CONTRIBUTIONS TO HYDROCARBON RETENTION IN GAS–LIQUID–SOLID CHROMATOGRAPHY WITH POLYETHYLENE GLYCOL 6000 AS STATIONARY PHASE

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SUMMARY

The contributions of interfacial adsorption and bulk solution partition to hydrocarbon solute retention on polyethylene glycol 6000 (PEG 6000) were investigated by gas–liquid–solid chromatography using Chromosorb P and modified alumina supports pre-heated at 900, 1000, 1100 and 1150°C. When using a solid support with low adsorption capacity such as Chromosorb P, the bulk solution partition controlled the retention volume of a given solute. On a solid support with high adsorption capacity, the interfacial adsorption was still important even at a high liquid loading. These results can be interpreted in terms of the thickness of the PEG 6000 layer on the solid support. On the modified alumina, at least a triple layer was required for the PEG 6000 to exhibit its bulk properties.

INTRODUCTION

In general, gas–liquid chromatography is conducted at a column temperature above the freezing point of the stationary liquid phase, and below this temperature gas–solid chromatography occurs. Some authors[1–10] have reported that gas–liquid–solid chromatography (GLSC) may occur at a temperature near the freezing point of the stationary liquid phase. Guillet and co-workers[11,12] determined the crystallinity of some polymers by GLSC. Annino and McCrea[13] studied the characteristics of a mixture of stearic and azelaic acids as a stationary liquid phase. However, few authors have reported the GLSC characteristics of the stationary liquid phase on an active solid adsorbent.

In the present study, the retention volume of some aliphatic hydrocarbons were determined as a function of column temperature on different amounts of polyethylene glycol 6000 (PEG 6000). Four kinds of modified alumina supports with specific surface areas of 90.1, 68.6, 23.1 and 16.2 m²/g and Chromosorb P with a nominal value of 4 m²/g were used as solid supports.

EXPERIMENTAL

Modified alumina supports with different adsorption capacities were prepared from active alumina, Neobead MS · C (60–80 mesh) (Mizusawa Industrial Chemicals, Tokyo, Japan), by heating at 900, 1000, 1100 and 1150°C for 2 h. A commercially available solid support, Chromosorb P, was used for comparison. PEG 6000 was used as a stationary liquid phase without further purification. The organic solutes used were n-pentane, n-hexane, cyclohexane, isohexane, 2-pentene and 1-hexene.

A 10-g amount of the modified alumina or 5 g of Chromosorb P were added to 25 ml of a dichloromethane solution containing the required amount of PEG 6000. The dichloromethane was gradually evaporated by warming with continuous stirring and PEG 6000 was thoroughly deposited on the solid support. The modified alumina or Chromosorb P coated with PEG 6000 was packed into stainless-steel columns (100 × 0.3 cm I.D.) after drying in vacuo at room temperature for 1 h.

A Hitachi Model 023 gas chromatograph equipped with a thermal conductivity detector was used. A Hitachi Model QPD 33 recorder was used to record the chromatograms at a chart speed of 10 mm/min. The organic solutes were chromatographed at a flow-rate of 40 ml/min (helium as carrier gas) and at column temperatures between 40 and 104°C.

The retention volumes of the solutes and the specific surface areas of the modified alumina were determined as described previously[14].

RESULTS AND DISCUSSION

Fig. 1 shows plots of the reduced retention volume, V'_R/W_S (where V'_R is a net retention volume and W_S the weight of liquid-free solid support packed into the column), of some solutes obtained by GLSC against the specific surface areas of the modified alumina pre-heated at 900, 1000, 1100 and 1150°C. All the lines have the same intercept on the abscissa, as shown previously[15]. This suggests that not all of the modified alumina surface was effectively utilized for the solute retention. However, the interaction of the solute molecule with the modified alumina surface is independent of the pre-heating temperature.

In Fig. 2, plots of $\log(V'_R/W_L)$ (where W_L is the weight of the liquid stationary phase packed into the column) versus the column temperature are shown. At any column temperature above 63°C, $\log(V'_R/W_L)$ is independent of the loading, but at lower temperatures, it and the slope of the linear plots decrease with increasing liquid loading. The temperature of the sudden decrease in $\log(V'_R/W_L)$, 63°C, is very close to the freezing point of PEG 6000. At column temperatures above 63°C the solute molecule may be retained chiefly by means of the bulk solution partition and at lower temperatures by the interfacial adsorption. In the transition region between the two linear parts of the plots, both bulk solution partition and interfacial adsorption may contribute to the solute retention. From these results, it is most probable that the surface of Chromosorb P is coated with the bulk PEG 6000 phase.

On the modified alumina pre-heated at 1150°C, the plots of $\log(V'_R/W_L)$ vs. $1/T$ were dependent upon the liquid loading even at column temperatures above 63°C (Fig. 3). A linear relationship still exists at 4% liquid loading, but above 5% the plots become curved. The magnitude of the sudden decrease in $\log(V'_R/W_L)$ increases
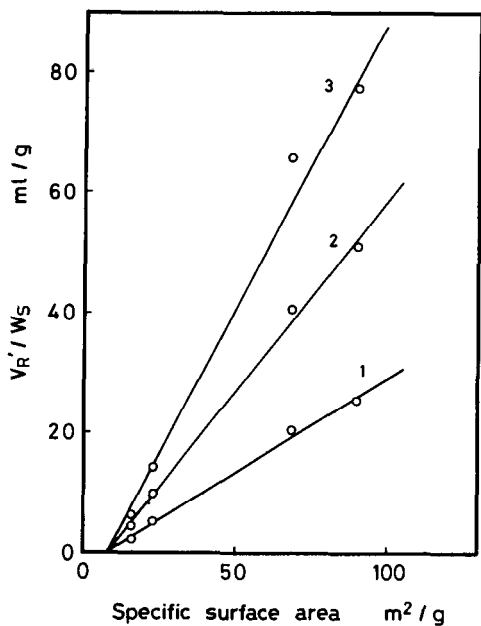
Fig. 1. Variation of V_R'/W_S for aliphatic hydrocarbons with the specific surface area of modified alumina pre-heated at 900, 1000, 1100 and 1150°C. Column temperature: 85°C. Solutes: 1 = n-pentane; 2 = cyclohexane; 3 = n-hexane.
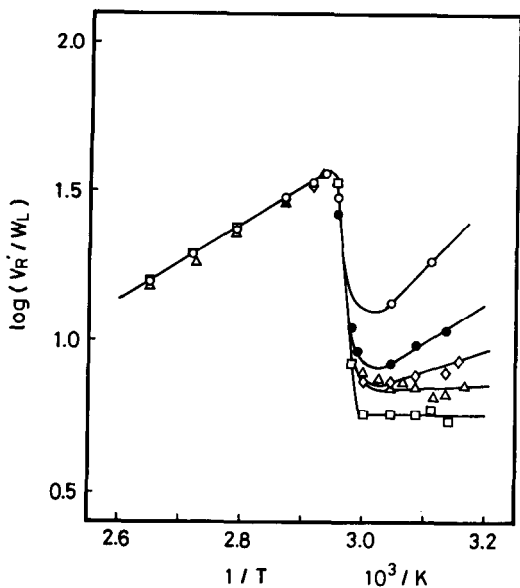

Fig. 2. Graph of $\log(V_R'/W_L)$ against $1/T$. Solid support: Chromosorb P. Stationary phase: PEG 6000. Liquid loadings: ○, 10%; ●, 15%; ◇, 20%; △, 25%; □, 30%. Solute: cyclohexane.
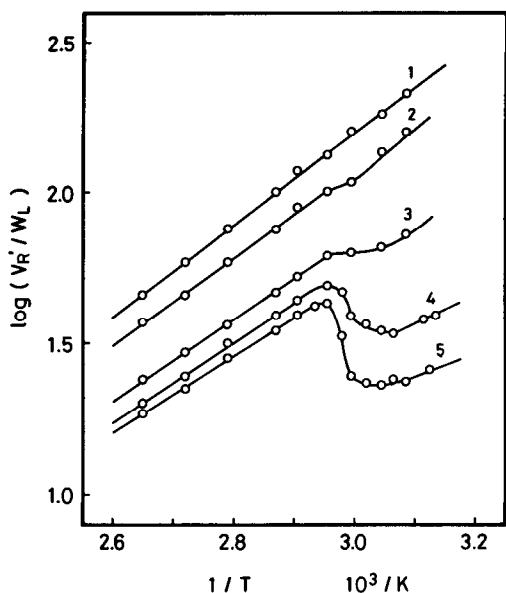
Fig. 3. Graph of log(V'_R/W_L) against $1/T$. Solid support: modified alumina pre-heated at 1150°C. Stationary phase: PEG 6000. Liquid loadings: 1, 4%; 2, 5%; 3, 10%; 4, 15%; 5, 20%. Solute: cyclohexane.

with increasing liquid loading but is still smaller than that in Fig. 2. From these results we conclude that the interfacial adsorption contributes to the solute retention even at temperatures above 63°C, because of the large specific surface area of the modified alumina. The effect of the interfacial adsorption is suppressed as the alumina surface is gradually covered with the bulk PEG 6000 phase.

On the modified alumina pre-heated at 1100°C the sudden decrease in log(V'_R/W_L) occurs at liquid loadings above 10% and at column temperatures lower than 63°C (Fig. 4). The magnitude of this decrease is smaller than that in Fig. 3. No sudden decrease takes place at high liquid loadings, e.g., 20 and 30%, when using the modified alumina pre-heated at 900 and 1000°C. The liquid loading at which the sudden decrease begins to occur increases with increasing specific surface area of the modified alumina.

With Chromosorb P, a linear plot of V'_R/W_S vs. W_L/W_S was obtained, which upon extrapolation passes through the origin (Fig. 5A). In this case, the bulk solution partition is the only mechanism of solute retention. On the modified alumina the plots were curved, but approached the above linear plot as the specific surface area decreased. This suggests an important role of the interfacial adsorption in the solute retention. No increase in V'_R/W_S with increasing W_L/W_S implies that the bulk solution partition effectively does not contribute to the solute retention. The value of V'_R/W_S starts to increase linearly at a lower liquid loading on the modified alumina with smaller specific surface area. The positive intercept obtained by extrapolation of this linear part indicates that the solute retention is still influenced by the interfacial adsorption.

At a column temperature of 55°C, V'_R/W_S is almost constant on Chromosorb P and on the modified alumina it passes through a maximum with increasing liquid
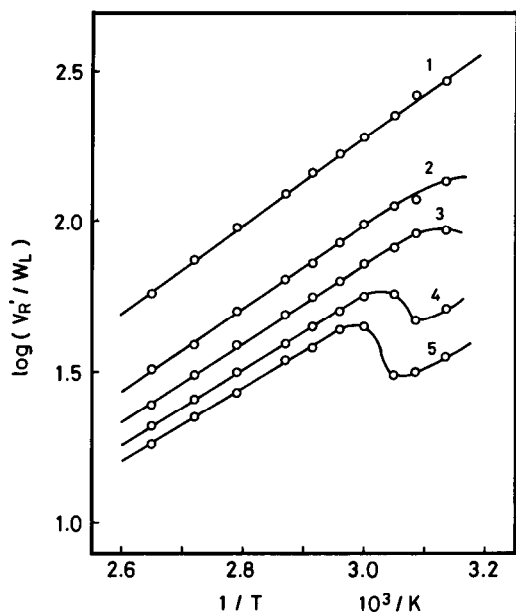
Fig. 4. Graph of $\log(V'_R/W_L)$ against $1/T$. Solid support: modified alumina pre-heated at 1100°C. Stationary phase: PEG 6000. Liquid loadings: 1, 5%; 2, 10%; 3, 15%; 4, 20%; 5, 25%. Solute: cyclohexane.

loading (Fig. 5B). The constant value on Chromosorb P is due to the fact that the specific surface area of the liquid-coated stationary phase hardly varies with W_L/W_S because of the considerably thick layer. The modified alumina is considered to be first covered with a thin film, then probably with small solid particles and finally with a solidified bulk layer. The different V'_R/W_S vs. W_L/W_S profiles are due probably to the fact that different sizes of solid particles are formed depending upon the specific surface area of the modified alumina.

Fig. 5C shows the V'_R/W_S vs. W_L/W_S curve for cyclohexane obtained at different column temperatures on the modified alumina pre-heated at 1100°C. At column temperatures above 63°C the similar profiles indicate that only one sorption process contributes to the solute retention. The somewhat different shapes of the curves observed at lower column temperatures suggest a change in the retention mechanism.

In the case of simultaneous contributions of the bulk solution partition and the interfacial adsorption to the solute retention, eqn. 1, proposed by Conder and co-workers[16,17], can be written

$$V'_R = K_L V_L + K_A A_L + K_S A_S \qquad (1)$$

where K_L is the gas–liquid partition coefficient, V_L the volume of the stationary liquid phase and K_A and K_S are constants pertaining to adsorption on the liquid surface (surface area: A_L) and on the solid surface (surface area: A_S), respectively. Dividing both sides of eqn. 1 by W_L, we obtain

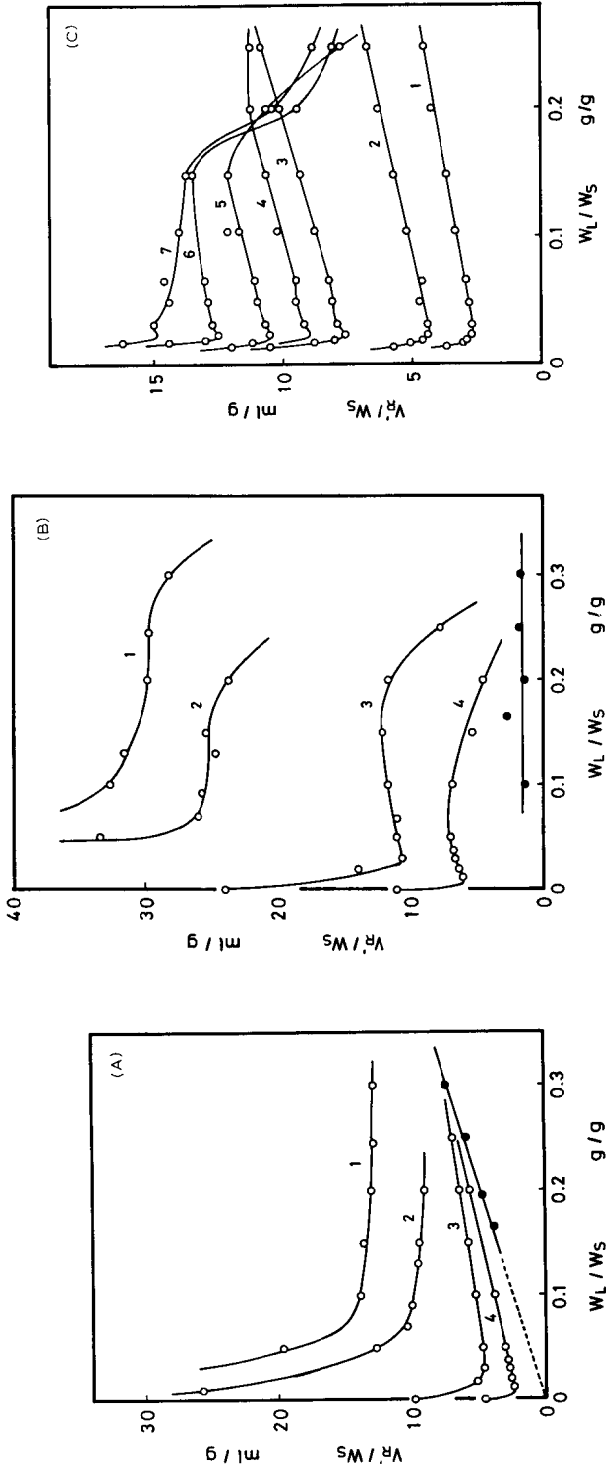$$V'_R/W_L = K'_L + (K_A \sigma_A + K_S \sigma_S)(W_S/W_L) \qquad (2)$$

Fig. 5. (A) Variation of V_R'/W_S with W_L/W_S at a column temperature of 85°C. Solid supports: ●, Chromosorb P; ○, modified alumina. Pre-heating temperatures: 1, 900°C; 2, 1000°C; 3, 1100°C; 4, 1150°C. Solute: cyclohexane. (B) Variation as in (A) but at a column temperature of 55°C. (C) Variation as in (A) but on modified alumina pre-heated at 1100°C. Column temperatures: 1, 104°C; 2, 85°C; 3, 65°C; 4, 60°C; 5, 55°C; 6, 51°C; 7, 46°C. Solute: cyclohexane.
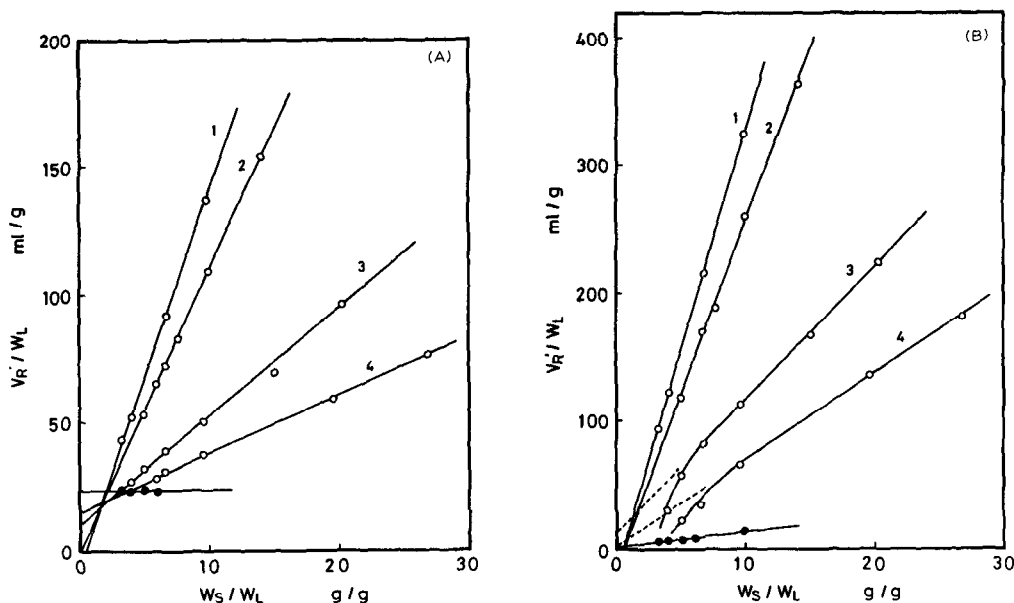
Fig. 6. Variation of V'_R/W_L with W_S/W_L at column temperatures of 85°C (A) and 55°C (B). Other details as in Fig. 5A.

where $K'_L = K_L/\rho_L$, W_L and ρ_L are the weight and density of the stationary liquid phase packed into the column, σ_A and σ_S are equal to A_L/W_S and A_S/W_S and W_S is the weight of the free solid support packed into the column. Eqn. 2 predicts linear plots of V'_R/W_L vs. W_S/W_L with K'_L as an intercept and $(K_A\sigma_A + K_S\sigma_S)$ as a slope, providing that $K_A\sigma_A$ and $K_S\sigma_S$ are independent of the liquid loading.

In Fig. 6A the plot of V'_R/W_L vs. W_S/W_L obtained on Chromosorb P is parallel to the abscissa, indicating that the predominant mechanism of solute retention is the bulk solution. In Fig. 6B, the positive slope and very small intercept obtained on Chromosorb P indicate a contribution from interfacial adsorption. On the modified alumina, curves having a linear part with different slopes and intercepts are found at both column temperatures. The slopes decrease but the intercepts increase with decreasing specific surface area of the modified alumina. Such behaviour is not predictable from eqn. 2.

The values of the slope and the intercept of these plots were calculated for each solute by the least squares method and are summarized in Tables I and II. Negative values for K'_L are hard to accept on the basis of eqn. 2. In order to interpret this discrepancy regarded σ_A and σ_S as linear functions of the liquid loading

$$\sigma_A = \sigma_A^0 [1 - \alpha(W_L/W_S)] \tag{3}$$

$$\sigma_S = \sigma_S^0 [1 - \beta(W_L/W_S)] \tag{4}$$

where α and β are constants. Substituting these relationships in eqn. 2, we obtain:

$$V'_R/W_L = K'_L - (\alpha K_A\sigma_A^0 + \beta K_S\sigma_S^0) + (K_A\sigma_A^0 + K_S\sigma_S^0)(W_S/W_L) \tag{5}$$

TABLE I

K_L (ml/g) ON MODIFIED ALUMINA AND ON CHROMOSORB P AT COLUMN TEMPERATURES OF 85 AND 55°C

Solute	Modified alumina								Chromosorb P	
	900°C		1000°C		1100°C		1150°C			
	85°C	55°C	85°C	55°C	85°C	55°C	85°C	55°C	85°C	55°C
n-Pentane	−10.8	−27.8	−9.82	−23.4	−2.34	−10.7	0.458	−4.66	4.32	0.0899
n-Hexane	−27.9	−71.2	−26.2	−66.2	−6.64	−26.0	−0.0458	−15.1	8.64	−0.315
Cyclohexane	−6.17	−23.3	−3.03	−15.8	10.5	11.9	16.1	5.54	24.2	2.02
Isohexane	−22.9	−63.8	−21.6	−54.5	−6.55	−22.7	−0.682	−13.6	5.56	−0.504
2-Pentene	−10.3	−23.2	−10.5	−23.9	0.102	−5.54	3.49	−1.94	6.41	0.866
1-Hexene	−25.6	−69.9	−13.7	−63.6	−3.54	−20.5	3.80	−10.3	11.8	0.299

TABLE II

$(K_A \sigma_A + K_S \sigma_S)$ (ml/g) ON MODIFIED ALUMINA AND ON CHROMOSORB P AT COLUMN TEMPERATURES OF 85 AND 55°C

| Solute	Modified alumina								Chromosorb P	
	900°C		1000°C		1100°C		1150°C			
	85°C	55°C	85°C	55°C	85°C	55°C	85°C	55°C	85°C	55°C
n-Pentane	6.76	15.4	5.32	11.7	2.02	4.59	1.10	2.54	0.0805	0.371
n-Hexane	16.0	39.3	12.7	30.7	4.55	11.5	2.46	6.54	0.120	0.998
Cyclohexane	14.4	35.1	11.2	27.2	4.09	10.3	2.21	6.48	−0.154	1.13
Isohexane	13.4	33.3	10.6	25.7	3.93	9.57	2.12	5.39	0.383	0.860
2-Pentene	7.72	16.8	6.12	13.5	2.15	4.95	1.17	2.81	0.235	0.359
1-Hexene	16.5	41.4	12.1	32.3	4.58	11.6	2.40	6.57	0.151	0.987
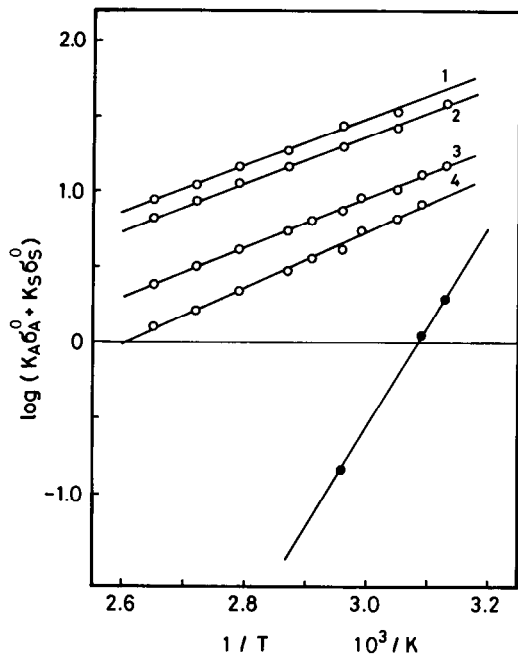
Fig. 7. Graph of $\log(K_A\sigma_A^0 + K_S\sigma_S^0)$ against $1/T$. Other details as in Fig. 5A.

The first term on the right-hand side of this equation, corresponding to the intercept of the V'_R/W_L vs. W_S/W_L plot, becomes negative if $K'_L < (\alpha K_A\sigma_A^0 + \beta K_S\sigma_S^0)$, i.e., the contribution of interfacial adsorption is larger than that of the bulk solution partition. Thus, this equation is applicable for interpreting the experimental data.

Linear plots of $\log(K_A\sigma_A^0 + K_S\sigma_S^0)$ against $1/T$ are obtained between 46 and 104°C (Fig. 7). The slopes of these curves are very similar on the modified alumina, but different from that on Chromosorb P. This implies the predominance of adsorption on the solid support acting through the liquid phase layer. Plots of $\log[K'_L - (\alpha K_A\sigma_A^0 + \beta K_S\sigma_S^0)]$ against $1/T$ exhibit a large decrease near 65°C, corresponding to that in $\log(V'_R/W_L)$ near 63°C (Fig. 8). It is concluded that the large decrease in $\log(V'_R/W_L)$ is caused by a correspondingly large decrease in the term involving the bulk solution partition.

Table III lists the thickness of the PEG 6000 layer formed on each solid support calculated from the liquid loading and the specific surface area of the solid support using 1.21 g/ml as the density of PEG 6000[18]. The values on the modified alumina are a quarter to one-twentieth of that on Chromosorb P at the same liquid loading. A thickness of 10–11 Å, calculated from the liquid loading at the minimum of the V'_R/W_S vs. W_L/W_S curve, is considered to represent a monolayer. A value of 26–37 Å, at which the large decrease in $\log(V'_R/W_L)$ starts, is thus about three times as large as this.

On plotting the apparent heat of solution against the thickness of the PEG 6000 layer, a monotonously decreasing curve was obtained independent of the nature of the modified alumina (Fig. 9). The monotonous decrease is due to changes in the
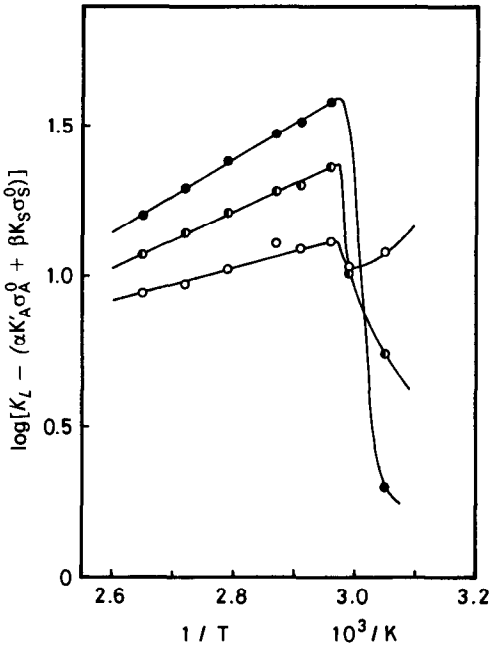
Fig. 8. Graph of log $[K'_L - (\alpha K_A \sigma_A^0 + \beta K_S \sigma_S^0)]$ against $1/T$. Solid supports: $\bigcirc$, modified alumina pre-heated at 1100°C; $\pmb{\circ}$, modified alumina pre-heated at 1150°C; $\bullet$, Chromosorb P. Solute: cyclohexane.

contributions of the different sorption processes to the solute retention. Thus, the selectivity of the gas chromatographic separation can be controlled to some extent by adjusting the thickness of the stationary liquid phase layer.

From these results, it is probable that, at low liquid loadings, the modified

TABLE III

THICKNESS OF THE STATIONARY PHASE (PEG 6000) (Å) ON MODIFIED ALUMINA AND ON CHROMOSORB P

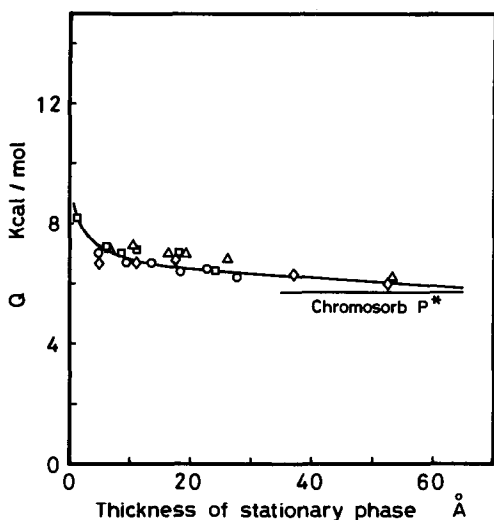| Liquid loading (%)	Modified alumina				Chromosorb P
	900°C	1000°C	1100°C	1150°C	
0.5	—	—	—	3.98	—
1	—	1.20	5.91	6.37	—
2	—	—	6.71	10.4	—
3	—	—	10.9	16.2	—
4	—	—	—	19.0	—
5	4.83	6.02	17.5	26.1	—
7	—	8.62	23.5	—	—
10	9.28	11.0	36.9	53.1	208
15	13.5	18.1	52.4	77.8	339
20	18.3	24.1	71.0	102	408
25	22.5	—	88.0	—	521
30	27.6	—	—	—	631

Fig. 9. Variation of apparent heat of solution for cyclohexane with the thickness of the PEG 6000 layer on the modified alumina. Pre-heating temperatures: O, 900°C; □, 1000°C; ◇, 1100°C; △, 1150°C. * The apparent heat of solution obtained at a thickness in the range of 208–631 Å.

alumina surface is covered with a thin film, a monolayer and a double layer, of PEG 6000. Such a thin film deactivates the surface of the modified alumina. Then, the deactivated surface is covered with a fixed thickness of the bulk PEG 6000 phase. The thickness of the bulk phase layer increases with increasing liquid loading. At least the thickness of the triple layer is necessary for the bulk phase properties of PEG 6000 to be shown on the modified alumina. Thus, our previous concept[19-21] can be applied for interpreting the dependence of the solute retention volume on the liquid loading. It should be noted that the thickness of the stationary liquid phase layer is an important factor in controlling the characteristics of the gas chromatographic system.

REFERENCES

1 O. Smidsrød and J. E. Guillet, *Macromolecules*, 2 (1969) 272.
2 J. Serpinet, *J. Chromatogr.*, 77 (1973) 289.
3 K. Shoji and M. Takeda, *Kobunshi Ronbunshu*, 31 (1974) 420.
4 Yu. S. Lipatov and A. E. Nesterov, *Macromolecules*, 8 (1975) 889.
5 J.-M. Braun, A. Lavoie and J. E. Guillet, *Macromolecules*, 8 (1975) 311.
6 J.-M. Braun and J. E. Guillet, *Macromolecules*, 8 (1975) 882.
7 G. J. Courval and D. G. Gray, *Macromolecules*, 8 (1975) 916.
8 J.-M. Braun and J. E. Guillet, *Macromolecules*, 9 (1976) 340.
9 J.-M. Braun and J. E. Guillet, *Macromolecules*, 9 (1976) 617.
10 G. J. Courval and D. G. Gray, *Can. J. Chem.*, 54 (1976) 3496.
11 J. E. Guillet and A. N. Stein, *Macromolecules*, 3 (1970) 102.
12 J.-M. Braun and J. E. Guillet, *Macromolecules*, 10 (1977) 101.
13 R. Annino and P. F. McCrea, *Anal. Chem.*, 42 (1970) 1486.
14 S. Moriguchi, K. Naito and S. Takei, *J. Chromatogr.*, 131 (1977) 19.
15 S. Moriguchi and S. Takei, *J. Chromatogr.*, 295 (1984) 73.

16 J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 700.
17 D. F. Cadogan, J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 708.
18 *The Merck Index*, Merck and Co., Rahway, NJ, 9th ed., 1976, p. 984.
19 T. Komaita, K. Naito and S. Takei, *J. Chromatogr.*, 114 (1975) 1.
20 K. Naito and S. Takei, *J. Chromatogr.*, 190 (1980) 21.
21 K. Naito, H. Ogawa, S. Moriguchi and S. Takei, *J. Chromatogr.*, 299 (1984) 73.