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GAS–MODIFIED SOLID CHROMATOGRAPHY USING ORGANIC VAPOURS AS CARRIER GAS

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SUMMARY

The vapour of an alcohol or other organic compound can be used as the carrier gas for gas–modified solid chromatography for the separation of mixtures of α- and β-naphthol, phenols and esters, using silica gel as solid adsorbent. The effect of four different carrier vapours (*n*-hexane, *n*-butyl chloride, ethyl acetate and ethanol) on the retention volume was examined using activated alumina and substituted benzenes as samples. It is suggested that the sample is retained by both multi-layer adsorption and on the adsorbent. The approximate calculation of ΔH at a constant column temperature has also been attempted.

INTRODUCTION

The use of water[1], ammonia[2], carbon dioxide[3], carbon tetrachloride[4], benzene[5] or other vapours[4,5] as carrier gas in gas–liquid chromatography (GLC) has been recommended for the analysis of polar compounds, and the partition coefficients of the samples obtained using these carrier gases vary in comparison with those obtained using permanent carrier gases. The gaseous diffusion coefficient for the solute in the organic carrier vapour has also been determined[4].

On the other hand, vapours of lower alcohols[6,7] and water[8–10] have been used as carrier gases in gas–solid chromatography with activated alumina, magnesium silicate, magnesia or diatomaceous firebrick as the adsorbent. When ethanol and activated alumina are used as the carrier gas and solid adsorbent, respectively, the retention volume (V_r) of benzene is about one-hundredth of that when nitrogen is used as carrier gas[6]. It has been suggested that the ethanol vapour is adsorbed on the surface of activated alumina and forms a thin layer of liquid[6,7,9]. This layer of alcohol on the adsorbent is formed by multi-layer physical adsorption when the pressure of the adsorbate is comparatively high[11].

The purpose of this paper is to describe the performance of such a chromatographic system using a UV detector and organic vapours as carrier gas, the separation of α- and β-naphthol, phenols, esters and substituted benzenes, and consideration of the separation mechanism.

EXPERIMENTAL

Procedure

A constant flow-rate liquid pump was utilized to pump the liquid into a vapourizer for the purpose of generating vapour[6,12]. One of the two sample injection ports of the Shimazu 4BPT gas chromatograph (Shimazu Seisakusho, Kyoto, Japan) was employed as a vapourizer. This port was maintained at 200–250 °C by an electric furnace. The two sample injection ports were connected with each other with a stainless-steel tube of length 30 cm and I.D. 1 mm. The sample was injected into the second injection port.

The effluent from the separation column was conducted directly into a small condenser[12] by a heated pipe-line of stainless-steel of length 30 cm and I.D. 1 mm.

In the condenser, the carrier gas vapour was condensed, and the liquid was then led into a UV absorption detector for detection at 254 or 280 nm (Laboratory Data Control, Riviera Beach, Fla., U.S.A.)[6,12]. The procedure was carried out as described earlier[6,12].

Adsorbents and columns

The solid adsorbents used were as follows: activated alumina (100–300 mesh, Brockman activity II–III; E. Merck, Darmstadt, G.F.R.); silica gel K 923 (100–200 mesh; Katayama Chemical Co., Osaka, Japan); silica gel (70–230 mesh; E. Merck); controlled pore glass (CPG-10-120; Electro-Nucleonics, Fairfield, N.J., U.S.A.); glass beads (30–60 mesh; Nishio Kogyo, Tokyo, Japan); porous glass (60–80 mesh; Gasukuro Kogyo, Tokyo, Japan); HS-Pellumina (H. Reeve Angel, Clifton, N.J., U.S.A.); and Chromosorb W AW (100–120 mesh; Johns-Manville, New York, N.Y., U.S.A.).

The columns used were stainless-steel tubes, length 50–100 cm and I.D. 3 mm. All chemicals used were of extra-pure grade. The recorder used was a Type 2H31G (Yokogawa Electric Works, Tokyo, Japan).

RESULTS AND DISCUSSION

Using activated alumina and ethanol or methanol as carrier vapour, a mixture of benzene, *p*-xylene, di-*n*-propyl ketone, naphthalene, diphenyl and anthracene, and a mixture of ketones, were separated[6]. By using this method, the isomers of anthracene and phenanthrene and *o*-, *m*- and *p*-dinitrobenzenes were completely separated[7], although these separations are very difficult to achieve by conventional GLC. When activated alumina was used as adsorbent, the phenols and naphthols were not eluted owing to the irreversible adsorption on the adsorbent[6].

Separation of α- and β-naphthol

As α-naphthol and β-naphthol have nearly same boiling points (288 and 285–286 °C, respectively), in order to separate them the selection of the most suitable stationary phase[13] or their conversion into their trimethylsilyl ethers[14] is important when using conventional gas chromatography. Using silica gel K 923, they are separated as shown in Fig. 1. The resolution of the two peaks[15] is 1.05.

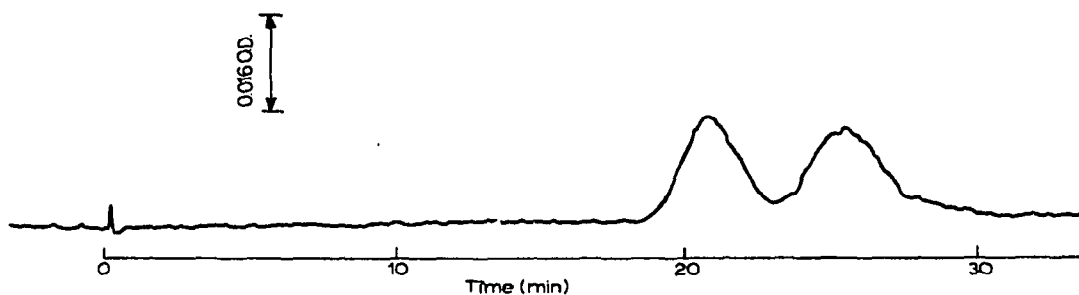The separation using 10 % water–ethanol vapour at a flow-rate of 250 µl (in liquid

Fig. 1. Chromatogram of α- and β-naphthol. α-Naphthol is eluted first and β-naphthol second. Carrier vapour, 10% water–ethanol; adsorbent, silica gel K 923 (100–200 mesh); column length, 50 cm; column temperature, 190 °C; wavelength of UV detector, 280 nm; amount of sample, 4 μl of ethanol solution containing 0.17% of α- and 0.18% of β-naphthol.

state)/min as carrier gas is better than when 100% ethanol vapour is used at the same flow-rate. Also, the retention times of naphthols using the former vapour are about 5–8 min longer than those using the latter. It is suggested that the retention time is dependent on the nature of the carrier vapour owing to changes in the nature of the thin liquid layer on the adsorbent. The same phenomenon is also observed for the retention volumes of dinitrobenzenes when a small amount of ethanol is added to methanol[7]. The length of the silica gel column is only 50 cm, although in conventional GLC the columns used are longer (e.g., 2–3 m)[13,14]. This gas–modified solid chromatography may be excellent in the separation of isomers.

Chromatography of phenols and esters

The separation of a mixture of phenols, such as dimethyl-, methyl-, ethyl- and nitrophenol, has been attempted. Typical chromatograms are shown in Fig. 2. There
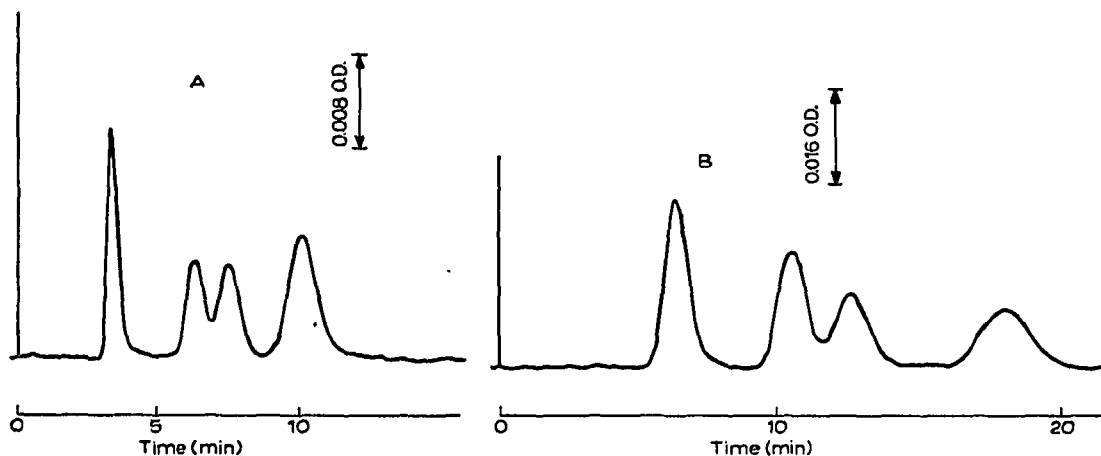

Fig. 2. Chromatograms of phenols. Carrier vapour, ethanol; adsorbent, silica gel K 923; column length, 50 cm; wavelength of UV detector, 280 nm. A: amount of sample, 5 μl of a solution containing 0.02% of o-nitrophenol, 0.09% of 2,5-, 0.09% of 2,3- and 0.05% of 3,4-dimethylphenol; column temperature, 170 °C. B: amount of sample, 2 μl of ethanol solution containing 0.4% of phenol, 0.25% of m-cresol, 0.1% of 2,4-dimethylphenol and 0.1% of p-ethylphenol.
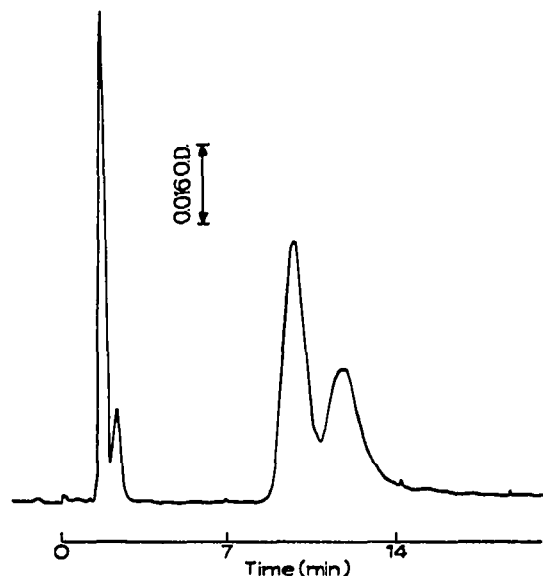
Fig. 3. Chromatogram of esters. Carrier vapour, ethanol; adsorbent, silica gel K 923; column temperature, 190 °C; wavelength of UV detector, 254 nm; amount of sample, 7 μl of ethanol solution containing 0.08 % of methyl benzoate, 0.09 % of p-tolyl acetate, 0.12 % of terephthalic acid dimethyl ester and 0.06 % of phthalic acid dimethyl ester.
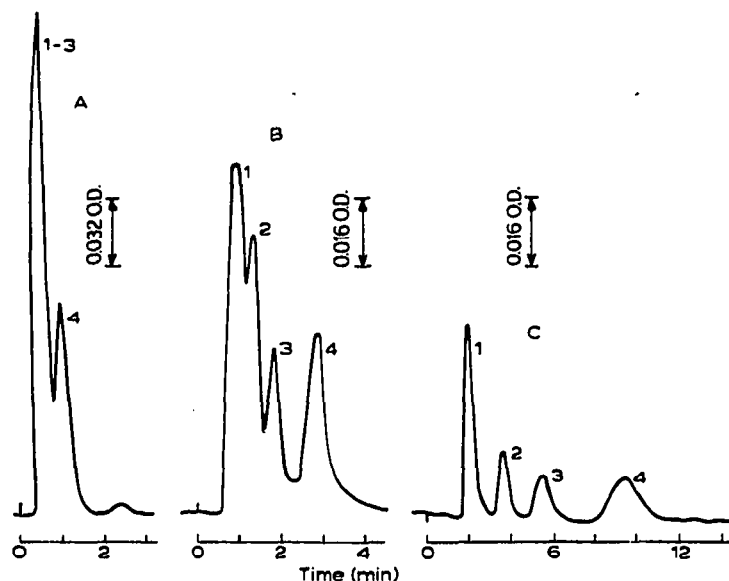

Fig. 4. Chromatograms obtained using (A) ethanol, (B) ethyl acetate and (C) n-hexane vapour. Adsorbent: activated alumina (100–300 mesh); column temperature, 150 °C; column length, 75 cm; amount of sample, 1–3 μl of ethanol solution containing about 1 % of benzene (1), toluene (2), ethylbenzene (3) and n-propylbenzene (4).

is a linear relationship between the boiling point of the sample (T_b) and ln V_r for the phenols, except *o*-nitrophenol, under the following experimental conditions: ethanol vapour and silica gel are used; column temperature 190°C; column length 50 cm. *o*-Nitrophenol has a large relative retention time owing to the action of the nitro group. The isomers of cresols and phenols are also separated by columns of controlled pore glass, porous glass and HS-Pellumina. The column efficiency using these adsorbents is not as high as with silica gel. The chromatogram of esters is shown in Fig. 3.

Effect of different carrier vapours on retention volume

A change of carrier vapour has a considerable effect on the retention volumes of the sample components, as shown in Figs. 4 and 5.
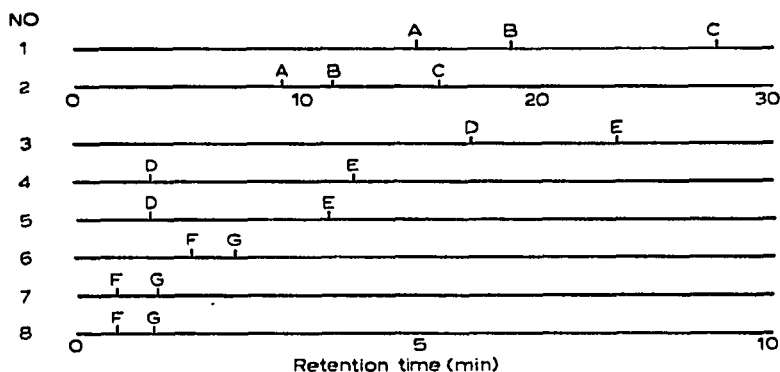

Fig. 5. Effect of different carrier vapours on retention time. Carrier vapours: benzene (1), 10% benzene–ethanol (2), 1% ethanol–isooctane (3 and 6), ethanol (4 and 7) and 1% water–ethanol (5 and 8). Flow-rates of carrier vapours were constant at 200 μl/min. A–G represent the peak positions of samples A–G: (A) phenol, (B) *o*-cresol, (C) *m*-cresol, (D) *p*-diisopropylbenzene and (E) its impurity, (G) cumene and (F) its impurity. Nos. 1 and 2: adsorbent, silica gel K 923; column, length 50 cm, I.D. 3 mm; column temperature, 140°C. Nos. 3–8: adsorbent, HS-Pellumina; column, length 1 m, I.D. 2 mm; column temperature, 150°C.

Using 1% ethanol–isooctane as carrier vapour, the thin liquid layer on the surface of silica gel may be composed of a mixture of ethanol and isooctane, but when 100% ethanol is used as carrier vapour, the layer is composed of ethanol molecules only. This difference is caused by the difference in the V_r values of the sample components. It is suggested that in this chromatography the sample is retained with the thin layer of liquid. The thickness of this layer of liquid will be discussed later[16]. In our preliminary experiment, the thickness was found to be about 2–10 molecules in the case of ethanol carrier vapour and activated alumina at a column temperature of 100–150 °C (ref. 16).

Using four different polar vapours (*n*-hexane, *n*-butyl chloride, ethyl acetate and ethanol) and three different adsorbents (glass beads, Chromosorb W AW and activated alumina), the V_r values of alkylbenzenes, halogenated benzenes and other compounds were examined at a column temperature of 150°C with a column length of 75 cm and a flow-rate of solvent of 200 μl/min. In the case of glass beads and Chromosorb W AW, the ratio of V_r with *n*-hexane to V_r with ethanol vapour is less

than 2, but in the case of activated alumina the corresponding ratio is 3–15. In the latter case, the effect of the carrier vapour on V_r is very large as the strongest adsorbent of the three is involved. Figs. 4 and 6 show the V_r values with four different carrier vapours using activated alumina.

The parameter ε, representing the relative strengths of the different solvents, are 0.00, 0.30, 0.58 and 0.88 for n-hexane, n-butyl chloride, ethyl acetate and ethanol, respectively[17,18]. The V_r values in Fig. 6 become larger as the value of ε becomes smaller. This tendency is similar to that in thin-layer and liquid chromatography.
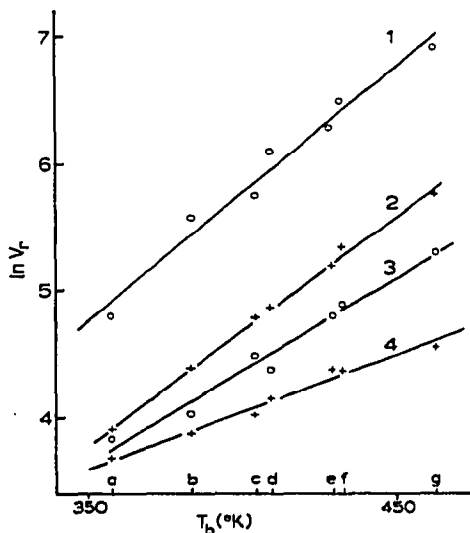

Fig. 6. Effect of different carrier vapours on retention volume on activated alumina. Carrier vapour: n-hexane (1), n-butyl chloride (2), ethyl acetate (3) and ethanol (4). Sample: toluene (b), ethylbenzene (d), n-propylbenzene (f), fluorobenzene (a), chlorobenzene (c), bromobenzene (e) and iodobenzene (g). Column temperature, 150 °C; flow-rate of each carrier vapour, 200 μl/min; sensitivity of UV detector, 0.32 or 0.16 O.D. The retention volume (V_r, ml) used was corrected with a factor for pressure drop in the column. The adsorbent was activated alumina (100–300 mesh), and the column length was 75 cm.

Approximate calculation of ΔH

The linear relationship between ln V_r and T_b has been observed for homologous series in conventional gas chromatography. Fig. 6 shows semi-logarithmic plots of V_r for alkyl benzenes and halogenated benzenes as a function of their boiling points, T_b (°K). The linear relationship is also valid in this chromatography. Then

$$\ln V_r = K_1 T_b + A_1 \tag{1}$$

where K_1 and A_1 are constants. The slope of the straight line (K_1) is large for n-hexane (0.0200), medium for n-butyl chloride (0.0180) and ethyl acetate (0.0145) and small for ethanol (0.00894), and the correlation coefficients are 0.986, 0.998, 0.988 and 0.987, respectively.

In the usual gas chromatography, the heat of evaporation of the solute from solution or its heat of desorption from the adsorbent, ΔH_s, is obtained by measuring the specific retention volume (V_g) at different column temperatures (T_c) using the following equation[19]:

$$\ln V_g = (\Delta H_s) (RT_c)^{-1} + A_2 \qquad (2)$$

where A_2 is a constant of integration. But in this chromatography, the thickness of multi-layer adsorption of the vapour and its nature may be varied with changes in column temperature. We therefore cannot obtain ΔH by using eqn. 2. At constant column temperature, we can obtain an approximate value for ΔH as follows.

The heat of evaporation is related to the boiling point of the solute by Trouton's rule by $\Delta H_v/T_b = 21$ cal·°K^{-1}·mole^{-1}. When the three alkylbenzenes and four halogenated benzenes in Fig. 6 are used as solutes, the mean value obtained by dividing their heats of evaporation (ΔH_v) at 150 °C (ref. 20) by each T_b is nearly constant (21.3), and the standard deviation is 1.32. It can be considered that ΔH_v and ΔH_s are nearly equal.

The following approximate relationship may be set up in this chromatography:

$$H_{150\ °C}/T_b = K_2 \qquad (3)$$

where K_2 is a constant. Eqn. 2 becomes

$$\ln V_g = (K_2 T_b) (RT_c)^{-1} + A_2 \qquad (4)$$

In considering retention volumes relative to a standard, the constant term is immaterial. Eqns. 1 and 4 become

$$\ln V_{r,i}/V_{r,1} = K_1 (T_{b,i} - T_{b,1}) \qquad (5)$$

and

$$\ln V_{g,i}/V_{g,1} = K_2 (T_{b,i} - T_{b,1}) (RT_c)^{-1} \qquad (6)$$

where the subscripts i and 1 represent the solute i in a homologous series and the standard solute, respectively. As the $\ln V_{r,i}/V_{r,1}$ values are equal to $\ln V_{g,i}/V_{g,1}$, one obtains

$$K_1 = K_2/RT_c \qquad (7)$$

Eqn. 7 shows that K_2 can be obtained from the slope of the straight line shown in Fig. 6 and the ΔH values are obtained using eqn. 3.

The ΔH values of the solutes used in this chromatography are shown in Table I, obtained using the above approximate calculation. It is suggested that the average deviation of ΔH may be within about 15% owing to the assumptions made in eqn. 3.

The value of ΔH for n-hexane carrier vapour is 1–2 kcal/mole lower than the value of the heat of evaporation, and about 8 kcal/mole lower than the heat of desorption on activated alumina[16], while the value of ΔH for alcohol carrier vapour, 2.7–3.5 kcal/mole, is 30–50% of the heat of evaporation. The values in Table I show

TABLE I

CALCULATED VALUES OF ΔH (kcal/mole) IN THE SYSTEM OF FOUR CARRIER VAPOURS AND ACTIVATED ALUMINA AT 150 °C

The ΔH_v values were calculated using the relation of Fig. 6.

Carrier vapour	ΔH_v*	Sample						
		$CH_3C_6H_5$	$C_2H_5C_6H_5$	$n\text{-}C_3H_7C_6H_5$	FC_6H_5	ClC_6H_5	BrC_6H_5	IC_6H_5
n-Hexane	5.33	6.5	6.9	7.3	6.0	6.8	7.2	7.8
n-Butyl chloride	6.12	5.8	6.2	6.6	5.4	6.1	6.5	7.0
Ethyl acetate	6.27	4.7	5.0	5.3	4.4	5.0	5.3	5.7
Ethanol	7.39	2.9	3.1	3.3	2.7	3.0	3.2	3.5
ΔH_v*		7.37	8.36	9.31		8.62	9.38	10.8

* ΔH_v at 150 °C was calculated from each ΔH_v at the boiling points, using the equation proposed by Sato[20].

that the surface of the adsorbent using carrier vapour is covered with condensed vapour and the solute is not adsorbed directly on the adsorbent, or the solute which is adsorbed directly is displaced by molecules of carrier vapour.

The small value of ΔH for ethanol vapour may be explained as follows. If the heat of evaporation of a solute from its ethanolic solution is more than about 1 kcal/mole higher than the heat of evaporation and the effect of solid adsorbent on the solute is about 1 kcal/mole, the solute on the thin layer of ethanol may be displaced by one ethanol molecule from the condensed thin layer of ethanol, and the calculated value of ΔH may be 2–3 kcal/mole. It is suggested that the small value of ΔH for ethanol vapour is favourable for the separation of high-boiling substances by this type of chromatography.

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