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Note

Gas chromatography using the vapours of carbon tetrachloride and other compounds as carrier gases

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Many different gases are used as carriers in gas chromatography (GC), such as inert gases, methane[1], ethane[1], acetylene[2], carbon tetrachloride[3], ethanol[3,4], water[5,6], etc. The value of the partition coefficient of a sample varies with different carrier gases[1–3,7].

Using CCl_4 vapor as a carrier gas in GC, gaseous interdiffusion coefficients ($D_{1,2}$) for solute–carrier gas pairs have been determined[8]. The $D_{1,2}$ values for hydrocarbons in a CCl_4 atmosphere were nearly one-tenth of those in a He atmosphere.

The present paper describes the effect of the gaseous diffusion coefficient on the height equivalent of theoretical plate (H), the effect of different carrier gases on retention volumes (V_R) and the determination of $D_{1,2}$ for ethane and *n*-butane in chloroform and dichloromethane atmospheres.

EXPERIMENTAL

The apparatus used was a commercial gas chromatograph with a thermal conductivity detector (TCD), Shimadzu Seisakusho Ltd., Type GC 4B-PT, and an organic vapour generator[8], from which organic vapour was led to the column. The generator consisted of a nitrogen cylinder, solvent tank (40 ml) and heated cupper tube packed with small lead shot. The solvent, under 1.5–2.0 atm pressure, led to the heated copper tube through a needle, so that the solvent was converted into vapour in the tube.

The vapour of CCl_4, chloroform, dichloromethane or ethanol was employed as carrier gas. Columns were of stainless steel, I.D. 3 mm, and length 10, 20 or 100 cm. Column packing materials were dioctyl phthalate (DOP), 20% (w/w) on Chromosorb W AW (80–100 mesh) and Porapak S and Q (Waters Ass., Framingham, Mass., U.S.A.).

The line for the determination of diffusion coefficients was an injector, the first empty column (4.7 mm × 107 cm), a TCD, the second empty column (4.7 mm × 510 cm) and a TCD, in that order[8]. Ethane and *n*-butane, injected amount of each, 0.2 ml, were used as solute.

H was calculated from the retention time and half-peak width[10].

RESULTS AND DISCUSSION

Diffusion coefficients for solute–carrier gas pairs

The diffusion coefficient, $D_{1,2}$, was obtained by the following equation for an empty column[11,12].

$$H \cdot u = 2D_{1,2} + C \cdot u^2 \tag{1}$$

where C is coefficient and u (cm/sec) is the linear gas velocity. The experimental values of H and u, about 10–20 determinations, were substituted in the above equation to obtain $D_{1,2}$, calculated by the method of least squares. $D_{1,2}$ for ethane and *n*-butane in chloroform and in dichloromethane atmospheres were measured, as shown in Table I. These $D_{1,2}$ values are somewhat larger than those in a CCl_4 atmosphere, but about one-eight that of $D_{1,2}$ in a He atmosphere.

TABLE I

INTERDIFFUSION COEFFICIENTS FOR SOLUTE–CARRIER GAS PAIRS

Values are given in cm²/sec, at 1 atm. Figures in brackets are the experimental temperatures (°C).

Solute	*Carrier gas*			
	CH_2Cl_2	*$CHCl_3$*	*CCl_4*	*He*
Ethane	(117.7) 0.121 ± 0.002	(117.8) 0.107 ± 0.004	(117.1) 0.095*	(117) 0.809**
Ethane	(184.2) 0.163 ± 0.002	(184.7) 0.141 ± 0.003	(187.1) 0.131*	
n-Butane	(117.7) 0.075 ± 0.002	(118.0) 0.069 ± 0.005	(115.6) 0.057*	(117) 0.636**
n-Butane	(184.4) 0.104 ± 0.001	(184.7) 0.087 ± 0.001	(185.1) 0.074*	
Benzene			(130) 0.0480**	(130) 0.616**

* From ref. 8.

** Calculated values using the equation proposed by Hirschfelder *et al.*[9].

Effect of gaseous diffusion coefficient on H

The usual equation relating H with u is

$$H = A + 2\gamma D_{1,2}/u + C' \cdot u \tag{2}$$

where A, γ and C' are coefficients. If γ is a function of the column type, $2\gamma D_{1,2}$ for CCl_4, chloroform or dichloromethane carrier vapour is also about one-eighth of that for helium. The relationship between H and u was examined under the following conditions: column, Porapak S or Q or DOP, 20% (w/w) on Chromosorb W AW (80–100 mesh); samples, benzene, ethylbenzene, *n*-decane and *n*-butane; carrier gases, CCl_4 and He; column temperature, 130 or 90°; outlet pressure, 1 atm. Typical relationships are shown in Figs. 1 and 2.

For u values above 1 cm/sec, the natures of the relationship between H and u with CCl_4 and He carrier gases are similar. As u decreases from 1.0 to 0.2 cm/sec, H sharply increases with He, while H is nearly constant with CCl_4, owing to the low value of $D_{1,2}$ in CCl_4 atmospheres.

The linear gas velocity at the minimum value of H was about 0.5 cm/sec with CCl_4 as carrier gas (Fig. 2), but 1.3–1.5 cm/sec with methane, ethane or nitrogen as carrier gas[1], and about 3.0 cm/sec with He as carrier gas (Fig. 2). These results

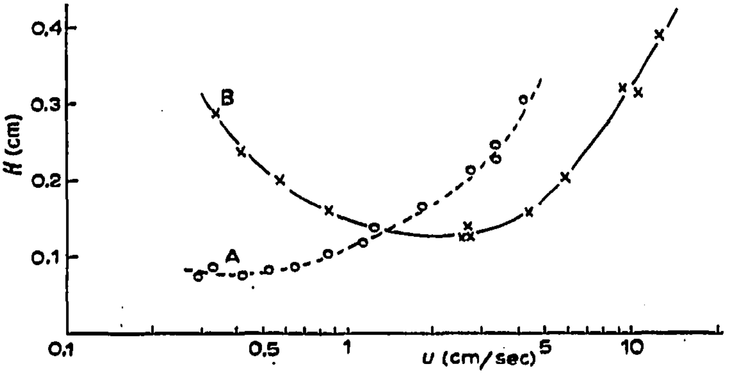

Fig. 1. Plot of H *vs.* u. Carrier gases of A and B are CCl_4 and He, respectively. Sample: benzene, 0.1 μl; column, 10 cm × 3 mm I.D., Porapak S (80–100 mesh); column temperature, 130°.

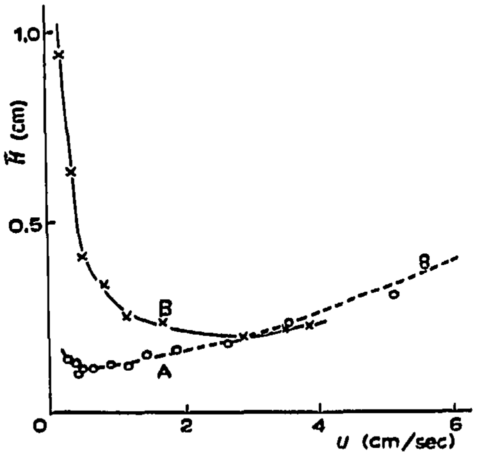

Fig. 2. Plot of H *vs.* u. Carrier gases of A and B are CCl_4 and He, respectively. Sample: ethylbenzene, 0.3 μl. Column: 20 cm × 3 mm I.D.; DOP, 20% (w/w) on Chromosorb W AW (80–100 mesh); temperature: 90°.

show that the value of u at minimum H depends on gas–gas diffusivities, in other words, the molecular weights of the carrier gases.

The chromatograms at minimum H (A′ and B) or at the same linear gas velocities (A and C) are shown in Fig. 3. The peaks in A′ are sharper than those in B; the peaks in C are very broad, but those in A are not. Fig. 3 shows the apparent effect of different carrier gases on chromatograms. It is suggested that a carrier gas of low diffusivity gives higher column efficiency at low gas velocity.

Ratio of retention volume

The effect of carrier gases on the retention volumes (V_R) are also examined, shown in Table II. The ratio of retention volumes is given by dividing the V_R of a sample with an organic carrier gas by the V_R of the sample with He or nitrogen as carrier gas. With liquid stationary phases, porous polymer and solid adsorbent the

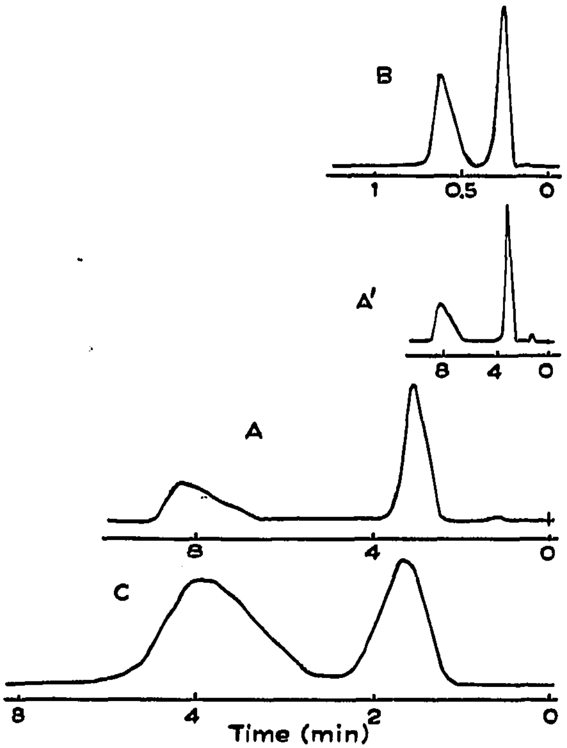

Fig. 3. Comparison of chromatograms. The sample is a mixture of ethylbenzene and *n*-decane, 0.7 μl. The first peak is identified as ethylbenzene, and the second as *n*-decane. Chromatograms A and B were obtained at minimum *H* values. Column: 20 cm × 3 mm I.D.; DOP, 20% (w/w) on Chromosorb W AW (80–100 mesh). A: Carrier gas, CCl_4; flow-rate, 0.5 cm/sec. B: Carrier gas, He; flow-rate, 3.8 cm/sec. C: Carrier gas, He; flow-rate, 0.48 cm/sec. Chromatograms A and A' are the same except for the time scale.

TABLE II

RATIO OF RETENTION VOLUMES WITH DIFFERENT CARRIER GASES

Column	*Carrier gas pair*	*Sample*	*Ratio of retention volumes*
DOP, 20% (w/w)	CCl_4,He	Ethylbenzene and *n*-decane	1.7–1.6
Silicone oil, 25 % (w/w)	CCl_4, N_2	*n*-Propanol, *n*-octane and toluene	1.2–0.9
	C_2H_5OH, N_2	As above.	0.7–0.5*
	C_6H_6, N_2	As above.	1.4–1.1*
Porapak S	CCl_4, He	*n*-Hexane, cyclohexane and benzene	0.18–0.15
Porapak Q	CCl_4, N_2	Benzene	0.4
Activated alumina	C_2H_5OH, N_2	Benzene	0.01

* From ref. 3.

relative retention volumes are 1.7–0.5, 0.4–0.1 and 0.01, respectively. The effect of an organic carrier gas on V_R is strongest in the case of activated alumina (30–60 mesh,

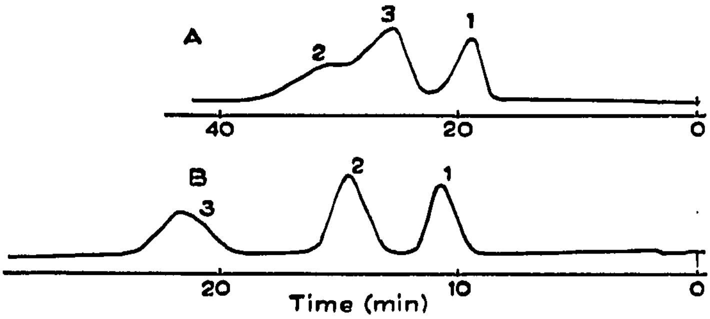

Fig. 4. Different elution orders with different carrier gases. The sample is a mixture of *n*-hexane (1), cyclohexane (2) and benzene (3), 0.3 μl. A: Carrier gas, He; flow-rate, 4.0 cm/sec. B: Carrier gas, CCl_4; flow-rate, 1.7 cm/sec. Column, 1 m × 3 mm, Porapak S (80–100 mesh).

Yanagimoto, Kyoto, Japan). It is suggested that the nature of a porous polymer is intermediate between those of liquid and solid adsorbents.

Fig. 4 shows the chromatograms with CCl_4 and He carrier gases. The elution order of samples in the chromatogram with He carrier gas is in the order of lower to higher boiling point, while that in the chromatogram with CCl_4 carrier gas is in the order of polarity of substances. Goldup *et al.*[7] also observed that the elution order of lower hydrocarbons varied when the carrier gas changed from hydrogen to nitrogen. It is suggested that the selection of carrier gas is an important factor in the separation of sample components in GC.

REFERENCES

1 K. L. Wagaman and T. G. Smith, *J. Chromatogr. Sci.*, 9 (1971) 241.
2 S. A. Greene and H. E. Roy, *Anal. Chem.*, 29 (1957) 569.
3 T. Tsuda, N. Tokoro and D. Ishii, *J. Chromatogr.*, 46 (1970) 241.
4 T. Tsuda, K. Ito and D. Ishii, *Bunseki Kagaku (Jap. Anal.)*, in press.
5 A. Nonaka, *Anal. Chem.*, 45 (1973) 483.
6 A. Nonaka, *Anal. Chem.*, 44 (1972) 271.
7 A. Goldup, G. R. Luckhurst and W. T. Swanton, *Nature (London)*, 193 (1962) 333.
8 T. Tsuda and D. Ishii, *Bunseki Kagaku (Jap. Anal.)*, 22 (1973) 528.
9 J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1967, Ch. 8.
10 G. L. Hargrove and D. T. Sawyer, *Anal. Chem.*, 39 (1967) 245.
11 G. L. Hargrove and D. T. Sawyer, *Anal. Chem.*, 39 (1967) 244.
12 J. C. Giddings and S. L. Seager, *J. Chem. Phys.*, 33 (1960) 1579.