

CHROM. 17 796

ADSORPTION EFFECTS IN GAS-LIQUID CHROMATOGRAPHY

SOLUTE RETENTION IN THE HYDROCARBON SOLUTE-POLAR STATIONARY PHASE (POLYPROPYLENE GLYCOL 2000) SYSTEM

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(First received May 29th, 1984; revised manuscript received April 1st, 1985)

SUMMARY

The solute retention mechanism in gas-liquid chromatography was studied in a non-polar hydrocarbon solute-moderately polar stationary phase (polypropylene glycol 2000) system. The dependences of the retention volume of a solute and the specific surface area of column packings on the liquid loading are quantitatively interpreted on the basis of a model for the distribution of a liquid phase on a solid support. In the model, the solid support surface is assumed to be successively covered with three different types of liquid phase layers, first with a monolayer, second with a double layer and finally with a bulk liquid layer, as the liquid loading increases. The changes in the enthalpy and entropy of solution and adsorption were calculated from distribution constants for bulk solution partition and for interfacial adsorption obtained by analysis at two column temperatures.

INTRODUCTION

In studies of the effects of interfacial adsorption on the retention volumes of solutes in gas-liquid chromatography (GLC), most workers have emphasized the preferential contribution of adsorption at the gas-liquid interface to the solute retention¹⁻¹¹. This applies only when the solid support surface is completely covered with a bulk liquid layer of a stationary phase. However, in such an instance, the retention volume of a given solute usually has a contribution from bulk solution partition and less significantly from the interfacial adsorption.

We used modified alumina as the solid support as it is possible to observe adsorption effects of a suitable magnitude and to use some hydrocarbons as solutes without the occurrence of phenomena such as irreversible adsorption on the column packing¹²⁻¹⁴. We interpreted the dependence of the retention volume of the solute and the specific surface area of the column packing on liquid loading on the basis of a liquid-phase distribution model. We postulated that the modified alumina surface

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was first covered with a monolayer, second with a double layer and finally with a bulk liquid layer of the stationary phase as the liquid loading increases. In previous work¹⁴, a large effect of interfacial adsorption and a small effect of bulk solution partition were observed by using a strongly polar stationary phase, Triton X-100. This result is considered to be partly due to the large specific surface area of the modified alumina used as the solid support.

In this paper, the retention volume of a given solute and the specific surface area of column packings, determined as a function of the liquid loading, are interpreted on the basis of the same reasoning used in the previous paper. The enthalpy and entropy changes are calculated from distribution constants obtained by analysis at two column temperatures.

EXPERIMENTAL

Modified alumina, prepared from Neobead MS.C (60–80 mesh) (Mizusawa

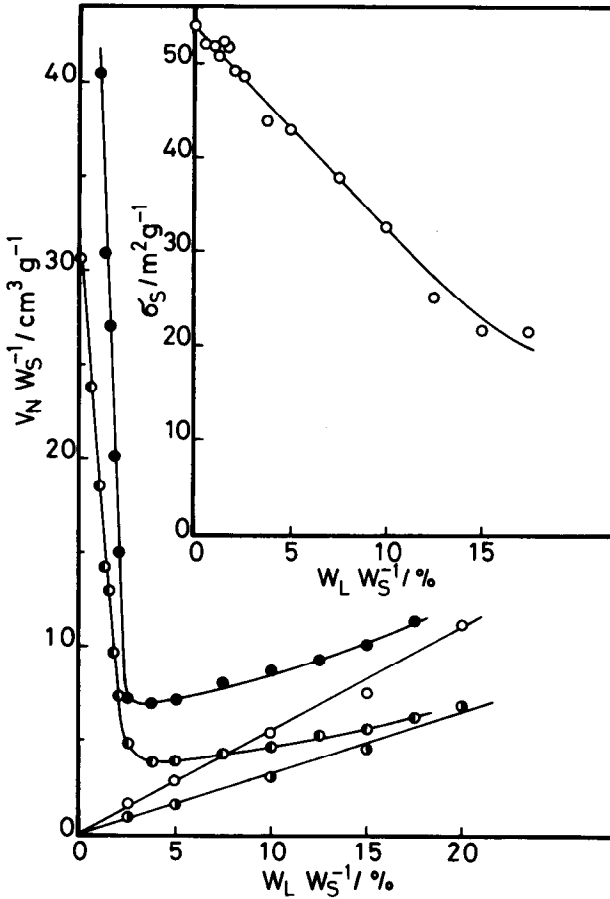


Fig. 1. Dependence of retention volume of *n*-hexane and specific surface area of column packings on liquid loading. Stationary phase: polypropylene glycol 2000. Column temperature and solid support: ●, 50°C, modified alumina; O, 50°C, Chromosorb P; ●, 70°C, Chromosorb P.

TABLE I
DISTRIBUTION CONSTANT FOR BULK SOLUTION PARTITION, K_L ($\text{cm}^3 \text{g}^{-1}$), OF SOLUTES

Solute	Column temperature			
	50°C		70°C	
	Chromosorb P	Al_2O_3	Chromosorb P	Al_2O_3
2-Methylpentane	40	42	22	22
<i>n</i> -Hexane	54	56	29	29
Cyclohexane	118	117	61	65
1-Hexene	60	58	30	33
2-Hexene	68	65	34	38
Cyclohexene	167	173	81	91
2-Methylhexane	102	92	52	57
<i>n</i> -Heptane	140	134	64	70
Benzene	226	249	110	122
1-Heptene	145	149	70	77
2-Heptene	179	184	85	93

Industrial Chemicals, Tokyo, Japan) by a previous method¹⁴, was used as the solid support. A commercially available solid support, Chromosorb P, was used as a reference. Polypropylene glycol 2000 (PPG 2000) (reagent for gas chromatography), a moderately polar stationary phase, was coated on these solid supports at different liquid loadings of 0–0.2 g/g of liquid-free solid support. Column packings prepared were packed into a stainless-steel tube (100 × 0.3 cm I.D.) after removing any volatile components under vacuum. The packed column was pre-conditioned under the same conditions as used previously.

A Hitachi K53 gas chromatograph equipped with a thermal conductivity detector was used in conjunction with a Hitachi 561 recorder for gas chromatography. Chromatographic measurements were carried out under the same conditions as applied previously, except for the column temperature; the column temperatures used were 50 and 70°C.

Previous procedures¹³ were applied to the determination of the retention volume of each solute and its correction. The specific surface areas of the column packings were measured by the BET method of adsorption of nitrogen at liquid nitrogen temperature. To prevent the fluctuation of the retention data with the amount of the column packings used, retention volumes are expressed as a reduced value per unit weight of liquid-free solid support packed into the column.

RESULTS AND DISCUSSION

When Chromosorb P support (specific surface area *ca.* 4 m² g⁻¹) was coated with various amounts of PPG 2000, the reduced retention volume, V_N/W_s , of a given solute increased linearly with increase in the liquid loading, W_L/W_s , at both column temperatures, where V_N is the net retention volume and W_L and W_s are the weight of stationary phase coated and the weight of liquid-free solid support packed into the column, respectively. From the small and positive intercept of the linear graph

(Fig. 1), bulk solution partition contributes predominantly to the solute retention in this instance. We assume that the slope of the linear graph corresponds to the K_L' value defined previously¹². The K_L' value of each solute is listed in Table I.

When using the modified alumina (specific surface area $54.0 \text{ m}^2 \text{ g}^{-1}$) coated with the same stationary phase, the graph of V_N/W_S against W_L/W_S is a hyperbolic curve with a minimum for each solute. This result is different from that for Triton X-100¹⁴ but similar to that for silicone DC 200¹³. The steep decrease in V_N/W_S with a small increase in W_L/W_S is attributed to deactivation by gradual occupation of the original active adsorption sites with molecules of PPG 2000 dispersed in a monomolecular form. The gradual increase in V_N/W_S with increasing W_L/W_S is considered to be due to successive expansion of the bulk liquid layer on the deactivated surface of the modified alumina.

By plotting the relative retentions of 1-hexene and *n*-heptane with respect to *n*-hexane against the negative logarithm of the amount of PPG 2000 per unit surface area of the modified alumina, a reversed L-shaped curve is obtained (Fig. 2), as shown previously¹⁴. The high liquid loading part of the curve can be smoothly con-

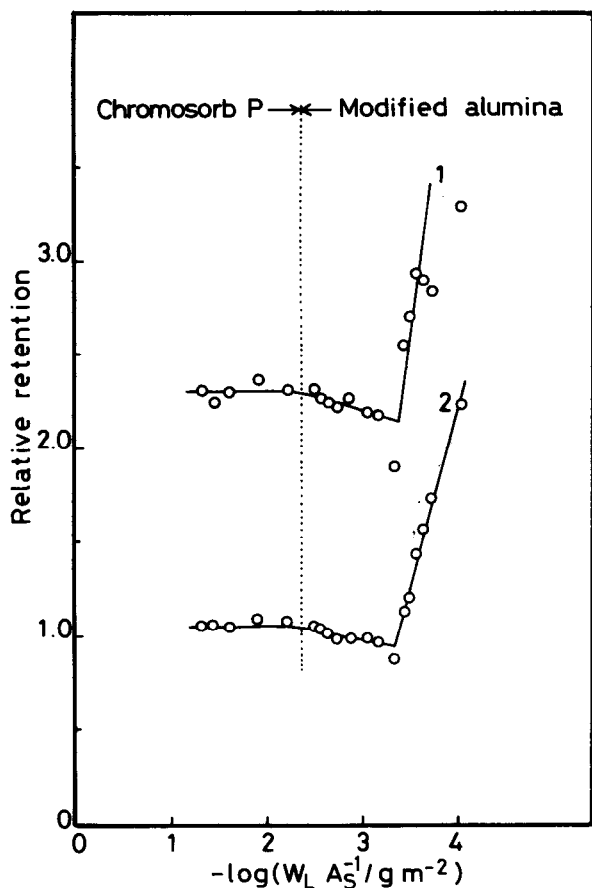


Fig. 2. Dependence of relative retention with respect to *n*-hexane on surface concentration of polypropylene glycol 2000. 1, *n*-Heptane; 2, 1-hexene.

nected to the curve for Chromosorb P. This result suggests that, at a high liquid loading, the distribution of the stationary phase on the modified alumina is very similar to that on Chromosorb P.

The BET surface area of the modified alumina coated with various amounts of PPG 2000, σ_s , decreases almost linearly with increasing W_L/W_S (Fig. 1). This decrease is not always comparable to that of V_N/W_S with W_L/W_S . Fig. 3 shows a graph of V_N/W_S vs. σ_s , consisting of two different parts, regions A and B. Region A corresponds to the low liquid loading range, where the modified alumina surface is gradually shielded with a thin film of the stationary phase as a monolayer and a double layer. An increase in V_N/W_S and a decrease in σ_s in region B indicate a smaller effect of the interfacial adsorption and a significant effect of the bulk solution partition on the solute retention.

The V_N/W_S vs. W_L/W_S curve can be approximated by means of the straight lines in five different liquid loading ranges. Two adjacent linear portions intersect at the same liquid loading regardless of the nature of the solute and the column temperature (Table II). As assumed previously¹⁴, W_L/W_S can be regarded as the liquid

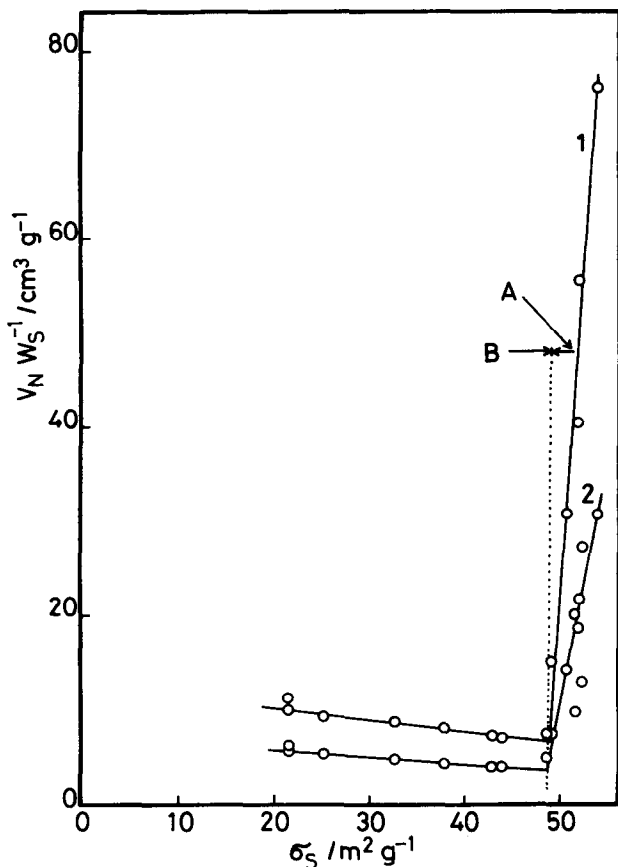


Fig. 3. Dependence of V_N/W_S on σ_s . Solute: *n*-hexane. Liquid loading range: A, region A; B, region B. Column temperature: 1, 50°C; 2, 70°C.

TABLE II

LIQUID LOADINGS AT THE POINTS OF INTERSECTION BETWEEN TWO ADJACENT STRAIGHT LINES (FIG. 3)

Solute	W_{L_1}/W_s (%, w/w)		W_{L_0}/W_s (%, w/w)		W'_{L_0}/W_s (%, w/w)		W_{L_2}/W_s (%, w/w)	
	50°C	70°C	50°C	70°C	50°C	70°C	50°C	70°C
2-Methylpentane	0.43	0.50	1.43	1.45	2.53	2.59	13.0	13.4
<i>n</i> -Hexane	0.48	0.50	1.46	1.52	2.54	2.71	13.5	12.8
Cyclohexane	0.47	—	1.27	1.32	2.55	2.61	13.0	13.2
1-Hexene	0.50	0.51	1.49	1.44	2.53	2.58	12.9	12.8
2-Hexene	0.50	0.50	1.45	1.48	2.54	2.58	13.0	12.8
Cyclohexene	0.50	0.48	1.44	1.54	2.56	2.63	12.9	13.1
2-Methylhexane	0.50	0.50	1.42	1.53	2.58	2.59	13.1	13.3
<i>n</i> -Heptane	0.50	0.51	1.48	1.41	2.54	2.57	12.7	13.1
Benzene	0.50	0.50	1.45	1.62	2.57	2.65	12.9	12.9
1-Heptene	0.50	0.51	1.44	1.41	2.54	2.56	12.4	13.2
2-Heptene	—	0.51	1.45	1.38	2.54	2.57	12.9	13.1

loading necessary to cover subsurface 1 completely with a monolayer of PPG 2000. W_{L_0}/W_s , W'_{L_0}/W_s and W_{L_2}/W_s correspond to the liquid loadings required for complete coverage of the modified alumina surface with a monolayer, a double layer and a bulk liquid layer of PPG 2000, respectively.

From these results, previous reasoning can be applied to interpret the present experimental data. Tables I, III and IV give the distribution constants for the bulk solution partition, K_L , and those for the interfacial adsorption, K_1 , K_2 , K_A , K'_A and K''_A , obtained through analysis, where K_1 , K_2 , K_A , K'_A and K''_A are distribution constants for adsorption on subsurface 1, on subsurface 2, on the monolayer of PPG 2000, on the double layer and on the bulk liquid layer, respectively.

It should be noted that the same value was determined for K'_L for a given solute

TABLE III

DISTRIBUTION CONSTANTS FOR ADSORPTION, K_1 , K_2 , K_A , K'_A AND K''_A (10^{-5} cm)

Column temperature: 50°C.

Solute	K_1	K_2	K_A	K'_A			K''_A		
				Region 1	Region 2	Region 3	Region 3	Region 4	Region 4
2-Methylpentane	10.8	10.3	3.9	4.0	4.0	1.1	1.2	1.1	1.1
<i>n</i> -Hexane	16.6	13.4	4.9	5.0	4.9	1.3	1.4	1.4	1.4
Cyclohexane	9.2	7.8	3.9	4.0	4.1	1.3	1.4	1.3	1.3
1-Hexene	110	29.7	8.4	6.7	6.2	1.2	1.3	1.3	1.3
2-Hexene	110	31.8	8.4	6.1	6.2	1.4	1.4	1.5	1.5
Cyclohexene	41.5	28.9	6.1	5.9	6.0	1.6	1.5	1.0	1.0
2-Methylhexane	37.2	35.7	12.3	12.3	12.6	2.8	1.9	2.0	2.9
<i>n</i> -Heptane	51.4	44.0	15.6	15.4	15.1	3.2	3.2	3.4	3.4
Benzene	231	78.1	11.8	9.4	9.3	2.1	1.9	0.5	0.6
1-Heptene	271	100	—	18.9	19.2	2.9	3.1	3.1	3.1
2-Heptene	—	115	—	19.6	19.8	3.3	3.4	3.4	3.4

TABLE IV

DISTRIBUTION CONSTANTS FOR ADSORPTION, K_1 , K_2 , K_A , K'_A AND K''_A (10^{-5} cm)

Column temperature: 70°C.

Solute	K_1	K_2	K_A			K'_A		K''_A	
			Region 1	Region 2	Region 3	Region 3	Region 4	Region 4	Region 5
2-Methylpentane	4.82	4.33	1.8	1.8	1.8	0.62	0.62	0.74	0.73
<i>n</i> -Hexane	5.83	5.59	2.3	2.3	2.2	0.86	0.71	0.87	0.87
Cyclohexane	3.56	3.70	1.9	2.0	2.0	0.74	0.72	0.76	0.76
1-Hexene	16.3	13.7	2.5	2.5	2.7	0.67	0.69	0.74	0.75
2-Hexene	17.2	13.4	2.6	2.7	2.7	0.71	0.73	0.81	0.82
Cyclohexene	15.8	11.1	2.7	2.9	2.7	0.84	0.76	0.69	0.69
2-Methylhexane	17.0	12.9	5.5	5.5	5.4	1.3	1.3	1.4	1.4
<i>n</i> -Heptane	25.1	19.0	6.0	5.8	6.2	1.5	1.6	1.7	1.7
Benzene	77.2	38.6	7.0	7.0	4.2	1.1	0.87	0.70	0.70
1-Heptene	73.6	45.3	6.5	6.1	7.6	1.3	1.5	1.6	1.6
2-Heptene	83.5	53.6	5.5	4.9	7.8	1.5	1.6	1.7	1.7

on using both solid supports with different surface properties. For any solute, the distribution constants for the interfacial adsorption decrease in the order $K_1 > K_2 > K_A > K'_A \approx K''_A$, which is different from the previously determined order¹⁴, $K_1 > K_2 > K_A \approx K'_A > K''_A$. The same value was determined for K_A for a given solute in three different liquid loading ranges. The same K_A values for an olefin and an alkane with the same number of carbon atoms indicate that the monolayer surface of PPG 2000 shows the same adsorption interaction toward both hydrocarbon solutes. This implies that, for adsorption of hydrocarbon molecules, the monolayer

TABLE V

ENTHALPY AND ENTROPY CHANGES, ΔH (kJ mol⁻¹) AND ΔS (J mol⁻¹ K⁻¹), OF BULK SOLUTION PARTITION IN POLYPROPYLENE GLYCOL 2000

Solute	Solid support				ΔH_i^* (kJ mol ⁻¹)
	Chromosorb P		Modified alumina		
	ΔH	ΔS	ΔH	ΔS	
2-Methylpentane	29	-59	30	-61	27.8
<i>n</i> -Hexane	30	-59	31	-62	28.9
Cyclohexane	31	-56	27	-45	33.0
1-Hexene	32	-63	27	-47	28.0
2-Hexene	31	-62	26	-44	29.1 (<i>cis</i> -isomer) 28.9 (<i>trans</i> -isomer)
Cyclohexene	33	-61	30	-49	-
2-Methylhexane	31	-59	24	-37	30.7
<i>n</i> -Heptane	36	-71	30	-52	31.7
Benzene	33	-59	33	-55	31.7
1-Heptene	34	-63	30	-52	-
2-Heptene	34	-63	32	-54	-

* Data from ref. 15.

TABLE VI

ENTHALPY AND ENTROPY CHANGES, ΔH (kJ mol⁻¹) AND ΔS (kJ mol⁻¹ K⁻¹), OF INTER-FACIAL ADSORPTION

Solute	Distribution constants for adsorption									
	K_1		K_2		K_A		K'_A		K''_A	
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
2-Methylpentane	40	-0.20	38	-0.19	36	-0.19	28	-0.18	20	-0.16
<i>n</i> -Hexane	51	-0.23	38	-0.19	37	-0.20	25	-0.17	21	-0.16
Cyclohexane	45	-0.22	34	-0.18	33	-0.19	29	-0.18	23	-0.17
1-Hexene	89	-0.33	29	-0.16	42	-0.21	29	-0.18	26	-0.17
2-Hexene	87	-0.33	33	-0.17	38	-0.20	30	-0.19	29	-0.18
Cyclohexene	52	-0.23	36	-0.18	35	-0.19	30	-0.19	16	-0.14
2-Methylhexane	48	-0.21	39	-0.19	38	-0.19	27	-0.17	15	-0.14
<i>n</i> -Heptane	35	-0.17	37	-0.18	43	-0.21	35	-0.19	30	-0.18
Benzene	48	-0.20	32	-0.16	-	-	33	-0.19	-	-
1-Heptene	66	-0.25	31	-0.16	48	-0.22	35	-0.19	32	-0.19
2-Heptene	-	-	35	-0.17	43	-0.20	35	-0.19	30	-0.18

surface of PPG 2000 can behave as an energetically homogeneous surface. It should be noted that the strong adsorption interaction between the olefin molecule and the original surface of the modified alumina can be significantly suppressed by shielding only with the monolayer. The same values of K'_A and K''_A for a given solute indicate that the double layer surface shows similar surface properties towards hydrocarbon solutes as those of the bulk liquid layer. However we consider that the double layer itself still has as dense a structure as the monolayer because of the polarity of PPG 2000.

Tables V and VI list the changes in the enthalpy and entropy of solution and adsorption, calculated from the corresponding distribution constants by using the relationships $\Delta G^0 = -RT \ln K$ and $\Delta H = \Delta H - T\Delta S$. For each solute, the same value is obtained for ΔH_s and ΔS_s , the changes in enthalpy and entropy of solution into the bulk liquid layer of PPG 2000, regardless of the nature of the solid support. The ΔH_s value agrees with heat of evaporation to within about 10% for each solute. It is likely that a hydrocarbon molecule interacts slightly with a PPG 2000 molecule in the bulk liquid layer.

On subsurface 1, the change in the enthalpy of adsorption of an unsaturated hydrocarbon is higher than that of a saturated hydrocarbon with the same number of carbon atoms. However such a difference is hardly observed on the other surface. The change in the enthalpy of adsorption of an unsaturated hydrocarbon on subsurface 1 is about three to four times larger than that on subsurface 2. However a saturated hydrocarbon solute shows similar changes in the enthalpy of adsorption on both subsurfaces. From these results, it is probable that an unsaturated hydrocarbon solute is adsorbed through specific interaction on subsurface 1 but through non-specific interaction on the other surface. Also, it is likely that a saturated hydrocarbon solute is adsorbed mainly through non-specific interaction on any surface.

We continue to take an interest in these aspects are studying GLC systems involving other types of stationary phase.

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