

CHROM. 11,197

THE RETENTION MECHANISM OF SOME ALKANE AND BENZENE DERIVATIVES ON OCTADECYLSILYL AND TRIMETHYLSILYL SILICA IN GAS CHROMATOGRAPHIC COLUMNS

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(First received March 1st, 1978; revised manuscript received May 16th, 1978)

SUMMARY

Gas chromatographic net retention data of a number of mono-substituted alkane and benzene derivatives on trimethylsilyl, octadecylsilyl (ODS) and trimethylchlorosilane treated ODS Porasil C have been measured at 160° and interpreted in terms of the adsorption model of Snyder. On the basis of plausible assumptions, the interaction of apolar samples with the ODS chains is separated from that with the adsorbent surface underneath. For polar samples, the effects of these two interaction mechanisms cannot be distinguished.

INTRODUCTION

The introduction of chemically modified adsorbents is one of the most interesting and promising developments in the field of chromatography in the last decade. In gas chromatography (GC), support deactivation with dimethyldichlorosilane is well known and indispensable in order to obtain reliable retention data and quantitative results. In liquid chromatography (LC), chemically modified silicas offer much better column stability and great flexibility with regard to the choice of the eluent and the column temperature. On account of their loose structures, bonded phases show high mass-transfer rates which implies high column efficiencies, even at high flow-rates of the mobile phase, and hence short analysis times.

Although a large number of applications of bonded phases in LC as well as GC has been reported¹ in the last few years, very little is known about the separation mechanism on these materials. Even the fundamental question whether solute retention is based on adsorption or on partition is usually difficult to answer unequivocally. It can be argued that the bound chains cannot be considered as a real liquid because they are anchored to the solid phase whereas their mutual distance is generally much larger than in a real liquid phase. In addition, the thickness of the bonded phase is usually only 25 Å or even less and it is doubtful whether such thin layers have bulk properties. Recently Pesek and Graham² reported that the sorption isotherm on octadecylsilyl (ODS) silica is of the Langmuir type and concluded that adsorption plays a dominant role.

In this paper we attempt to unravel some aspects of the intricate sorption mechanism of these "bristle" phases. The choice of GC, of the examined solute and the types of bonded phase was based on the following considerations. It was expected that interaction with the bound chains would be recognizable at best if the chains are surrounded by inert, non-adsorbing eluent molecules. This requirement is met in GC columns flushed by helium as carrier gas. In order to be able to distinguish the two types of sorption, *i.e.*, at the polar silica surface and to the molecules of the bonded phase, the bonded phase should be apolar, whereas both polar and apolar solutes should be examined. Since the layer thickness seems to be a relevant variable, the sorption properties of ODS and trimethylsilyl (TMS) groups on silica were examined.

THEORETICAL

Separation of the effects of interaction of the sample with the bonded phase and with the adsorbent surface underneath

Suppose that the bonded phase has bulk properties and that solute retention is controlled by sorption in the bonded phase layer and at the silica. Then the net retention volume, *i.e.*, the retention volume corrected for gas hold-up, column pressure and the difference between room and column temperature, per gram adsorbent, is given by the well-known equation³:

$$V_N/W = KV_L + K_a A \quad (1)$$

wherein W is the weight (g) of the adsorbent in the column, K is the partition coefficient and V_L the volume of the stationary phase per gram adsorbent (cm^3/g); K_a is the adsorption coefficient (cm) and A the specific area of the adsorbent (cm^2/g) (see Glossary of terms). In the following derivations, the adsorption contribution to V_N/W will be interpreted in terms of Snyder's adsorption model⁴, wherein the adsorption coefficient is defined as the ratio of the mole fractions of the adsorbate at the adsorbent and in the mobile phase. This coefficient K_a^0 is dimensionless and should be multiplied by a specific volume V_a (cm^3/g) in order to replace the $K_a A$ term in eqn. 1:

$$V_N/W = KV_L + K_a^0 V_a \quad (2)$$

It can easily be shown that V_a is the volume of adsorbed mobile phase per gram adsorbent. In liquid-solid chromatography (LSC), approximately one monolayer of eluent is adsorbed. Snyder⁴ showed that, for a large number of eluents on both alumina and silica, V_a can be calculated from the equation:

$$V_a = 3.5 \cdot 10^{-8} A - 0.01 \text{ wt. \% H}_2\text{O} \quad (3)$$

which means that the monolayer is 3.5 \AA thick and that one volume of adsorbed water replaces an equal volume of adsorbed eluent at the surface. In gas-solid chromatography (GSC), eqn. 3 holds equally well, although for non-adsorbing gases V_a merely has a formal significance.

In order to separate the retention contributions of sorption to the ODS chains and at the bare silica underneath, the following assumptions are made:

(1) the contribution of partition on TMS silica is negligible: $(KV_L)_1 = 0$

(2) the contributions of sorption to the ODS chains are equal for trimethylchlorosilane-treated and untreated ODS silica. In other words the reaction of TMCS with the remaining silanol groups only affects the activity of the adsorbent surface: $(KV_L)_{18/1} = (KV_L)_{18}$

(3) the contributions of adsorption at the TMS layers of TMS silica and TMCS-treated ODS silica are equal: $(K_a^0V_a)_1 = (K_a^0V_a)_{18/1}$

These assumptions seem to be plausible, provided that the TMCS treatment of C1 and the C18/1 packings have the same yield (to be verified experimentally), and give the following relationships:

$$(V_N/W)_1^{\text{ads.}} = (K_a^0V_a)_1 = (V_N/W)_1 \quad (4)$$

$$(V_N/W)_{18/1}^{\text{part.}} = (KV_L)_{18/1} = (V_N/W)_{18/1} - (V_N/W)_1 \quad (5)$$

$$(V_N/W)_{18}^{\text{ads.}} = (K_a^0V_a)_{18} = (V_N/W)_{18} - (V_N/W)_{18/1}^{\text{part.}} \quad (6)$$

In eqns. 5 and 6 the interaction with the ODS chains has been denoted by the superscript part., but this is a shorthand notation for a sorption mode specified as adsorption-like partition. The superscript ads. denotes the familiar adsorption at a solid surface (silica or TMS silica).

Application of Snyder's theory to the adsorption contribution to the retention volume

If it is supposed that, on adsorption of any solute molecule (x), m eluent molecules (e) have to be desorbed, the net standard partial molar free energy of this adsorption process $\Delta\bar{F}^0$ is given by:

$$\Delta\bar{F}^0/2.3RT \equiv \Delta\bar{F} = \log K_a^0 = \bar{F}_x - m\bar{F}_e \quad (7)$$

In eqn. 7 it is assumed that specific solute-eluent interactions, that would give rise to a $\bar{F}_{x,e}$ term in eqn. 7, are absent. This is true for GSC systems at moderate column pressures and is often a useful approximation in LSC systems. $\Delta\bar{F}$ can be divided into contributions arising from specific and dispersive (*i.e.*, London) interactions⁵:

$$\Delta\bar{F} = (\bar{F}_x - m\bar{F}_e) + (\bar{F}_x - m\bar{F}_e)_d \quad (8)$$

If one type of specific interaction plays a dominant role, Snyder showed that \bar{F} can be described simply by $\bar{F} = \alpha S^0$ where α is the adsorbent activity and S^0 is the (reduced) free energy of the adsorbed molecule (solute or eluent) on adsorption at a standard adsorbent ($\alpha = 1$). The same applies to dispersive forces: $\bar{F}_d = \alpha_d S_d^0$. The number of desorbed eluent molecules per adsorbed solute molecule (m) is equal to the ratio of their molecular surface areas: $m = A_x/A_e$. An eluent strength parameter has been defined as $\varepsilon^0 = \bar{F}_e/A_e$. Substitution of these relationships into eqn. 8 gives the general equation of the adsorption model of Snyder⁵:

$$\Delta\bar{F} = \alpha(S^0 - A_x\varepsilon^0) + \alpha_d(S_d^0 - A_x\varepsilon_d^0) \quad (9)$$

This equation has been successfully applied by Snyder to polar and apolar adsorbent systems, in LSC as well as GSC columns. Besides, the model has a great heuristic value because of its simplicity. Since dispersion forces are approximately proportional to the molecular surfaces of the interacting molecules, it holds that $S_{d,x}^0/A_x \doteq S_{d,e}^0/A_e \equiv \varepsilon_d^0$. Therefore the dispersive term in eqn. 9 can be omitted in LSC systems.

On apolar adsorbents such as pure charcoal, $\alpha = 0$. Hence, LSC separations on charcoal are mainly based on specific solute-eluent interactions, *i.e.*, on an $\bar{F}_{x,e}$ term.

When applied to GSC systems, eqn. 9 should be adjusted for the loss of entropy of the solute on adsorption from the vapour phase. Snyder showed that this correction is independent of the solute, but its magnitude appears to be dependent on the adsorbent type^{5,6} and the temperature. Since it cannot be calculated straightforwardly for the complex bonded phase layers considered, a parameter C should be added to eqn. 9 to account for it. Further, it is obvious that ε^0 and ε_d^0 are zero if a non-adsorbing carrier gas is used. Hence, for GSC systems, eqn. 9 becomes:

$$\Delta \bar{F} = \alpha S^0 + \alpha_d S_d^0 + C = \alpha S^0 + \beta A_x + C \quad (10)$$

Combination of eqns. 10, 7 and 4 or 6 gives the desired description of $\log(V_N/W)^{\text{ads}}$ in terms of adsorbent and solute parameters:

$$\log(V_N/W)_i^{\text{ads}} = \log(V_a)_i + \alpha_i S^0 + \beta_i A_x + C_i \quad (11)$$

where i denotes the adsorbent. This equation is essentially the same as that applied by Snyder to GSC retention data on charcoal⁵ and alumina-2.7% water⁶.

Finally, a few remarks should be made on how to handle eqn. 11. The required S^0 and A_x values can be calculated by adding group contributions. These additivity rules fail if flat adsorption is hampered by steric effects. This problem and those arising from the heterogeneity⁴ of the silica surface and intramolecular electronic effects⁴ have been avoided by an appropriate choice of the solutes in the present investigation. The A_x values can be calculated from the Van der Waals radii (enlarged by 0.5 Å) of the solute groups⁴. The values given in Table II are normalized to $A_x(\text{benzene}) = 6$.

Although the S^0 values given in Table II are based on retention data on bare silica at ambient temperature, they can be used for the description of the adsorption at the bare silica surface beneath the ODS bristles at higher temperatures. The variation of S^0 with temperature can be taken into account by use of a temperature-dependent value of α for solutes similar to those examined in this work^{4,5}. The same holds for the temperature variation of the dispersive term $\beta_i A_x$ in eqn. 11 (ref. 5). The applicability of the S^0 values to bonded phases on silica has been established from LSC data on ODS silica and will be reported elsewhere¹⁵. Whether these A_x and S^0 values can also be applied to the TMCS-treated silicas is doubtful, due to the high surface concentration of the TMS groups.

Since the $\log V_a + C$ term is assumed to be independent of the solute, β can be obtained by plotting $\log(V_N/W)^{\text{ads}}$ data of n -alkanes ($S^0 = 0$) versus their A_x values. α can be computed from the deviations (αS^0) of data of other substances from this line. Both α and β depend only on the adsorbent type and the temperature. In

this work, however, the parameters mentioned above are evaluated simultaneously per class of solutes (substituted hexanes and benzenes) by means of multiple regression analysis. In doing so, the rather uncertain assumption that C is independent of solute type can be avoided.

EXPERIMENTAL

Preparation of the bonded phases

Porasil C (100–150 mesh) (Waters Assoc., Milford, Mass., U.S.A.) was activated by boiling with 1 *N* HCl for 4 h, rinsing with distilled water until free from chloride and heating at 1 mmHg and 150° for 3 h to remove the surface water. About 15 g activated silica were transferred directly to a three-necked round-bottomed flask containing 50 ml of carefully dried tetrahydrofuran (THF), and flushed with a stream of dry nitrogen. The reagent, 10 ml hexamethyldisilazane (HMDS) and 1 ml trimethylchlorosilane (TMCS), was added from a separation funnel. The reaction mixture was gently swirled occasionally and refluxed under nitrogen at 75° for 6 h.

Another portion of *ca.* 15 g activated silica was allowed to react with 10 ml octadecyltrichlorosilane in 50 ml dry THF by refluxing under nitrogen at 75° for 6 h.

After completion of the reactions, both products were thoroughly extracted with dry THF, rinsed with acetone and distilled water and dried at 1 mmHg and 150° for 4 h.

Weighed amounts of these adsorbents were packed in cleaned stainless-steel tubes (as specified in Table I) and mounted in the gas chromatograph. The extent of silylation of the C1 column was judged from the effect of 25- μ l injections of HMDS on the magnitude of the net retention volume of a series of polar solutes at 150°. The retention data did not appear to change and hence it was concluded that the surface coverage of TMS groups on Porasil was complete. The same *in situ* silylation procedure has been applied to the packing of the C18 column after the measurements on this column were finished. Net retention volumes were measured after each 25- μ l injection of HMDS until they remained constant, after which 50 μ l HMDS (in excess) was injected.

TABLE I
COLUMN AND BONDED PHASE SPECIFICATIONS

<i>Column code</i>	<i>C1</i>	<i>C18</i>	<i>C18/1</i>
Column dimensions	175 cm \times 4 mm I.D.	175 cm \times 4 mm I.D.	175 cm \times 4 mm I.D.
Weight (g) of packing in the column	10.66	11.04	\sim 11.04
Wt. % bound carbon	1.52	5.22	5.62
Surface concentration (μ moles/m ²)*	5.48	3.14	4.58
Plate number (m ⁻¹)**	1700	2000	1800

* μ moles/m² = $10^4 \times$ wt. % bound carbon / (mol. wt. of carbon skeleton \times specific surface area).

** Solute, toluene; flow-rate, 5 cm/sec.

Characterization of the adsorbents

The specific surface area and the pore size distribution of Porasil C (Batch 223) were determined by nitrogen adsorption (BET) according to the method of Broekhoff and Linsen⁷, using a Carlo Erba Sorptomatic (Type 1810) equipped with a pressure transducer and a digital pressure read-out. The specific surface area ($77 \pm 1 \text{ m}^2/\text{g}$) and the pore diameter range (*ca.* 200–500 Å) are in accord with the rough specifications given by the supplier.

Thermal gravimetric and differential thermal analysis of these bonded phases in oxygen-free argon confirmed their stability⁸ up to *ca.* 300°. Heating above *ca.* 200° in argon containing 10% oxygen caused a rapid oxidation of the bound molecules, especially of the ODS chains.

Total carbon analyses were performed by the TNO Institute for Organic Chemistry, Utrecht. The results are given in Table I, together with the surface concentrations ($\mu\text{mole}/\text{m}^2$) of the bound species.

Chemicals

TMCS and HMDS were obtained from Fluka (Buchs, Switzerland) and octadecyltrichlorosilane from Aldrich (Milwaukee, Wisc., U.S.A.). The other chemicals were supplied by Fluka, J. T. Baker (Phillipsburg, N.J., U.S.A.) or BDH (Poole, Great Britain) and were of the highest purity available. All of the chemicals were used as received, except THF which was dried and distilled before use.

Apparatus and measuring technique

The apparatus employed was manufactured by Packard-Becker, Delft, The Netherlands. The column temperature was regulated at 160° with an air thermostat and measured with an Anschütz thermometer to 0.1°. Oxygen-free helium was used as carrier gas. The retention volumes were corrected for gas hold-up, the difference between room and column temperature, the compressibility of the carrier gas and the water vapour in the (calibrated) soap-film flow meter. The eluted substances were detected by a flame ionization detector and recorded by a Servogor recorder.

The samples, injected directly on to the column packing, were as small as possible (down to microlitres of vapour). Symmetrical peaks (skew ratio, $\eta = 0.8$ –1) were obtained, except for benzonitrile ($\eta = 0.5$), nitrohexane and benzaldehyde ($\eta = 0.4$). Since the net retention data are based on the position of the peak maximum, the data for these very polar solutes are slightly less accurate than those of the other solutes (duplicate runs gave a precision of 2%). The net retention volumes, measured at a carrier gas flow-rate of *ca.* 10 ml/min, are independent of the flow-rate (examined range: 5–10 ml/min).

RESULTS AND DISCUSSION

General characterization of the bonded phase sorbents

Surface concentrations of the bonded phase monomers are given in Table I. The coverage by TMS groups ($5.5 \mu\text{moles}/\text{m}^2$) appears to be complete since the effective area occupied by a TMS group on the silica corresponds to the maximum radius of the TMS group (*ca.* 2.9 Å). If it is assumed that the Porasil surface is covered with *ca.* 8 μmoles of silanol groups per m^2 (ref. 9), 2.5 $\mu\text{moles}/\text{m}^2$ of unchanged

silanol groups are left. The activity of these silanol groups will be reduced because of steric shielding by adjacent TMS groups.

The surface concentration of ODS groups is only $3.1 \mu\text{moles/m}^2$ owing to the mutual hindrance of these bulky reagent molecules. The surface concentration is slightly higher than that reported by Hemetsberger *et al.*¹⁰ ($2.68 \mu\text{moles/m}^2$)*. If the ODS coverage is complete, the effective occupation area of an ODS chain is *ca.* 48 \AA^2 .

An important question is whether the ODS molecules react with one or with two silanol groups. Bohemen *et al.*¹¹ have suggested that dimethyldichlorosilane can react simultaneously with two geminal (or bound) silanol groups. However, Gilpin and Burke¹² showed that only one chloro group reacts with the silica, whereas a part of the bound DMCS monomers dimerizes subsequently by the action of trace amounts of water. This dimerization requires a short distance between the monomers on the silica surface and can be ruled out for bulkier silanes. It can be estimated from data of Unger and Gallei⁹ that *ca.* 88% phenyltrichlorosilane molecules react simultaneously with two silanol groups. However, even if 100% of the ODS molecules react with two silanol groups, $4.9 \mu\text{moles/m}^2$ of more or less shielded free silanol groups are left.

TMCS treatment of the ODS packing material reduces this surface concentration of silanol groups by *ca.* $1.4 \mu\text{moles/m}^2$. Hence the C18/1 adsorbent contains slightly more free silanol groups than the C1 adsorbent. Since the silylation procedure applied was the same for both materials and achieved optimal deactivation, it was concluded that both TMS layers have about the same activity and that a part of the free silanol groups on the C18/1 material is completely shielded. Hence, eqn. 5 may be regarded as a useful approximation.

Separation of the effects of adsorption-like partition and adsorption

In columns 4–6 of Table II experimental V_N/W data on the three chromatographic columns are given for a series of monosubstituted hexanes, benzenes and a few other substances. From these data (V_N/W)_{18/1}^{part.} and (V_N/W)₁₈^{ads.} values are calculated using eqns. 5 and 6. The contribution of "partition" (column 8) appears to be substantial, compared to that of adsorption at the TMS layer (column 4) and at the bare silica beneath the ODS bristles (column 7) (except for the polar solutes, as expected). Since the ODS chain length is only 22 \AA and the mean mutual distance of the bristles is *ca.* 8 \AA , the sorption process to the single ODS chains can be characterized best as adsorption-like partition. From the nearly constant increase of the $\ln(V_N/W)$ _{18/1}^{part.} data (relative values are given in Table II, column 9) with the number of carbon atoms of *n*-alkanes, it can be concluded that, at least up to *n*-nonane, all of the methylene groups adsorb equally well to the ODS chain. This contribution of a methylene group, in *n*-alkanes and *n*-alkylbenzenes, is given in Table III, together with the corresponding data for a conventional stationary phase. The latter data were calculated from data on Apiezon M, a nearly apolar hydrocarbon polymer¹⁴ (Table II, column 10). The similarity of the data on both phases is striking and points to a strong interaction of the solutes with the ODS chains, notwithstanding the loose structure of the ODS layer. However, it follows from a comparison of columns 9 and 10 of Table II that the ODS chains and Apiezon M behave differently towards

* See footnote to Table I.

TABLE II

LITERATURE DATA ON A_x AND S^0 , EXPERIMENTAL DATA ON V_N/W FOR TMS SILICA, ODS SILICA AND TMS-TREATED ODS SILICA AND LITERATURE DATA ON $\ln(V_N/W)$ FOR APIEZON M AT 160°, AND CALCULATED CONTRIBUTIONS OF ADSORPTION AT THE SILICA SURFACE AND TO THE ODS CHAINS OF ODS SILICA

Solutes are monosubstituted hexanes and benzenes and a few other compounds.

Substances or substituents	A_x^*	S^{0**}	$(V_N/W)_1$	$(V_N/W)_{18}$	$(V_N/W)_{18/1}$	$(V_N/W)_{18}^{nd.s.}$	$(V_N/W)_{18/1}^{part.}$	$\Delta \ln(V_N/W)_{18/1}^{part.}$	$\Delta \ln(V_N/W)_{AP}^{s.}$
<i>n</i> -Pentane	5.9	0	0.300	1.006	0.925	0.381	0.625	-0.599	—
Hexanal	7.2	4.97	3.380	23.06	5.35	21.09	1.97	0.551	—
Hexanes									
H	6.8	0	0.433	1.723	1.571	0.585	1.138	0.000	0.000
CH ₃	7.7	0	0.663	2.891	2.599	0.955	1.936	0.531	0.556
C ₂ H ₅	8.6	0	0.921	4.878	4.236	1.563	3.315	1.069	1.120
C ₃ H ₇	9.5	0	1.333	8.05	6.80	2.581	5.47	1.570	1.664 ^{§§}
Cl	7.6	1.74	0.953	7.19	4.299	3.844	3.346	1.078	1.500
Br	7.9	1.94	1.231	11.00	6.23	6.00	5.00	1.480	2.003
CHO	8.1	4.97	4.343	41.08	8.86	36.56	4.52	1.379	—
NO ₂	8.4	5.71	4.620	57.79	8.14	54.27	3.52	1.130	2.315
Dipropyl ether	7.3	3.61	0.823	12.15	2.197	10.78	1.37	0.188	—
Benzenes									
H	6.0	1.50	0.457	1.755	1.667	0.545	1.210	0.061	0.544 ^{§§}
CH ₃	6.8	1.61	0.680	3.172	2.850	1.002	2.170	0.645	1.227
C ₂ H ₅	7.7	1.62	0.947	5.77	4.476	2.244	3.529	1.132	1.716
C ₃ H ₇	8.6	1.63	1.325	9.01	6.88	3.45	5.56	1.586	—
F	6.4	1.35	0.483	2.979	1.633	1.829	1.150	0.010	0.461
Cl	6.7	1.30	0.840	7.41	3.864	4.383	3.024	0.977	1.692
Br	7.0	1.33	1.093	11.99	5.78	7.31	4.68	1.415	2.245
OCH ₃	7.1	3.33	1.316	25.10	5.05	21.37	3.73	1.188	—
CN	6.6	4.85	3.170	61.1	7.32	56.98	4.15	1.294	2.108
CHO	7.1	4.93	6.44	69.4	10.50	65.32	4.06	1.271	2.135

* Calculated values given by Snyder⁴.

** Experimental data given by Snyder⁴ for narrow pore silica.

*** Relative to *n*-hexane.

§ Relative to *n*-hexane, $\Delta \ln(V_N/W)_{AP} = \Delta \ln(V_N^0/RT)$, where $\Delta \ln^0$ is the standard chemical potential of vaporization of the solute from an infinitely dilute solution in Apiezon M at 160°¹³.

§§ Experimental value used in ref. 14.

TABLE III

CONTRIBUTION OF METHYLENE GROUPS TO $\ln(V_N/W)$ FOR INTERACTION WITH CHEMICALLY BONDED ODS CHAINS AND WITH APIEZON M AT 160°

Parent compound	$\Delta \ln(V_N/W)$	
	ODS silica	Apiezon M
Hexane	0.54	0.55
Benzene	0.54	0.59

polar substituents and towards the hexyl and the phenyl moiety. This may be due to the Apiezon's content of aromatic material. These results suggest that the contributions from adsorption to the bare silica (or TMS silica) and from adsorption-like partition to the ODS chains are independent, as expressed in the eqns. 1 and 4-6. Hence, it is expected that the $\log(V_N/W)_{18}^{ads}$ values can be described by eqn. 11.

Application of Snyder's theory to the $\log(V_N/W)_{18}^{ads}$ values

The parameters $\log V_a + C$, α and β in eqn. 11 for the substituted hexanes and benzenes are given in Table IV. The results, obtained from multiple regression analysis, are within error in accord with those obtained from the alternative graphical procedure outlined in the Theoretical section. The $\log V_a + C$ and the β values obtained from $\log(V_N/W)_1$ and $\log(V_N/W)_{18}^{ads}$ data are about equal and within error independent of the solute type. Apparently, the apolar non-specific interaction contributions are not significantly affected by the TMCS treatment, *i.e.*, they are almost independent of the polarity of the adsorbent. The activity α , however, depends on the polarity of the adsorbent (as expected) and on the solute type. This dependence of α on the solute type is not expected from Snyder's adsorption model, applied to the adsorption on bare adsorbents (see Theoretical section). Therefore, it must be ascribed to the influence of the ODS chains on the polar adsorption contribution. Probably, the ODS chains are able to bend back to the adsorbent surface underneath and to form a network which hampers the adsorption on the silica or TMS silica surface. This sieve is apparently more effective towards the rod-like hexanes than towards the more compact benzenes. As a result of the mechanical restriction exerted

TABLE IV

VALUES OF THE PARAMETERS IN EQN. 11 FOR THE C1, C18 AND C18/1 PACKINGS AND THE STANDARD ERROR OF THE FIT (s)

Parameters	$(V_N/W)_1$	$(V_N/W)_{18}^{ads}$	$(V_N/W)_{18}$	$(V_N/W)_{18/1}$
<i>Hexanes</i>				
$\log V_a + C$	-1.60 ± 0.18	-1.61 ± 0.36	-1.31 ± 0.24	-1.17 ± 0.36
β	0.18 ± 0.03	0.21 ± 0.04	0.23 ± 0.03	0.21 ± 0.04
α	0.14 ± 0.01	0.29 ± 0.02	0.20 ± 0.01	0.08 ± 0.02
s	0.05	0.09	0.06	0.09
<i>Benzenes</i>				
$\log V_a + C$	-1.55 ± 0.45	-1.46 ± 1.21	-1.14 ± 0.81	-1.22 ± 0.46
β	0.16 ± 0.06	0.17 ± 0.17	0.19 ± 0.11	0.22 ± 0.06
α	0.22 ± 0.03	0.43 ± 0.08	0.33 ± 0.06	0.12 ± 0.03
s	0.13	0.36	0.24	0.14

by the ODS layer, the adsorption-like partition at the ODS bristles and the adsorption to the adsorbent surface underneath are mutually dependent. Hence, eqns. 1 and 4–6 cannot be applied unless S^0 is zero (*i.e.*, for apolar solutes). Obviously, the ODS chains should be considered as apolar adsorption sites of the ODS silica which are able to deactivate the adsorbent sterically to an amount which depends on the molecular shape of the solute molecules.

Therefore, we also applied eqn. 11 straightforwardly to the $\log (V_N/W)_{18}$ and $\log (V_N/W)_{18/1}$ data. In doing so, the interaction of the solutes with the ODS chains is considered as adsorption to apolar adsorption sites of the ODS silica. The results of this procedure are given in columns 4 and 5 of Table IV. It follows from the values of s that the fit of this straightforward procedure is good. We observe an increase of the apolar non-specific interaction parameter β compared to TMS silica, as expected. Again it is found that the α values for the substituted benzenes are larger than those for the hexanes. The activity α of the ODS–TMS silica is even smaller than that of the TMS silica, although the number of free silanol groups on the former is larger.

The $\log (V_N/W)$ data of hexanal and *n*-dipropyl ether were excluded from the regression analysis in order to examine the effect of the alkyl chain length and of the position of the polar group in the solute molecule. The $\log (V_N/W)$ data of hexanal can be calculated with the parameters for the substituted hexanes (mean deviation 0.06). The same holds for dipropyl ether, except on the C1 and the C18/1 adsorbents where the experimental data are 0.31 smaller than those calculated. Obviously, the propyl groups hinder adsorption of the ether group to the TMS layer. This finding is consistent with the striking discrepancy between the α values of the hexanes and benzenes on the investigated adsorbents.

CONCLUSIONS

The contribution of the interaction of the solutes with the ODS chains is substantial, but it can only be estimated quantitatively for apolar solutes.

Snyder's equation for adsorption chromatography gives a good description of the retention data on the investigated chemically modified adsorbents. The ODS chains sterically hinder the adsorption of solutes at the polar adsorbent surface underneath. This shielding effect appears to be most pronounced for the rod-like substituted hexanes. As a consequence, the adsorbent activity α in Snyder's equation is smaller for substituted hexanes than for benzenes.

GLOSSARY

A	specific area of the adsorbent
A_x, A_e	adsorbed area of a solute (x) or eluent (e) molecule relative to that of benzene ($A_x = 51 \text{ \AA}^2 \sim 6$ units)
C_i	parameter which accounts for the loss of degrees of freedom of the solute on adsorption to an adsorbent (i) from the perfect vapour phase
$\Delta \bar{F}^0$	standard partial molar free energy of adsorption from infinitely dilute solution (vapour)
$\Delta \bar{F}$	$\equiv \Delta \bar{F}^0 / 2.3 RT$

$\bar{F}_x, \bar{F}_e, \bar{F}_{x,e}$	standard partial molar free energy of the solute (\bar{F}_x) or the eluent (\bar{F}_e) in the adsorbed state, and of the solute in the eluent ($\bar{F}_{x,e}$)
K	partition coefficient
K_a	adsorption coefficient (cm)
K_a^0	adsorption coefficient (0)
S^0, S_d^0	contribution of specific interaction forces (S^0) and of dispersive interaction forces (S_d^0) to \bar{F} on adsorption at a standard adsorbent (equal to \bar{F} and \bar{F}_d , respectively)
V_a	volume of adsorbed mobile phase per gram adsorbent
V_L	volume of bonded (stationary) phase per gram adsorbent
V_N	net retention volume
$(V_N/W)_{18/1}^{\text{part.}}$	$\equiv (V_N/W)_{18/1} - (V_N/W)_1$
$(V_N/W)_{18}^{\text{ads.}}$	$\equiv (V_N/W)_{18} - (V_N/W)_{18/1}^{\text{part.}}$
W	weight of the adsorbent (GSC column); weight of conventional stationary phase (GLC column)
m	$\equiv A_x/A_e$, number of desorbed eluent molecules per adsorbed solute molecule
α	specific (polar) adsorbent activity
α_d	non-specific (dispersive) adsorbent activity
β	$\equiv \alpha_d S_d^0/A_x$, contribution of dispersive interaction forces to $\Delta\bar{F}$ per unit of (adsorbed) molecular area
$\varepsilon^0, \varepsilon_d^0$	eluent strength parameter arising from specific (polar) and from non-specific (dispersive) eluent-adsorbent interaction forces, respectively
η	skew ratio, <i>i.e.</i> , the ratio of the slopes of the rear (trailing) and the front (leading) boundary of the peak at the points of inflection
$\Delta\mu^0$	standard chemical potential of vaporization of the solute from an infinitely dilute solution to the perfect vapour phase

ACKNOWLEDGEMENTS

The authors are indebted to Mr. P. A. Elbertse and Dr. L. A. M. Hermans for their accurate BET measurements, and to Mr. A. Broersma for his TGA and DTA analyses of the bonded phases.

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