ADSORPTION EFFECTS IN GAS-LIQUID CHROMATOGRAPHY: SOLUTE RETENTION IN THE HYDROCARBON SOLUTE-POLAR LIQUID STATIONARY PHASE (TRITON X-100) SYSTEM

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SUMMARY

A model for the distribution of liquids on modified alumina is described, in which the solid support is successively covered first with a monolayer, then with a double layer and finally with a bulk liquid layer of Triton X-100. On the basis of this model, the solute retention can be interpreted as a linear combination of concurrent contributions of possible sorption equilibria on the subsurfaces and/or in the bulk liquid layer. Acceptable results were obtained by analysis of experimental data.

INTRODUCTION

Solute retention in gas–liquid chromatography (GLC) is concurrently contributed to from bulk solution partition and from adsorption at gas–solid, gas–solid and/or liquid–solid interfaces, depending on the nature of the solute, the liquid stationary phase and the solid support and also depending on the liquid loading. Conder and co-workers[1,2], Suprynowicz and co-workers[3–7] and Berezkin[8,9] independently reported that the solute retention volume, V_R, in such a case can be experessed as a linear combination of contributions of the bulk solution partition, $K_L V_L$, and the interfacial adsorptions, $K_A A_L$ and $K_S A_S$:

$$V_R = K_L V_L + K_A A_L + K_S A_S$$

In order to apply the above equation, A_S and A_L must be determined as a function of the liquid loading. In the most of earlier studies, the BET surface areas of the bare solid support and the column packings coated with a liquid stationary phase were regarded as A_S and A_L, respectively. This idea is true only when the solid support is completely covered with the liquid phase layer. A certain amount of the liquid phase is required for complete coverage of the solid support surface and, at a liquid loading lower than this, the BET surface area of the column packings involves the surface areas of an uncovered part of the solid support and the liquid layer expanding on

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the solid support. For a correct interpretation of interfacial adsorption effects on the solute retention, a reasonable relationship between the interfacial area and the liquid loading must be established by taking into account the distribution of the liquid phase on the solid support.

In order to detect such interfacial adsorption effects on the solute retention in GLC with reasonable precision, we used modified alumina with a large specific surface area as a solid support. In our previous model for the liquid phase distribution, the modified alumina is successively covered with two different types of liquid films, a monolayer and a bulk liquid layer, depending on the liquid loading. Experimental retention volumes of a given solute, determined as a function of the liquid loading, were successfully analysed by fitting some linear relationships derived on the basis of the liquid phase distribution model[10]. Applying the same reasoning, we have quantitatively interpreted the dependence on the salt loading of the solute retention volume on a salt-modified alumina adsorbent in gas–solid chromatography (GSC)[11].

This paper is concerned with a quantitative interpretation of the solute retention in a non-polar solute–polar liquid stationary phase system. As we expected an important effect of adsorption on the liquid phase layer in the solute retention in this GLC system, the specific surface area of the liquid-coated column packings was determined by the BET method. This BET surface area was used without further correction, although it may not always correspond to the surface area available for the solute retention in GLC.

EXPERIMENTAL

The modified alumina was prepared from Neobead MS · C (60–80 mesh) (Mizusawa Industrial Chemicals, Tokyo, Japan) by ignition at 1100°C for 1 h and by resieving to obtain the 60–80 mesh fraction. A commercially available solid support, Chromosorb P, was used as a reference without further treatment. Column packings were prepared by coating the solid support with a strongly polar liquid stationary phase, Triton X-100. The liquid loading was calculated as the weight ratio of the liquid phase to the solid support. The packings was packed into a stainless-steel tube (100 × 0.3 cm I.D.) after removing any volatile components for 3 h *in vacuo*. The column was preconditioned for 15 h in a stream of nitrogen and then for 1 h in a stream of helium at 120°C.

A Hitachi K53 gas chromatograph equipped with a thermal conductivity detector was used in conjunction with a Hitachi 561 recorder for gas chromatography. Gas chromatographic measurements were carried out under the same conditions as used in previous studies[10,12]. The procedure described previously was applied for the determination of the retention volume of the solute and its correction. The specific surface area of the modified alumina, uncoated and coated with Triton X-100, was measured by the BET method of nitrogen adsorption at liquid nitrogen temperature.

RESULTS AND DISCUSSION

When Triton X-100 was coated on Chromosorb P, a plot of the retention volume of a given solute, V_N/W_S, against the liquid loading, W_L/W_S, was a linear graph (Fig. 1). From the small intercept of this graph, it is considered that the major

contribution to solute retention in this instance is from the bulk solution partition rather than the interfacial adsorption. Hence, the slope of the graph gives a value of K'_L defined in a previous paper[12] (Table I). In the non-polar solute–polar liquid phase system, this small intercept is probably due to the contribution of adsorption at the gas–liquid interface.

When the modified alumina with a large surface area was used as a solid support, the V_N/W_S vs. W_L/W_S plots were hyperbolic curves with and without a minimum for cyclohexane, cyclohexene, benzene and for other solutes (Fig. 2). At liquid loadings higher than the minimum, the slopes of these curved graphs increase in the order cyclohexane < cyclohexene < benzene, which is in accordance with the increasing order of their K'_L values.

In this liquid loading range, the contribution of the bulk solution partition is greater than that of the interfacial adsorption to the solute retention of the above solutes. For the other solutes, it appears that the interfacial adsorption effects are even more significant than the bulk solution partition effects. From the large interfacial adsorption effects, it would be expected that the V_N/W_S values would be correlated with the specific surface area of the column packings, σ_S. However, the V_N/W_S vs. W_L/W_S curve does not correspond to the σ_S vs. W_L/W_S curve, which suggests that the retention volume cannot be described as a simple function of the specific surface area of the column packings.

Fig. 3 shows the converse L-form of the V_N/W_S vs. σ_S curve. This curve consists of three different parts, region A, where V_N/W_S decreases considerably with a small
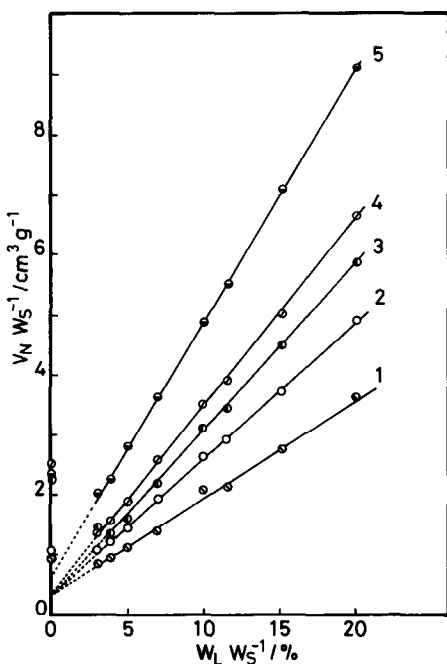

Fig. 1. Dependence of solute retention volume on liquid loading. Liquid phase stationary: Triton X-100. Solid support: Chromosorb P. Solutes: 1 = 2-methylpentane; 2 = n-hexane; 3 = 1-hexene; 4 = 2-hexene; 5 = 2-methylhexane.

TABLE I

GAS–LIQUID PARTITION CONSTANTS, K_L (ml/g), OF SOLUTES IN TRITON X-100

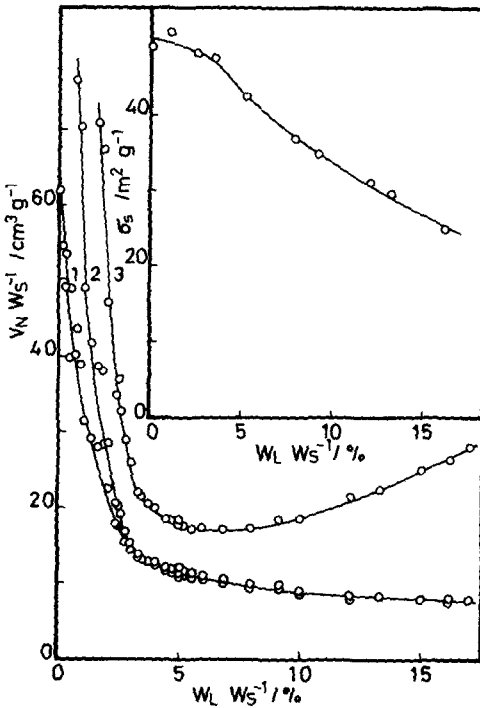| Solute	Solid support	
	Chromosorb P	Modified alumina
2-Methylpentane	16	18
n-Hexane	22	24
Cyclohexane	56	57
1-Hexene	27	27
2-Hexene	31	33
Cyclohexene	88	100
2-Methylhexane	42	43
n-Heptane	52	59
Benzene	166	176
1-Heptene	66	66
2-Heptene	80	84

Fig. 2. Dependence of solute retention volume and specific surface area of column packings on liquid loading. Liquid phase stationary: Triton X-100. Solid support: modified alumina. Solutes: 1 = n-hexane; 2 = 1-hexene; 3 = benzene.

decrease in σ_S, region B, where V_N/W_S decreases or increases with a relatively large decrease in σ_S, and a transition part between regions A and B. In region A, corresponding to a low liquid loading range, the highly adsorptive surface of the solid support is gradually covered with a low adsorptive monolayer of the liquid phase with increasing liquid loading. It is probably that such a gradual coverage causes a large decrease in V_N/W_S and a slight reduction in σ_S. In the transition region, both V_N/W_S and σ_S decrease with increasing liquid loading. This change indicates that the interfacial adsorption is important but the bulk solution partition is less significant in the solute retention in this instance. We therefore considered that the solid support, covered with the monolayer, is successively covered with a thin film of the liquid phase without bulk liquid properties. In region B, the bulk solution partition contributes to the retention volume of cyclohexane, cyclohexene and benzene. It is reasonable to conclude that the solid support covered with the above thin film is further covered with a bulk liquid layer of Triton X-100. After complete coverage with the bulk liquid layer, the thickness of the bulk liquid layer increases with further increase in the liquid loading.

Fig. 4 shows that the V_N/W_S vs. W_L/W_S curve can be well approximated by five linear graphs. The liquid loading ranges for which five linear relationships were obtained are called region 1 for the lowest, region 2 for the second, region 3 for the
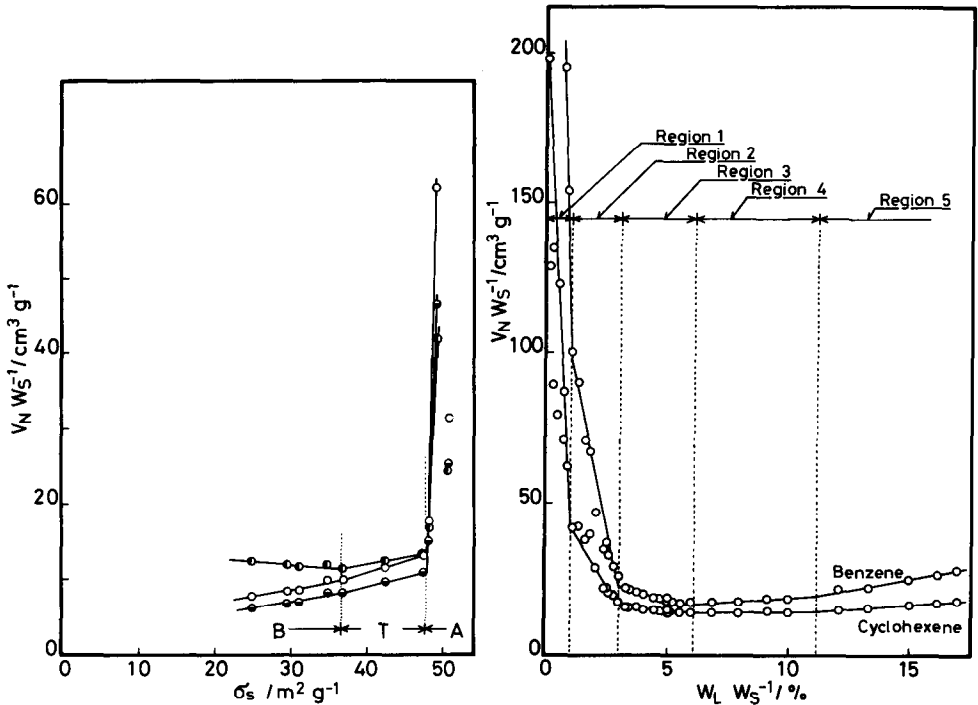

Fig. 3. Dependence of V_N/W_S on σ_S. Liquid loading range: A, region A; B, region B; T, transition region. ◑, 2-Methylpentane; ○, n-hexane; ◐, cyclohexane.

Fig. 4. Dependence of solute retention volume on liquid loading on modified alumina coated with Triton X-100.

third, region 4 for the fourth and region 5 for the highest liquid loading range. By comparison between the graphs in Figs. 3 and 4, region A corresponds to regions 1 and 2, the transition region to region 3 and region B to regions 4 and 5, respectively.

Table II shows that the liquid loading at an intersection between two adjacent linear graphs has almost the same value, irrespective of the nature of the solute. The number of moles of Triton X-100 per unit surface area of the solid support, calculated from the values of W_{L1}/W_S, W_{L0}/W_S, W'_{L0}/W_S and W_{L2}/W_S, are 0.3, 1.0, 1.9 and 3.5 μmol/m^2, respectively. From previous results[10,11], the W_{L0}/W_S and W_{L2}/W_S values can be regarded as the requirements for complete coverage of the solid support with a monolayer and with a bulk liquid layer of Triton X-100, respectively. Also the W'_{L0}/W_S value, which is double the W_{L0}/W_S value, can be considered as the requirement for complete coverage with a double layer of Triton X-100. Supposing that the modified alumina surface consists of two different subsurfaces with higher and lower surface activities for adsorption, the W_{L1}/W_S value can be regarded as the liquid loading required for complete coverage of the higher adsorptive subsurface (subsurface 1) with a monolayer of Triton X-100. The σ_S *vs.* W_L/W_S curve can also be approximated by four straight lines. Three liquid loadings at the intersections between two adjacent lines on the above graph correspond well to the W_{L0}/W_S, W'_{L0}/W_S and W_{L2}/W_S values calculated from the retention data.

We formulated a model for the distribution of Triton X-100 on the modified alumina support in which the solid support is successively covered with three different types of liquid phase layers, first with a monolayer, second with a double layer and finally with a bulk liquid layer, depending on the liquid loading. We assumed that the surface area of the column packings available for the solute retention, equal to the BET surface area, is the sum of some subsurface areas in contact with a gas phase at any liquid loading.

In region 1, subsurface 1 (surface area: $A_1 = \sigma_1 W_S$) is considered to be partly covered with a monolayer of Triton X-100. The solid support surface (surface area: $As^\circ = \sigma^\circ_S W_S$) involves a higher adsorption activity of subsurface 1 and a lower

TABLE II

LIQUID LOADINGS OF INTERSECTION, W_{L1}/W_S, W_{L0}/W_S, W'_{L0}/W_S and W_{L2}/W_S, BETWEEN TWO ADJACENT STRAIGHT LINES ON THE V_N/W_S *vs.* W_L/W_S DIAGRAM

Solid support: modified alumina.

Solute	W_{L1}/W_S	W_{L0}/W_S	W'_{L0}/W_S	W_{L2}/W_S
2-Methylpentane	0.0104	0.0299	0.0613	0.113
n-Hexane	0.0103	0.0310	0.0608	0.112
Cyclohexane	0.0104	0.0302	0.0610	0.113
1-Hexene	0.0104	0.0307	0.0608	0.106
2-Hexene	0.0104	0.0307	0.0605	0.111
Cyclohexene	0.0104	0.0303	0.0609	0.112
2-Methylhexane	0.0104	0.0308	0.0612	0.111
n-Heptane	0.0105	0.0302	0.0601	0.114
Benzene	0.0104	0.0309	0.0606	0.114
1-Heptene	0.0104	0.0308	0.0612	0.113
2-Heptene	0.0104	0.0306	0.0606	0.112

adsorption activity of subsurface 2 ($A_2 = \sigma_2 W_S$), that is, $As^\circ = A_1 + A_2$. The BET surface area of the column packings, As, is equal to the sum of the areas of an uncovered subsurface 1 ($A_1 - A_{SL}$), subsurface 2 (A_2) and the monolayer surface (A_{LM}). A_{SL}, the surface area of the solid support covered with the monolayer, and A_{LM} are proportional to an amount of the liquid phase coated, W_L; $A_{SL} = \alpha W_L$ and $A_{LM} = \beta W_L$, where α and β are proportionality constants. Then, the retention volume of a given solute can be regarded as the sum of contributions of adsorption equilibria on these three subsurfaces. Thus, we can write

$$As = As^\circ - (\alpha - \beta)W_L \tag{1}$$

and

$$V_N = K_1(A_1 - A_{SL}) + K_2 A_2 + K_A A_{LM}$$

or

$$V_N = K_{ad}^\circ As^\circ - (\alpha K_1 - \beta K_A)W_L \tag{2}$$

where $K_{ad}^\circ As^\circ$, equal to the sum $K_1 A_1 + K_2 A_2$, is the net retention volume at zero liquid loading and K_1, K_2 and K_A are distribution constants for adsorption on subsurface 1, subsurface 2 and the monolayer surface, respectively. Then, eqns. 1 and 2 can be converted into the forms

$$\sigma_S = \sigma_S^\circ - (\alpha - \beta)(W_L/W_S) \tag{3}$$

and

$$V_N/W_S = K_{ad}^\circ \sigma_S^\circ - (\alpha K_1 - \beta K_A)(W_L/W_S) \tag{4}$$

If $\alpha > \beta$ and $K_1 > K_2 > K_A$, these two equations can be fitted to the experimental data.

In region 2, the monolayer of Triton X-100 expands on subsurface 2 after completion of monolayer coverage of subsurface 1. The surface area of the column packings, As, is equal to the sum of the areas of subsurface 2 ($As^\circ - A_{SL}$) and the monolayer surface (A_{LM}). Then, the net retention volume of a certain solute has contributions from adsorption equilibria on both subsurfaces. Supposing that α and β have the same values as those in region 1 and considering that K_A is the same for both monolayer surfaces formed on subsurfaces 1 and 2, As can be expressed as eqn. 3 and V_N can be written in the form

$$V_N = K_2(As^\circ - A_{SL}) + K_A A_{LM}$$

and then

$$V_N/W_S = K_2 \sigma_S^\circ - (\alpha K_2 - \beta K_A)(W_L/W_S) \tag{5}$$

In region 3, the liquid phase further covers the solid support covered completely with the monolayer (surface area: A_M°) to form a double layer. The surface area of the monolayer covered with the thin film of Triton X-100, A_{MD}, and that of the double layer formed, A_{LD}, are considered to be proportional to the amount of the liquid phase necessary to cover the monolayer surface, $W_L - W_{L0}$; $A_{MD} = \alpha'(W_L - W_{L0})$ and $A_{LD} = \beta'(W_L - W_{L0})$. W_{L0} is the requirement for complete coverage of the solid support surface with the monolayer of Triton X-100. The coefficients α' and β' are proportionality constants and it is assumed that $\alpha' > \beta'$. The BET surface area of the column packings consists of the uncovered monolayer surface ($A_M^\circ - A_{MD}$) and the newly formed double layer surface (A_{LD}). Then, it can be considered that the solute retention volume has contributions from two adsorption equilibria on the monolayer and on the double layer surface. We assumed that the double layer of Triton X-100 is as dense a film as the monolayer. It is probable that the solute molecule is adsorbed with difficulty directly on the solid support or on the monolayer surface by passing through the double layer. Under these conditions, As and V_N in this region can be written as

$$As = A_M^\circ - (\alpha' - \beta')(W_L - W_{L0})$$

and

$$V_N = K_A[A_M^\circ - \alpha'(W_L - W_{L0})] + K_A'\alpha'(W_L - W_{L0})$$

Then,

$$\sigma_S = \sigma_M^\circ + (\alpha' - \beta')(W_{L0}/W_S) - (\alpha' - \beta')(W_L/W_S) \tag{6}$$

and

$$V_N/W_S = [K_A\sigma_M^\circ + (\alpha'K_A - \beta'K_A')(W_{L0}/W_S)] - (\alpha'K_A - \beta'K_A')(W_L/W_S) \tag{7}$$

where K_A' is a distribution constant for adsorption on the double layer surface and $K_A' \leqslant K_A$. These equations can also be applied for analysis of the experimental data.

In region 4, the bulk liquid layer of Triton X-100 expands on the solid support covered with the double layer (surface area: A_D°). The surface area of the double layer covered with the bulk liquid layer, A_{DB}, and that of the bulk liquid layer, A_{LB}, are proportional to the amount of bulk liquid layer, $W_L - W_{L0}'$; $A_{DB} = \alpha''(W_L - W_{L0}')$ and $A_{LB} = \beta''(W_L - W_{L0}')$. The quantities α'' and β'' are proportionality constants and W_{L0}' is the requirement for complete coverage with the double layer. The BET surface area of the column packings can be regarded as the sum of the surface area of the uncovered double layer ($A_D^\circ - A_{DB}$) and that of the bulk liquid layer (A_{LB}). Then, it is considered that the solute retention volume has concurrent contributions from two adsorption equilibria on the uncovered double layer and on the bulk liquid layer surface, and from the bulk solution partition. Thus, the following equations can be written:

$$As = A_D^\circ - (\alpha'' - \beta'')(W_L - W_{L0}')$$

and

$$V_N = K'_A[A^\circ_D - \alpha''(W_L - W''_{L0})] + K'_A\beta''(W_L - W'_{L0})$$

Then,

$$\sigma_S = \sigma^\circ_D + (\alpha'' - \beta'')(W'_{L0}/W_S) - (\alpha'' - \beta'')(W_L/W_S) \tag{8}$$

and

$$V_N/W_S = K'_A\sigma^\circ_D + K'_{exp}(W'_{L0}/W_S) - K'_{exp}(W_L/W_S) \tag{9}$$

where $K'_{exp} = K'_L - \alpha''(K'_A - K'_S) + \beta''K'_A$ and K'_A, K'_S and K'_L are distribution constants for adsorption on the bulk liquid layer and on the double layer surface covered with the bulk liquid layer, and a partition constant in the bulk liquid layer, respectively. If $\alpha'' > \beta''$, $K'_A > K'_A$ and $K'_A > K'_S$, eqns. 8 and 9 can be fitted to the experimental data.

In region 5, the bulk liquid layer of Triton X-100 covers completely the solid support surface. In this instance, an increase in the liquid loading causes an increased thickness of the bulk liquid layer and a subsequent decrease of the surface area of the column packings. The surface area and the amount of the bulk liquid layer of Triton X-100 with which the solid support is completely covered are defined as A°_L and W_{L2}, respectively. Then, we assumed that a decrease of the surface area of the column packings, $A^\circ_L - As$, is proportional to the excess amount of the liquid phase, $W_L - W_{L2}$. In this region, the solute retention volume has contributions from two adsorption equilibria on the liquid layer and on the double layer surface covered with the bulk liquid layer and from the bulk solution partition. The surface area of the column packings and the net retention volume can be expressed as

$$As = A^\circ_L - \lambda(W_L - W_{L2})$$

and

$$V_N = K'_S A^\circ_D + K''_A[A^\circ_L - \lambda(W_L - W_{L2})] + K'_L(W_L - W'_{L0})$$

Thus,

$$\sigma_S = \sigma^\circ_L + \lambda(W_{L2}/W_S) - \sigma(W_L/W_S) \tag{10}$$

and

$$V_N/W_S = K'_S\sigma^\circ_D + K''_A[\sigma^\circ_L + \lambda(W_{L2}/W_S)] - K'_L(W'_{L0}/W_S)$$

$$+ (K'_L - \lambda K''_A)(W_L/W_S) \tag{11}$$

If $K'_L < \lambda K''_A$, that is, the solute retention has a greater contribution from an adsorption equilibrium on the bulk liquid layer surface than the bulk solution partition,

the linear graph represented by eqn. 11 will have a negative slope. For solutes other than cyclohexane, cyclohexene and benzene, the V_N/W_S vs. W_L/W_S graphs in this region had a negative slope. Therefore, these equations can be applied to the analysis of the experimental data.

Using the equations derived above, the values of the slope and intercept can be determined by the least-squares regression method for each straight line in Fig. 4. From these values and the liquid loading of intersections, unknown constants except for K_S can be calculated. These distribution constants are listed in Table III. The value of the distribution constant for adsorption essentially satisfied all the assumptions used in deriving the above equations. For a give solute, the same value of K_A is determined in three different liquid loading regions. The K'_A value was also determined as the same value in two different regions. It should be noted that the K'_A value is very similar to the K_A value for a given solute. This finding suggests that the double layer of Triton X-100, as assumed previously, is as dense a film as the monolayer. The K'_L value determined on the modified alumina support is consistent with that obtained on Chromosorb P, as shown in Table I. From this result, Triton X-100 can be distributed on the modified alumina support in the same form as that on Chromosorb P. The results of the analysis indicate that any contribution of adsorption equilibrium at a liquid–solid interface such as an interface between the double layer and the bulk liquid layer need not be taken into account in the analysis. Therefore, the K_S term can be neglected in eqns. 9 and 11.

Fig. 5 shows the dependence of each contribution of sorption equilibrium on the subsurface or in the bulk liquid layer on the liquid loading. The solid line, indicating the calculated value of V_N/W_S, passes through the observed points. From this result, the analysis of the experimental data was carried out with reasonable precision. It can be seen that a large amount of Triton X-100 is necessary for the contribution of the bulk solution partition to appear in the solute retention because of the large specific surface area of the modified alumina support. As the specific surface area of the Chromosorb P support is one thirteenth of that of the modified alumina support,

TABLE III

DISTRIBUTION CONSTANTS FOR ADSORPTION, K_1, K_2, K_A, K'_A and K''_A (all × 10^{-5} cm), ON MODIFIED ALUMINA

| Solute	K_1	K_2	K_A			K'_A		K''_A
			Region 1	Region 2	Region 3	Region 3	Region 4	
2-Methylpentane	16.8	6.7	2.3	2.3	2.3	2.3	2.3	1.8
n-Hexane	22.7	8.3	2.7	2.8	2.8	2.7	2.7	2.2
Cyclohexane	14.3	6.1	2.8	2.8	2.8	2.8	2.9	2.6
1-Hexene	79.8	13.5	3.0	2.9	2.8	2.6	2.6	2.1
2-Hexene	77.1	13.5	3.3	3.1	3.0	2.8	2.8	2.3
Cyclohexene	95.7	11.2	3.4	3.2	3.3	3.4	3.4	2.7
2-Methylhexane	47.4	16.7	5.9	5.6	5.6	5.4	5.4	4.3
n-Heptane	104	26.7	7.8	7.0	7.2	6.7	6.7	5.2
Benzene	247	28.6	4.5	4.8	4.6	4.0	4.0	3.5
1-Heptene	267	47.0	8.3	7.5	7.2	6.5	6.5	5.0
2-Heptene	337	52.5	9.0	7.8	7.8	7.2	7.2	5.5
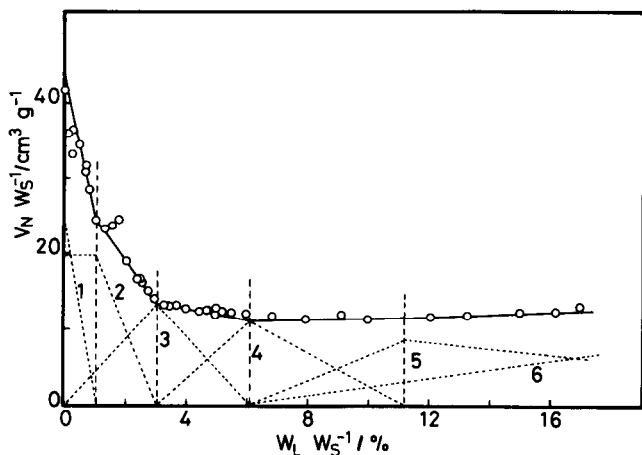
Fig. 5. Contribution of each interfacial adsorption and bulk solution partition to solute retention volume on modified alumina coated with Triton X-100. Solute: cyclohexane; (O), observed value of V_N/W_S; (——), calculated value of V_N/W_S (----); calculated value of each sorption contribution. 1, Adsorption on subsurface 1; 2, adsorption on subsurface 2; 3, adsorption on monolayer of Triton X-100; 4, adsorption on double layer of Triton X-100; 5, adsorption on bulk liquid layer of Triton X-100; 6, bulk solution partition in bulk liquid layer of Triton X-100.

the liquid loading range corresponding to regions 1–4 is so narrow that region 5 can appear at a low liquid loading. Thus, the contribution of the interfacial adsorption is less important but that of the bulk solution partition has a great effect on the solute retention on Chromosorb P.

In Fig. 6, the ratios of the net retention volumes of 1-hexene and n-heptane to that of n-hexane are plotted against the weight of Triton X-100 per unit surface area of the solid support. The high liquid loading part of the curve for the modified alumina support can be smoothly connected to the curve for Chromosorb P. This finding suggests that the same concept can be applied to the interpretation of the experimental data on Chromosorb P. Eqn. 11 can be fitted to the linear graph on the V_N/W_S vs. W_L/W_S diagram by a slight modification for a small specific surface area of Chromosorb P. As the $K'_S\sigma^\circ_D$ term is neglected and $\lambda K''_A \ll K'_L$, eqn. 11 can be modified to

$$V_N/W_S = K''_A[\sigma^\circ_L + \lambda(W_{L2}/W_S)] - K'_L(W'_{L0}/W_S) + K'_L(W'_L/W_S) \qquad (12)$$

Thus, the intercept of the linear graph in Fig. 1 is

$$\text{Intercept} = K''_A[\sigma^\circ_L + \lambda(W_{L2}/W_S)] - K'_L(W'_{L0}/W_S) \qquad (13)$$

In eqn. 13, the $\sigma^\circ_L + \lambda(W_{L2}/W_S)$ and W'_{L0}/W_S terms are constant, regardless of the nature of the solute. Then, by using the K''_A and K'_L values determined on the modified alumina support, plotting intercept/K'_L against K''_A/K'_L gives a linear graph with a slope of $\sigma^\circ_L + \lambda(W_{L2}/W_S)$ and an intercept of $-W'_{L0}/W_S$. The intercept of this linear graph is actually determined to be -0.0046. This value is about one thirteenth of
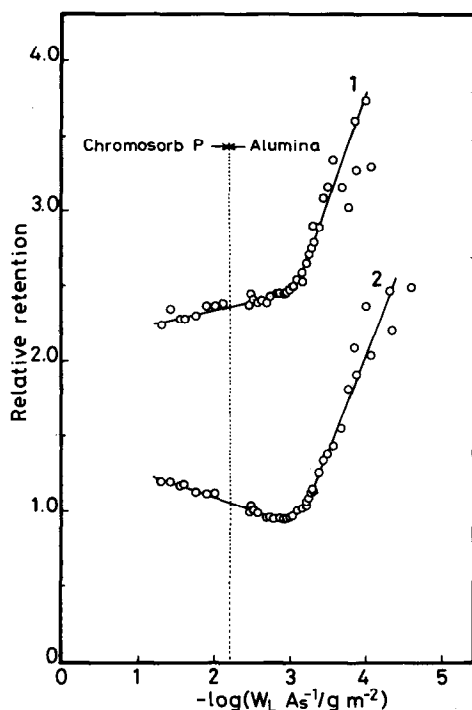
Fig. 6. Dependence of relative retention on surface concentration of Triton X-100. Relative retention: 1, *n*-heptane/*n*-hexane; 2, 1-hexene/*n*-hexane.

the requirement for complete coverage of the modified alumina with the double layer of Triton X-100. This result indicates the same cross-sectional area of Triton X-100 molecule for the double layer cover of Chromosorb P and the modified alumina support. On Chromosorb P, Triton X-100 begins to cover partly with a bulk liquid layer at a liquid loading above 0.5% and completely at about 1–2%. On using a support of small specific surface area such as Chromosorb P, the adsorption equilibrium at the gas–liquid interface can thus be regarded as a preferential phenomenon in the non-polar solute–polar liquid stationary phase system.

The dependence of the specific surface area of the column packings and the solute retention volume of a given solute on the liquid loading can be interpreted by taking into account changes in the distribution of three different types of liquid layer, a monolayer, a double layer and a bulk liquid layer, depending on the liquid loading. By the same reasoning, solute retention on Chromosorb P can be readily understood.

We continue to take an interest in this problem and are now studying GLC systems involving other types of polar liquid stationary phase.

REFERENCES

1 J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 700.
2 D. F. Cadogan, J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 708.
3 Z. Suprynowicz, *Chem. Anal. (Warsaw)*, 17 (1972) 267.
4 Z. Suprynowicz, *Chem. Anal. (Warsaw)*, 18 (1973) 15.

5 Z. Suprynowicz, *Chem. Anal. (Warsaw)*, 18 (1973) 251.
6 A. Waksmundzki, W. Rudziński, Z. Suprynowicz and J. Rayss, *J. Chromatogr.*, 74 (1972) 3.
7 Z. Suprynowicz, A. Waksmundzki and W. Rudziński, *J. Chromatogr.*, 67 (1972) 21.
8 V. G. Berezkin, *J. Chromatogr.*, 65 (1972) 267.
9 V. G. Berezkin, *J. Chromatogr.*, 159 (1978) 359.
10 K. Naito and S. Takei, *J. Chromatogr.*, 190 (1980) 21.
11 K. Naito, M. Endo, S. Moriguchi and S. Takei, *J. Chromatogr.*, 253 (1982) 205.
12 T. Komaita, K. Naito and S. Takei, *J. Chromatogr.*, 114 (1975) 1.