CHARACTERISTICS OF GAS-LIQUID CHROMATOGRAPHY

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Abstract—The effects of sample size, liquid loading, particle size, column length, and column temperature on retention volumes were studied and separation factor, column efficiency, partition coefficient, and heat of solution were also obtained by gas-liquid chromatography. The feed materials were chosen by similar boiling points as diethylether, dimethoxymethane and dichloromethane.

The relations between retention volume and above mentioned various variables were obtained. Separation factor was more affected by column temperature than other variables, and decreased with the temperature. HETP increased almost linearly with sample size. From the exponential relationship between partition coefficient and column temperature heat of solution of each material was calculated.

INTRODUCTION

Gas chromatography (GC) has been used for separating components from mixtures of volatile compounds. In most applications, the separations are made to identify and determine the quantity of each component in a mixed sample.

After the first work on gas-liquid chromatography (GLC) by James and Martin, subsequent works showed that adsorption on the solid support played a relatively important role in GLC[1]. In recent years, much efforts have been made to determine the transport properties[2]. Due to complexity of random pore shape and size, exact phenomena of distribution of stationary liquid phase (SLP) on the solid support have not been clarified.

The purpose of this study is to examine the variables affecting on the efficiency of the chromatrgraphic column and to obtain heat of solutions of three sample materials by GLC.

EXPERIMENTAL

Reagents

Non-acid washed Chromosorb A(Manville Co.) was used as solid support and its characteristics are[3]: (1) use in preparative scale GC (2) good capacity to hold the SLP (25% liquid loading maximum) (3) surface that is not highly adsorptive (4) structure that does not readly break down with handling. Dichloromethane (DCM), diethylether (DEE) and dimethoxymethane (DMM) were used as sample materials and their boiling points are 39.8°C, 34.6°C and 41.5°C, respectively.

As a stationary liquid phase, dinonylphthalate [DNP: $C_6H_4(COOC_9H_{19})_2$] was used, and its recomended maximum temperature is 175°C. Liquid coating on Chromosorb A was done by vacuum rotary evaportor (Brinkmann Co.) and chloroform was used as solvent. The column was packed with the Chromosorb A by a vibrator, and both ends were filled with glass wool.

Apparatus and Operating Conditions

Fig. 1 is a block diagram of the experimential apparatus. Helium from a cylinder passed successively through the flow controller, the chromatographic column, the thermal conductivity cell, and the bubble flowmeter. Samples for analysis were injected at S with a microliter syringe (Hamiltonian Co.) and a HP 3390A integrator analysed their output peaks.

A gas chromatograph (GOW MAC 550P TCD) was used to obtain retention volume of each component and the column was made by 1/8" copper tube, and the detector temperature was fixed at 250°C. Table 1 shows the operation conditions.

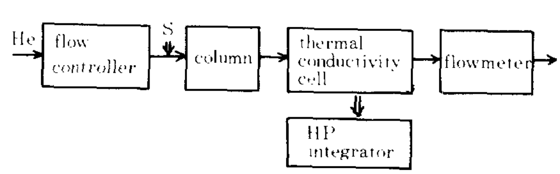

Fig. 1. Schematic diagram of analytical gas chromatography.

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RESULTS AND DISCUSSION

Effect of Variables on Retention Volume

The effect of variables on retention volume are presented in Figs. 2 to 4 as plot of liquid loading versus retention volume. The variables are mesh size, column length and column temperature in Figs. 2, 3, and sample material in Fig. 4. They show that the retention volume increases with the liquid loading. SLP-loading on the solid support is expressed as the percentage ratio of the weight of SLP to that of solid support. But in the case of 60/80 mesh and 30% liquid loading, separation is not completed and the retention volume decreases sharply.

As shown in the previous results, the retention volume was influenced by the liquid loading, mesh size, and column length. The retention volume was correlated by these variables and the result is expressed by the following equation:

$$V_N = a_1 W^{a_2} R_p^{a_3} L^{a_4} \qquad (1)$$

where W, R_p, and L are the liquid loading, average particle radius, and column length, respectively. The Chromosorb A of three particle sizes (R_p = 1.00, 1.36, 3.13 mm) were used, and average particle size were determined by screen analysis.

Table 2 shows the parameters in Eq. (1) at different experimental cases. And Figs. 5 and 6 represent the comparisons between experimental data and correlations.

Figs. 7 and 8 represent the effect of sample size. The retention volume decreses as increasing sample size slightly. There are probably two principal reasons for the variation of retention volume with sample size[4]: (1)

Table 1. Operating Conditions.

Column temp. (℃)	55 – 120
Column length (cm)	150, 200, 250, 400
Packing size (mesh)	20/30, 45/60, 60/80
Liquid loading (%)	10, 20, 25, 30
Sample volume (μl)	1, 3, 5, 10, 20

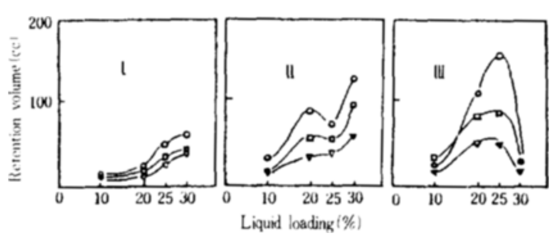

Fig. 2. Effect of liquid loading on retention volume

(column temperature, 55℃; 5μl sample size, DEE; I: 20/30 mesh, II: 45/60 mesh, III: 60/80 mesh; column length, △ = 1.5m, □ = 2.0m, ○ = 2.5m).

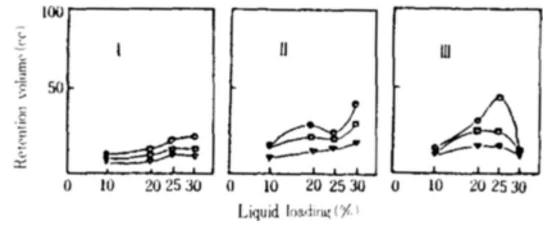

Fig. 3. Effect of liquid loading on retention volume

(column temperature, 120℃; 5μl sample size, DEE; I: 20/30 mesh, II: 45/60 mesh, III: 60/80 mesh; column length, △ = 1.5m, □ = 2.0m, ○ = 2.5m).

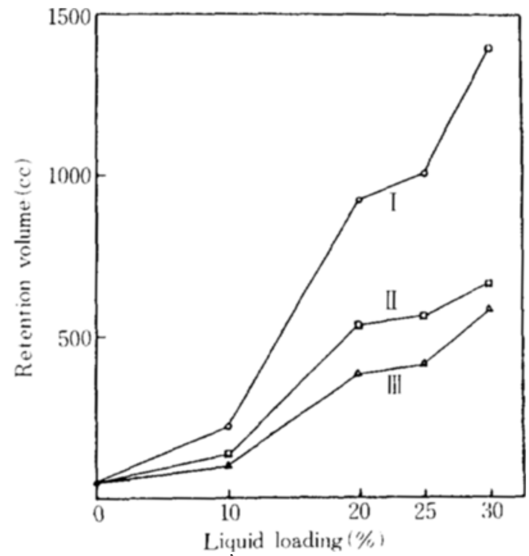

Fig. 4. Effect of liquid loading on retention volume

(55℃; 4m column length; 45/60 mesh; I: DCM, II: DEE, III: DMM).

Table 2. Parameters of Regression.

Temperature	Material	a_1	a_2	a_3	a_4
55℃	DEE	4.78	1.26	−0.82	1.26
	DMM	5.01	1.32	−0.89	1.30
	DCM	7.64	1.53	−0.96	1.30
120℃	DEE	1.05	0.56	−0.59	1.11
	DMM	1.64	0.68	−0.66	1.15
	DCM	1.98	0.93	−0.75	1.21

$V_N = a_1 W^{a_2} R_p^{a_3} L^{a_4}$

non-sharp input distribution and (2) finite vapor concentration in the column. Because the samples adopted in this experiment are very volatile at the column temperature, the effect of (1) is negligible. The latter, (2) is important under the condition of small cross-sectional area of column with volatil material. Effect of the finite vapor concentration in the column is to cause retention volumes to decrease with increase in sample size, and

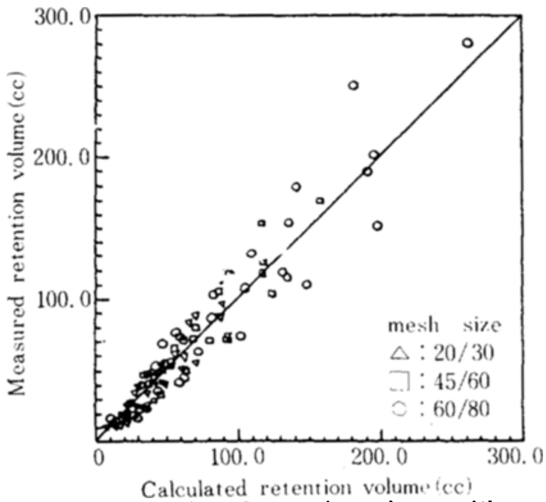

Fig. 5. Correlation of retention volume with respect to liquid loading, column length, particle size
(column temperature; 55℃).

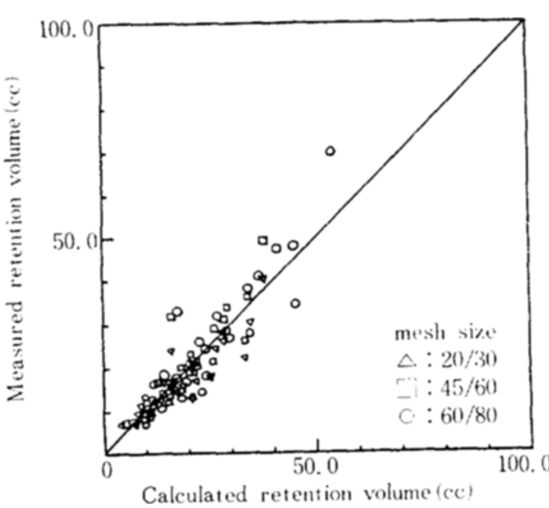

Fig. 6. Correlation of retention volume with respect to liquid loading, column length, particle size
(column temperature; 120℃).

so the chromatographic curves become skewed (Fig. 8). As decreasing the retention volume, analysis was done rapidly but resolution was worse.

Separation Factor (S.F.)

Retention volumes have been widely used in quantitative analyses aimed at identifying chromatographic zones[5], and separation factor is defined as:

$$S.F. = \frac{V_a}{V_b} \tag{2}$$

where V_a and V_b are retention volume of component a and b, respectively.

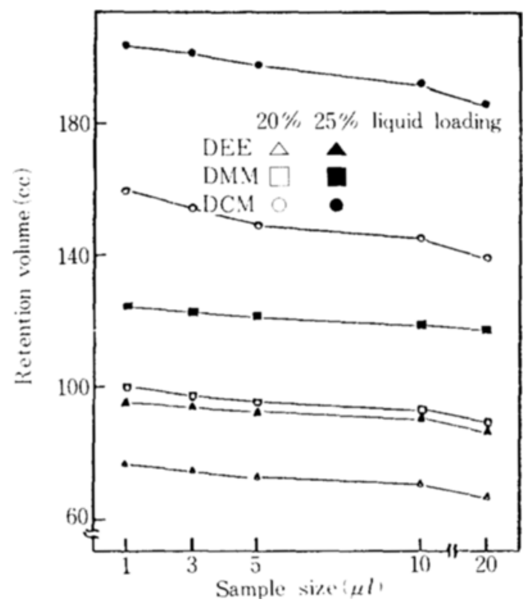

Fig. 7. Effect of sample size on retention volume
(2m column length, 60/80 mesh, 55℃).

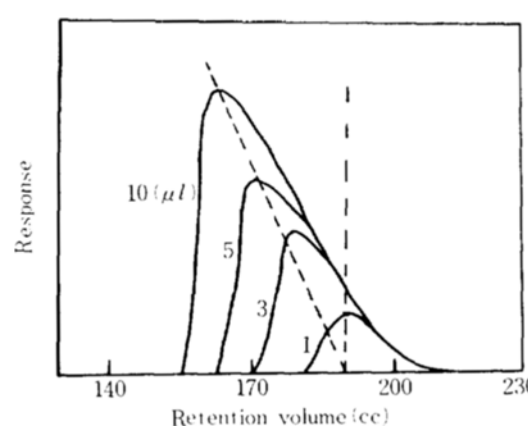

Fig. 8. Effect of sample size on retention volume
(2m column length, 60/80 mesh, 20% liquid loading, DCM).

Separation factor was calculated as shown in the Table 3 under the various conditions of column length, liquid loading, and particle size. It shows that although effects of column length and particle size were not so

Table 3. Separation Factor.

Temp. / S. F. / Case	55℃ DMM/DEE	55℃ DCM/DEE	120℃ DMM/DEE	120℃ DCM/DEE
A 2 a	1. 22	1. 67	#	#
A 2 b	1. 29	2. 05	1. 12	1. 55
A 2 c	1. 28	2. 06	#	#
A 2 d	1. 28	2. 15	#	#
A 3 a	1. 25	1. 83	#	#
A 3 b	1. 32	2. 17	1. 18	1. 59
A 3 c	1. 30	2. 12	1. 17	1. 65
B 1 c	1. 21	1. 99	#	#
B 2 a	1. 13	1. 51	#	#
B 2 b	1. 29	2. 06	1. 14	1. 59
B 2 c	1. 29	2. 10	1. 16	1. 62
B 2 d	1. 31	2. 21	1. 18	1. 74
B 3 a	1. 31	1. 98	#	#
B 3 b	1. 30	2. 08	1. 17	1. 58
B 3 c	1. 30	2. 14	1. 19	1. 69
C 1 c	1. 30	2. 05	#	#
C 2 a	1. 26	1. 78	#	#
C 2 b	1. 31	2. 14	1. 18	1. 62
C 2 c	1. 30	2. 11	1. 17	1. 60
C 2 d	1. 31	2. 22	1. 21	1. 76
C 3 a	1. 21	1. 70	#	#
C 3 b	1. 33	2. 21	1. 20	1. 63
C 3 c	1. 33	2. 28	1. 22	1. 73
average	1. 28	2. 03	1. 18	1. 64

(5μl sample size)
(# : mixture is not separated)

Table 3(1). Conditions of Table 3.

Liquid loading (%)		Column length (cm)		Particle size (mesh)	
a	10	A	150	1	20/30
b	20	B	200	2	45/60
c	25	C	250	3	60/80
d	30				

larged, S.F. was increased with higher liquid lacdling. The effect of column temperature is shown in Fig. 9. Two kinds of S.F. was linearly decreased with the column temperature. As in the general case, the value of S.F. in a component at same temperature was not so different and this meant that S.F. of each material has its own value against certain SLP, and was slightly affected by column length, liquid loading, and mesh size.

Column Efficiency

The efficiency of GLC columns is measured in terms of the total number of theoretical equilibrium plates, or the height equivalent to a theoretical plate (HETP), H. The plate concept came from distillation processes. The number of theoretical plates exhibited by a column for a specific liquid phase, temperature, and solute can be calculated in several ways, all of which are a measure of the degree the peak spreads relative to its residence time in the column. The number of theoretical plates, N, is given by:

$$N=16\left(\frac{x}{y}\right)^2 \qquad (3)$$

where y is the length of the baseline cut by the two tangents, and x is the distance from injection to peak maximum.

The HETP is the length of column necessary for the attainment of solute equilibrium between mobile phase and SLP. This is related to N by:

$$H=\frac{L}{N} \qquad (4)$$

where L is the length of the chromatographic column, usually in centimeters[1].

As predicted in the Van Deemter equation [6], Table 4 shows that HETP was linearly increased as increasing the particle size. According to Klinkenberg and Sjenitzer

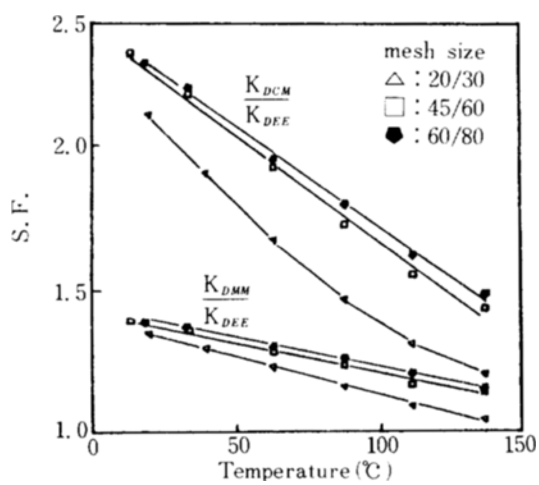

Fig. 9. Relation between column temperature and separation factor.

Table 4. HETP of Various Experimental Conditions(cm).

Material		DEE			DCM		
Column length (cm)	mesh / **	20/30	45/60	60/80	20/30	45/60	60/80
150	10	4.31	2.59	1.71	4.14	2.55	1.25
	20	4.53	0.99	0.41	6.02	1.06	0.21
	25	4.30	1.58	0.39	3.66	1.33	0.19
	30	10.33	1.04	5.50	7.92	0.58	3.97
200	10	5.78	2.25	0.57	6.01	2.43	0.59
	20	4.33	1.00	0.47	4.09	1.00	0.27
	25	3.95	1.15	0.80	3.49	1.19	0.62
	30	12.54	1.47	6.63	9.79	1.11	4.82
250	10	3.07	1.14	1.40	6.04	1.45	2.64
	20	9.78	0.62	0.29	9.39	0.69	0.29
	25	3.79	1.17	0.43	3.04	0.98	0.37
	30	6.07	1.73	8.25	4.23	1.07	5.57
average*		4.87	1.39	0.69	5.10	1.41	0.72

* : 30% liquid loading is not contained ** :Liquid loading(%) (55℃, 5μl sample size)

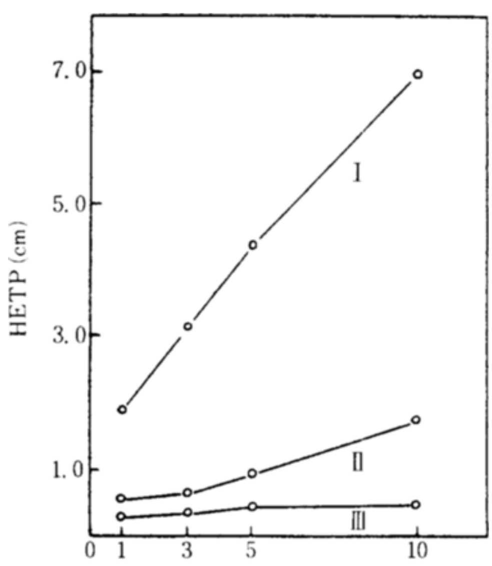

Fig. 10. Effect of sample size on HETP

(2m column length; 20% liquid loading;55 ℃; DEE; I: 20/30 mesh, II: 45/60 mesh, III: 60/80 mesh).

[7], it is easier to obtain regular packing with large rather than small particles. And the more the irrequlari-ty in packing, the greater the value of HETP. But at 30% liquid loading its tendency was irregular since it seems to be a phenomenon of pool within the porous solid support[8].

Fig. 10 shows that the greater the mass of sample chromatographed, the lower the performance of the apparatus as in most of other cases[9, 10]. The effect of the finite vapor concentration in the column makes an extra band spreading. So from the definition of HETP, Eq. (3) and (4), increasing the sample volume makes increasing the HETP and decreasing the column efficiency.

Partition Coefficient and Heat of Solution

The great emphasis in the application of GC to physicalanalytical measurements has been placed on the determination of activity coefficients, thermodynamic properties and kinematic transport coefficients. The partition coefficient, K, is defined as:

$$K=\frac{\text{amount of solute/unit volume of SLP}}{\text{amount of solute/unit volume of mobile phase}} \tag{5}$$

Partition coefficient is high when most of a substance is retained in the SLP. Thus, the greater the difference in their values, the fewer the plates that is required to achieve a good resolution[11].

The partition coefficient may be related to the corrected retention volume and the column packing. And its relation is derived[14] as:

$$K=\frac{V_N}{V_L}=\frac{\text{net retention volume}}{\text{volume of SLP}} \tag{6}$$

where V_N = (retention volume-air retention volume)

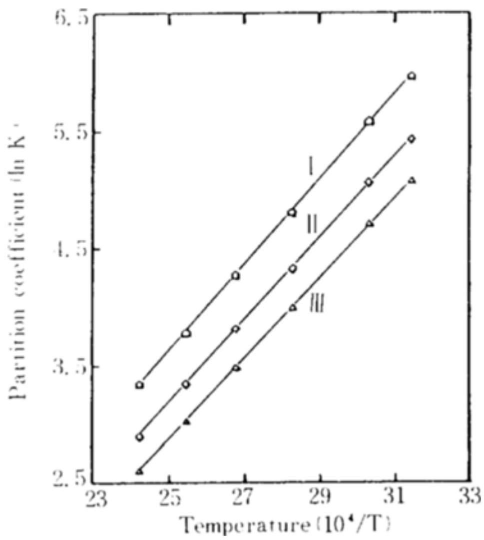

Fig. 11. Effect of column temperature on partition coefficient
(I, DCM, II, DMM, III, DCM).

Table 5. Comparison between Calculated and Published K.

	This study		Fitch et al. (9)
	20℃	30℃	room temperature
DEE	224	152	145
DMM	310	210	221
DCM	536	360	359

x correction factor (7)

Partition coefficients were calculated at 2m column length, 20% liquid loading for six different temperatures and three different mesh sizes. The heat of solution of a volatile solute in a nonvolatile solvent may be determined by GC without the need of preparing purified samples [12]. Littlewood et al.[13] showed that a plot of log K vs. 1/T for a component was linear and that the slope of this plot was a function of the heat of solution. And this was defined as follows:

$$K = K_o \exp(-\Delta H_s/RT) \quad (8)$$

Fig. 11 shows the plot of ln K vs. 1/T for 60/80 mesh size. From the results of linear regression the following relations between partition coefficient and column temperature were obtained.

for DEE $K = 1.67\times10^{-3}\exp(-6875/RT)$ (9)

for DMM $K = 2.31\times10^{-3}\exp(-6875/RT)$ (10)

for DCM $K = 2.98\times10^{-3}\exp(-7044/RT)$ (11)

where R = 1.987 cal/g mole °K.

Table 6. Comparison between ΔH_s and ΔH_v.

	This study	Published
	$-\Delta H_s$ (cal/gmole)	$-\Delta H_v$ (cal/gmole)
DEE	6875	6946 (14)
DMM	6875	6835 (15)
DCM	7044	7572 (14)

To compare the above correlations with others Table 5 is provided. It shows that the difference is not so large.

From the above equations the heat of solution, ΔH_s, is obtained. It was compared with the heat of vaporization, ΔH_v. Littlewood et al.[13] showed that the values of the two were almost identical. Table 6 shows the comparison.

CONCLUSION

The effects of the liquid loading, particle size, column length, and material on retention volume were examined and could be expressed by the following correlation for each material:

$$V_N = a_1 W^{a2} R_p^{a3} L^{a4}$$

Regardless of different experimental conditions, separation factor was almost constant at given temperature. Column efficiencies expressed as HETP were cosidered under various conditions, and the HETP increased almost linearly with sample size. Heat of solution was obtained for each material by regression analysis of partition coefficients.

NOMENCLATURE

a_1, a_2, a_3, a_4	:	values used in Eq. (1)
DCM	:	dichloromethane
DEE	:	diethylether
DMM	:	dimethoxymethane
DNP	:	dinonylphthalate
HETP, H	:	height equivalent to a theoretical plate, cm
ΔH_s	:	heat of solution, cal/gmol
ΔH_v	:	heat of vaporization, cal/gmol
K, K_i	:	partition coefficient and of i component, respectively
K_o	:	constant defined in Eq. (8)
L	:	column length, cm
N	:	number of theoretical plates
R	:	gas constant (= 1.987 cal/gmol °K)
R_p	:	average particle radius, mm
S.F.	:	separation factor
SLP	:	stationary liquid phase
T	:	column temperature, °K

V_L : volume of SLP, cc
V_N : net retention volume, cc
V_a, V_b : retention volume of component a, b, respectively, cc
W : liquid loading, %
x : distance from injection to peak maximum, cm
y : length of the baseline cut by the two tangents, cm

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