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Adsorption effects on retention behaviour of hydrocarbons in gas–liquid and gas–solid chromatography with the use of modified alumina coated with diphenyl phthalate as column packings

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Abstract

Adsorption effects on the retention of hydrocarbons were investigated in gas–liquid–solid chromatography using modified alumina beads, preheated at 1150 and 1200°C, coated with diphenyl phthalate as column packings. At a column temperature above the melting point of diphenyl phthalate, the same method as used in a previous study could be applied for interpreting the solute retention behaviour. At a column temperature below the melting point of the stationary phase, the retention mechanism could be successfully understood by considering that some adsorption equilibria took part in solute retention on the basis of the distribution of diphenyl phthalate in a solid form on the modified alumina surface.

1. Introduction

A jump in $\log(\text{retention volume})$ near the melting point of a stationary phase has been observed when the former was plotted against the reciprocal of the absolute column temperature. This phenomenon is caused by the phase transition of the stationary phase between the liquid and solid forms. Gas–liquid and gas–solid chromatography can be performed at column temperatures above and below the melting point, respectively, and in the transition range of the column temperature gas–liquid–solid chromatography can be conducted [1–3].

We previously studied the dependence of the

retention volume of hydrocarbons on column temperature using the modified alumina coated with polyethylene glycol 6000 (PEG 6000) as column packing. It was found that no jump in $\log(\text{retention volume})$ of a given solute took place at low stationary phase loadings when modified alumina with a low adsorption capacity was coated with PEG 6000 and even at high stationary phase loadings when modified alumina with a high adsorption capacity was used as a solid support. We drew the important conclusion that the thickness of a triple layer was at least required for a polar stationary phase to exhibit the same properties as those of a bulk liquid [4].

In this study, the retention volume of various solutes was examined as a function of stationary phase loading using modified alumina preheated

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at 1150 or 1200°C and coated with diphenyl phthalate. In addition, we examined the retention behaviour of each solute at a column temperature below the melting point of diphenyl phthalate.

2. Experimental

Modified alumina beads were prepared by preheating activated alumina beads, Neobead MS·C (60–80 mesh) (Mizusawa Industrial Chemicals, Tokyo, Japan), at 1150 and 1200°C for 3 h. Diphenyl phthalate (m.p. 73°C) was used as a stationary phase without further purification. Some C₆–C₇ saturated and unsaturated hydrocarbons were used as organic solutes. A 10-g amount of the modified alumina was added to 25 cm³ of dichloromethane solution containing the required amount of diphenyl phthalate. Diphenyl phthalate was thoroughly deposited on the modified alumina beads by evaporating the dichloromethane gradually with continuous stirring. The column packings so prepared were packed into a stainless-steel column (100 × 0.3 cm I.D.) after drying at 120°C for 2 h.

A Hitachi Model 023 gas chromatograph equipped with a thermal conductivity detector was used in conjunction with a Hitachi Model QPD 33 recorder for gas chromatography. Gas chromatographic measurements and the determination of the specific surface area of the modified alumina coated with diphenyl phthalate were carried out as described previously [5].

3. Results and discussion

The net retention volume of each solute, V'_R , was measured as a function of column temperature between 104 and 46°C, which included the melting point of diphenyl phthalate. Fig. 1 shows an experimental plot of $\log V_{NL}$ ($V_{NL} = V'_R/W_L$) against $1/T$ for *n*-hexane using the modified alumina preheated at 1150°C as solid support, where W_L is the mass of diphenyl phthalate packed in the column and T (K) is the column temperature. $\log V_{NL}$ increased linearly with

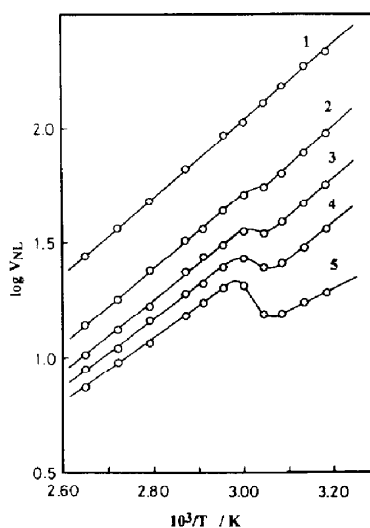


Fig. 1. Graph of $\log V_{NL}$ against $1/T$. Solid support, modified alumina preheated at 1150°C; stationary phase, diphenyl phthalate with the following loadings: 1 = 5%; 2 = 10%; 3 = 15%; 4 = 20%; 5 = 25%. Solute, *n*-hexane.

increase in $1/T$. With increase in stationary phase loading, a jump in $\log V_{NL}$ occurred more sharply near a column temperature of 60°C. This temperature is almost the same regardless of the stationary phase loading but is slightly lower than the melting point of diphenyl phthalate. This phenomenon is usually referred to as the phase transition of the stationary phase used, fusion or solidification. Hence the occurrence of this phenomenon is evidence that a liquid layer with the same properties as those of the bulk phase of the stationary phase is formed on the solid support. According to this idea, it is clear that no bulk liquid layer is formed on the modified alumina at a stationary phase loading of 5%, because a plot of $\log V_{NL}$ against $1/T$ showed no jump in the former parameter. At stationary phase loadings above 10%, diphenyl phthalate is present in the liquid form on the modified alumina at column temperatures above ca. 60°C and in the solid form at lower column temperatures. Similar results were obtained for the other solutes.

Fig. 2 shows plots of reduced retention volume, V_{NR} ($V_{NR} = V'_R/W_S$), against stationary phase loading, X_L ($X_L = W_L/W_S$), for *n*-heptane

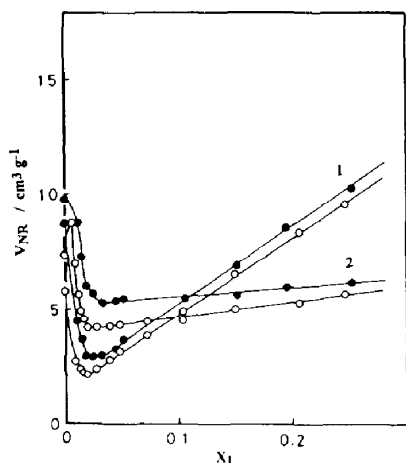


Fig. 2. Variation of V_{NR} with X_{L1} at a column temperature of 85°C. Solid supports, modified alumina preheated at (●) 1150 and (○) 1200°C; stationary phase, diphenyl phthalate. Solutes: 1 = cyclohexene; 2 = *n*-heptane.

and cyclohexene when the modified alumina preheated at 1150 and 1200°C was coated with various amounts of diphenyl phthalate, where W_S is the mass of bare solid support in the column. For both hydrocarbon solutes, V_{NR} rapidly decreased to a minimum and then increased linearly with increasing X_{L1} . The rapid decrease in V_{NR} with X_{L1} indicates that deactivation of the modified alumina surface occurred owing to gradual occupation of active sites for adsorption with diphenyl phthalate molecules. During this deactivation, the modified alumina surface was completely covered with a monolayer of diphenyl phthalate. A further increase in X_{L1} results in the formation of a bulk liquid layer of diphenyl phthalate on the deactivated surface of the modified alumina. The linear increase in V_{NR} with X_{L1} in this range of X_{L1} can thus be caused by a dominant contribution of solution partitioning into a liquid layer of diphenyl phthalate. The value of V_{NR} for each solute is always smaller when using the modified alumina preheated at 1200°C (specific surface area 26.7 m² g⁻¹) than when using the modified alumina preheated at 1150°C (specific surface area 32.8 m² g⁻¹). This result indicates that interfacial adsorption equilibria still contribute significantly to solute retention in this instance.

Fig. 3 shows plots of V_{NL} against $1/X_{L1}$ for the

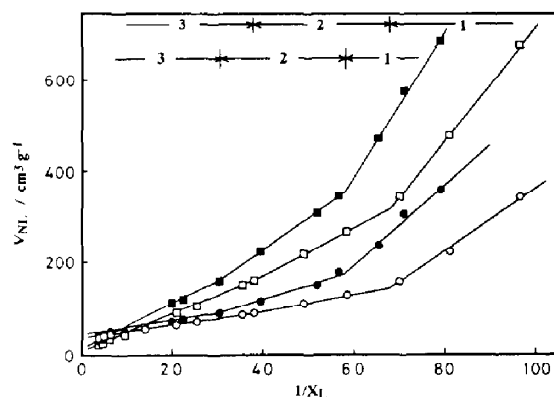


Fig. 3. Variation of V_{NL} with $1/X_{L1}$ at a column temperature of 85°C. Solid supports, modified alumina preheated at (●, ■) 1150 and (○, □) 1200°C. Stationary phase, diphenyl phthalate. Solutes: ○, ● = cyclohexene; □, ■ = *n*-heptane.

same solutes as in Fig. 2. The plot of V_{NL} against $1/X_{L1}$ for each solute can be well approximated with a straight line in each of three $1/X_{L1}$ ranges. Two stationary phase loadings, X_{L1} and X_{L0} , were calculated as fixed values regardless of the nature of the solutes at the intersection of two adjacent straight lines (Table 1).

Both X_{L1} and X_{L0} determined on the modified alumina preheated at 1200°C are smaller than the corresponding stationary phase loadings determined on the modified alumina preheated at 1150°C. We thought that these stationary phase loadings are meaningful where the solid support surface was completely covered with a monolayer of stationary phase used. The occupying area of a molecule of diphenyl phthalate (0.54 nm²), calculated from X_{L0} and the BET surface area of liquid-free modified alumina, is in good agreement with the cross-sectional area of the same molecule (0.53 nm²) calculated from the density [6] and the molecular mass of diphenyl phthalate according to Emmett and Brunauer's equation [7]. This result supports the above idea that the modified alumina surface is first covered with a monolayer of diphenyl phthalate. Thus, X_{L0} corresponds to a stationary phase loading where the modified alumina surface is completely covered with a monolayer of diphenyl phthalate. According to a previous model for solid surfaces [8] in which the modified alumina sur-

Table 1
Liquid phase loadings at two intersection points between two adjacent straight lines in Fig. 3

Solute	W_{11}/W_s (% w/w)		W_{10}/W_s (% w/w)	
	A	B	A	B
<i>n</i> -Hexane	1.76	1.42	3.14	2.78
2-Methylpentane	1.79	1.42	3.09	2.96
1-Hexene	1.77	1.38	3.11	2.69
2-Hexene	1.81	1.40	3.05	2.96
Cyclohexane	1.72	1.43	2.95	2.64
Cyclohexene	1.82	1.41	3.13	2.33
<i>n</i> -Heptane	1.77	1.45	3.02	2.52

(A) Modified alumina preheated at 1150°C; (B) modified alumina preheated at 1200°C. Column temperature, 85°C.

face includes two subsurfaces with high and low adsorption capacities. X_{11} corresponds to a stationary phase loading where the subsurface with a high adsorption capacity (subsurface 1) is completely covered with a monolayer of diphenyl phthalate.

In the range of stationary phase loadings below X_{L1} (region 1), subsurface 1 is considered to be partly covered with a monolayer of diphenyl phthalate. Hence the modified alumina surface includes an uncoated part of subsurface 1, bare surface of subsurface 2 (subsurface with low adsorption capacity) and surface of a monolayer of diphenyl phthalate. We assumed that a monolayer of diphenyl phthalate had such a dense structure that no solute molecule can penetrate or dissolve in the monolayer. Taking account of the concurrent contribution of adsorption equilibria on these three subsurfaces to solute retention, the following equation can be written:

$$V_{NL} = -(K_1 - K_A)(s_1 N_{Av} / M_L) + K_S \sigma_{S0} / X_L \quad (1)$$

where K_1 and K_A are distribution constants for adsorption on subsurface 1 and a monolayer of diphenyl phthalate, respectively, and K_S is an apparent distribution constant for adsorption on the solid surface of modified alumina. $K_S \sigma_{S0}$ is equal to the net retention volume at $X_L = 0$ and $K_S \sigma_{S0} = K_1 S_1 + K_2 S_2$, where K_2 is the distribution constant for adsorption on subsurface 2. S_1 and S_2 are the specific surface areas of subsurfaces 1 and 2, respectively, and $\sigma_{S0} = S_1 + S_2$. s_1

is the occupying area of a diphenyl phthalate molecule, M_L is the molecular mass of diphenyl phthalate, N_{Av} is Avogadro's number and σ_{S0} is the specific surface area of liquid-free modified alumina.

In the range of stationary phase loadings between X_{L1} and X_{L0} (region 2), subsurface 2 is considered to be gradually covered with a monolayer of diphenyl phthalate after subsurface 1 is completely covered. In this instance, the modified alumina surface consists of the bare surface of subsurface 2 and the surface of a monolayer of diphenyl phthalate. Adsorption equilibria on these two subsurfaces contribute to solute retention. We assumed that K_A is the same for both adsorption equilibria on the surface of the monolayer formed on subsurfaces 1 and 2. Then the retention volume of a solute in this region can be written in the following form:

$$V_{NL} = -(K_2 - K_A)(s_2 N_{Av} / M_L) + K_2 \sigma_{S0} / X_L \quad (2)$$

In the range of stationary phase loadings above X_{L0} (region 3), the deactivated surface of modified alumina (bare surface of a monolayer of diphenyl phthalate) is considered to be further covered with a bulk liquid-like layer. In this instance, solution partitioning into a bulk liquid-like layer becomes more important, and adsorption equilibria on the deactivated surface of modified alumina and the surface of a bulk liquid-like layer become less significant with respect to solute retention. Considering that such

Table 2
Distribution coefficients for adsorption, K_s (cm), K_1 (cm) and K_2 (cm)

Solute	$K_s \times 10^5$		$K_1 \times 10^5$		$K_2 \times 10^5$	
	A	B	A	B	A	B
<i>n</i> -Hexane	2.43	2.44	3.40	3.62	1.19	1.09
2-Methylpentane	2.01	2.05	2.74	3.06	1.07	0.888
1-Hexene	3.38	4.06	5.07	6.62	1.23	1.10
2-Hexene	3.23	3.98	4.79	6.50	1.25	1.08
Cyclohexane	2.27	2.08	3.25	3.10	1.03	0.911
Cyclohexene	3.32	3.76	5.01	6.18	1.16	0.981
<i>n</i> -Heptane	6.15	6.24	8.73	9.33	2.85	2.68

(A) Modified alumina preheated at 1150°C; (B) modified alumina preheated at 1200°C. Column temperature, 85°C.

sorption equilibria take part concurrently in solute retention, the retention volume of a solute can be expressed as follows:

$$V_{NL} = K'_{exp} + [K_A \sigma_{S0} - K'_{exp} X_{L0}] / X_L \quad (3)$$

where $K'_{exp} = K'_L - \alpha(K_A - K'_S)$ and α is a proportionality constant relating $X_L - X_{L0}$ to the surface area of the deactivated surface covered with a bulk liquid-like layer.

Table 2 gives values of K_s , K_1 and K_2 calculated from retention data observed at a column temperature of 85°C.

As assumed previously, K_1 is always larger than K_2 for each solute. The apparent adsorption constant, K_s , of each solute is almost the same

for both modified aluminas used as solid supports. Subsurface 1 of modified alumina preheated at 1200°C has a larger K_1 value than that preheated at 1150°C, whereas subsurface 2 of modified alumina preheated at 1200°C, has a smaller K_2 value than that preheated at 1150°C. Table 3 shows very similar values of K_A for each solute calculated separately in three regions. Similar values of K_A are also obtained regardless of preheating temperature of modified alumina. This result means that the surface properties of modified alumina can be shielded with a monolayer of diphenyl phthalate.

Fig. 4 shows a plot of V_{NR} vs. X_L for each solute at a column temperature of 46°C, at which diphenyl phthalate loaded on modified alumina

Table 3
Distribution coefficients for adsorption, K_A (cm)

Solute	$K_A \times 10^5$					
	Region 1		Region 2		Region 3	
	A	B	A	B	A	B
<i>n</i> -Hexane	0.796	0.891	0.895	0.895	0.909	0.891
2-Methylpentane	0.702	0.748	0.739	0.760	0.758	0.750
1-Hexene	0.776	0.693	0.894	0.882	0.915	0.882
2-Hexene	0.920	0.881	0.971	0.972	0.996	0.958
Cyclohexane	0.857	1.01	1.01	0.997	1.03	0.998
Cyclohexene	1.16	1.08	1.18	1.15	1.19	1.17
<i>n</i> -Heptane	1.91	2.13	2.10	2.02	2.16	2.04

(A) Modified alumina preheated at 1150°C; (B) modified alumina preheated at 1200°C. Column temperature, 85°C.

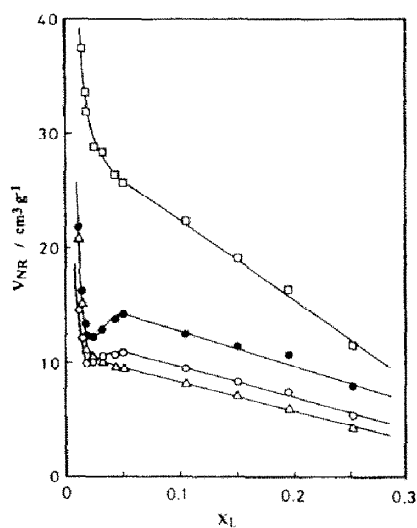


Fig. 4. Variation of V_{NR} with X_L at a column temperature of 46°C. Solid support, modified alumina preheated at 1150°C; stationary phase, diphenyl phthalate. Solutes: ○ = cyclohexane; ● = cyclohexene; △ = 1-hexene; □ = *n*-heptane.

is thought to exist in the solid form. With increasing X_L , V_{NR} of cyclohexane and cyclohexene rapidly decreased to a minimum, then increased to a maximum and finally decreased linearly with a further increase in X_L beyond 5%. For *n*-heptane and 1-hexene, V_{NR} suddenly decreased and then decreased linearly with increasing X_L . Such different profiles of the V_{NR} vs. X_L curves are probably related to different solubilities of diphenyl phthalate in the adsorbed layer of each solute: diphenyl phthalate can be easily dissolved in such a layer of cyclic solutes but only slightly in a layer of linear solutes. This phenomenon is observed only when a thin, solidified bulk liquid layer of diphenyl phthalate is formed on a monolayer in a small amount compared with the amount of the solute injected. Fig. 5 shows the dependence of the specific surface area of liquid-coated modified alumina, A_S , on X_L .

The profile of A_S vs. X_L for liquid-coated modified alumina preheated at 1150°C is similar to that of the V_{NR} vs. X_L plots for *n*-heptane and 1-hexene. Fig. 6 shows a plot of V_{NR} vs. A_S . In the range of X_L above 5%, a straight line was

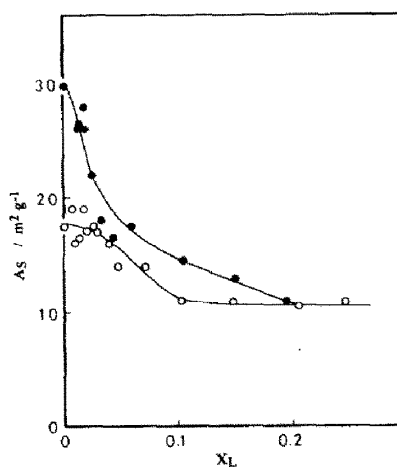


Fig. 5. Variation of A_S with X_L . Solid supports, modified alumina preheated at (●) 1150 and (○) 1200°C. Stationary phase, diphenyl phthalate.

drawn on the V_{NR} vs. A_S diagram. We thought that the decrease in V_{NR} in this region was caused by that of A_S . The previous method was applied to analyse the retention data in this instance, taking account of the contribution of adsorption equilibria on the solid surface of the modified alumina and the organic surface of diphenyl phthalate in the solid form.

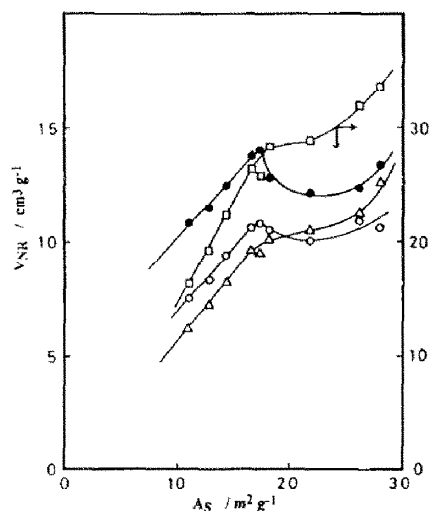


Fig. 6. Graph of V_{NR} against A_S . Solid support, modified alumina pre-heated at 1150°C; stationary phase, diphenyl phthalate. Solutes: ○ = cyclohexane; ● = cyclohexene; △ = 1-hexene; □ = *n*-heptane. Column temperature, 46°C.

In regions 1 and 2, the same retention mechanism as used previously could be applied to interpret the dependence of the retention volume of each solute on stationary phase loading. Hence Eqs. 1 and 2 were valid for the experimental data observed in these two regions. In region 3, the diphenyl phthalate loaded is present in a solid form on modified alumina surface, so we considered that two adsorption equilibria on the bare surface of a monolayer and the surface of the solidified bulk liquid layer of the stationary phase took part in solute retention. The reduced retention volume, V_{NR} , can be written as follows:

$$V_{NR} = K_A[\sigma_{S0} - \alpha(X_L - X_{L0})] + K'_S\alpha(X_L - X_{L0}) \quad (4)$$

where K'_S is a distribution constant for adsorption on the surface of the solidified bulk liquid layer of diphenyl phthalate. Eq. 4 can be expressed as

$$V_{NR} = -K''_{exp}X_L + K_A\sigma_{S0} + K''_{exp}X_{L0} \quad (5)$$

where $K''_{exp} = \alpha(K_A - K'_S)$. Dividing both sides of the above equation by X_L , the following equation is obtained:

$$V_{NL} = -K''_{exp} + [K_A\sigma_{S0} + K''_{exp}X_{L0}]/X_L \quad (6)$$

Eq. 5 indicates that a plot of V_{NR} against X_L gives a linear graph with a slope of $-K''_{exp}$ and an intercept of $K_A\sigma_{S0} + K''_{exp}X_{L0}$. This equation can

be fitted to a linear part of a V_{NR} vs. X_L plot shown in Fig. 4.

Calculated distribution constants for adsorption, K_S , K_1 , K_2 and K_A , are given in Tables 4 and 5. Table 4 shows that K_1 is always larger than K_2 for each solute. In this instance, similar values were obtained for K_S , K_1 and K_2 for each solute, regardless of the preheating temperature of the modified alumina used. This result means that both modified alumina supports show very similar surface properties for the adsorption of hydrocarbons under this condition. In Table 5, almost the same values of K_A are calculated separately in each of three regions regardless of the preheating temperature of the modified alumina.

Plotting logarithms of K_1 , K_2 and K_A against $1/T$ gave linear graphs for each solute. Fig. 7 shows such linear graphs for *n*-heptane. Hence, it is reasonable to consider that a monolayer of diphenyl phthalate has a rigid structure like as solid crystals, so that no solute molecule can penetrate into the monolayer. It is surprising that the heterogeneous characteristics of the solid surface of modified alumina could be converted into deactivated, homogeneous characteristics by covering it with a thin layer such as a monolayer of diphenyl phthalate.

We conclude that reasonable results were obtained through the above analysis of the experimental data on the basis of a previous model for the solid surface of modified alumina and the distribution of the stationary phase on

Table 4
Distribution coefficients for adsorption, K_S (cm), K_1 (cm) and K_2 (cm)

Solute	$K_S \times 10^5$		$K_1 \times 10^5$		$K_2 \times 10^5$	
	A	B	A	B	A	B
<i>n</i> -Hexane	10.2	11.6	15.0	17.6	4.22	4.55
2-Methylpentane	8.39	9.33	12.2	14.1	3.50	3.69
1-Hexene	15.1	18.3	23.2	30.0	4.66	4.64
2-Hexene	15.0	17.8	23.1	29.0	4.69	4.84
Cyclohexane	8.73	8.84	12.6	13.4	3.68	3.47
Cyclohexene	15.5	17.2	24.2	28.5	4.26	4.06
<i>n</i> -Heptane	36.3	34.4	54.6	52.5	13.1	13.3

(A) Modified alumina preheated at 1150°C; (B) modified alumina preheated at 1200°C. Column temperature, 46°C.

Table 5
Distribution coefficients for adsorption, K_A (cm)

Solute	$K_A \times 10^3$		Region 2		Region 3	
	Region 1		A	B	A	B
	A	B				
<i>n</i> -Hexane	3.43	3.14	3.55	3.30	3.56	3.30
2-Methylpentane	2.84	2.59	2.88	2.70	2.83	2.69
1-Hexene	3.07	2.89	3.53	3.30	3.55	3.31
2-Hexene	3.49	3.37	3.88	3.62	3.89	3.58
Cyclohexane	3.28	3.38	3.63	3.54	4.01	3.64
Cyclohexene	3.92	3.78	4.45	4.27	5.20	4.51
<i>n</i> -Heptane	8.95	9.86	9.78	9.33	9.63	9.34

(A) Modified alumina preheated at 1150°C; (B) modified alumina preheated at 1200°C. Column temperature, 46°C.

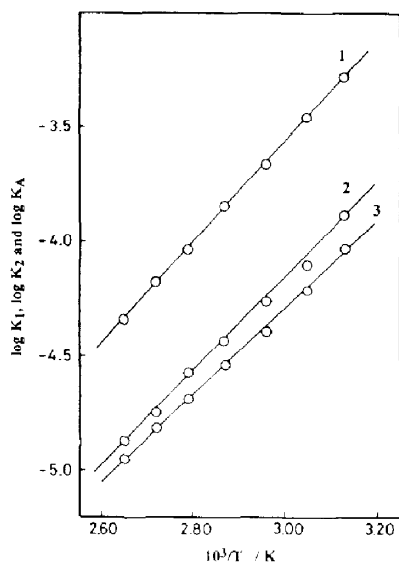


Fig. 7. Graphs of (1) $\log K_1$, (2) $\log K_2$, and (3) $\log K_A$ against $1/T$. Solute, *n*-heptane; solid support, modified alumina preheated at 1200°C; stationary phase, diphenyl phthalate.

modified alumina under the conditions where diphenyl phthalate was present in either the liquid or solid form. Our results show that a mixed retention mechanism is very useful for interpreting the dependence of retention data on stationary phase loading in gas-liquid and gas-solid chromatography.

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