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ADSORPTION EFFECTS IN GAS–LIQUID PARTITION CHROMATOGRAPHY*

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SUMMARY

Contributions of adsorption on the surface of the support and/or stationary phase in gas–liquid partition chromatography were investigated by using an adsorption-active support and squalane, di-*n*-octyl phthalate, di-*n*-octyl sebacate or 1,2,3-tris(2-cyanoethoxy)propane as stationary phase. Adsorption effects vary with the adsorptivity of the support, the polarity of the stationary phase and the amount of the phase loaded on the support. Retention volumes of saturated and unsaturated hydrocarbons in the low liquid-loading range can be expressed in terms of the gas–liquid partition and adsorption on clean and liquid-coated support surfaces. The interaction of the solute with the surface of support is also discussed.

INTRODUCTION

Since the first studies by Martin[1,2], there have been a number of investigations by gas–liquid partition chromatography (GLC)[3–12] on the effects of adsorption of a solute on a support and/or liquid phase on the retention volume. The contributions of solution and adsorption equilibriums to the retention of a solute are thus, quantitatively, better understood. However, most investigations have been made with commercially available supports that have small specific surface areas and adsorptivities for solutes. There is, therefore, the danger of incomplete appreciation of the adsorption effects as these are relatively small.

In order to appreciate these effects completely, it is necessary to adjust the experimental conditions so as to optimize the contribution of the effects. One such method is to use supports with large specific surface areas and adsorptivities for solutes.

A method of preparation of adsorbent for gas–solid adsorption chromatography (GSC) was presented by our laboratory[13]. This consisted of treatment of alumina beads with hydrofluoric acid–potassium fluoride solution followed by ignition at high temperature. Adsorbents prepared in this way have large specific surface areas

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and adsorptivities compared with those of commercially available supports, and these properties can be varied continuously by variation of the ignition temperature. Adsorption effects may be clarified more precisely by using this adsorbent as the support for GLC and loading the support with stationary phases of different polarity.

EXPERIMENTAL

The modified alumina was prepared by immersion of Neobead MS. C (60–80 mesh) (Mizusawa Industrial Chemicals, Tokyo, Japan) in 2 *M* hydrofluoric acid–2 *M* potassium fluoride solution for 3 h followed by ignition at 500–800° for 1 h. Squalane, di-*n*-octyl phthalate (DNOP) and di-*n*-octyl sebacate (DNOS), and 1,2,3-tris(2-cyanoethoxy)propane (TCEP) were used as the non-polar, moderately polar and highly polar stationary phases, respectively. These liquids were loaded on to the support without further purification. The solutes were saturated, unsaturated and cyclic aliphatic hydrocarbons, containing five to eight carbon atoms, and benzene and toluene. Commercially available Chromosorb P, W and G supports were used for comparison.

A Hitachi 023 gas chromatograph equipped with a thermal-conductivity detector and stainless-steel (100 × 0.3 cm I.D.) columns was used. The carrier gas (helium) flow-rate was 40 ml/min. The sample was injected by means of a 1-μl microsyringe. The column temperature was 60°. The packed column was pre-conditioned for 12 h in a stream of nitrogen and for 1 h in a stream of helium at 120°. When the support was not loaded with liquid phase, the pre-conditioning in nitrogen was omitted.

Retention volumes measured from air peak to peak maximum were corrected for water pressure at a soap-film flow-meter and for the pressure drop in the column. The specific surface area of the modified alumina was measured by the BET method and by the method of adsorption of *p*-nitrophenol from benzene solution (PNP method)[14]. The modified alumina was examined with a Hitachi scanning electron-microscope HSM-2B (magnification, 7500 times) and by X-ray diffraction with a Geigerflex (Rigaku Denki).

RESULTS AND DISCUSSION

Adsorptivities of modified aluminas used as the support were investigated by GSC. As shown in Fig. 1 the apparent adsorptivity of the modified alumina decreased with increasing ignition temperature. Variations in the retention volumes with the ignition temperature were significant for the unsaturated aliphatic and aromatic hydrocarbons, and the retention volumes for the unsaturated hydrocarbons were greater than those of the saturated hydrocarbons having the same number of carbon atoms and similar structure. These results suggest that this adsorbent shows specific interaction with π electrons of the solute and belongs to type II as classified by Kiselev[15]. The order of elution from the column containing this adsorbent was cyclic, branched and straight chain for saturated hydrocarbons of almost the same boiling point, and *trans*- and *cis*-isomers for the 2-olefins. This suggests that steric factors of the solute affect the adsorption on this adsorbent. From the X-ray diffraction patterns, characteristic peaks of γ-alumina only and those of α-alumina and

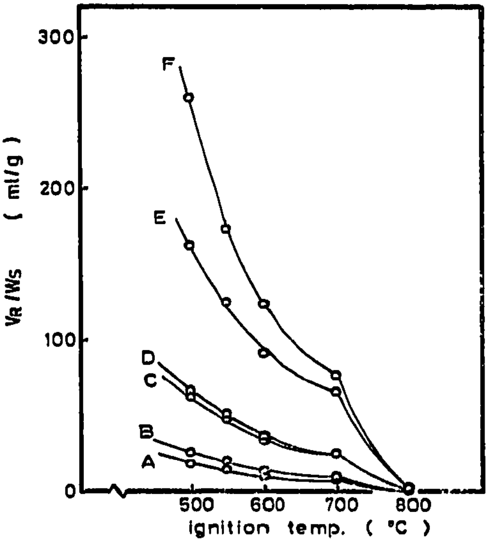


Fig. 1. Variation of apparent adsorptivity, V_R/W_s, of the modified alumina with the ignition temperature. Solutes: A = cyclohexane; B = *n*-hexane; C = *n*-heptane; D = 1-hexene; E = 1-heptene; and F = benzene.

K_3AlF_6 were observed for modified alumina ignited at 500–700° and 800°, respectively. With the scanning electron microscope, crystallization and pronounced crystal growth were observed for alumina ignited at 500–600° and 700–800°, respectively. From the X-ray diffraction observation, this crystal growth is seen to be K_3AlF_6.

The specific surface area of the modified alumina, as measured by the BET and PNP methods, decreased with increasing ignition temperature as shown in Fig. 2.

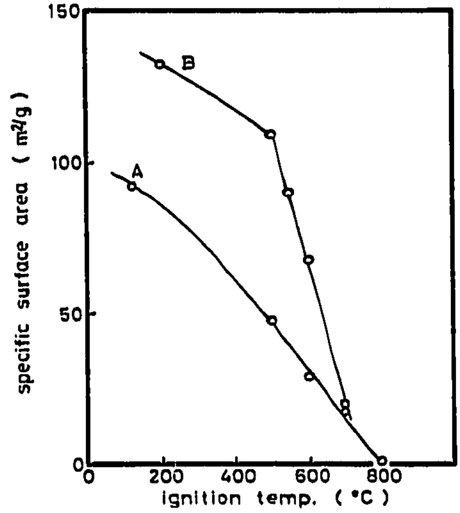


Fig. 2. Variation of the specific surface area of the modified alumina with the ignition temperature. The surface area was determined (A) by the PNP method, (B) by the BET method.

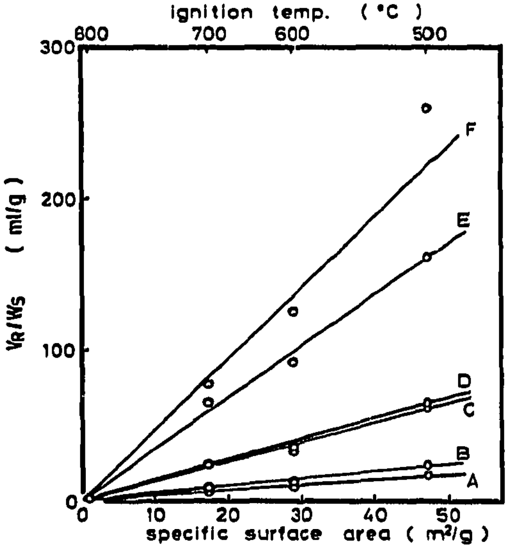


Fig. 3. Graphs of the retention volume per gram of alumina, V_R/W_s, against the specific surface area of the modified alumina adsorbent as determined by the PNP method. Solutes: A = cyclohexane; B = *n*-hexane; C = *n*-heptane; D = 1-hexene; E = 1-heptene; and F = benzene.

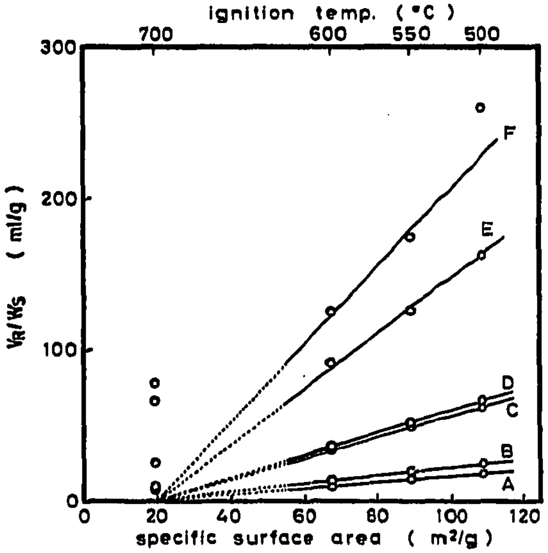


Fig. 4. Graphs of the retention volume per gram of alumina, V_R/W_s, against the specific surface area of the modified alumina adsorbent as adetermined by the BET method. Solutes: A = cyclohexane; B = *n*-hexane; C = *n*-heptane; D = 1-hexene; E = 1-heptene; and F = benzene.

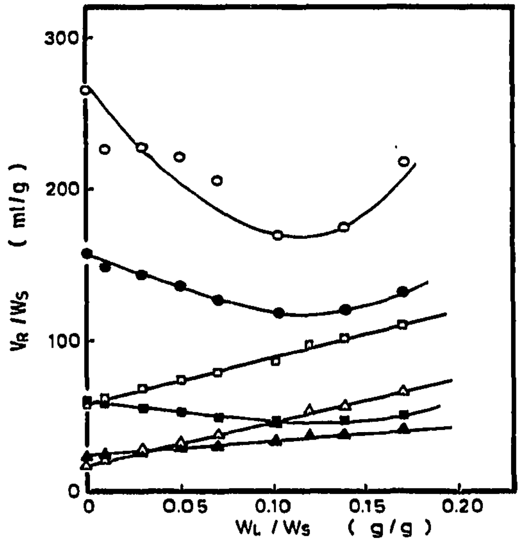
The fact that the specific surface area measured by the PNP method is smaller than that obtained by the BET method is considered to be due to the existence of micropores into which *p*-nitrophenol cannot enter. In Figs. 3 and 4 the specific surface area of the alumina obtained by both methods is plotted against retention volume per gram of alumina for each solute. In Fig. 3 the specific surface area obtained by the PNP method shows a linear relation with V_R/W_s for each solute which can be extrapolated to the origin, where V_R and W_s are the corrected retention volume and the weight of adsorbent in the column, respectively. This result shows that the apparent variations of the adsorptivity of the adsorbent with the ignition temperature are due to the variation of the specific surface area, but not to the adsorptivity per unit surface area of the adsorbent when the specific surface area obtained by the PNP method is adopted. However, when the specific surface area obtained by the BET method is adopted (Fig. 4), the graph of V_R/W_s against surface area is linear but cannot be extrapolated to the origin, and gives zero retention volume at a specific surface area of *ca.* 20 m^2/g. The modified alumina ignited at 700° has a specific surface area of *ca.* 20 m^2/g and this is responsible for the retention volume of each solute. It is concluded that the effective adsorption surface of the solute can be measured by the PNP method and the adsorption constant K_s for each solute on this adsorbent may be obtained from the slope of each line in Fig. 3. The results are shown in Table I. The apparent adsorptivity of the modified alumina ignited at 800° is as small as that of Chromosorb P used as comparison.

TABLE I

ADSORPTION CONSTANTS, K_s AND K_l, ON THE MODIFIED ALUMINA AND ON THE LIQUIDCOATED ALUMINA IGNITED AT 500° AND 600° IN THE LOW LIQUID LOADING RANGE

Solute	K_s ($\times 10^5$ cm)	K_l ($\times 10^5$ cm)							
		Squalane		*DNOP*		*DNOS*		*TCEP*	
		500°	*600°*	*500°*	*600°*	*500°*	*600°*	*500°*	*600°*
n-Pentane	1.8	2.0	2.0	2.4	2.4	—	—	2.2	2.1
n-Hexane	4.8	5.1	5.3	6.3	6.3	6.4	6.6	5.4	5.5
2-Methylpentane	4.3	4.6	4.7	5.5	5.5	5.5	5.7	4.7	4.9
Cyclohexane	3.9	3.8	4.3	5.6	4.8	5.0	5.3	4.2	4.4
1-Hexene	13.0	12.4	14.1	14.9	15.1	15.3	15.0	13.1	12.0
trans-2-Hexene	12.4	—	13.0	14.6	13.9	14.7	14.1	12.6	11.4
cis-2-Hexene	—	—	16.5	—	17.2	—	17.3	—	13.7
Cyclohexene	11.7	12.8	12.9	14.1	14.0	14.4	15.1	12.0	11.4
n-Heptane	12.3	12.5	13.4	15.6	16.1	16.1	16.8	13.4	13.7
2-Methylhexane	10.4	11.3	11.5	13.0	—	13.1	14.2	10.7	11.3
1-Heptene	33.3	31.6	35.5	37.3	37.1	38.7	38.9	31.9	29.4
trans-2-Heptene	—	—	32.0	—	—	—	37.3	—	28.3
cis-2-Heptene	36.9	—	39.7	42.6	43.4	43.6	43.8	36.0	36.7
n-octane	31.9	31.0	33.7	39.3	39.6	40.2	43.1	33.1	34.2
2-Methylheptane	20.6	19.5	20.6	23.5	23.2	24.1	26.5	20.3	20.9
1-Octene	82.7	77.5	88.4	98.2	97.1	94.7	96.6	80.9	74.2
trans-2-Octene	—	—	82.3	—	95.5	—	91.7	—	70.8
cis-2-Octene	85.2	—	97.8	95.9	116.0	107.2	106.8	90.3	82.5
Benzene	43.8	51.1	54.9	54.7	51.1	50.2	45.6	43.8	32.6
Toluene	154	181	193	190	169	182	159	150	108

When these adsorption-active modified aluminas are used as the column support in GLC the elution, behaviour of the solute varies with the support and the stationary phase used. Figs. 5–7 show the variation of retention volume of a number of solutes on the modified alumina ignited at 500° using squalane, DNOP and TCEP as the stationary phase, respectively. With squalane (Fig. 5), the retention volumes of saturated aliphatic hydrocarbons show a linear relation with the amount of liquid loaded, W_L/W_s, and the intercepts of these lines agree well with the retention volumes obtained for the clean support. On the other hand, the retention volumes of unsaturated aliphatic and aromatic hydrocarbons first decrease and then increase linearly with increasing amount of liquid loaded, and the amount of liquid required to give the minimum retention volume is almost constant, independent of the solute. With DNOP (Fig. 6), the variations in the retention volume of the solutes are similar to those of the unsaturated aliphatic and aromatic hydrocarbons with squalane. The moderately polar stationary phase DNOS gave similar results to DNOP. With the highly polar TCEP phase (Fig. 7), the retention volumes of the solutes decrease with increasing liquid loading, except for benzene, and the decrease is most pronounced in the low liquid-loading range. The amount of the liquid required to give the minimum retention volume decreases with decreasing adsorptivity of the support used as shown in Fig. 8.



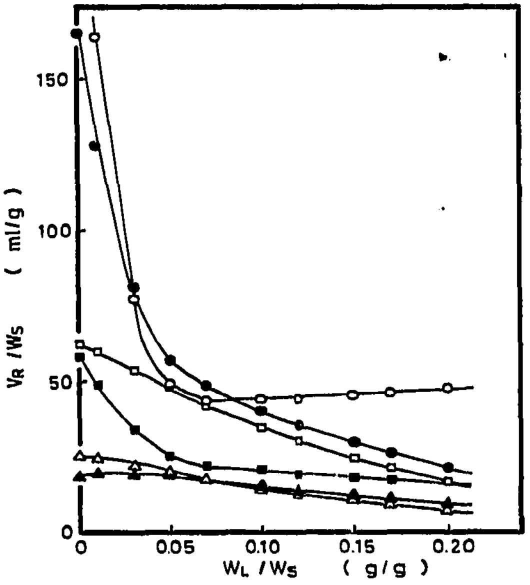


Fig. 5. Variation of the retention volume per gram of alumina, V_R/W_s, with the liquid loading, W_L/W_s. Support, modified alumina ignited at 500°. Stationary phase, squalane. Solutes: ▲—▲, *n*-hexane; ■—■, 1-hexene; △—△, cyclohexane; □—□, *n*-heptane; ●—●, 1-heptene; and ○—○, benzene.

Fig. 6. Variation of the retention volume per gram of alumina, V_R/W_s, with the liquid loading, W_L/W_s. Support as in Fig. 5. Stationary phase, DNOP. Solutes: △—△, *n*-hexane; ■—■, 1-hexene; ●—●, benzene; ○—○, 1-octene; and □—□, *n*-octane.

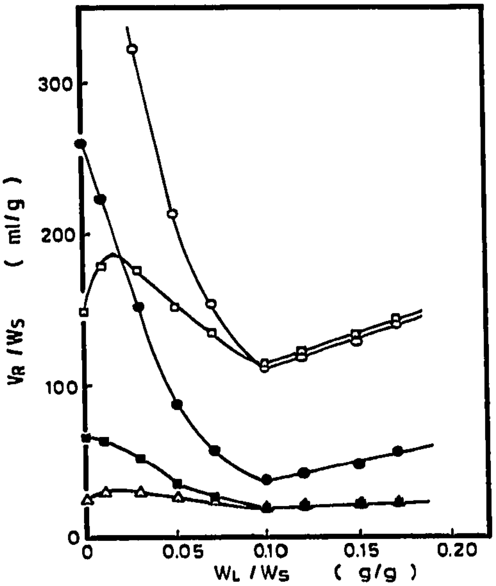


Fig. 7. Variation of the retention volume per gram of alumina, V_R/W_s, with the liquid loading, W_L/W_s. Support as in Fig. 5. Stationary phase, TCEP. Solutes: △—△, *n*-hexane; ▲—▲, cyclohexane; ■—■, cyclohexene; □—□, *n*-heptane; ●—●, 1-heptene and ○—○, benzene.

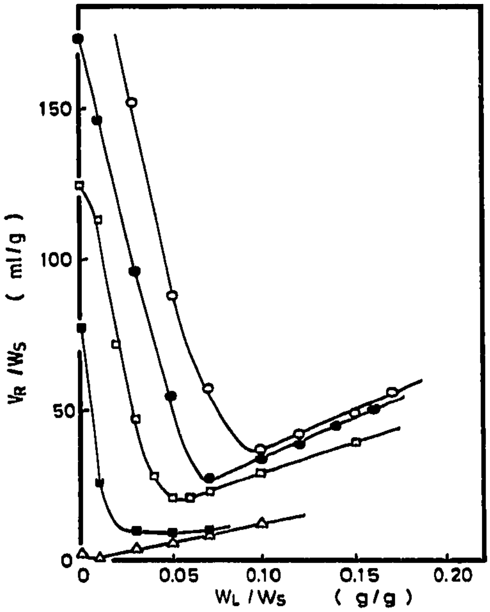


Fig. 8. Graph of the retention volume per gram of alumina, V_R/W_s, against the liquid loading, W_L/W_s, for benzene. Support: modified alumina, ignited at (○) 500, (●) 550, (□) 600, (■) 700, and (△) 800°. Stationary phase, DNOP.

When Chromosorb G, P and W were used as supports, graphs of the retention volume against the amount of the liquid loaded were linear for each liquid–solute pair, except at very low liquid loadings, and values of the gas–liquid partition constants, K_L', of the solutes obtained from the slopes of such graphs were independent of the kind of the support used, where K_L' is based on the weight of the liquid loaded rather than its volume. The mean value of K_L' for each solute is given in Table II.

TABLE II

GAS–LIQUID PARTITION CONSTANTS, K_L' (ml/g), OF SOLUTES WITH SQUALANE, DNOP AND DNOS AS STATIONARY PHASES ON CHROMOSORB AND ON MODIFIED ALUMINAS IGNITED AT 500 AND 600°, RESPECTIVELY

Solute	*Squalane*			*DNOP*			*DNOS*		
	Chromosorb	*Modified alumina*		*Chromosorb*	*Modified alumina*		*Chromosorb*	*Modified alumina*	
		500°	*600°*		*500°*	*600°*		*500°*	*600°*
n-Pentane	45	25	24	29	12	9	—	—	—
n-Hexane	115	36	76	75	45	32	92	71	68
2-Methylpentane	—	42	41	56	23	13	70	36	41
Cyclohexane	212	278	236	156	171	111	177	201	196
1-Hexene	96	51	8	77	42	32	94	69	76
2-Hexene	113	110	49	89	68	50	103	88	84
Cyclohexene	228	159	162	203	241	177	227	271	271
n-Heptane	287	287	242	190	136	97	230	195	205
2-Methylhexane	222	141	157	152	105	—	180	141	167
1-Heptene	242	151	70	198	161	111	233	204	237
2-Heptene	291	268	110	240	219	152	281	274	305
n-Octane	664	790	698	468	407	346	572	570	690
2-Methylheptane	245	79	75	174	46	22	212	96	167
1-Octene	559	500	354	476	430	376	578	545	648
2-Octene	665	757	491	—	567	488	685	699	788
Benzene	162	—	225	247	272	201	273	291	309
Toluene	469	—	793	635	771	622	710	805	855

The variations in the retention volumes of the solutes with the support, liquid phase and the amount of phase loaded on the column are considered to be due to the contribution of adsorption of the solutes on the surface of the support and/or liquid in addition to the gas–liquid partition. The retention volumes are analysed by the procedure of Conder *et al.*[8] who considered that the retention volume can be expressed as in eqn. 1, where K_L is the gas–liquid partition constant, V_L the volume of liquid

$$V_R = K_L V_L + K_A A_L + K_s A_s \tag{1}$$

loaded, K_A the constant for adsorption on the liquid surface and A_L and A_s are the total surface areas of the liquid and support in the column, respectively. By using the retention volume per unit weight of a support, eqn. 2 is obtained, where σ_A and σ_s are

$$\frac{V_R}{W_s} = \frac{K_L V_L}{W_s} + K_A \sigma_A + K_s \sigma_s \tag{2}$$

$$\frac{V_R}{V_L} = K_L + \frac{(K_A \sigma_A + K_s \sigma_s) W_s}{V_L} \tag{3}$$

specific surface areas of the support and the liquid on the support, respectively. From eqn. 2, relation 3 is obtained, and the contributions of gas–liquid partition and adsorption on the surface of the support and/or liquid to the retention volume of the solute can be estimated by plotting V_R/V_L against W_s/V_L. The experimental results were thus analysed, but in this work W_L is used instead of V'_L and K'_L contains the density of the stationary phase at the column temperature.

In Figs. 9–11 graphs of V_R/W_L against W_s/W_L are shown for squalane, DNOP and TCEP, respectively, as liquid phase on the modified alumina ignited at 500°. For squalane (Fig. 9), the graph is approximated by two straight lines, except that the saturated hydrocarbons each give one straight line. It is clear that the contribution of adsorption varies with the amount of liquid loaded. Since similar graphs for squalane and DNOP on the chromosorb supports gave straight lines of zero slope, the contribution of adsorption on the liquid surface is considered to be negligible. Therefore, on these liquid-loaded columns, it is only necessary to consider adsorption on the support. However, the graph for TCEP on Chromosorb gave a straight line of positive slope, and here contributions of adsorption on both surfaces must be considered.

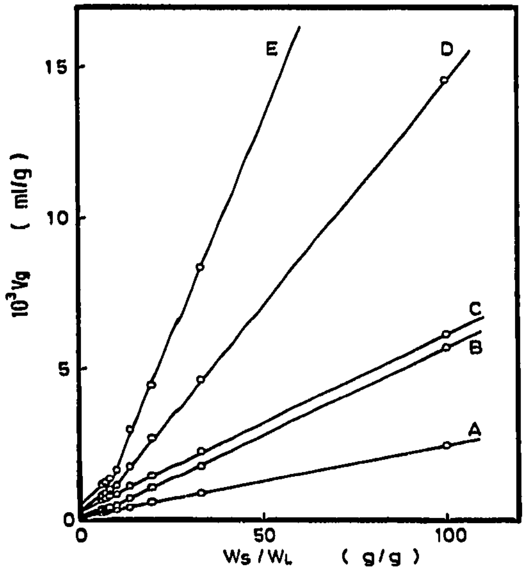
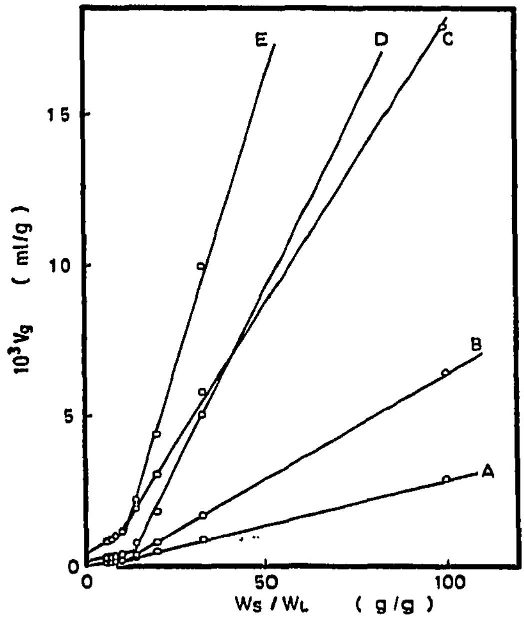


Fig. 9. Graph of V_g (= V_R/W_L) against W_s/W_L. Support, modified alumina ignited at 500°. Stationary phase, squalane. Solutes: A = *n*-hexane; B = 1-hexene; C = *n*-heptane; D = 1-heptene; and E = benzene.

The straight lines in the low liquid-loading range in Figs. 9–11 have negative intercepts, and cannot be explained by eqn. 3. However, the adsorption constants, K_1, obtained from the slopes of the straight lines and the specific surface areas of the supports agree well with the adsorption constants, K_s, on the clean support (Table I). Secondly, the intercepts of the straight lines in the high liquid-loading range are fairly close to the gas–liquid partition constants, K'_L, obtained on the Chromosorb supports (Table II). The agreement is not as good as that of K_1 and K_s, and the intercepts with



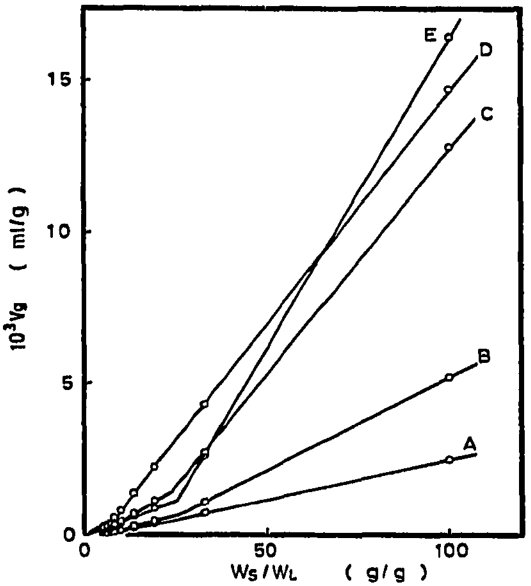


Fig. 10. Graph of V_g (= V_R/W_L) against W_s/W_L. Support as in Fig. 9. Stationary phase, DNOP. Solutes: A = *n*-hexane; B = 1-hexene; C = *n*-octane; D = benzene; and E = 1-octene.

Fig. 11. Graph of V_g (= V_R/W_L) against W_s/W_L. Support as in Fig. 9. Stationary phase, TCEP. Solutes: A = *n*-hexane; B = 1-hexene; C = 1-heptene; D = *n*-octane; and E = benzene.

TCEP as stationary phase gave negative values, except for benzene and toluene. The result with TCEP seemed to be due partly to the very small K_L' value; however, the straight line in the high liquid-loading range must be considered to be an approximation. It is reasonable that the slope decreases gradually and is not constant, that is the adsorption constant on the support coated with the liquid decreases gradually with increasing thickness of the liquid film. It is concluded that it is difficult to measure K_L' values using adsorption-active supports and eqn. 3.

The adsorption constants obtained from the slopes of the straight lines in the high liquid-loading range and the specific surface areas of the supports are smaller than K_1 (Table III).

Similar results were obtained when the modified alumina ignited at 600° and DNOS were used as the support and stationary phase, respectively (Tables I–III). The amount of liquid loaded at the point of intersection of the two straight lines agrees well with that giving the minimum retention volumes. The thickness of the DNOP film on the support which gives the minimum retention volume may be calculated from the specific surface area measured by PNP method and the density of DNOP at 20°, 0.978 g/ml (ref. 16). Values of 19–20 Å were obtained regardless of the support used. The minimum thickness of the liquid film which gives the gas–liquid partition-controlled retention volume is thus considered to be constant, independent of the adsorptivity of the support, and to be of the order of a monomolecular layer. The adsorptivity of the support decreases considerably on coating with the liquid monolayer and is almost constant on further increasing the film thickness.

TABLE III

ADSORPTION CONSTANTS, K_2, ON LIQUID-LOADED SUPPORTS WITH VARIOUS STATIONARY PHASES IN THE HIGH LIQUID-LOADING RANGE

Solute	*K_2 (× 10^5 cm)*					
	Modified alumina support					
	500°			*600°*		
	Squalane	*DNOP*	*DNOS*	*Squalane*	*DNOP*	*DNOS*
n-Pentane	—	1.4	—	—	1.3	—
n-Hexane	—	3.1	3.3	—	3.2	3.3
2-Methylpentane	—	2.9	3.1	—	2.9	3.0
Cyclohexane	—	1.6	1.5	—	2.7	1.6
1-Hexene	8.4	3.1	3.0	10.0	2.9	2.8
2-Hexene	7.2	2.8	3.0	9.3	3.0	3.3
Cyclohexene	—	1.0	0.8	—	2.2	0.8
n-Heptane	—	7.3	8.0	—	7.5	7.7
2-Methylhexane	—	5.9	6.6	—	—	6.0
1-Heptene	21.4	6.2	7.0	25.3	7.1	6.2
2-Heptene	22.4	6.2	6.8	28.3	7.7	6.1
n-Octane	—	15.6	18.2	—	14.7	15.1
2-Methylheptane	—	10.8	12.1	—	10.1	10.4
1-Octene	52.9	14.5	16.6	61.1	13.6	14.3
2-Octene	50.2	13.8	16.8	59.8	13.5	14.6
Benzene	—	2.0	1.7	31.3	3.1	1.3
Toluene	—	3.4	3.7	103	5.8	2.8

From these considerations the retention volume on the low liquid-loading support may be expressed as in eqns. 4 and 5,

$$V_R = K_L' W_L + K_s A_{s1} + K_2 A_{s2} + K_A A_{s2} \tag{4}$$

$$A_s^0 = W_s \sigma_s = A_{s1} + A_{s2} \tag{5}$$

where A_{s1} and A_{s2} are the surface areas of clean and liquid-coated support, respectively, and the surface area of the liquid film is assumed to be equal to A_{s2}. By using the molecular weight of the stationary liquid, M_L, the cross-sectional area of the liquid molecule, σ_L, and the Avogadro number N_A, the following relation is obtained from eqn. 4.

$$\frac{V_R}{W_L} = K_L' + \frac{N_A \sigma_L [(K_2 + K_A) - K_1]}{M_L} + \frac{K_s \sigma_s W_s}{W_L} \tag{6}$$

Eqn. 6 is able to explain the fact that the adsorption constant K_1 obtained from the slope of the straight line in the low liquid-loading range is equal to the adsorption constant on the clean support, K_s. If the straight line in the low liquid-loading range can be fully explained by eqn. 6, the sum of the constant terms in this equation must be negative. However, the cross-sectional areas of these liquids are unknown and cannot be calculated accurately. For DNOP–solute pairs, the sum of the constant terms was calculated on the assumption that the cross-sectional area of DNOP is the same as that of *p*-nitrophenol, 52.5 Å (ref. 14), a negative value was obtained for each solute. If the cross-sectional area of DNOP is larger than that of *p*-nitrophenol, then the sum of the constant terms cannot be positive even if the accurate value of the cross-sectional area is adopted.

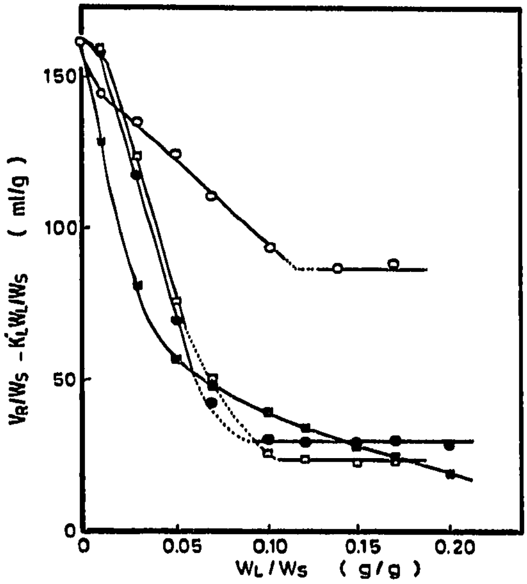
From these results it is concluded that the straight lines in the low liquid-loading range can be explained adequately by eqn. 6. As shown in Fig. 9 for squalane, the graphs of V_R/W_L against W_s/W_L for the saturate hydrocarbons each give one straight line, and the adsorption constants K_1, obtained from the slopes of the lines agree fairly well with K_s; moreover, the intercepts of the lines agree fairly well with K'_L (Table II). These results suggest that there is little variation in the adsorptivity of the support on coating with squalane. As mentioned above, the contribution of the adsorption on the liquid surface cannot be neglected when TCEP is used as the stationary phase, and the slope of the straight line in Fig. 11 contains the contribution of adsorption on the surfaces of the support and of the liquid film. However, as shown in Table IV, the value of K_2 for *n*-hexane obtained from the slope of the straight line in Fig. 11 agrees well with that obtained by the same procedure from the retention volume on the Chromosorb support. The fact that the K_2 value of the light hydrocarbon, whose K'_L value is small, obtained from supports of different adsorptivity agrees well suggests that K_2 is the adsorption constant on the liquid surface, K_A, and that the contribution of adsorption on the surface of the support coated with TCEP can be neglected.

TABLE IV

GAS–LIQUID PARTITION CONSTANTS, K_L', WITH TCEP AS THE STATIONARY PHASE AND ADSORPTION CONSTANTS, K_2, WITH TCEP ON CHROMOSORB AND MODIFIED ALUMINAS IGNITED AT 500 AND 600°, RESPECTIVELY

Solute	K_L' (*ml/g*)	K_2 (× 10^5 *cm*)		
		Chromosorb	*Modified alumina*	
			500°	*600°*
n-Hexane	3	3.3	4.5	4.3
2-Methylpentane	2	2.3	3.8	3.9
Cyclohexane	11	1.9	4.2	4.4
1-Hexene	5	3.1	5.1	5.2
2-Hexene	6	3.4	5.2	5.0
Cyclohexene	26	2.1	5.1	5.4
n-Heptane	3	7.6	10.7	10.4
2-Methylhexane	4	6.2	8.4	8.3
1-Heptene	9	8.2	12.1	11.5
2-Heptene	12	9.1	13.0	12.5
n-octane	3	18.1	24.3	23.3
2-Methylheptane	2	10.1	13.4	12.7
1-Octene	14	19.7	27.3	26.7
Benzene	108	2.6	8.4	8.9
Toluene	193	10.3	21.7	23.8

In Figs. 12 and 13 the contributions of the adsorption, obtained by subtraction of the contribution of the gas–liquid partition from the retention volumes of 1-heptene and 1-heptane, are plotted against the amount of the liquid loaded. In Fig. 12 the



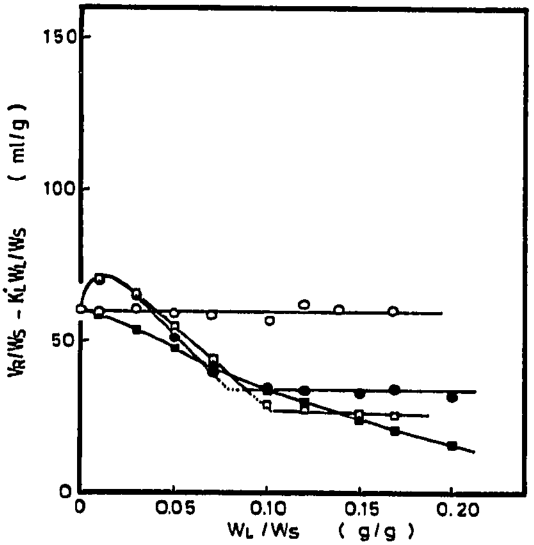


Fig. 12. Variation of the contribution of adsorption to the retention of 1-heptene with liquid loading. Support as in Fig. 9. Stationary phases: ○—○, squalane; ●—●, DNOS; □—□, DNOP; and ■—■, TCEP.

Fig. 13. Variation of the contribution of adsorption to the retention of *n*-heptane with liquid loading. Support as in Fig. 9. Stationary phases as in Fig. 12.

decrease in the contribution of adsorption to the retention of 1-heptene with loading of squalane, DNOP and DNOS in the low loading range, and constant contribution in the high loading range, are considered to be due to the blocking of specific active sites to adsorption (as classified by Kiselev[15]) by the liquid molecule and to the non-specific interaction of the solute with non-specific and non-specified active sites by the liquid molecule, respectively. The high constant contribution of adsorption with the squalane phase is considered to be due to imperfect blocking of the active sites by the non-polar squalane. As shown in Fig. 13, the variations in adsorption contributions to *n*-heptane are similar to those for 1-heptene. In the high loading range of DNOP and DNOS, the contributions of adsorption to *n*-heptane and 1-heptene, whose molecular sizes are almost the same, are identical. This suggests that, in this range, the interactions of these solutes with the surface of the support are both non-specific. The decrease in the contribution of adsorption to *n*-heptane in the low loading range of the polar liquid suggests that *n*-heptane has some specific interactions with the clean support. The constant contribution of adsorption to *n*-heptane with squalane may be due to the very small change in adsorptivity of the support on loading with squalane. The lack of the constant contribution of adsorption with the TCEP phase is considered to be due to the continuous variation in the surface area of the liquid film with increasing amount of liquid loaded, as the adsorption on the liquid surface is the main factor in this system.

Thus the contribution of adsorption in GLC can be clarified in more detail by using adsorption-active supports. Contributions of adsorption in GLC vary with the adsorptivity of the support and the polarity of the liquid phase, and, therefore, in order to utilize the adsorption effects in separations of complex mixtures, preparations of supports with various adsorptivities and investigations of the elution behaviour of solutes on liquid phases of various polarities on those supports are necessary. These are now in progress.

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