Adsorption effect on the retention volume of hydrocarbons and dialkyl ethers in gas–liquid chromatography using a polar stationary phase and silica gel support

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SUMMARY

The mechanism of solute retention in gas–liquid chromatography was studied by using silica gel coated with different amounts of polyethylene glycol 20 000 (PEG 20M). The retention volumes of aliphatic hydrocarbons, aromatic hydrocarbons and dialkyl ethers were determined as a function of liquid phase loading. The silica gel surface showed homogeneous characteristics on adsorption of saturated hydrocarbons and a heterogeneous nature on adsorption of the other solutes. The experimental data could be interpreted on the basis of a model in which the silica gel surface was covered first with a monolayer and then with a double layer of PEG 20M. Distribution constants of adsorption on the silica gel, on the monolayer and on the double layer were calculated.

INTRODUCTION

For the quantitative interpretation of the effect of interfacial adsorption on solute retention in gas–liquid chromatography, several workers have proposed the following equation[1-7]:

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

where V_R is the retention volume of a given solute and K_L, K_A and K_S are distribution constants of bulk solution partitioning into a bulk liquid layer (volume V_L) and adsorption equilibria on the liquid layer (surface area A_L) and the solid surface (surface area A_S), respectively. For practical use of the above equation, a reasonable relationship must be established between the surface areas, A_L and A_S, and the liquid phase loading.

In previous studies using modified alumina as a solid support[8-12], we found that the experimental plot of the retention volume of a given solute against liquid phase loading could be divided into four or five regions and each part of the plot could be

fitted to a straight line. From this result, we proposed a model in which the modified alumina surface, involving two subsurfaces with low and high adsorption capacities, was incrementally covered with three different types of the liquid layer, a monolayer, a double layer and a bulk liquid layer, as the liquid phase loading was increased. On the basis of this model, the retention volume of a given solute and the specific surface area of the liquid-coated, modified alumina could be written as a linear function of liquid phase loading in each region. These relationships allowed the distribution constants to be determined for bulk solution partitioning and adsorption equilibria.

In this study, we used silica gel, which had milder and more homogeneous surface characteristics than modified alumina, as a solid support and polyethylene glycol 20 000 (PEG 20M) as a liquid stationary phase. On the basis of the previous model, we tried to interpret the effect of interfacial adsorption on the retention volumes of some hydrocarbons and dialkyl ethers which were determined as a function of liquid phase loading.

EXPERIMENTAL

Fujigel KC-3 silica gel for preparative column chromatography was used as a solid support after sizing into a 60–80-mesh fraction. Chromosorb P was used as a reference support. A 10-g amount of silica gel or 7 g of Chromosorb P were dried at 120°C for 3 h, weighed accurately and suspended in a dichloromethane solution containing the desired amount of PEG 20M. The stationary phase was deposited on the solid support as evenly as possible by evaporating the solvent with occasional stirring. These column packings were packed into stainless-steel tubes (100 × 0.3 cm I.D.) after drying under vacuum at room temperature to remove any volatile components. The newly packed columns were conditioned at 120°C for 15 h in a stream of nitrogen and then for 3 h in a stream of helium.

A Hitachi Model 263-30 gas chromatograph equipped with a thermal conductivity detector was used in conjunction with a Hitachi Model 561 recorder. Gas chromatographic measurements were made at a column temperature of 120°C and with helium as carrier gas at a flow-rate of 40 cm^3 min^{-1}. The reduced retention volume, $V_{N,R}$, and liquid phase loading, X_L, were also calculated as described previously[8].

RESULTS AND DISCUSSION

When Chromosorb P was coated with different amounts of PEG 20M, the reduced retention volume of each solute increased linearly with increasing liquid phase loading. Fig. 1 shows linear plots of $V_{N,R}$ against X_L for some hydrocarbons. These linear plots indicate the dominance of bulk solution partitioning in solute retention. In this instance, the slope of the $V_{N,R}$ vs. X_L line corresponds to the distribution constant of bulk solution partitioning, K'_L, which was defined previously[12]. The K'_L values of solutes are listed in Table I. The presence of a small positive intercept for the $V_{N,R}$ vs. X_L curve suggests the concurrent contribution of the interfacial adsorption equilibrium to solute retention. This intercept is probably caused by the effect of adsorption at the gas–liquid interface of the bulk liquid layer of PEG 20M, because the surface of Chromosorb P is completely covered with a liquid layer even at low liquid phase loadings.
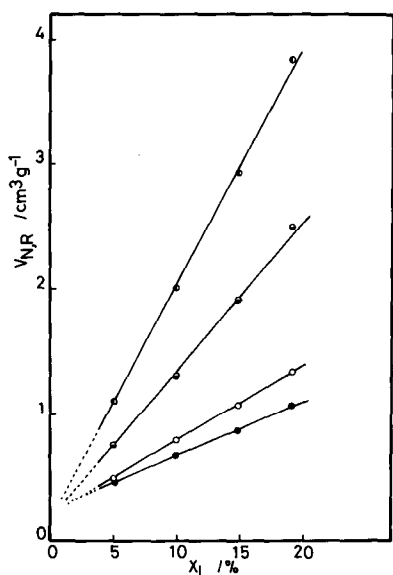
Fig. 1. Dependence of reduced retention volume on liquid loading. Solutes: ●, *n*-hexane; ○, 1-hexene; ◐, cyclohexane; ◑, cyclohexene. Solid support: Chromosorb P.

When silica gel was coated with PEG 20M, the reduced retention volume of unsaturated aliphatic hydrocarbons, aromatic hydrocarbons and dialkyl ethers decreased, first rapidly and then slowly, with increasing X_L. The profile of this curve is similar to those of the $V_{N,R}$ vs. X_L curves observed in previously studies[8-12]. The decrease in $V_{N,R}$ vs. X_L suggests that interfacial adsorption dominates solute retention and does not always correspond to a monotonous decrease in the specific surface area of column packings (Fig. 2). According to the previous view, the rapid decrease in $V_{N,R}$ with increasing X_L up to 11% is due to the deactivation of original solid surface by occupying active sites with molecules of PEG 20M. The slow decrease in $V_{N,R}$ with

TABLE I

DISTRIBUTION CONSTANT FOR THE BULK SOLUTION PARTITION, K_L'

| Solute	K_L' $(cm^3 \ g^{-1})$	Solute	K_L' $(cm^3 \ g^{-1})$
2-Methylpentane	3.0	Ethylbenzene	104
n-Hexane	4.3	*o*-Xylene	139
Cyclohexane	12.3	*m*-Xylene	111
1-Hexene	6.1	*p*-Xylene	107
2-Hexene	6.7	*tert.*-Butyl methyl ether	7.4
Cyclohexene	19.2	Methyl *n*-propyl ether	7.2
n-Heptane	8.3	Ethyl *n*-propyl ether	8.0
1-Heptene	10.8	Di-*n*-propyl ether	12.7
2-Heptene	13.1	Diisopropyl ether	6.4
Benzene	38.7	Diethyl ether	4.6
Toluene	65.9		
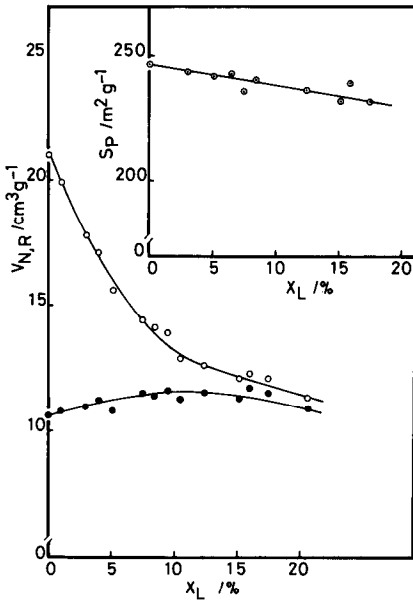
Fig. 2. Dependence of the specific surface area of the column packings and the reduced retention volume on the liquid loading. Solutes: ●, n-hexane, ○, 1-hexene. Solid support: silica gel.
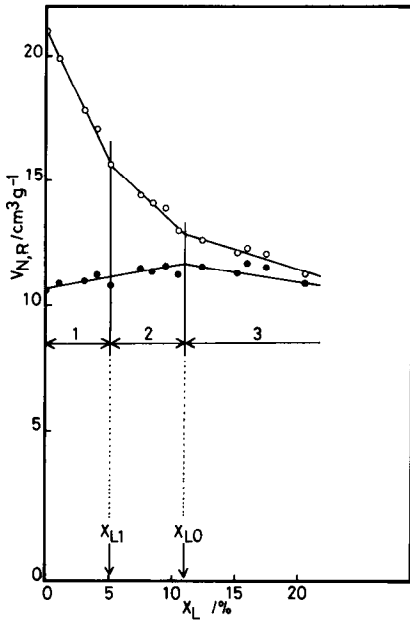

Fig. 3. Linear approximation of the $V_{N,R}$ vs. X_L curve. Solutes: ●, n-hexane; ○, 1-hexene. X_{L1} is the liquid loading at which the subsurface 1 is completely covered with a monolayer of PEG 20M.

further increase in X_L is caused by a gradual decrease in the specific surface area of the liquid-coated silica gel.

For saturated hydrocarbons, $V_{N,R}$ increased to a maximum and then decreased with increasing X_L. The almost linear increase in $V_{N,R}$ with X_L up to 11% suggests that bulk solution partitioning is important for solute retention, but the slope is inconsistent with the K'_L value of the corresponding solute listed in Table I. In this range of X_L, molecules of PEG 20M are fixed at active sites on the silica gel surface, so that a bulk liquid layer is not yet formed; there is only a thin liquid film like a monolayer or a double layer on the solid surface. Therefore, interfacial adsorption equilibria must dominate solute retention. From the evidence, we believe that saturated hydrocarbons can interact more strongly with the thin liquid film than with the solid surface, whereas the reverse is true for more polar solutes.

The experimental plot of $V_{N,R}$ against X_L can be approximated by two straight lines for saturated hydrocarbons and three for unsaturated aliphatic hydrocarbons, aromatic hydrocarbons and dialkyl ethers (Fig. 3). Two adjacent lines intersect at the same liquid phase loading (about 11%) for every solute. We took this liquid phase loading as X_{L0}, the liquid phase loading at which the silica gel surface is completely covered with a monolayer of PEG 20M. At liquid phase loadings lower than 11%, the $V_{N,R}$ vs. X_L curve can be approximated by only one straight line for saturated hydrocarbons and with two lines for the other solutes. This result indicates that the original surface of silica gel shows homogeneous characteristics on adsorption of saturated hydrocarbons but a heterogeneous nature on adsorption of the other solutes. The original surface of silica gel essentially involves two subsurfaces with low and high adsorption capacities towards unsaturated aliphatic hydrocarbons, aromatic hydrocarbons and dialkyl ethers. The subsurface with a high adsorption capacity (subsurface 1) corresponds to a part of the silica gel surface containing the surface hydroxyl groups which interact strongly with polar groups such as π-bonds and oxygen atoms of solute molecules. The subsurface with a low adsorption capacity (subsurface 2) corresponds to a different part of the silica gel surface.

Taking this model of the solid surface into account, first the subsurface 1 and then the subsurface 2 should be predominantly covered with a monolayer of PEG 20M in regions 1 and 2, respectively. X_{L1} (about 5%) is the liquid phase loading at which the subsurface 1 is completely covered with a monolayer of PEG 20M. In region 3, the silica gel surface covered completely with a PEG 20M monolayer is further covered with another type of liquid layer of PEG 20M. An apparent adsorption constant, K_{ad}, calculated by dividing the reduced retention volume by the specific surface area of the column packings, was given as a constant value for each hydrocarbon solute regardless of the liquid phase loadings in region 3. This result suggests that the liquid layer formed on the PEG 20M monolayer in this region has the same surface characteristics as the monolayer. Thus, we regarded this liquid layer as a double layer of PEG 20M.

In regions 1 and 2, the specific surface area of the column packing, S_p, is equal to the sum of the surface area of the uncoated part of the solid surface and of the PEG 20M monolayer. S_P can be formulated in the same form as described in a previous paper[8]:

$$S_P = S_S^0 - (\alpha - \beta)X_L \tag{1}$$

where S_S^0 is the specific surface area of the liquid-free silica gel and α and β are proportionality constants for relating X_L with the occupied area and the surface area of the PEG 20M monolayer. Taking K_S and K_A as distribution constants of adsorption equilibria on the uncoated part of the solid surface and on the monolayer, $V_{N,R}$ can be expressed for saturated hydrocarbons as follows:

$$V_{N,R} = K_S S_S^0 + (\beta K_A - \alpha K_S)X_L \tag{2}$$

For the other solutes, $V_{N,R}$ can be described with the same equations as described in the previous paper[8]:

$$V_{N,R} = K_{ad}^0 S_S^0 - (\alpha K_1 - \beta K_A)X_L \tag{3}$$

and

$$V_{N,R} = K_2 S_S^0 - (\alpha K_2 - \beta K_A)X_L \tag{4}$$

in regions 1 and 2, respectively. K_{ad}^0 is the apparent distribution constant of adsorption on the solid surface and is defined by $K_{ad}^0 S_S^0 = K_1 S_1 + K_2 S_2$, where K_1 and K_2 are distribution constants of adsorption equilibria on subsurface 1 (surface area S_1) and subsurface 2 (surface area S_2). These equations can be fitted to the experimental data if $K_A > K_S$ for saturated hydrocarbons, $K_1 > K_2 > K_A$ for the other solutes and $\alpha > \beta$.

In region 3, the silica gel surface has been completely covered with a monolayer of PEG 20M and partly with a double layer of PEG 20M. The specific surface area of column packings is the sum of the surface areas of the double layer and the uncoated part of the monolayer. The following equation can be written for S_P:

$$S_P = S_{LM}^0 + (\alpha' - \beta')X_{L0} - (\alpha' - \beta')X_L \tag{5}$$

where S_{LM}^0 is the specific surface area of column packings at a liquid phase loading of X_{L0} and α' and β' are proportionality constants to relate $X_L - X_{L0}$ with the occupied area and the surface area of the double layer of PEG 20M. In this case, $V_{N,R}$ can be written as

$$V_{N,R} = K_A S_{LM}^0 + K_{exp}'' X_{L0} - K_{exp}'' X_L \tag{6}$$

where

$$K_{exp}'' = \alpha' K_A - \beta' K_A' - K_L'' \tag{7}$$

K_A' and K_L'' are distribution constants of adsorption on the double layer and solution partitioning into the double layer.

In this study, we could not find regions 4 and 5 on the experimental plot of $V_{N,R}$ vs. X_L, in which a bulk liquid layer was formed on the solid surface, because we failed in uniformly loading such large an amount of PEG 20M on silica gel. The liquid phase loading, X_{L0}', at which the silica gel surface was completely covered with a double layer of PEG 20M could not be directly determined from the experimental data. The

TABLE II

DISTRIBUTION CONSTANTS (10^{-5} cm) FOR ADSORPTION EQUILIBRIA

Solute	K_S		K_A		K'_A
			Regions 1 and 2	Region 3	
2-Methylpentane	0.39		0.44	0.43	0.44
n-Hexane	0.43		0.49	0.49	0.49
Cyclohexane	0.43		0.51	0.51	0.50
2-Methylhexane	0.73		0.81	0.79	0.80
n-Heptane	0.80		0.91	0.91	0.95

Solute	K_1	K_2	K_A			K'_A
			Region 1	Region 2	Region 3	
1-Hexene	0.99	0.73	0.55	0.54	0.54	0.51
2-Hexene	1.18	0.84	0.56	0.55	0.56	0.56
Cyclohexene	1.51	0.94	0.61	0.62	0.61	0.60
1-Heptene	1.84	1.39	0.98	0.99	1.01	0.96
2-Heptene	2.48	1.63	1.06	1.05	1.03	0.99
Benzene	2.87	1.68	0.82	0.83	0.85	0.80
Toluene	7.85	3.65	1.49	1.63	1.64	1.50
Ethylbenzene	14.7	6.74	2.61	2.90	3.06	2.46
o-Xylene	21.9	8.23	3.88	3.58	3.50	3.19
m-Xylene	21.2	7.62	2.82	3.20	3.20	2.79
p-Xylene	21.1	7.36	2.81	3.24	3.18	2.76
tert.-Butyl methyl ether	—	32.0	—	2.77	2.16	0.61
Methyl n-propyl ether	32.4	12.6	1.47	1.48	1.07	0.37
Ethyl n-propyl ether	—	24.0	—	2.00	1.75	0.62
Di-n-propyl ether	—	33.9	—	3.52	2.85	1.10
Diisopropyl ether	—	28.5	—	1.88	1.90	0.73
Diethyl ether	34.1	14.0	1.74	1.28	1.01	0.32

proportionality constants α' and β' were calculated by using the relationships $\alpha' = S^0_{LM}/(X'_{L0} - X_{L0})$ and $\beta' = S^0_{LD}/(X'_{L0} - X_{L0})$, by assuming that $X'_{L0} = 2X_{L0}$. S^0_{LD} is the specific surface area of column packings at X'_{L0} and is obtained by extrapolating the experimental relationship between S_P and X_L.

By fitting the equations to the experimental data in the respective regions, distribution constants of adsorption equilibria were determined as listed in Table II. The results show that $K_A > K_S$ for saturated hydrocarbons and $K_1 > K_2 > K_A$ for the other solutes. Similar values of K_A were determined for each solute in two or three different regions. The relatively large fluctuation in the K_A values of dialkyl ethers is due to poor reproducibility of the retention data of the skewed peaks.

The K''_L value of each hydrocarbon was calculated from the slope of the $V_{N,R}$ vs. X_L plot in region 3 by assuming that $K'_A = K_A$ and that K'_A was equal to K_{ad} in region 3. The two values of K''_L were different and inconsistent with the K_L value of the corresponding solute listed in Table I. Negative values of K''_L were obtained for unsaturated aliphatic hydrocarbons and aromatic hydrocarbons. From these results, we considered that solution partitioning into a double layer of PEG 20M did not take

part in solute retention in this instance. By neglecting the effect of solution partitioning, eqn. 7 can be rewritten as

$$K''_{exp} = \alpha' K_A - \beta' K'_A \tag{8}$$

The K'_A value of each hydrocarbon solute is in good agreement with the K_A value of the corresponding solute. That $K_A > K'_A$ for dialkyl ether implies that the surface of the PEG 20M monolayer still has polar adsorptive characteristics, which can be effectively suppressed by coverage with a thin liquid film of PEG 20M. In other words, the original surface activity of silica gel is significantly reduced with a monolayer of PEG 20M with respect to adsorption of hydrocarbons but a double layer is required for similar reduction with adsorption of dialkyl ethers. In this study, adsorption dominated the retention of all solutes used.

REFERENCES

1 J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1972) 700.
2 V. G. Berezkin, *J. Chromatogr.*, 65 (1972) 227.
3 V. G. Berezkin, *J. Chromatogr.*, 159 (1978) 358.
4 Z. Suprynowicz, A. Waksmunzki and W. Rudzinski, *J. Chromatogr.*, 67 (1972) 21.
5 A. Waksmunzki, W. Rudzinski and Z. Suprynowicz, *J. Chromatogr.*, 74 (1972) 3.
6 J. A. Jönsson and L. Mathiasson, *J. Chromatogr.*, 179 (1979) 1.
7 D. F. Fritz, A. Sahil and E. Sz. Kováts, *J. Chromatogr.*, 186 (1978) 63.
8 K. Naito, H. Ogawa, S. Igarashi and S. Takei, *Anal. Sci.*, 4 (1988) 185.
9 K. Naito, S. Wada and S. Takei, *Anal. Sci.*, 4 (1988) 105.
10 K. Naito, N. Ohwada, S. Moriguchi and S. Takei, *J. Chromatogr.*, 330 (1985) 193.
11 K. Naito, H. Ogawa, S. Moriguchi and S. Takei, *J. Chromatogr.*, 229 (1984) 73.
12 K. Naito and S. Takei, *J. Chromatogr.*, 190 (1980) 21.