CHROM. 12,503

ADSORPTION EFFECTS IN GAS–LIQUID PARTITION CHROMATOGRAPHY

QUANTITATIVE EVALUATION

KUNISHIGE NAITO and SHINSUKE TAKEI

Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Hitachi 316 (Japan)

(First received June 19th, 1979; revised manuscript received September 24th, 1979)

SUMMARY

The retention mechanism in gas–liquid chromatography has been studied for hydrocarbon–silicone DC 200 and –Oronite polybutene 128 systems. Plots of V_R/W_L against W_L/W_L for each solute could be approximated by four straight lines with different slopes and intercepts and three straight lines when silicone DC 200 and Oronite polybutene 128 were loaded on modified alumina, respectively. Satisfactory results were obtained on analysis of the retention data with the equations that describe these straight lines, derived on the basis of the possible distribution of the liquid phase on the solid support with heterogeneous surface dispersing more and less adsorptive sites.

INTRODUCTION

The quantitative interpretation of the retention mechanism in gas–liquid chromatography (GLC) can serve to evaluate some physico-chemical parameters from gas chromatographic data and to enable desirable characteristics of the solid support for GLC to be achieved. This problem has been better understood by considering the contributions of concurrent solution and adsorption equilibria on the retention of the solute, as expressed in the form

$$V_R = K_L V_L + K_A A_L + K_s A_s \qquad (1)$$

where K_L is the gas–liquid partition constant, V_L is the volume of the liquid phase loaded, K_A and K_s are constants for adsorption equilibria between the liquid phase surface and the solid support, and A_L and A_s are the total surface areas of the liquid phase and the solid support in the column, respectively. The determination of the K_L, K_A and K_s values by analysis of chromatographic data with eqn. 1 has been independently proposed by Conder and co-workers[1,2], Berezkin[3] and Suprynowicz and co-workers[4-8].

Previously, several workers[9-16] have demonstrated adsorption effects at the gas–liquid interface and solute retention in GLC by establishing experimentally the relationship between the specific surface area of the liquid phase layer, A_L, on the solid support and the amount of the liquid phase loaded, V_L. In these investigations

it was accepted that the surface of the solid support was completely covered with the liquid phase layer at very low liquid loading because of the small specific surface area of the commercially available solid supports used. The specific surface area of the liquid-coated solid support, measured by the BET method, was regarded as that of the liquid phase layer spreading on the solid support surface. However, as pointed out by Urone and Parcher[17] and later by Serpinet[18], this is not acceptable because such a BET surface area cannot correspond precisely to the surface area of the liquid phase layer in the liquid state. Further, some workers[19,20] have emphasized that adsorption equilibrium at a gas–solid interface contributes to the retention of the solute on a GLC column packed with an adsorption-active solid support coated with the liquid phase. Therefore, it is necessary for the characterization of adsorption effects on solute retention at interfaces to establish theoretically or empirically the relationship between the specific surface area of the liquid phase layer and the amount of the liquid phase loaded.

Berezkin[3] and Serpinet[21,22] tried to interpret qualitatively changes in the distribution of the liquid phase loaded on the solid support according to the equilibrated thin film–capillary liquid model proposed by Giddings[23,24]. However, they made no attempt to develop a quantitative relationship between the specific surface area of the liquid phase or the solid support and the liquid loading on the basis of this model. Nikolov and co-workers[25,26,27] successfully derived a semi-empirical equation for describing the change in the specific surface are aof the liquid phase with variation in the liquid loading when some liquid phases were loaded on commercially available solid supports. This equation has the significant disadvantage that some unknown constants must be determined experimentally, and this may prevent the equation from becoming generally used.

We have previously reported that the retention volume of the solute, measured at low liquid loadings, could be interpreted quantitatively fairly well by considering the contributions of adsorption equilibria between the clean surface of the solid support and the monolayer of the liquid phase spread on its surface[28]. In this paper, the equations that describe the quantitative relationship between the retention volume of the solute and the liquid loading will be developed by considering the heterogeneous adsorptivities of the solid support surface and different sources of the solute retention on the basis of the possible distribution of the liquid phase on the solid support. Modified alumina, a solid support with a large adsorptivity, was used in order to ensure maximal adsorption effects on the retention of the solute. The solutes used were hydrocarbons that were not subject to irreversible adsorption or catalytic reactions on the solid support surface. Two commercially available liquid phases, silicone DC 200 and Oronite polybutene 128, were used as a non-polar and a weakly polar liquid phases, respectively, without the possibility of unusual interactions with the solutes.

EXPERIMENTAL

The modified alumina was prepared from Neobead MS. C (60–80 mesh fractions) (Mizusawa Industrial Chemicals, Tokyo, Japan) by ignition at 1000° for 2 h. Silicone DC 200 and Oronite polybutene 128 were loaded on the solid support without further purification. The solutes were saturated, unsaturated and cyclic

aliphatic hydrocarbons containing six and seven carbon atoms and benzene. A commercially available Chromosorb P support was used for comparison.

Hitachi K53 and K23 gas chromatographs equipped with thermal conductivity detectors and stainless-steel columns (100 × 0.3 cm I.D.) were used. The carrier gas (helium) flow-rate was 40 ml/min, the sample was injected with a 10-μl microsyringe and the column temperature was 60°. The packed column was pre-conditioned for 16 h in a stream of nitrogen and for 1 h in a stream of helium at 120°.

Retention volumes measured from the air peak to the particular peak maxima were corrected for water vapour pressure measured with a soap-film flowmeter and for pressure drop in the column. The specific surface area of the modified alumina ($\sigma^0 = 51.6$ m²/g) was measured by the method of adsorption of p-nitrophenol from benzene solution (PNP method)[29].

RESULTS AND DISCUSSION

When Chromosorb P was used as the solid support, graphs of retention volume against liquid loading were linear for each solute–liquid phase pair, except at very low liquid loadings (Figs. 1 and 2).

Such linear graphs suggest that bulk solution partition is the main contributor to solute retention, although the straight lines have small positive intercepts on the
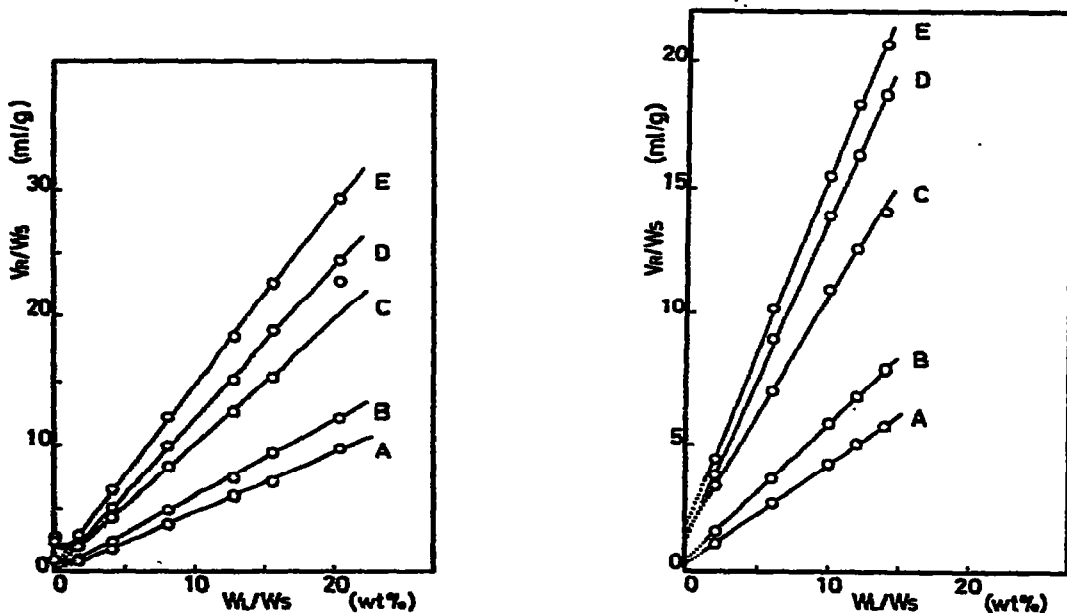

Fig. 1. Graphs of retention volume per gram of solid support, V_R/W_s, against liquid loading, W_L/W_s. Solid support: Chromosorb P. Stationary liquid phase: silicone DC 200. Solutes: A, 2-methylpentane; B, n-hexane; C, benzene; D, cyclohexene; E, n-heptane.

Fig. 2. Graphs of retention volume per gram of solid support, V_R/W_s, against liquid loading, W_L/W_s. Solid support: Chromosorb P. Stationary liquid phase: Oronite polybutene 128. Solutes: A, 2-methylpentane; B, n-hexane; C, benzene; D, cyclohexene; E, n-heptane.

ordinate due to the contribution of adsorption. Using the equations $V_L = W_L/\varrho_L$, $A_L = \sigma_L W_s$ and $A_s = \sigma_s W_s$, eqn. 1 can be written in the form:

$$V_R/W_s = K_L'(W_L/W_s) + K_A\sigma_L + K_s\sigma_s \qquad (2)$$

where $K_L' = K_L/\varrho_L$, ϱ_L is the density of the liquid phase at the column temperature and σ_L and σ_s are the surface area of the liquid phase coated and the solid support per unit weight of the free solid support in the column respectively. Eqn. 2 described the linear graphs shown in Figs. 1 and 2 if the terms $K_A\sigma_L + K_s\sigma_s$ were held constant for any liquid loading. Thus, a value of K_L' for each solute can be determined from the slope of the straight line and the results are given in Table I. The intercept of this straight line does not correlate with the retention volume of the solute on the clean surface of the solid support, so that the effects of adsorption on the solute retention cannot be described by means of eqn. 2.

TABLE I

GAS–LIQUID PARTITION CONSTANTS, K_L' (ml/g), OF SOLUTES

Solid support: Chromosorb P.

Solute	Liquid phase	
	Silicone DC 200	Oronite polybutene 128
n-Hexane	60	54
2-Methylpentane	45	39
Cyclohexane	106	110
1-Hexene	55	46
2-Hexene	63	53
Cyclohexene	118	125
n-Heptane	141	139
2-Methylhexane	109	107
2-Heptene	153	142
Benzene	96	92

When adsorption-active modified alumina was used as solid support, plots of V_R/W_s against W_L/W_s gave hyperbolic curves with minimum values for all solute–liquid phase pairs (Figs. 3 and 4). A steep decrease in the retention volume to its minimum value could be qualitatively understood to be due to progressive shielding of adsorption-active sites on the solid support with an expanding thin film of the liquid phase. Also a linear increase in retention volume beyond the minimum could be interpreted as being due to increasing contributions of bulk solution partition over the others after complete shielding of all of the active sites on the solid support with the thin film.

These retention volumes were analysed by the procedure of Conder and co-workers[1,2], as was done successfully previously[28]. In Figs. 5 and 6, it can be seen that graphs of V_R/W_L against W_s/W_L gave four straight lines when silicone DC 200 was used as the liquid-phase and three when Oronite polybutene 128 was used. The liquid loading ranges for which linear relationships were obtained are called region
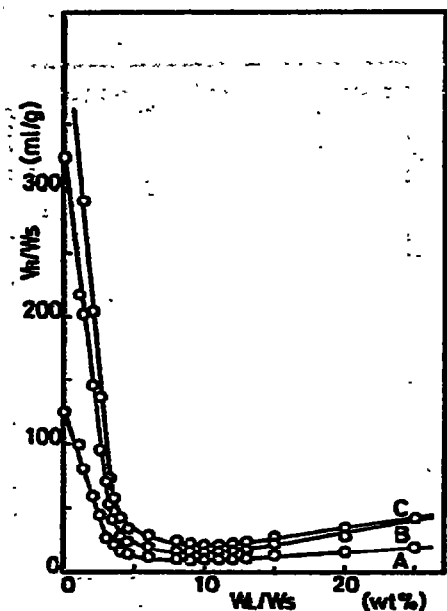
Fig. 3. Variation of retention volume per gram of solid support, V_R/W_s, with liquid loading, W_L/W_s. Solid support: modified alumina. Stationary liquid phase: silicone DC 200. Solutes: A, n-hexane; B, cyclohexene; C, n-heptane.
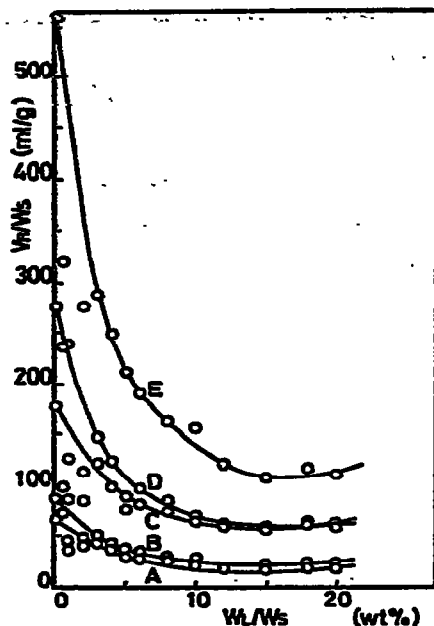
Fig. 4. Variation of retention volume per gram of solid support, V_R/W_s, with liquid loading, W_L/W_s. Solid support: modified alumina. Stationary liquid phase: Oronite polybutene 128. Solutes: A, 2-methylpentane; B, n-hexane; C, cyclohexene; D, n-heptane; E, benzene.

1 for the lowest, region 2 for the second, region 3 for the third and region 4 for the highest range.

Although in a preceding paper[28] the graph of V_R/W_L against W_s/W_L could be approximately described by two straight lines for each solute, with a break near the liquid loading giving the minimum retention volume, a number of measurements at short intervals in the present study revealed detailed profiles of the graph. Because the results can be described by several straight lines with different slopes and intercepts, separate retention mechanisms are believed to dominate the different regions of the liquid loading. The liquid loading at the point of intersection between two adjacent linear graphs, as shown in Table II, is regarded as a meaningful value because it remains almost constant, regardless of the nature of the solute.

The solid support surface was previously considered to be completely covered with a monolayer of the liquid phase near the liquid loading giving the minimum retention volume. Such a liquid loading, according to a previous concept, can be decided in the present paper as 4.36 wt.-% for silicone DC 200 and 12.6 wt.-% for Oronite polybutene 128 loaded on to the modified alumina support. If the liquid loading is lower, it is expected that the effects of adsorption on the clean surface of the solid support and/or on the liquid phase monolayer formed on it will contribute to the retention of the solute. Assuming that the solute retention is due only to adsorption on the clean surface of the solid support with uniform adsorptivity of the
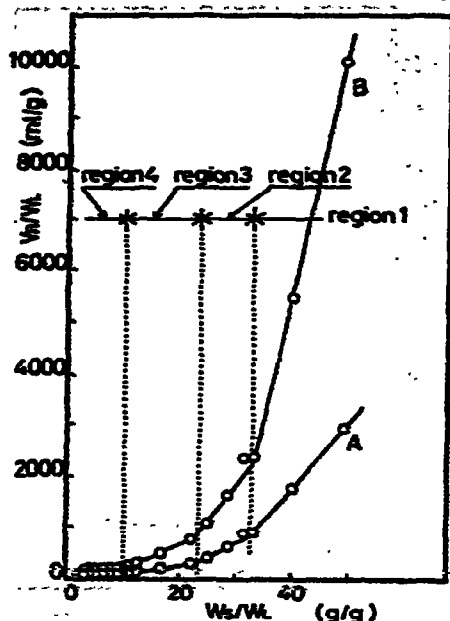
Fig. 5. Graphs of V_R/W_L against W_s/W_L. Solid support: modified alumina. Stationary liquid phase: silicone DC 200. Solutes: A, n-hexane; B, n-heptane.
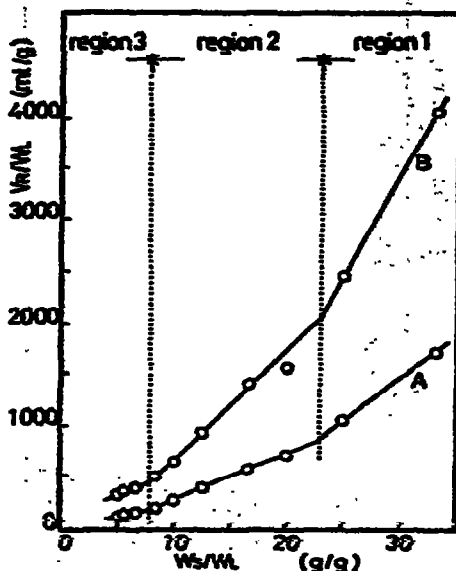
Fig. 6. Graphs of V_R/W_L against W_s/W_L. Solid support: modified alumina. Stationary liquid phase: Oronite polybutene 128. Solutes: A, n-hexane; B, cyclohexene.

TABLE II

LIQUID LOADINGS AT THE POINTS OF INTERSECTIONS BETWEEN TWO ADJACENT STRAIGHT LINES IN REGIONS 1 AND 2, IN REGIONS 2 AND 3 AND IN REGIONS 3 AND 4

Solid support: modified alumina.

Solute	Liquid phase				
	Silicone DC 200			Oronite polybutene 128	
	$W_{1,2}/W_s$ (%, w/w)	$W_{2,3}/W_s$ (%, w/w)	$W_{3,4}/W_s$ (%, w/w)	$W_{1,2}/W_s$ (%, w/w)	$W_{2,3}/W_s$ (%, w/w)
n-Hexane	3.08	4.31	10.3	4.36	12.6
2-Methylpentane	2.94	4.29	10.3	4.32	12.7
Cyclohexane	2.98	4.32	10.3	4.45	11.5
1-Hexene	3.80	4.45	9.90	4.62	12.6
2-Hexene	2.95	4.22	10.7	5.12	12.6
Cyclohexene	3.01	4.27	9.86	4.57	13.0
n-Heptane	3.03	4.42	10.1	4.22	12.6
2-Methylhexane	2.96	4.36	9.87	4.29	12.5
1-Heptene	3.82	4.26	9.95	4.33	13.0
2-Heptene	3.53	4.66	10.2	4.11	12.8
Benzene	2.95	4.66	10.1	4.30	13.1

solute and decreases in proportion to the surface area of the clean surface with an increase in the liquid loading, the retention volume can be expressed as

$$V_R/W_s = \bar{K} s_a^0 - (s_L N_{av}/M_L)(W_L/W_s) \tag{3}$$

where σ^0 is the specific surface area of the solid support, N_{av} is Avogadro's number and s_L and M_L are the cross-sectional area of a molecule and the molecular weight of the liquid phase, respectively.

When silicone DC 200 was used as liquid phase, graphs of V_R/W_s against W_L/W_s for n-hexane and 1-hexene, as shown in Fig. 7, gave the curved solid lines drawn under the respective straight broken lines predicted by eqn. 3. Similar results were obtained for the other solutes when the same liquid phase and even when Oronite polybutene 128 was used as liquid phase. Plots of experimental data for each solute can be expected to appear above the broken line predicted by eqn. 3 because the retention volume observed is subject to the contribution of adsorption on the liquid phase monolayer as well as that on the clean surface of the solid support. Fig. 7 shows that the retention volume of the solute decreased more than predicted by eqn. 3 when the liquid phase was loaded on to the modified alumina. Assuming heterogeneous adsorptivities of the modified alumina surface for the solute, these results can be reasonably interpreted as being due to preferential shielding of more strongly adsorptive sites with the liquid phase as a monolayer. Heterogeneity of the surface properties of any metal oxide generally occurs because of the presence of surface functional groups such as hydroxyl groups. It is probable
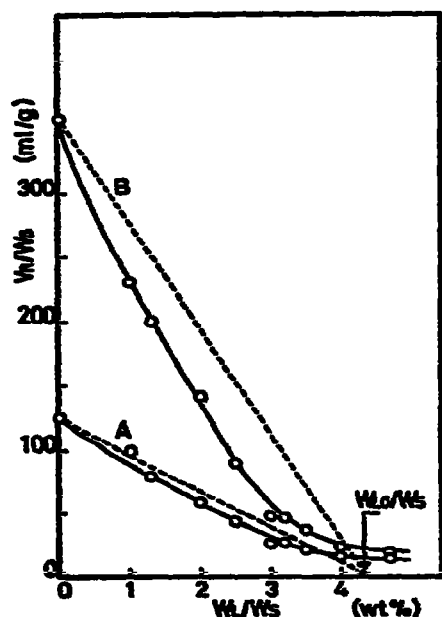

Fig. 7. Variation of retention volume per gram of solid support, V_R/W_s, with liquid loading, W_L/W_s, at low liquid loadings. Solid lines, observed data; broken lines, calculated data from eqn. 3. Solid support: modified alumina. Stationary liquid phase: silicone DC 200. Solutes: A, n-hexane; B, 1-hexene.

that some different sites with their various adsorptivities for the solute were dispersed on the modified alumina surface. The graph of V_R/W_L against W_s/W_L for any solute can be described by two straight lines at liquid loadings lower than that required for complete coverage of the modified alumina surface with a monolayer. It is considered that the modified alumina surface consists of two subsurfaces dispersing more and less adsorptive sites. Thus, the W_{Li}/W_s value for each solute listed in Table II can be regarded as the liquid loading required for complete coverage of the subsurface with more adsorptive sites with a monolayer of the liquid phase. At such lower liquid loadings, the peak shape was improved and the difference between the retention volumes of an n-alkane and the 1-alkene with the same number of carbon atoms but with different adsorptivities for the solid support surface decreased with increasing liquid loading. These observations indicate that the surface of the liquid phase monolayer shows a homogeneous adsorptivity for the solute regardless of the adsorptivities of the solid support surfaces under the monolayer. The loading of the liquid phase consequently resulted in an apparently decreasing adsorptivity of the solid support and the occurrence of a homogeneous surface.

At liquid loadings higher than that required for complete coverage of the solid support with a monolayer, the graph of V_R/W_L against W_s/W_L can be described by two straight lines with different slopes and intercepts when silicone DC 200 was used and one straight line when Oronite polybutene 128 was used.

Fig. 8 shows plots of the relative retention against liquid loading for 1-hexene and n-hexane, which have similar molecular sizes and boiling points but very different adsorptivities for the solid support surface. The relative retention decreased similarly for either liquid phase loaded on to Chromosorb P with an increase in the liquid
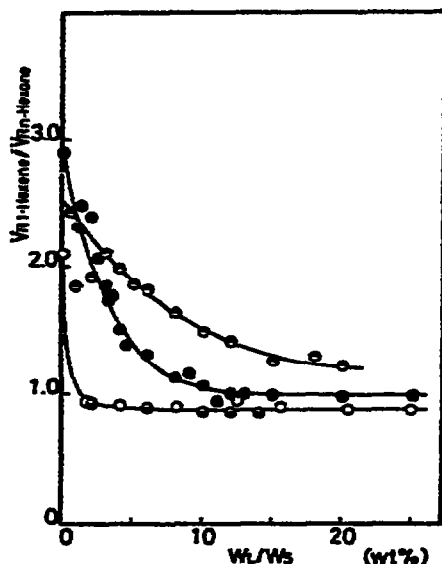

Fig. 8. Variation in the ratio of the retention volumes of 1-hexene and n-hexane, $V_{R(1-Hexene)}/V_{R(n-Hexane)}$, with liquid loading. O, Silicone DC 200 loaded on Chromosorb P; ◒ Oronite polybutene 128 loaded on Chromosorb P; ● silicone DC 200 loaded on modified alumina; ◓ Oronite polybutene 128 loaded on modified alumina.

loading, and reached a constant value near unity at very low liquid loading. This result indicates that, in the range where the relative retention is held constant, bulk solution partition is the major contributor to the retention of the solute. On using the modified alumina support, the relative retention decreased more rapidly for silicone DC 200 than for Oronite polybutene 128 with increasing the liquid loading; it became constant at about 12 wt.-% loading of silicone DC 200 but had not become constant even at 20 wt.-% loading of Oronite polybutene 128. The distribution of the liquid phase on the modified alumina became similar to that on Chromosorb P when silicone DC 200 was loaded at a liquid loading higher than 12 wt.-%, corresponding region 4 in Fig. 5. When Oronite polybutene 128 was loaded on to the modified alumina, Fig. 8 shows that further liquid loading leads to the appearance of region 4. Thus, when the liquid loading is greater than that required for complete coverage of the solid support with a monolayer, the liquid phase is considered to expand as a bulk liquid-like layer on the homogeneous surface of the monolayer with increasing the liquid loading. At these loadings, the contribution of adsorption on the monolayer surface to the solute retention decreases and that of bulk solution partition increases. The occurrence of a predominating contribution of bulk solution partition to the retention of the solute indicates the achievement of complete coverage of the solid support surface with the liquid phase as a bulk liquid-like layer. The W_{L2}/W_s value obtained for silicone DC 200 can be regarded as the liquid loading required for such complete coverage. A further increase in the liquid loading causes only an increase in the thickness of the bulk liquid-like layer covering the solid support surface.

From these considerations, the retention mechanism can be discussed on the basis of the four different models for distribution of the liquid phase on the modified alumina support, depending on the liquid loading. As mentioned above, the surface of the modified alumina support is assumed to consist of two different subsurfaces, surface 1 with a large and surface 2 with a small adsorptivity.

In region 1, surface 1 (surface area: $A_1 = \sigma_1 W_s$) is considered to be partly covered with the liquid phase as a monolayer. Using the relation where the total surface area of the solid support in the column, $A_s^0 = \sigma^0 W_s$, is equals to the sum of surface area of surfaces 1 and 2, $A_1 + A_2$, and using the surface area of the monolayer, A_L, the following equations can be written:

$$A_s^0 = (A_1 - A_L) + A_2 + A_L \tag{4}$$

and

$$A_L = (s_L N_{av}/M_L)W_L \tag{5}$$

where W_L is the total weight of the liquid phase in the column. An apparent adsorptivity of the solid support surface, $K_s A_s^0$, which is equal to the retention volume observed at zero liquid loading, V_{RO}, can be written by using the intrinsic adsorptivities of two subsurfaces, $K_1 A_1$ for surface 1 and $K_2 A_2$ for surface 2:

$$K_s A_s^0 = K_1 A_1 + K_2 A_2 \tag{6}$$

Considering that effects of adsorption equilibria on surface 1 (surface area: $A_1 - A_L$),

surface 2 (A_2) and the monolayer surface (A_L) contribute to the retention of the solute, the retention volume can be expressed as

$$V_R = K_1(A_2 - A_L) + K_2 A_2 + K_A A_L \qquad (7)$$

where K_A is Henry's constant for adsorption equilibrium on the monolayer and is assumed to be smaller than either K_1 or K_2. Substituting eqns. 4, 5 and 6 into eqn. 7, the following equation can be written:

$$V_g = -(K_1 - K_A)(s_L N_{av}/M_L) + K_2 \sigma_s^0 (W_s/W_L) \qquad (8)$$

where $V_g = V_R/W_L$.

In region 2, the monolayer of the liquid phase expands on surface 2 after complete coverage of surface 1, with increasing liquid loading. Assuming that K_A is the same for both of the monolayer surfaces formed on surfaces 1 and 2, effects of adsorption on surface 2 [surface area: $A_2 - (A_L - A_1)$] and the monolayer surface (A_L) contribute to the retention of the solute. Then, the retention volume in this region can be written in the form

$$V_R = K_2[A_2 - (A_L - A_1)] + K_A A_L \qquad (9)$$

Rearranging eqn. 9 by using eqns. 4 and 5, the specific retention volume can be expressed in the form

$$V_g = -(K_2 - K_A)(s_L N_{av}/M_L) + K_2 \sigma_s^0 (W_s/W_L) \qquad (10)$$

In region 3, the liquid phase provides further coverage as a bulk liquid-like layer on the monolayer with which the solid support surface is completely shielded. Effects of adsorption on the surface of the bulk liquid-like layer can be neglected because of the relatively large solubilities of the solute in both of the liquid phases under study. Considering that effects of bulk solution partition and of adsorption equilibria at the bulk liquid-like layer–monolayer and gas–monolayer interfaces contribute to the solute retention, the retention volume can be written as

$$V_R = K_L'(W_L - W_{L0}) + K_A(A_s^0 - A_{LB}) + K_s' A_{LB} \qquad (11)$$

where W_{L0} is the weight of the liquid phase required for complete coverage of the solid support surface as a monolayer, K_s' is Henry's constant for adsorption equilibrium at the bulk liquid-like layer–monolayer interface, and A_{LB} is the area of the monolayer covered with the bulk liquid-like layer [$A_{LB} = \alpha(W_L - W_{L0})$], the specific retention volume can be expressed as

$$V_g = K_{exp}' + [K_A \sigma_s^0 - K_{exp}'(W_{L0}/W_L)](W_s/W_L) \qquad (12)$$

where $K_{exp}' = K_L' \alpha(K_A - K_s')$; the proportionality factor, α, can be expected to have a constant value for a particular liquid phase–solid support pair, regardless of the nature of the solute.

In region 4, the monolayer surface is completely covered with the bulk liquid-like layer and a further increase in the liquid loading increases the thickness of the layer. The retention volume of the solute can be expected to be subject to contribu-

tions of bulk solution partition and of adsorption at the bulk liquid-like layer–monolayer interface. Hence the retention volume can be written as

$$V_R = K_s' A_s^0 + K_L' (W_L - W_{L_0})$$ (13)

and then

$$V_e = K_L' + [K_s' \sigma_s^0 - K_L'(W_{L_0}/W_s)] (W_s/W_L)$$ (14)

    With eqns. 8, 10, 12 and 14 derived as above, the values of the slope and the intercept can be determined by the least-squares method for each straight line drawn in Figs. 3 and 4. With these values and the liquid loadings at three intersections listed in Table II, all of the unknown constants involved in the above four equations can be determined for silicone DC 200 and, except for K_L', α and K_s', for Oronite polybutene 128. The resulting values are given in Tables III–VI.

TABLE III

$K_s \sigma_s$ VALUES CALCULATED FROM THE SLOPE OF THE STRAIGHT LINE IN REGION 1 AND RETENTION VOLUMES OF THE SOLUTES AT ZERO LIQUID LOADING, V_{R_0}/W_s
Solid support: modified alumina.

Solute	Liquid phase			
	Silicone DC 200		Oronite polybutene 128	
	$K_s \sigma_s$ (ml/g)	V_{R_0}/W_s (ml/g)	$K_s \sigma_s$ (ml/g)	V_{R_0}/W_s (ml/g)
n-Hexane	121	124	78	88
2-Methylpentane	104	98	57	68
Cyclohexane	88	76	52	56
1-Hexene	322	350	179	181
2-Hexene	317	309	158	198
Cyclohexene	300	324	193	177
n-Heptane	460	—	219	276
2-Methylhexane	273	266	127	166
1-Hexene	1123	—	490	639
2-Hexene	1008	—	601	984
Benzene	965	—	414	559

    In Table III, the value of the slope of the straight line in region 1 is in good agreement with the V_{R_0}/W_s value of each solute observed at zero liquid loading. The results obtained showed that, as assumed previously, K_1 is always larger than K_2 and K_4 is always smaller than the K_1 and K_2 values for each solute.

    Tables IV and V show fairly good agreement between three values of K_4 obtained separately for the different solutes except for 2-heptene on silicone DC 200 and 2-hexene and 2-heptene on Oronite polybutene 128.

    In Table VI, the value of K_L' for each solute obtained on the modified alumina column is consistent with that obtained on the Chromosorb P column with silicone DC 200. The proportionality factor, α, had the same value for all solutes.

    As satisfactory results were obtained by analysis of the experimental data with the equations derived here, it can be concluded that the model for distribution

TABLE IV

ADSORPTION CONSTANTS, K_1 (cm), K_2 (cm) AND K_4 (cm), ON MODIFIED ALUMINA, AND K'_{exp} VALUES (ml/g)

Liquid phase: silicone DC 200.

Solute	$K_1 \times 10^{-5}$	$K_2 \times 10^{-5}$	$K_4 \times 10^{-5}$			K'_{exp}
			Region 1	Region 2	Region 3	
n-Hexane	29.1	11.1	2.7	2.3	2.4	−58
2-Methylpentane	30.0	9.5	1.6	2.0	2.1	−65
Cyclohexane	20.7	8.8	2.5	2.4	2.3	−11
1-Hexene	78.9	25.9	1.7	2.5	3.3	−137
2-Hexene	79.9	20.7	2.7	3.1	3.2	−132
Cyclohexene	73.1	25.1	3.6	3.5	3.9	−109
n-Heptane	116	29.8	7.2	6.2	6.0	−203
2-Methylhexane	66.7	22.7	4.3	4.8	4.8	−161
1-Heptene	289	61.7	9.5	7.6	8.8	−471
2-Heptene	251	53.0	40.5	10.5	8.3	−350
Benzene	244	60.7	6.3	9.4	6.1	−277

TABLE V

ADSORPTION CONSTANTS, K_1 (cm), K_2 (cm) AND K_4 (cm), ON MODIFIED ALUMINA, AND K'_{exp} VALUES (ml/g)

Liquid phase: Oronite polybutene 128.

Solute	$K_1 \times 10^{-5}$	$K_2 \times 10^{-5}$	$K_4 \times 10^{-5}$			K'_{exp}
			Region 1	Region 2	Region 3	
n-Hexane	32.4	8.6	4.0	4.3	4.3	1.22
2-Methylpentane	24.7	6.9	3.2	3.4	3.4	0.41
Cyclohexane	17.9	7.0	6.0	5.8	6.1	10.1
1-Hexene	67.9	17.4	7.7	5.6	5.6	−0.43
2-Hexene	77.0	17.6	—	5.7	5.7	−0.15
Cyclohexene	59.6	20.8	11.7	10.9	10.5	15.2
n-Heptane	105	25.5	8.5	11.2	11.2	3.10
2-Methylhexane	58.9	17.7	8.2	8.7	8.8	0.78
1-Heptene	258	51.1	14.0	15.4	14.5	−1.16
2-Heptene	428	62.4	—	18.9	18.5	−8.66
Benzene	217	49.7	19.9	21.9	20.8	9.94

of the liquid phase on the solid support is valid for the quantitative interpretation of the retention mechanism in the GLC system under study. Also, the surface of the porous solid can be simply approximated as a plane wettable with the liquid phase.

From these considerations, at low liquid loadings, adsorption equilibria on the clean surface of the modified alumina and on the liquid phase monolayer formed on it are the main factors in the GLC system. At high liquid loadings, the observed effects of adsorption are due to contributions of adsorption equilibria at the gas–monolayer and the bulk liquid-like layer–monolayer interfaces. It was found that the adsorption-active modified alumina required a large amount of liquid phase for complete coverage of its surface with a monolayer and more for the occurrence of a predominating contribution of the bulk solution partition to the solute retention.

TABLE VI

ADSORPTION CONSTANTS, K_i' (cm), PROPORTIONALITY FACTORS, α (m^2/g), AND GAS–LIQUID PARTITION CONSTANTS, K_L' (ml/g), OF SOLUTES

Liquid phase: silicone DC 200. Solid support: modified alumina.

Solute	$K_s' \times 10^{-4}$	K_L'		$\alpha \times 10^2$
		Al_2O_3	Chromosorb P	
n-Hexane	0.98	62	58	8.7
2-Methylpentane	0.78	48	45	8.7
Cyclohexane	1.01	110	106	10.1
1-Hexene	0.80	65	55	8.1
2-Hexene	0.91	70	63	8.7
Cyclohexene	1.42	127	118	9.4
n-Heptane	2.12	144	141	9.0
2-Methylhexane	1.94	111	108	9.4
1-Heptene	2.04	160	129	9.2
2-Heptene	2.51	160	152	8.8
Benzene	1.70	116	94	9.0

This approach to the quantitative interprepation of the retention mechanism in GLC can be expected to provide information on the heterogeneity in the surface properties of the solid, and studies on this aspect are now in progress.

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 V. G. Berezkin, J. Chromatogr., 65 (1972) 227.
4 Z. Suprynowicz, Chem. Anal. (Warsaw), 17 (1972) 267.
5 Z. Suprynowicz, Chem. Anal. (Warsaw), 18 (1973) 15.
6 Z. Suprynowicz, Chem. Anal. (Warsaw), 18 (1973) 251.
7 A. Waksmundzki, W. Rudziński, Z. Suprynowicz and J. Rayss, J. Chromatogr., 74 (1972) 3.
8 Z. Suprynowicz, A. Waksmundzki and W. Rudziński, J. Chromatogr., 67 (1972) 21.
9 R. L. Martin, Anal. Chem., 33 (1961) 347.
10 R. L. Pecsok, A. de Yllana and A. Abdul-Karim, Anal. Chem., 36 (1964) 452.
11 H. L. Liao and D. E. Martire, Anal. Chem., 44 (1972) 498.
12 J. R. Conder, Anal. Chem., 48 (1976) 917.
13 J. F. Parcher and C. L. Hussey, Anal. Chem., 45 (1973) 188.
14 D. E. Martire, Advan. Anal. Chem. Instrum., 6 (1967) 93.
15 D. C. Locke, Advan. Chromatogr., 14 (1976) 87.
16 V. G. Berezkin, D. Kouřilová, M. Krejčí and V. M. Fateeva, J. Chromatogr., 78 (1973) 261.
17 P. Urone and J. F. Parcher, Advan. Chromatogr., 6 (1968) 299.
18 J. Serpinet, Anal. Chem., 48 (1976) 2264.
19 P. Urone and J. F. Parcher, Anal. Chem., 38 (1966) 270.
20 D. E. Martire, in J. H. Purnell (Editor), Progress in Gas Chromatography, Interscience, New York, 1968, p. 93.

21 J. Serpinet, *Chromatographia*, 8 (1975) 18.
22 J. Serpinet, *J. Chromatogr. Sci.*, 12 (1974) 832.
23 J. C. Giddings, *Anal. Chem.*, 34 (1962) 458.
24 J. C. Giddings, *Anal. Chem.*, 35 (1963) 439.
25 R. N. Nikolov, *Chromatographia*, 6 (1973) 451.
26 R. N. Nikolov, *Chromatographia*, 7 (1974) 6.
27 R. N. Nikolov, L. D. Petkova and M. D. Shopova, *Chromatographia*, 7 (1974) 376.
28 T. Komaita, K. Naito and S. Takei, *J. Chromatogr.*, 114 (1975) 1.
29 C. H. Giles, A. P. D'silva and A. S. Trivedi, *J. Appl. Chem.*, 20 (1970) 37.