C}_2\text{H}_4$ is less affected by temperature; the trend should be the same, but the lower temperature range is difficult to investigate because of the very long retention time below 190 °K.

The separation for the pair $\text{C}_2\text{D}_2\text{-C}_2\text{H}_2$ cannot be realized on Porapak Q as the separation factor is almost united and hardly affected by temperature. No peak separation has been obtained by operating on the pair $\text{H}_2\text{S-D}_2\text{S}$, but by performing separate chromatograms on the single isotopic species, a noticeable difference of retention time is measured and significant information is obtained. This pair exhibits a normal isotopic effect, the separation factor increasing by decreasing the temperature. Measurements have been limited to the temperature range 273–330 °K using column c; at lower temperatures the peaks are strongly tailed and do not allow any satisfactory determination.

Separation of liquid compounds

A set of polar and non-polar isotopic pairs has been investigated. The operating temperature range (320°–450 °K) is quite limited as the capacity ratio (K') strongly increases by decreasing the temperature; on the other hand, an increase of temperature decreases the separation factor; in several cases, however, a partial separation of the various systems has been realized. As an example, in Fig. 3 is shown the separation of a non-polar system (cyclohexane–deuterocyclohexane) and a polar system (acetone–deuteroacetone) performed on column d.

The results obtained for various liquid systems are expressed in terms of the

logarithm of the retention volumes ratio, $\log V_h/V_a$, and are plotted *vs.* $1/T$ in Fig. 4. In the same graph have been reported the retention volume ratios obtained in GLC on stationary phases of different polarity (squalane, SE 30, triethyleneglycol)². It seems that the interaction of most isotopic pairs on Porapak Q enhances the isotopic effect, measured in GLC. It has to be pointed out that measurements have been performed at higher temperatures where usually the isotopic effect is less relevant.

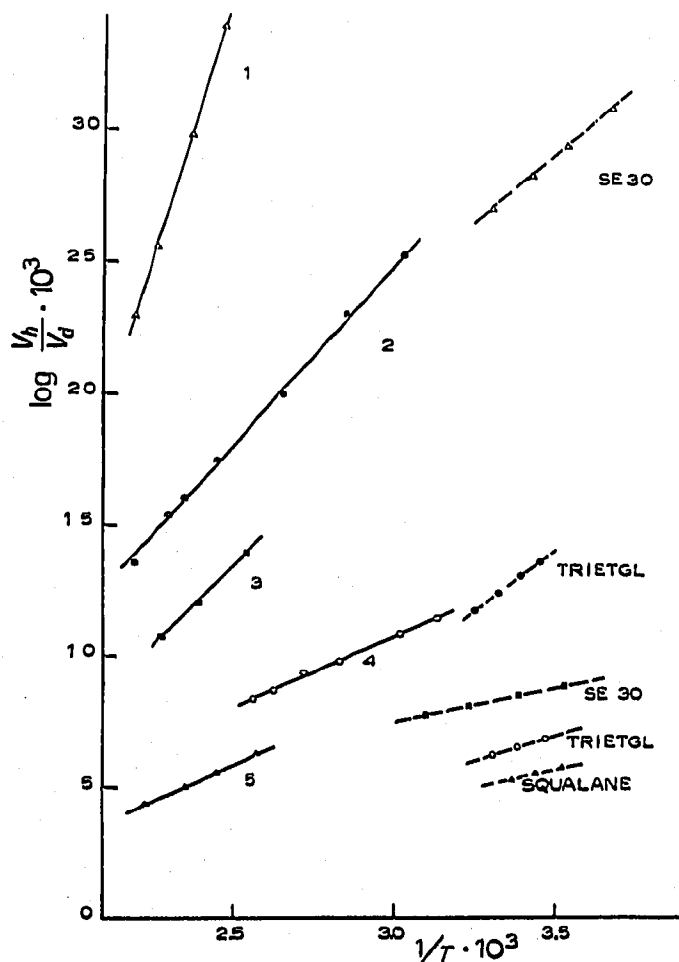


Fig. 4. Plots of logarithm $\times 10^3$ of ratio of retention volumes *vs.* $1/T \cdot 10^3$ for liquid isotopic pairs on Porapak Q (continuous line) and by GLC (dotted line) on silicone oil, triethyleneglycol and squalane. Δ = $C_6H_{12}-C_6D_{12}$; \bullet = $CH_3COCH_3-CD_3COCD_3$; \blacksquare = $C_6H_6-C_6D_6$; \circ = CH_3OH-CD_3OH ; \blacktriangle = $CHCl_3-CDCl_3$.

DISCUSSION

In Table I are collected the most favourable experimental separation factors on Porapak Q for various isotopic pairs at the indicated temperature, together with the separation factors obtained in adsorption gas chromatography on graphitized carbon black (GCB)³, on etched glass (EG)⁴ and on partition chromatography on squalane⁵. In all gaseous systems a higher separation factor has been measured; for liquid systems, the separation factor is usually favourable but it is obtained at a higher working temperature. The mechanism of gas chromatographic separations on

TABLE I
EXPERIMENTAL SEPARATION FACTORS

	Porapak <i>Q</i>	°K	GCB	°K	EG	°K	Squalane	°K
CH ₄ -CD ₄	1.075	193	1.056	143	1.016	152		
C ₂ H ₂ -C ₂ D ₂			1.070	77	1.075	77		
C ₂ H ₄ -C ₂ D ₄	1.065	193	1.051	175	0.973	190		
C ₂ H ₆ -C ₂ D ₆	1.095	251	1.087	175	1.043	164		
C ₇ H ₈ -C ₇ D ₈	1.030	431	1.056	352	0.987	277	1.059	273
C ₆ H ₆ -C ₆ D ₆	1.033	393	1.050	327	0.984	277	1.042	273
C ₃ H ₁₂ -C ₃ D ₁₂	1.086	400					1.107	273

TABLE II
DIFFERENCES OF ENTHALPY AND ENTROPY CHANGES OF ISOTOPIC SYSTEMS

	$(\Delta H_{chr})_h - (\Delta H_{chr})_d \text{ cal mol}^{-1}$	$(\Delta S_{chr})_h - (\Delta S_{chr})_d \text{ e.u.} \times 10^2$
C ₆ H ₁₂ -C ₆ D ₁₂	-191.8	-32.1
C ₆ H ₆ -C ₆ D ₆	-73.1	-8.6
CH ₃ COCH ₃ -CD ₃ COCD ₃	-62.6	-7.1
C ₂ H ₅ OH-C ₂ D ₅ OH	-29.7	-41.0
CH ₃ OH-CD ₃ OH	-25.1	-24.0
CHCl ₃ -CDCl ₃	-22.8	-3.0

microporous polymers is not yet elucidated; both partition and adsorption take place and the enhancement of the isotopic effect should be related to factors concerning chromatographic resolution connected to the mass transfer in the gas phase, in the mobile phase, and in the adsorption-desorption; all processes should, to a certain extent, be affected by isotopic substitution. To obtain some quantitative information on the magnitude of the isotopic effect, the differences of enthalpy and entropy changes of various isotopic pairs have been calculated for the systems where a linear relationship has been found between the logarithm of the ratio of the retention volumes and I/T . These values are collected in Table II. The enthalpy differences are, in most cases, much larger than the same values determined on other adsorption media.

As an adsorption medium, Porapak, being a copolymer between ethylvinylbenzene and divinylbenzene, can be considered mainly responsible for a non-specific interaction, as its molecule does not carry specific functional groups. It should be considered, however, that because of the presence of aromatic nuclei with easily polarizable electrons, a weak specific effect may also be expected, namely with molecules having lone electron pairs, π bonds or positively charged groups like protonic hydrogen atoms.

As it was expected, most isotopic pairs exhibit a reverse isotopic effect, due to a polarizability difference⁶ since a non-specific interaction takes place. In the case of the isotopic pair H₂S-D₂S, a prevailing specific interaction takes place on Porapak because of the presence of protonic hydrogen atoms; this pair thus exhibits a normal isotopic effect. If, however, the C₆H₆-C₆D₆ is examined, which on silica exhibits a

normal isotopic effect, in spite of the presence of π bonds, a reverse isotopic effect is still observed. The specific interaction due to Porapak on the adsorption of an isotopic pair seems, therefore, to be very slight.

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