Mixed retention mechanism in gas–liquid chromatography of hydrocarbon and dialkyl ether solutes on squalane-coated silica gel

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ABSTRACT

A mixed retention mechanism in gas–liquid chromatography was studied in order to elucidate the dependence of the retention volume of some hydrocarbons and dialkyl ethers on squalane-coated silica gel on the liquid phase loading. Two adsorption equilibria on the solid surface of silica gel and the surface of a monolayer of squalane dominantly contribute to solute retention until the monolayer of squalane is formed on the silica gel surface. Subsequently, excess of squalane formed a double layer on the deactivated surface of the silica gel, so bulk solution partition concurrently contributes to solute retention together with adsorption equilibria on the monolayer and/or the double layer of squalane. The distribution constants of bulk solution partition and adsorption equilibria on the solid surface of silica gel and the surface of the monolayer of squalane were calculated as reasonable values for any solute.

INTRODUCTION

It is well known that interfacial adsorption equilibria, together with bulk solution partition, contribute to solute retention in gas–liquid chromatography at different rates depending on the nature of the solute, the type of solid support and the polarity of and the loaded amount of liquid stationary phase. In such cases, the retention volume of a given solute, V_R, can be written as a linear combination of contributions of bulk solution partition and interfacial adsorption equilibria taking part in solute retention [1–8]:

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

where K_L, K_A and K_S are distribution constants of solution partition into a bulk liquid layer (volume V_L) and adsorption equilibria on the liquid layer (surface area A_L) and on the solid surface (surface

area A_S), respectively. V_R and V_L can be experimentally determined but A_L and A_S cannot be directly measured when the solid support surface is partly covered with the liquid layer. For practical use of the above equation it is therefore necessary to establish a reasonable relationship relating A_L and A_S to the liquid phase loading.

In a previous study using silica gel as a solid support [9], we found that the experimental plot of the reduced retention volume of a given solute, V_{NR}, against the liquid phase loading, X_L, could be divided into two or three parts. The respective parts were fitted with straight lines of different slopes and intercepts. From this result, we proposed a model in which the silica gel surface essentially consisted of two subsurfaces with high and low adsorption capacities and was gradually covered first with a monolayer of the liquid phase and then with a double layer with increasing liquid phase loading. On the basis of this model, the specific surface area of liquid-coated silica gel and the reduced retention volume of a given solute could be written as a linear function of the liquid phase loading in each part. By

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fitting these relationships to the experimental data, distribution constants could be calculated for adsorption equilibria on the solid surface and the monolayer of the liquid stationary phase, but the distribution constant of bulk solution partition could not be calculated. Because of the large specific surface area of silica gel and the strong polarity of the liquid stationary phase, the effects of interfacial adsorption equilibria dominated over the contribution of bulk solution partition to solute retention.

In this study, silica gel with a smaller specific surface area than that studied previously was used as a solid support for avoiding the dominant effects of interfacial adsorption equilibria on the retention volume of any solute. A non-polar liquid stationary phase, squalane, was used to observe the contribution of bulk solution partition to solute retention. The retention volume of a given solute and the specific surface area of liquid-coated silica gel were determined as a function of the liquid phase loading. The experimental data were analysed and are discussed on the basis of the previous model of the solid support surface and the distribution of the liquid phase on the solid support.

EXPERIMENTAL

Fujigel KC-5, silica gel for preparative column chromatography, was used as a solid support after sizing into a 60–80 mesh fraction. Chromosorb P NAW (60–80 mesh) was used as a reference solid support without further purification. Ten grams of Chromosorb P and silica gel were dried at 120°C for 3 and 12 h, respectively, and weighed accurately. They were suspended in dichloromethane containing the desired amount of squalane. Squalane was deposited on the solid support as evenly as possible by evaporating the solvent with occasional stirring. After drying under vacuum at 50°C for 3 h for removal of any volatile component, the material was packed into a stainless-steel tube (100 × 0.3 cm I.D.) with tapping. The newly packed column was conditioned at 120°C for 15 h in a stream of nitrogen (flow-rate 40 cm³ min⁻¹) and then for 3 h in a stream of helium (flow-rate 40 cm³ min⁻¹) before use.

A Hitachi Model 263-30 gas chromatograph equipped with a thermal conductivity detector was used in conjunction with a Hitachi Model 561 re-

corder. Chromatographic measurements were made at a column temperature of 120°C using helium as the carrier gas at a flow-rate of 40 cm³ min⁻¹. The retention volume of a given solute was measured from the air peak to the particular peak maximum and corrected for the vapour pressure of water in a flow meter and the pressure drop in the column. The specific surface area of the column packings was determined by the BET nitrogen adsorption method at liquid nitrogen temperature. To account for any variations of the retention data with different amounts of the column packings used, the reduced retention volume, V_{NR}, was calculated by dividing the net retention volume by the weight of liquid-free solid support packed into the column. The liquid phase loading, X_L, was taken as the
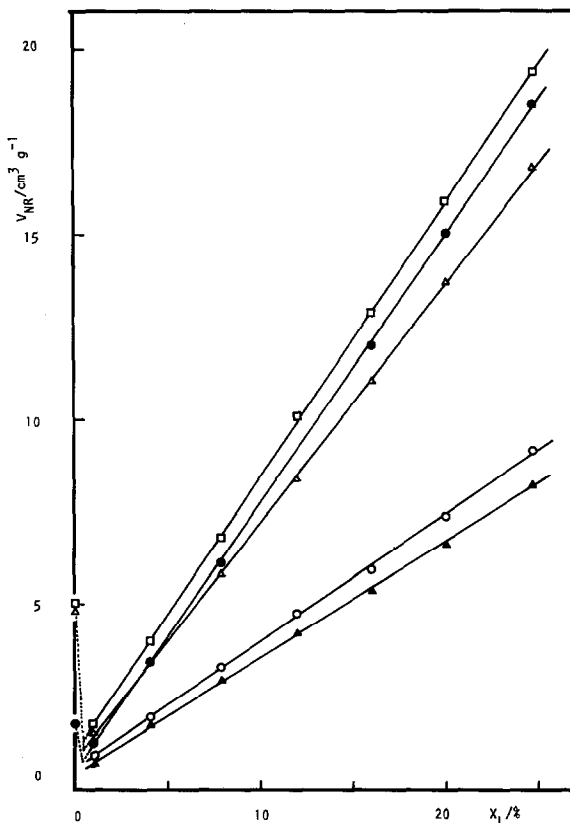

Fig. 1. Dependence of reduced retention volume on liquid phase loading on squalane-coated Chromosorb P. Solutes: ▲ = 1-hexene; ○ = n-hexane; △ = 1-heptene; ● = n-heptane; □ = 2-heptene.

weight ratio of the liquid stationary phase to the solid support.

RESULTS AND DISCUSSION

When Chromosorb P was coated with different amounts of squalane, the reduced retention volume of any solute increased linearly with increasing liquid phase loading. Fig. 1 shows such linear plots of V_{NR} vs. X_L for some hydrocarbon solutes. The small, positive intercepts of these graphs on the ordinate suggest less importance of concurrent contributions of interfacial adsorption equilibria to solute retention in this instance. Thus, the slope of the V_{NR} vs. X_L graph is regarded as the distribution constant of the bulk solution partition, K_L', for each solute.

Table I summarizes the K_L' values calculated from the experimental data. The K_L' values show that all the solutes except tert.-butyl methyl ether are readily soluble in the bulk liquid layer of squalane under the present conditions. The K_L' values of alkenes are very close to those of alkanes with the same carbon number and similar molecular shape, suggesting very similar solubilities of these compounds in squa-

lane. The V_{NR} vs. X_L graphs of dialkyl ethers and aromatic hydrocarbons gave larger intercepts on the ordinate than those of aliphatic hydrocarbons. Taking their large K_L' values into account, possible interfacial adsorption in this instance is considered to occur at the liquid–solid interface but not at the gas–liquid interface. Only one straight line was fitted to the experimental data except for a zero liquid phase loading for each solute. This indicates that a bulk liquid layer of squalane is formed on the surface of the Chromosorb P support even at low liquid phase loadings.

When silica gel was coated with squalane, the reduced retention volume of alkanes and cyclohexene increased monotonically. V_{NR} of aromatic hydrocarbons and alkenes except cyclohexene first decreased and then increased with increasing liquid phase loading. The profiles of these curves are different from those of the corresponding graphs ob-
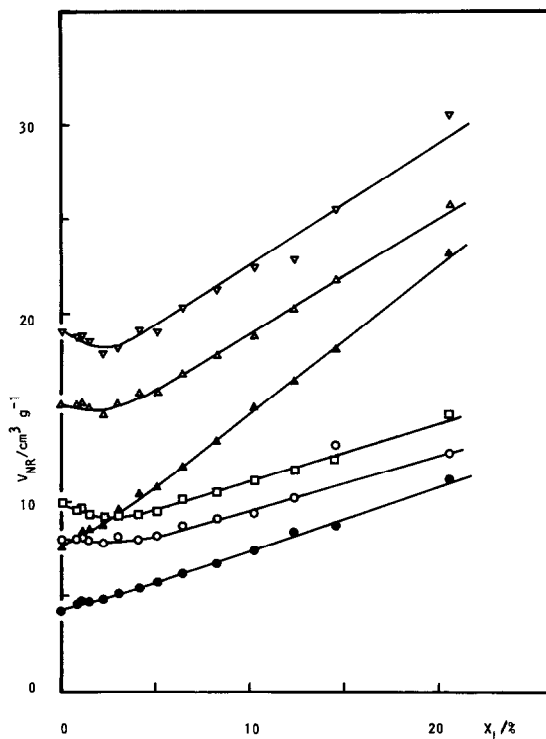
TABLE I

DISTRIBUTION CONSTANTS OF BULK SOLUTION PARTITION, K_L', and K_{exp}'

Solute	K_L' (cm³ g⁻¹)	K_{exp}' (cm³ g⁻¹)
2-Methylpentane	28	31
n-Hexane	36	37
Cyclohexane	62	66
1-Hexene	31	28
2-Hexene	35	29
Cyclohexene	66	76
2-Methylhexane	73	74
n-Heptane	73	81
1-Heptene	65	65
2-Heptene	74	68
Benzene	51	56
Toluene	108	106
Ethylbenzene	205	205
Diethyl ether	34	−169
tert.-Butyl methyl ether	8.3	−460
Di-n-propyl ether	183	−873
Diisopropyl ether	51	−492
Methyl n-propyl ether	48	−174
Ethyl n-propyl ether	75	−508

Fig. 2. Dependence of reduced retention volume on liquid phase loading on squalane-coated silica gel. Solutes: ● = n-hexane; ○ = 1-hexene; □ = 2-hexene; ▲ = n-heptane; △ = 1-heptene; ▽ = 2-heptene.

tained previously using modified alumina as a solid support [10]. In Fig. 2, the V_{NR} vs. X_L curve for any hydrocarbon solute shows no sudden decrease at low liquid phase loadings. It appears that the silica gel surface is less adsorptive than the modified alumina surface towards hydrocarbon solute molecules. An increase in V_{NR} with increasing X_L indicates that the non-polar surface of the thin film of squalane can interact more strongly than the polar surface of silica gel with hydrocarbon solute molecules. The reduced retention volumes of alkenes are always larger than those of the corresponding alkanes, although their K_L' values are very similar. The difference in the V_{NR} values of these compounds gradually decreases with increasing X_L. This result indicates that, with increasing X_L, interfacial adsorption equilibria become less signifi-

cant and bulk solution partition becomes more important with respect to solute retention. Even at high liquid phase loadings, the apparent effects of interfacial adsorption equilibria remain in V_{NR} because of the considerable difference in the V_{NR} values of the solutes.

Fig. 3 shows plots of V_{NR} vs. X_L for some dialkyl ethers. Their reduced retention volumes decrease with increasing X_L. The profiles of these graphs are similar to those for the experimental data measured on the modified alumina coated with polar stationary liquid phases [11,12]. This suggests that dialkyl ether molecules may interact more strongly with the polar surface of silica gel than with the non-polar surface of the thin layer of squalane. The decrease in V_{NR} of each dialkyl ether with increasing X_L is probably due to deactivation of the silica gel surface
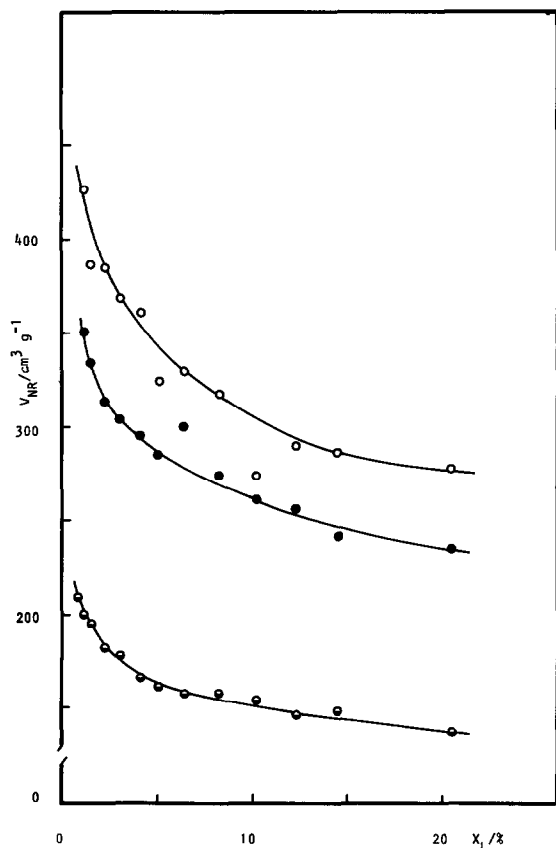

Fig. 3. Dependence of reduced retention volume on liquid phase loading on squalane-coated silica gel. Solutes: ◒ = diethyl ether; ● = ethyl n-propyl ether; ○ = diisopropyl ether.

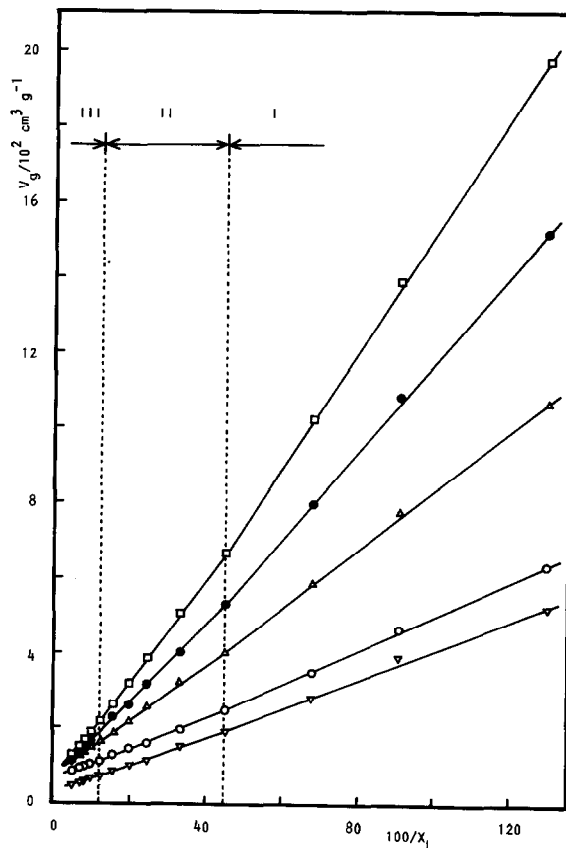Fig. 4. V_g vs. $1/X_L$ plot. Solutes: ▽ = 2-methylpentane; ○ = cyclohexane; △ = n-heptane; ● = cyclohexene; □ = 1-heptene. 1 = region 1; II = region 2; III = region 3.

caused by gradual coverage with some types of liquid layers of squalane. In this instance interfacial adsorption equilibria may play an important role in solute retention.

As shown in Fig. 4, the V_g vs. $1/X_L$ curves are divided into three linear parts. Two liquid phase loadings, X_{L1} and X_{L0}, were calculated as 2.23 and 8.27%, respectively, at the intersection of two adjacent straight lines regardless of the nature of the solutes. The occupied area of a squalane molecule (0.99 nm²), calculated from the X_{L0} value and the specific surface area of liquid-free silica gel, is consistent with the cross-sectional area of the same molecule (0.99 nm²), calculated from density and molecular weight of squalane according to Emmett and Brunauer's equation [13]. Thus, we regarded X_{L0} as the liquid phase loading at which the silica gel surface was completely covered with a monolayer of squalane. This supports the idea that the silica gel surface is first covered with a monolayer of squalane when the squalane is loaded on silica gel.

The specific surface area of the liquid-coated silica gel, S_P, decreased linearly, at first rapidly with increasing X_L up to about 8% and then slowly with further increase in X_L. The S_P vs. X_L curve can be approximated by two straight lines which intersect near X_{L0}. This result shows that the decrease in S_P is proportional to X_L or $X_L - X_{L0}$. The V_{NR} vs. X_L curve for hydrocarbons hardly reflected this change in S_P with X_L. Althought the V_{NR} vs. X_L curve for ethers showed a decreasing trend similar to that of the S_P vs. X_L curve, V_{NR} of ethers was not always proportional to S_P. These results indicate that the surface of the liquid-coated silica gel involves some types of subsurfaces at different ratios depending on X_L. We then examined the quantitative interpretation of the experimental X_L dependence of V_{NR} and S_P by considering a model for the solid surface of silica gel and the distribution of the liquid stationary phase on the solid surface.

At liquid phase loadings below X_{L0}, the V_g vs. $1/X_L$ curve can be approximated by two straight lines. This means that the original surface of the silica gel shows essentially heterogeneous characteristics on adsorption of solute molecules. We simply considered that the original surface of the silica gel consisted of two subsurfaces with high and low adsorption capacities, as assumed previously [9–12]. As previously, we regarded the subsurface with a

high adsorption capacity (subsurface 1) as being occupied first with squalane molecules and then the subsurface with a low adsorption capacity (subsurface 2) was covered. Hence X_{L1} (2.23%) should correspond to the liquid phase loading at which subsurface 1 was completely covered with the monolayer of squalane.

At liquid phase loadings above X_{L0}, one straight line of V_g vs. $1/X_L$ was drawn for each solute. For hydrocarbon solutes, the intercepts of these linear graphs are in good agreement with the K_L' values for the corresponding solutes listed in Table I. However, for dialkyl ethers, this linear graph gave a negative intercept on the ordinate, indicating that interfacial adsorption equilibria still contribute significantly to solute retention. According to previous considerations [9,10], a double layer of squalane should be formed on the silica gel surface in this region. We expect that, on the deactivated surface of silica gel, shielded with a monolayer of squalane, a double layer of squalane may possess a loose structure like a bulk liquid, because non-polar molecules of squalane cannot orient to the silica gel surface as strongly as polar molecules. It is likely that such a loose structure will lead to the same sorption properties as those of a bulk liquid layer. Hence we considered that, in this region, the silica gel surface is also covered with the same type of bulk liquid layer of squalane as is formed on a Chromosorb P support.

At liquid phase loadings below X_{L1} (region 1), the monolayer of squalane gradually expands on subsurface 1 of the silica gel surface with increasing X_L. The surface of the liquid-coated silica gel involves an uncoated part of subsurface 1, bare subsurface 2 and the surface of the monolayer of squalane with which subsurface 1 was partly covered. Then, the specific surface area of the liquid-coated silica gel, S_P, can be written as the sum of the surface areas of the above three surfaces:

$$S_P = S_1 - a X_L + S_2 + b X_L$$
$$= S_S^0 - (a - b) X_L$$

where $S_S^0 = S_1 + S_2$, S_S^0, S_1 and S_2 are the specific surface area of the liquid-free silica gel, subsurface 1 and subsurface 2, respectively, and a and b are proportionality constants that relate X_L to the covered area and surface area of the monolayer of squalane. We considered that the monolayer of squalane has

such a rigid structure that solute molecules cannot penetrate or dissolve in the monolayer. In this instance, interfacial adsorption equilibria on these three surfaces take part in solute retention. Hence the reduced retention volume of a given solute can be written as a linear combination of the contributions of these adsorption equilibria:

$$V_{NR} = K_1 (S_1 - a X_L) + K_2 S_2 + K_A b X_L \quad (1)$$

where K_1, K_2 and K_A are distribution constants of adsorption equilibria on subsurface 1, subsurface 2 and the surface of the monolayer of squalane, respectively. Dividing both sides of eqn. 1 by X_L and using the relationship $K_{ad} S_S^0 = K_1 S_1 + K_2 S_2$, the specific retention volume, V_g, can be expressed as

$$V_g = b K_A - a K_1 + K_{ad} S_S^0 / X_L \quad (2)$$

where $K_{ad} S_S^0$ is equal to V_{NR} at $X_L = 0$. Eqn. 2 should give a straight line with a positive intercept on the ordinate of the V_g vs. $1/X_L$ plot if $b K_A > a K_1$ and with a negative intercept if $b K_A < a K_1$.

In the range of liquid phase loadings between X_{L1} and X_{L0} (region 2), the monolayer of squalane completely covered subsurface 1 and gradually expanded on subsurface 2 with increasing X_L. The specific surface area of the liquid-coated silica gel in this region is the sum of the surface areas of an uncoated part of subsurface 2 and the surface of the monolayer of squalane. S_P can be written as the same linear function of X_L using the same a and b as defined in region 1:

$$S_P = S_S^0 - (a - b) X_L$$

This equation can be fitted to the experimental plot of S_P vs. X_L if $a > b$. In this instance, adsorption equilibria on these surfaces take part in solute retention. We considered that the distribution constant of adsorption was the same on the monolayer of squalane formed on subsurface 1 and on subsurface 2. The following equation can be written:

$$V_{NR} = K_2 (S_S^0 - a X_L) + K_A b X_L \quad (3)$$

Dividing both sides of eqn. 3 by X_L, V_g can be expressed as follows:

$$V_g = b K_A - a K_2 + K_2 S_S^0 / X_L \quad (4)$$

This equation should plot as a straight line of V_g vs. $1/X_L$ with a positive slope. The intercept of this linear graph on the ordinate is positive if $b K_A > a K_2$

and negative if $b K_A < a K_2$. We assumed that $K_1 > K_2$, so it is valid that $b K_A > a K_2$ if $b K_A > a K_1$, but it is not always true that $b K_A < a K_2$ when $b K_A < a K_1$.

At liquid phase loadings above X_{L0} (region 3), the silica gel surface was completely covered with a monolayer of squalane and further partly covered with a double layer of squalane. The surface of the liquid-coated silica gel involves the surface of an uncoated part of the monolayer and the double layer. Hence the specific surface area of the liquid-coated silica gel can be written as

$$\begin{aligned} S_P &= S_{LM} - a' (X_L - X_{L0}) + b' (X_L - X_{L0}) \\ &= S_{LM} + (a' - b') X_{L0} - (a' - b') X_L \end{aligned}$$

where a' and b' are proportionality constants that relate the excess liquid loading to the covered area and the surface area of the double layer of squalane. We simply assumed that the covered area and the surface area of the double layer of squalane were proportional to the excess liquid loading, $X_L - X_{L0}$. Assuming that the double layer of squalane shows the same sorption properties as a bulk liquid layer of squalane, solute molecules can dissolve in the double layer. In this instance, bulk solution partition, together with interfacial adsorption equilibria on the surface of the monolayer and/or the double layer, takes part in solute retention. V_{NR} can be written as

$$\begin{aligned} V_{NR} &= K_A [S_L^0 - a' (X_L - X_{L0})] + \\ &+ K_S a' (X_L - X_{L0}) + K_A' b' (X_L - X_{L0}) + \\ &+ K_L' (X_L - X_{L0}) \end{aligned} \quad (5)$$

where K_S and K_A' are distribution constants of adsorption equilibria on the monolayer through the double layer (at the liquid–solid interface) and the surface of the double layer of squalane (at the gas–liquid interface). Using the relationship $K_{exp}' = K_L' - (a' K_A - b' K_A') + a' K_S$ and dividing both sides of eqn. 5 by X_L, the following equation can be written:

$$V_g = K_{exp}' + (K_A S_L^0 - K_{exp}' X_{L0}) / X_L \quad (6)$$

If $K_L' < a' K_A - b' K_A' - a' K_S$, K_{exp}' will be negative, indicating that adsorption equilibrium on the monolayer surface is important in solute retention. If $K_L' \gg a' K_A - b' K_A' - a' K_S$, K_{exp}' will be equal to K_L', that is, bulk solution partition contributes dominantly to solute retention.

TABLE II

DISTRIBUTION CONSTANTS OF ADSORPTION, K_1, K_2 AND K_A

Solute	K_1 (10⁻⁵ cm)	K_2 (10⁻⁵ cm)	K_A (10⁻⁵ cm)		
			Region 1	Region 2	Region 3
2-Methylpentane	0.39	0.31	0.73	0.72	0.73
n-Hexane	0.45	0.36	0.87	0.86	0.86
Cyclohexane	0.51	0.35	1.15	1.15	1.14
1-Hexene	0.89	0.64	1.16	1.17	1.16
2-Hexene	1.07	0.75	1.33	1.33	1.33
Cyclohexene	1.27	0.91	1.86	1.86	1.92
2-Methylhexane	0.76	0.56	1.46	1.46	1.46
n-Heptane	0.77	0.64	1.60	1.70	1.67
1-Heptene	1.77	1.17	2.23	2.25	2.24
2-Heptene	2.24	1.44	2.70	2.70	2.68
Benzene	2.60	1.65	2.87	2.92	2.92
Toluene	5.88	3.87	6.61	6.61	6.60
Ethylbenzene	9.21	7.18	12.2	12.2	12.2
Diethyl ether	26.4	16.4	19.8	19.9	19.9
tert.-Butyl methyl ether	55.4	37.9	43.0	43.2	43.3
Di-n-propyl ether	79.2	46.7	54.3	56.3	56.4
Diisopropyl ether	53.7	35.2	40.1	39.9	40.0
Methyl n-propyl ether	25.7	15.1	19.5	18.7	19.1
Ethyl n-propyl ether	47.4	28.2	34.4	34.5	34.6

For each solute, the equations derived could be well fitted to the corresponding linear parts of the experimental plot of V_g vs. $1/X_L$. Distribution constants as unknown constants in these equations could be calculated from the intercepts and slopes of the respective straight lines. For hydrocarbons, K'_{exp} is in good agreement with K'_L, indicating the dominant contribution of bulk solution partition to solute retention in region 3. However, negative values of K'_{exp} for dialkyl ethers indicate dominant effects of adsorption equilibria on V_{NR} even at high liquid phase loadings. Unfortunately, distribution constants of bulk solution partition for dialkyl ethers could not be calculated from K'_{exp} because a' and b' were not determined from experimental data.

Almost the same value could be calculated as K_A for each solute separately in three regions of the liquid phase loading (Table II). This indicates that heterogeneous characteristics of the solid surface of silica gel on adsorption of solute molecules could be converted into homogeneous surface properties. As K_A of an unsaturated hydrocarbon is still larger than that of the corresponding saturated com-

pound, the original surface properties of silica gel were not completely shielded with a monolayer of squalane. Table II shows that the previous assumption that $K_1 > K_2$ is satisfied for any solute. It appears that hydrocarbon molecules can interact more strongly with the non-polar surface of silica gel, as $K_A > K_1$ and $K_A > K_2$. It is strange that $K_A > K_2$ for dialkyl ethers, although V_{NR} decreases monotonously with increasing X_L. It is probable that non-polar alkyl groups of ether molecules can interact through non-specific interaction with the squalane monolayer although specific interactions through ether-type oxygen are weakened significantly by shielding with the monolayer of squalane.

From the above results and discussion, we concluded that adsorption equilibria on the bare surface of the silica gel and the surface of the monolayer of squalane contributed dominantly to solute retention until the silica gel surface was completely covered with a monolayer of squalane. Subsequently, bulk solution partition and adsorption equilibria on the monolayer and/or the double layer of squalane concurrently contributed to solute retention

when an excess amount of squalane was loaded on silica gel. It was found that a considerable amount of squalane was necessary for deactivation of the surface of a solid support such as silica gel with a large surface area. A mixed retention mechanism was successfully applied for understanding the dependence of the retention volume of a solute on the liquid phase loading, taking into account a model of the solid surface and the distribution of the liquid phase molecules on the solid support.

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