GAS CHROMATOGRAPHY USING THE VAPOUR OF ORGANIC SOLVENTS AS CARRIER GASES

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SUMMARY

The vapour of organic solvents, such as ethanol, benzene and carbon tetrachloride was used as a carrier gas in gas chromatography. The effect of the vapour on the retention volume was examined at the liquid phase of polyethylene glycol, dioctyl phthalate and silicone oil. The experimental value of (gaseous diffusion coefficient for N_2 and octane)/(that for carbon tetrachloride and octane) was 2.3, which showed good coincidence with the calculated values.

INTRODUCTION

The carrier gases in gas chromatography (GC) usually used are permanent gases, while in some cases the vapour of formic acid[1] or water[2-5] is added to the permanent gas to reduce tailing in order to obtain reproducible and quantitative results. The use of water[6,7] or carbon dioxide[8] as a carrier gas has been recommended in the analysis of polar compounds, and the values of the partition coefficients of the samples obtained using the latter carrier gases vary in comparison with those obtained using permanent carrier gases.

This study attempts to use the vapour of organic solvents as carrier gas in GC, such as in other chromatographic methods that use many development solvents, and examines the effect of organic vapours on partition and diffusion coefficients in comparision with nitrogen as carrier gas.

EXPERIMENTAL

Apparatus

Fig. 1 shows the schematic flow system of a gas chromatograph consisting of three parts: (1) gas generator part, (2) separation column and (3) condensing part of organic carrier vapour. The three parts were maintained at constant temperature, and the connecting gas lines were heated with tape heaters. The 400-ml cupper tanks (A and B in Fig. 1), resistant column (D) (I.D. 4.5 mm) and a thermal conductivity
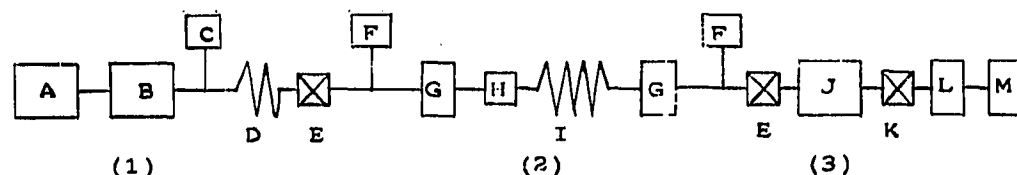
Fig. 1. Flow system consisting of (1) gas generator part, (2) separation column and (3) condensing part of organic carrier vapour. A = generator tank, B = buffer tank, C = pressure gauge, D = resistant column, E = needle valve, F = compound pressure gauge, G = detector, H = injector, I = column, J = trap for condensing of organic vapour, cooled with dry ice–methanol or water, K = stopcock, L = CaCl₂ trap, M = vacuum pump.

detector having tungsten filaments of 22 Ω were connected in order. Columns were of cupper tube, I.D. 4.5 mm, and supports were of 40–60 mesh of firebrick C-22. Temperature of the column was maintained at 125°. Silicone oil (DC-550), polyethylene glycol, dioctyl phthalate and other reagents were extra pure grade.

Procedure

The generator tank (A) contained approximately 300 ml of organic solvent. The system was evacuated by vacuum pump at room temperature and after evacuation the stopcock (K) was closed. Then the generator part (1) was heated to an adequate temperature (80–110°) at which the vapour of the solvent reached a pressure of 1–2 kg/cm². The flow rate of the solvent vapour was adjusted by controlling the inlet and the outlet pressures of the column, using needle valves (E). The column pressure and the temperature of the generator (1) were adjusted for a minimum noise level at the baseline. In some experiments the condensing part (3) was immersed in a water bath which was regulated at constant temperature, and the flow rate of organic carrier vapour was controlled by the temperature difference between generator part and condensing part without using needle valves. Before operating the gas chromatograph, the system was allowed to condition for several hours to reach an equilibrium of the organic vapour with the coating liquid. The flow rate was calculated by dividing the dead volume of the separation column by the retention time of hydrogen at the organic carrier vapour.

The vapour of carbon tetrachloride, benzene or ethanol was employed as a carrier gas. In most cases, 0.1–5 μl of a sample solution were injected. The gas chromatograph was usually operated at the reduced pressure.

Ratio of retention volume (RRv)

The ratio of the retention volume is given by dividing the retention volume (Rv) of a sample with an organic carrier vapour by a standard retention volume of the same sample with nitrogen carrier gas. Since a retention volume of octane vapour with nitrogen carrier gas was independent of the mean absolute pressure, from 150 to 800 mm Hg, the retention volume of each sample was taken as the standard retention volume when the outlet pressure of a column was 1 atm.

RESULTS AND DISCUSSION

The gas chromatograph using organic vapour as a carrier gas gave an excellent baseline and sensitivities which were nearly equal to the ordinary gas chromatograph

with nitrogen carrier gas. An example of the chromatogram with organic carrier vapour is shown in Fig. 2.

Relation between Rv and mean absolute column pressure

It is shown in Fig. 3 that the retention volumes of n-octane and toluene depended on the absolute column pressure, while the retention volume of n-propanol did not. The higher the mean absolute column pressure, the more soluble was the vapour of organic solvent into a liquid phase according to Henry's law. Then it is suggested that the nature of the silicone oil was somewhat altered due to the dissolution of carbon tetrachloride vapour in it. The tendency of the retention volumes shown in Fig. 3 might be explained by the above reason.
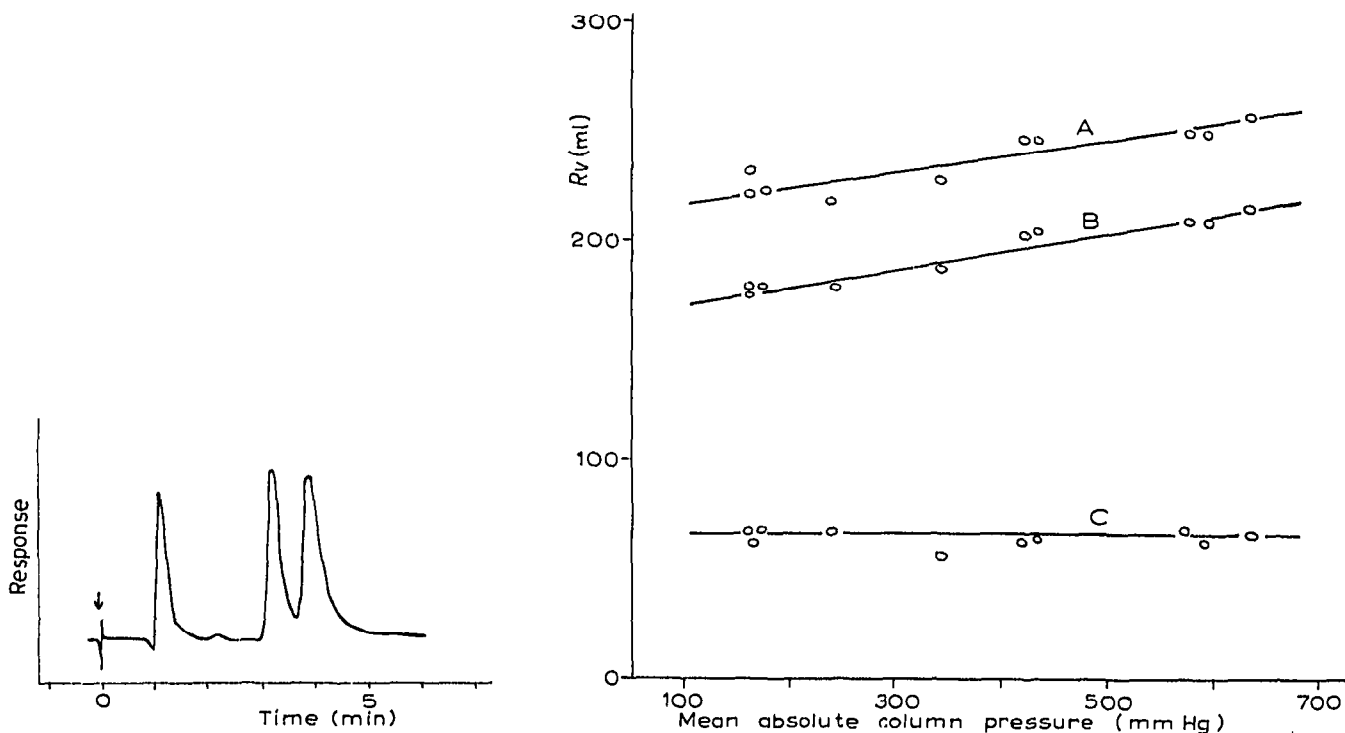

Fig. 2. Chromatogram using CCl_4 vapour as a carrier gas. Column, silicone oil 25% on firebrick C-22, temperature, 125°; column pressure, P_i, 515 mm Hg; P_o, 145 mm Hg; flow rate, 60 ml/min; sample, 0.5 μl of a mixture of toluene, n-octane and n-propanol.

Fig. 3. The relation between the mean absolute column pressure and retention volume with CCl_4 carrier vapour. A = n-octane, B = toluene, C = n-propanol. Column, silicone oil 25% on firebrick C-22; temperature, 125°; flow rate, 32–20 ml/min.

Second virial coefficients for carrier vapours and solute vapours

The second virial coefficient (B_{12}) characterizes the interaction between unlike molecules. The calculated values of B_{12} for CCl_4-n-octane, N_2-n-octane, CCl_4-toluene and N_2-toluene are — 1020, —220,— 1010 and —241 cm^3·mole^{-1}, respectively. They were calculated using the empirical formulas proposed by GUGGENHEIM AND McGLASHAN[9]. Since the values of the second virial coefficients for carbon tetrachloride vapour and solute vapours are more negative than coefficients for nitrogen and solute vapours, the state of the former gas deflects more than the latter from that of an ideal gas.

TABLE I

RATIO OF RETENTION VOLUMES WITH TWO DIFFERENT ORGANIC CARRIER VAPOURS AND THREE DIFFERENT LIQUID PHASES

Sample	Liquid phase	Polyethylene glycol		Dioctyl phthalate		Silicone oil	
	Organic carrier vapour	C_2H_5OH	C_6H_6	C_2H_5OH	C_6H_6	C_2H_5OH	C_6H_6
Ethanol					1.7		1.9
n-Propanol		0.9	1.0	0.8	1.2	0.7	1.4
n-Octane		0.7	0.8	0.8	1.0	0.5	1.3
Toluene		0.7	0.9	0.7	1.0	0.6	1.1

It is reasonable to assume that the gas state of other organic carrier and solute vapours, same as carbon tetrachloride and solute vapours, deflects from an ideal gas state in comparison with nitrogen and solute vapours.

Ratio of retention volume with two different organic carrier vapours and three different liquid phases

It was suggested that the two factors, which were mentioned above, had an important effect upon GC with the organic carrier vapour. The experimental values shown in Table I were given mostly under the following experimental conditions: column 170 cm × 4.5 mm I.D.; liquid phase 25 w/w % on firebrick C-22; temperature 125°; column pressure, P_t, 280–150 mm Hg; P_o, 120–60 mm Hg; flow rate, 20–40 ml/min.

The RRv with the ethanol carrier vapour on silicone oil is remarkably smaller than one, and the RRv with benzene carrier vapour on polyethylene glycol was comparatively smaller than the RRv with benzene carrier vapour on silicone oil. The result is that the RRv is relatively small when the polarity of the organic carrier vapour has the reverse polarity of the liquid phase.

The sample of alcohols generally showed a large RRv with benzene carrier vapour in comparison with other sample. It is suggested that a thin adsorption layer of benzene existed on the surface of liquid phase, and this delayed transfer of the sample into the gas phase. The phenomenon of the surface adsorption of organic vapour, solute, on the surface of liquid phase in gas chromatography with helium carrier gas was also reported by MARTIN[10], MARTIRE[11] and PECSOK et al.[12]. The existance of the surface layer was suggested in GC using a gas mixture of water vapour and helium as a carrier gas[4].

It is also suggested that the small RRv of n-propanol with ethanol carrier vapour is due to the retention of the sample in the surface adsorption layer and/or to the interaction between n-propanol and ethanol in the gas phase. The small values of octane and toluene with ethanol carrier vapour are explained by the altered nature of the liquid phase resulting in the dissolution of ethanol into it.

Gas diffusion coefficient (D_{gas})

An equation relating the height equivalent to a theoretical plate (H) with the linear gas velocity (u) is[13]

$$H = 2\lambda d_p + \frac{2\gamma D_{gas}}{u} + \frac{8}{\pi^2} \cdot \frac{k'}{(1 + k')^2} \cdot \frac{d_f^2}{D_{liq}} \cdot u$$

The symbols are defined as in the report of BOHEMEN AND PURNELL[14]. For convenience in discussion, the equation is written more simply

$$H = A + B/u + Cu$$

The linear gas velocity at the minimum H was about 5.2 cm/sec with carbon tetrachloride carrier vapour but 7.4 cm/sec with nitrogen carrier gas under the following experimental conditions: column (170 cm × 4.5 mm I.D.); silicone oil, 25w/w% on firebrick C-22 (40–60 mesh); temperature, 125°; column pressure, P_0, 80 mm Hg; sample, n-octane.

The values of A evaluated by the usual graphical method for the data obtained in the above experimental condition were negative. Since negative values of A are unacceptable to the theory, the eddy diffusion term, A, might be flow dependent, and the van Deemter equation should be written

$$H = (A + B)/u + Cu \tag{1}$$

Eqn. 1 is proposed by BOHEMEN AND PURNELL[14]. According to eqn. 1 the plot of Hu vs. u^2 should be linear, of slope C and intercept $A + B$. Fig. 4 shows such a graph for the data obtained under the above experimental condition.
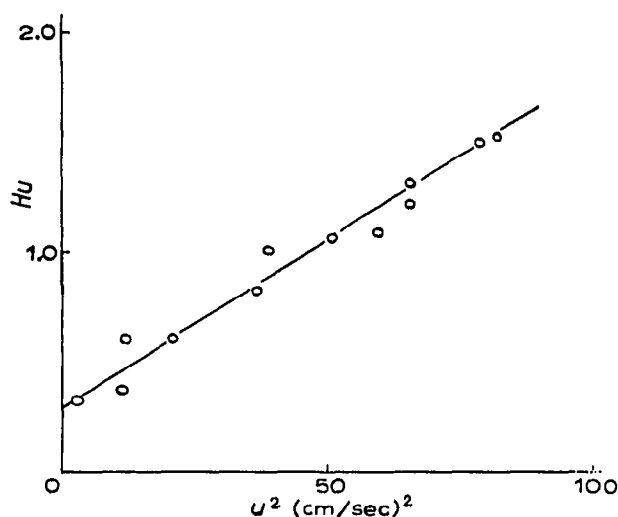

Fig. 4. Plot of Hu vs. u^2. Column, silicone oil 25% on firebrick C-22 (40–60 mesh); temperature, 125°; organic carrier vapour, CCl$_4$; sample, n-octane (1 μl).

Assuming $\lambda = 2$, the value of A was calculated, then the value of B was evaluated. The value of B_1/B_2 is equal to $D_{gas,1}/D_{gas,2}$, which is defined as the relative diffusion coefficient. The experimental value obtained by dividing the D_{gas} for nitrogen and n-octane by the D_{gas} for carbon tetrachloride and n-octane was 2.3. This experimental value of relative diffusion coefficient for n-octane–carrier vapour pairs shows good coincidence with the calculated value using the empirical formula of GILLILAND[15], 2.5, and using the formula derived by HIRSCHFELDER et al.[16], 2.0. We believe that GC using the vapours of organic solvents as a carrier gas will prove to be a new tool for the determination of gaseous diffusion coefficients.

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