STRUCTURE AND PROPERTIES OF n-ALKYLDIMETHYLSILYL BONDED SILICA REVERSED-PHASE PACKINGS

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SUMMARY

The effects of the modifier functionality and the chain length of n-alkylchlorosilanes on the surface structure of packings and on their retention behaviour in reversed-phase chromatography were investigated.

Comparative retention studies on three silica packings that had been treated to maximum conversion with n-octyltrichlorosilane (I), n-octylmethyldichlorosilane (II) and n-octyldimethylmonochlorosilane (III) showed that the most pronounced reversed-phase character is obtained by using III as the modifying reagent. A series of n-alkyldimethylsilyl bonded silica packings were prepared with widely differing n-alkyl chain lengths. Although the packings are very hydrophobic, the maximum surface concentration is 2–4 μmole/m^2 and a high population of hydroxyl groups (ca. 3–4 μmole/m^2) can still be detected by the isotopic exchange method.

The retention characteristics of hydrocarbons in methanol–water as the eluent were measured on these packings. The variation of the capacity factors of solutes could be well correlated with the following molecular quantities that characterize the solute and the type of bonded group: the total hydrocarbonaceous surface area of the bonded n-alkyldimethylsilyl group, the total hydrocarbonaceous surface area of the solute and the molecular dipole moment of the solute.

INTRODUCTION

Although reversed–phase materials are now the most popular packings in high-performance liquid chromatography (HPLC) and are widely used in routine analysis, there is no general agreement about the choice of an appropriate silanized support, particularly in terms of its chain length, for a given separation problem. The reasons for this situation are firstly that it is possible to apply a variety of reagents and procedures in surface silanization, which consequently results in different surface structures and hence leads to differences in the retention behaviour of reversed-phase packings, and secondly that the retention mechanism itself is still not well understood[1].

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Depending on the functionality (mono-, di- or tri-) of a particular silanizing reagent and on the water contents of the surface and the reactant, widely differing surface structures are produced, ranging from a bonded monolayer to polymerized layers with a considerable thickness. It is obvious that the type of surface layer and its structure significantly affect the kinetic properties and the stability of the packing.

An important variable in surface modification is the chain length of the n-alkylchlorosilane used as modifier. The shortest alkyl chain is produced by reaction with methylchlorosilane and long chains by reaction with n-octadecylchlorosilane[2–4]. With longer chains, the organic content per unit mass of packing increases, which results in larger capacity factors[4,5]. On the other hand, longer n-alkyl chains need more pore space than shorter chains so that the pore size of the support has to be carefully adjusted to the size of the modifier[1,6,7].

In the formation of a monolayer, depending on the reaction conditions the coverage may vary from zero to complete. However, even with a dense monolayer that is assumed to represent the maximum conversion some hydroxyl groups remain unreacted at the surface of the packing[2,5,8]. Although the role of these hydroxyl groups in the reversed-phase mechanism is not yet clear, it has been shown that they contribute to the retention of the solutes.

From the above discussion it is evident that studies of the retention behaviour of solutes in reversed-phase chromatography will provide information on the preparation procedure and the surface structure of packings.

The purpose of this work was to characterize the properties of a series of reversed-phase silica packings that differ in the type of n-alkyl group bonded. In order to study the effect of the modifier functionality on the surface structure and chromatographic properties, a set of packings was prepared by reaction of silica with n-octylchlorosilane homologues. A second set of samples were synthesized by reaction of silica with n-alkyldimethylchlorosilanes with widely differing chain lengths in order to study the influence of chain length. The capacity factors of a large number of hydrocarbon solutes were measured on the n-alkyldimethylsilyl bonded packings at a constant eluent composition. An attempt has been made to correlate the surface structure parameters of the packing with the retention characteristics of solutes.

EXPERIMENTAL

Silanization and characterization of the support

A batch of spherical silica prepared according to a procedure of Unger et al.[9] and with a narrow size range effected by means of the elutriation technique was used as support for silanization. The packing properties were as follows: mean particle diameter $(d_p) = 10 \ \mu m$; specific surface area $(S_{BET}) = 376 \ m^2/g$; and mean pore radius $(r_{max.}) = 6.7 \ nm$, where $r_{max.}$ corresponds to the maximum value of the relative pore volume distribution calculated from the nitrogen desorption isotherm using the method of Pierce[10].

n-Octyltrichlorosilane, n-octyldimethylchlorosilane, dimethyldichlorosilane and trimethylchlorosilane were purchased from Wacker Chemie (Burghausen, G.F.R.). All n-alkyldimethylchlorosilanes were prepared by a Grignard reaction using dimethyldichlorosilane and the corresponding n-alkyl bromide. The final products were distilled under vacuum and stored in closed glass ampoules.

The surface modification was carried out according to a procedure described previously[6]. The reaction temperature in all modifications was maintained at 473° K. The surface concentration of bonded n-alkyl groups ($\alpha_{n\text{-alkyl}}$ μmole/m^2) was estimated from the carbon content of the modified packing, the molar weight of bonded carbon atoms and the specific surface area (S_{BET}) of the starting silica, the last value being corrected for the weight increase resulting from the surface modification[6]. The concentration of hydroxyl groups (α_{OH}) of the initial silica support and the modified derivatives was measured using the heterogeneous isotopic exchange method with tritium-labelled water (HTO)[11]. The support samples were de-gassed at 473° K for 8 h under vacuum ($p \leqslant 1 \cdot 10^{-4}$ Torr) before and after the exchange.

Packing procedure

The supports were packed in 25 cm × 4.3 mm I.D. stainless-steel tubes (Type 304, Nennen Chemicals, Dreieichenhain, G.F.R.) by means of the slurry technique under the following conditions: slurry liquid, tetrachloromethane (reagent grade, E. Merck, Darmstadt, G.F.R.); slurry concentration, 10% (w/w); packing pressure, 350 bar; second immiscible liquid, n-heptane (reagent grade, Merck).

Equipment

The chromatograph used was a DuPont Model 830 instrument with a DuPont UV photometer of wavelength 254 nm and an 8-μl cell volume. The columns were terminated by porous stainless-steel frits of pore size <2 μm and thickness 1 mm (Type PSSH, Pall, Sprendlingen, G.F.R.). The column fittings were 1/4-in. Swagelok components. Connections were made with a capillary tube of I.D. 0.1 mm.

Solutes were introduced by septum injection using a Hamilton HP 305 syringe (G. Schmidt, Hamburg, G.F.R.). The injection volume was 5 μl. The columns were operated (i) at 293° K with dry n-heptane (reagent grade, Merck) in order to control the residual polarity of reversed-phase packings and (ii) at 323° K with methanol–water (65:35, v/v) as eluent. All samples used as solutes were of reagent grade (Merck).

Calculations

In measuring the capacity factors of solutes, tetrachloromethane was used as a t_0 marker in the non-polar eluent and methanol in the polar eluent.

RESULTS AND DISCUSSION

Characterization of surface-silanized packings

As reversed-phase chromatography is especially useful for the separation of polar molecules in aqueous and polar eluents, the main objective in the preparation of reversed-phase packings should be to produce an essentially hydrophobic surface with a high degree of uniformity. From this point of view a dense monolayer of bonded n-alkyl groups should fit these requirements better than a deposited polymer layer or a monolayer exhibiting a partial coverage, for the following reasons:

(i) A polymer layer consisting of branched n-alkylsiloxanes and prepared, for instance, by hydrolysis of trifunctional n-alkylchlorosilanes in the presence of water

cannot be built up with a high degree of uniformity in crosslinking and thickness because the growth of a polymer network in a porous system is sterically hindered to a large extent.

(ii) When tri- or bifunctional n-alkylchlorosilanes are employed as a modifier and water is carefully excluded from the reaction, a high population of hydroxyl groups is still formed after reaction by hydrolysis of unreacted Si–Cl groups. Because of the polar nature of hydroxyl groups, the hydrophobic character of the surface of a modified packing will be drastically reduced.

(iii) A similar type of surface will be obtained by applying conditions in the reaction between silica and a monofunctional n-alkylchlorosilane that result in partial coverage of the surface. In addition to the decrease in hydrophobicity, the residual hydroxyl groups cause an additional complication: the chemical stability of such partially covered reversed-phase packings towards aqueous solutions, particularly at pH > 7, is lowered owing to the solubility of the silica.

With respect to an essential hydrophobic surface, the question arises of whether it is really possible to achieve a closely packed monolayer of bonded n-alkyl groups. The preliminary conditions to produce this type of surface structure are as follows:

(i) use a fully hydroxylated silica with the highest population of hydroxyl groups as possible ($\alpha_{OH} = 8$–9 μmole/m^2) and free of physisorbed water[1];

(ii) employ a monofunctional modifier that permits the simplest stoichiometry with the hydroxyl groups present;

(iii) choose drastic reaction conditions in order to achieve the maximal conversion that is finally determined by the area and volume requirements of the modifier molecule.

There is a limitation in the realization of these conditions because the average cross-sectional area of one hydroxyl group, $A_m(OH)$, is about 0.2 nm^2 while the A_m value of the smallest modifier molecule (trimethylchlorosilane) is about 0.4 nm^2. Thus, the maximal surface concentration of trimethylsilyl groups is expected to be about 4 μmole/m^2 owing to their area requirement. In fact, it is found that the maximal conversion corresponds to this predicted value and 50% of the initial hydroxyl groups remain unreacted as they are shielded by trimethylsilyl groups[12]. This shielding cannot be expected to be complete so that a fraction of hydroxyl groups will still be accessible for solute–adsorbent interactions. The accessibility, however, will be a function of the size and shape of the solute molecules.

Some of the statements made previously will be proved by the experimental results presented here. The first is the influence of the functionality of the modifier on the surface structure. This problem was discussed generally in an earlier paper[6] on the basis of a stoichiometric factor (F), which corresponds to the molar ratio of hydroxyl groups reacted to modifier reacted. In reversed-phase chromatography, it can be exemplified by using the three homologues n-octyltrichlorosilane, n-octylmethyldichlorosilane and n-octyldimethylchlorosilane as modifier. The maximal conversions of the modified products, which are designated as OTCS-, OMDCS- and ODMCS-silica, respectively, are given in Table I. It can be seen that the $\alpha_{n\text{-alkyl}}$ values of the three products are of the same order of magnitude, which would be expected because the replacement of a chloro group by a methyl group does not significantly change the corresponding A_m value. Table I also gives the corresponding α_{OH} values measured for the modified products by means of the isotopic exchange method with tritium-

labelled water (HTO)[11]. In contrast to $\alpha_{n\text{-alkyl}}$, the α_{OH} values decrease rapidly in the sequence OTCS-silica > OMDCS-silica > ODMCS-silica. ODMCS is able to react only with a simple 1:1 stoichiometry ($F = 1$), leaving a population of 3.73 μmole/m^2 of hydroxyl groups unreacted. The higher α_{OH} value for the OMDCS-silica indicates that $1 < F < 2$ and the hydrolysis of some unreacted Si–Cl groups causes a further increase in α_{OH}. The highest hydroxyl group concentration is obtained for OTCS-silica, being four times higher than that of n-alkyl groups. These results indicate that again $1 < F < 2$ and the unreacted Si–Cl groups make a considerable contribution to α_{OH}.

TABLE I

PROPERTIES OF SILANIZED SUPPORTS

Type of modifier	Designation of product	C (%)	Surface concentration (μmole/m^2)		Total hydrocarbonaceous surface area of n-alkyldimethylsilyl group (nm^2 per group)
			$\alpha_{n\text{-alkyl}}$	α_{OH}	
n-Octyltrichlorosilane	OTCS-silica	7.36	2.35	11.70	—
n-Octylmethyldichloro-silane	OMDCS-silica	8.43	2.40	6.74	—
n-Octyldimethylchloro-silane	ODMCS-silica	9.24	2.35	3.73	—
Trimethylchlorosilane	TMCS-silica	4.18	3.37	2.98	1.29
n-Butyldimethylchloro-silane	BDMCS-silica	7.13	2.97	3.68	1.96
n-Octyldimethylchloro-silane	ODMCS-silica	10.43	2.71	3.73	2.86
n-Dodecyldimethylchloro-silane	DDMCS-silica	11.73	2.20	3.81	3.76
n-Hexadecyldimethyl-chlorosilane	HDMCS-silica	15.67	2.36	4.24	4.65
	Original silica	—	—	7.63	—

The influence of residual hydroxyl groups on the chromatographic behaviour of the packings in non-polar and polar eluents with selected solutes was examined. As shown in Table II, in dry n-heptane as eluent ODMCS-silica gave the smallest capacity factor (k') for benzo[a]pyrene. The capacity factors of acetone, methanol and diethyl ether were ca. 0.1 on all columns. In the polar eluent, OTCS-silica gave the smallest capacity factor of all three of the packings investigated, which reflects its high hydroxyl group concentration. From these results it can be concluded that the n-octyldimethylsilyl bonded reversed-phase packing is more hydrophobic than the other two derivatives obtained by reaction with tri- and bifunctional n-octylchlorosilanes. Also, the measurement of surface polarity in a non-polar eluent provides a useful and easy means of monitoring the hydrophobicity of reversed-phase packings, but hydroxyl groups are still present on the modified surface, as detected by the isotopic exchange method.

TABLE II

CAPACITY FACTORS (k') OF SOLUTES ON DIFFERENT n-OCTYLSILYL BONDED
SILICA PACKINGS IN TWO TYPES OF ELUENTS

Eluent	Solute	OTCS-silica	OMDCS-silica	ODMCS-silica
Dry n-heptane	Acetone	~0.1	~0.1	~0.1
	Benzo[a]pyrene	0.33	0.1	0.03
Methanol–water (70:30, v/v)	Anthracene	0.41	0.63	1.07

In addition to functionality, an important variable in the optimization of reversed-phase packings is the chain length of the n-alkyl groups. Commercial packings mostly provide methyl-, n-octyl- and n-octadecyl bonded groups[1]. In this study, five n-alkyldimethylsilyl bonded packings were prepared that covered this range (Table I).

Again, reaction conditions were chosen so as to achieve the maximal conversion. Although the chain length spans a wide range, the $\alpha_{n\text{-alkyl}}$ values vary between about 2 and 4 μmole/m^2 for all samples (Table I), which is in agreement with the findings of other workers[2,13]. It is also evident from Table I that the $\alpha_{n\text{-alkyl}}$ values decrease as the n-alkyl chain length increases, which is caused by the increasing molecular cross-sectional area of the modifier. In agreement with this result, the α_{OH} value increase on going from short-chain to long-chain silica. The sum of $\alpha_{n\text{-alkyl}} + \alpha_{OH}$ is nearly constant for all packings, supporting a 1:1 stoichiometry of the reaction. From the $\alpha_{n\text{-alkyl}}$ values, average molecular cross-sectional areas (A_m) of the silyl groups can be calculated to be trimethylsilyl 0.49, n-butyldimethylsilyl 0.56, n-octyldimethylsilyl 0.61, n-dodecyldimethylsilyl 0.76 and n-hexadecyldimethylsilyl 0.70 nm^2 per group.

The mean distance between two adjacent n-alkyl groups is then 0.80 nm for the trimethylsilyl groups and 0.94 nm for the n-hexadecylsilyl groups. This oversimplified pattern, as shown in Fig. 1, does not represent the real surface but is still useful as a model. The n-alkyl chains bonded at one end to the original silica surface via a siloxane bridge will have some freedom of rotational mobility, particularly when the chain is long. This behaviour will perhaps lead to an attachment of chains, which is favoured by dispersion attraction forces in the polar eluent.

The molecular cross-sectional area, however, is only one factor in the structural characteristics of packings. Another important feature is the volume requirement in the pore space of the support and the thickness of an n-alkyl group. It is apparent that with an increase in the chain length the fraction of the pore volume occupied by the bonded groups increases considerably. Again, it is difficult to make a clear distinction between the free pore space available and the space filled by the bonded layer because the bonded layer presents a relatively open spatial network that may be penetrated by solvent molecules and perhaps show swelling properties.

If we assume a cylindrical pore of length l and a radius r, the surface area before modification will be
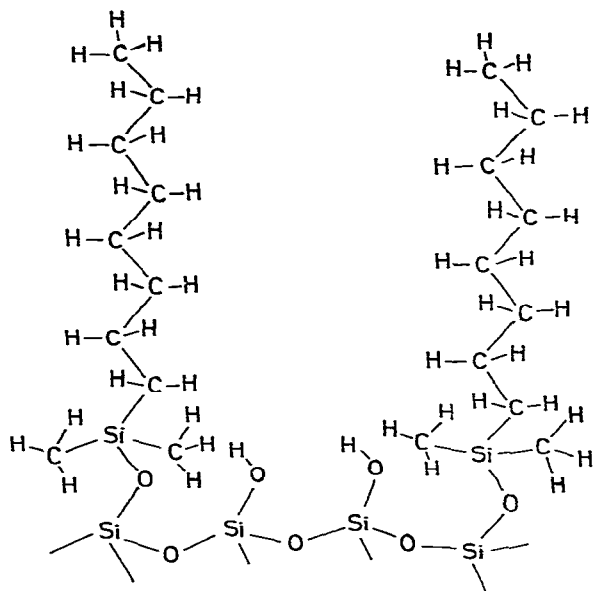
$$S = 2\pi r l \tag{1}$$

Fig. 1. Schematic diagram of the surface of an n-octyldimethylsilyl bonded silica packing.

and the volume will be

$$V = \pi r^2 l \tag{2}$$

After modification, the radius of the pore is decreased by the thickness (t) of the bonded layer. The surface of the modified pore can then be written as

$$S_{\text{mod}} = 2\pi(r-t)l \tag{3}$$

and the volume of the modified pore as

$$V_{\text{mod}} = \pi(r-t)^2 l \tag{4}$$

Combining eqns. 1 and 3, one obtains

$$\frac{S_{\text{mod}}}{S} = \frac{2\pi(r-t)\,l}{2\pi r\,l} = \frac{r-t}{r} \tag{5}$$

Similarly, eqns. 2 and 4 give

$$\frac{V_{\text{mod}}}{V} = \frac{\pi(r-t)^2\,l}{\pi r^2\,l} = \frac{(r-t)^2}{r^2} \tag{6}$$

In order to prove the validity of this model, one has to use measurable quantities for S and V, which are the specific surface area according to the B.E.T. method (S_{BET}) and the specific pore volume according to the Gurvitsch rule (V_p)[10]. These quantities are

TABLE III

VARIATION OF PORE STRUCTURE PARAMETERS BY MEANS OF SURFACE MODIFICATION

S_{BET} = specific surface area according to the B.E.T. method[10]; V_p = specific pore volume according to the Gurvitsch rule[10]; t = thickness of the bonded layer; $r_{max.}$ = most frequent pore radius of the relative pore volume distribution[10].

Designation of product	S_{BET} (m^2/g)	V_p (ml/g)	t (nm)	$\dfrac{S_{BET(mod)}}{S_{BET}}$	$\dfrac{r_{max.} - t}{r_{max.}}$	$\dfrac{r'_{max.}}{r_{max.}}$	$\dfrac{V_{p(mod)}}{V_p}$	$\left(\dfrac{r_{max.} - t}{r_{max.}}\right)^2$	$\left(\dfrac{r'_{max.}}{r_{max.}}\right)^2$
Original silica	376	1.258	—	—	—	—	—	—	—
TMCS-silica	205	1.168	0.299	0.55	0.95	—	0.93	0.90	—
BDMCS-silica	277	1.034	0.689	0.74	0.89	—	0.82	0.79	—
ODMCS-silica	252	0.910	1.197	0.67	0.82	0.82	0.72	0.67	0.67
DDMCS-silica	244	0.883	1.729	0.65	0.74	0.72	0.70	0.54	0.52
HDMCS-silica	205	0.784	2.261	0.55	0.67	0.70	0.62	0.45	0.49

listed in Table III for the modified silica and the original silica; the ratios $S_{BET(mod)}/S_{BET}$ and $V_{p(mod)}/V_p$ are also given. The pore radius of the original silica, determined from the nitrogen desorption isotherm using the method of Pierce, is 6.7 nm. The ratios $r-t/r$ and $(r-t/r)^2$ were obtained in two different ways. In the first approach, the thickness of the bonded n-alkyl layer was estimated from molecular models of the chain using the corresponding Van der Waals radii (see column 4 in Table III). The ratios $r-t/r$ and $(r-t/r)^2$ were calculated using $r_{max.}$ = 6.7 nm and the corresponding t value. In the second approach $r-t$ was expressed by the effective $r'_{max.}$ of the given modified packing and r in the dominator again was taken to be 6.7 nm. The corresponding ratios are also listed in Table III. Comparison of these ratios as given in eqns. 5 and 6 shows a relatively poor agreement between $S_{BET(mod)}/S_{BET}$ and the radius ratio whereas $V_{p(mod)}/V_p$ to the radius ratio squared agree fairly well. Deviations are observed with the long-chain silicas.

On the basis of the results, one can draw the following conclusions about the surface structure of n-alkyldimethylsilyl bonded packings. The layer of bonded n-alkyl groups extends in thickness from 0.3 nm for the shortest chain (trimethylsilyl) to about 2.3 nm for the longest chain (n-hexadecyldimethylsilyl). The thickness of the longest chain then corresponds to about one third of the average pore radius ($r_{max.}$) of the original silica. Correspondingly, the n-hexadecyldimethylsilyl groups occupy a substantial fraction of the original pore space (about 40%). The bonded n-alkyl groups are separated by a distance of about 0.8 nm. They are relatively closely packed but space is still available between them. The dimethylsiloxane groups operate as anchor groups for the n-alkyl chains and also shield the remaining hydroxyl groups. The Si–O–Si–C link of these groups may also have an influence on the chemical stability of the packing. Owing to the heterogeneity of the surface, the Si–O–Si bond angle deviates considerably from a tetrahedral arrangement and hence the siloxane bond can be expected to be very sensitive to the attack of nucleophilic and electrophilic reagents.

Retention behaviour of n-alkyldimethylsilyl bonded packings

To explain the retention mechanism in reversed-phase chromatography, two hypotheses have been put forward. In the first approach, the bonded n-alkyl layer is considered to be a liquid exhibiting bulk properties and separation is discussed in

terms of the solubility of the solutes between two liquid phases[14]. The advantage of this approach is the possible estimation of distribution coefficients of solutes from static measurements and their prediction from thermodynamic properties. However, with the monolayer type of reversed-phase packings the layer is only a few molecules thick and the structure of the *n*-alkyl chains is very different from that of a liquid *n*-alkane. The second approach is based on the assumption that the retention is largely controlled by competitive adsorption between solutes molecules, solvent molecules and the non-polar adsorption sites of the *n*-alkyl chain, occurring at the interfacial layer. This treatment, however, also involves a simplification because the interaction by dispersion forces is governed mainly by kinetic effects due to the spatial orientation of the bonded groups within the pore system.

The approach in this work is more pragmatic and attempts to correlate the measured capacity factors with the surface structure parameters of reversed-phase packings and the molecular properties of solutes. The effect of the eluent composition, which also influences the retention, is not considered here.

The most easily measurable parameter of a reversed-phase packing is its carbon content, which is a measure of the mass of "stationary phase" bonded[5,15]. The carbon content is a quantity that controls the maximal surface concentration of a reversed-phase packing but it is insufficiently specific when comparing retention data on packings with various *n*-alkyl chain lengths.

An attempt to explain the solute interactions in reversed-phase chromatography comprehensively on the basis of molecular properties was made by Horváth *et al.*[16] using the solvophobic theory. In the underlying model of this theory, the interaction between the solute, S, and the hydrocarbonaceous ligand, L ($\equiv$ bonded *n*-alkyl group), is considered as a reversible association process:

$$S + L \rightleftharpoons SL \tag{7}$$

By a thermodynamic treatment, an equation was derived that expresses the dependence of the capacity factor on the solute and ligand properties at constant column dimensions, column temperature, eluent composition and flow-rate, as follows:

$$\ln k' = A' + B' \cdot \frac{1-\lambda}{2\lambda} \cdot \frac{\mu_S^2}{v_S} \cdot \frac{1}{\left(1 - \dfrac{\alpha_S}{v_S}\right)} + C' \Delta A \tag{8}$$

where A', B' and C' are constants, μ_S the molecular dipole moment of the solute, α_S the volume polarizibility of the solute, v_S the molecular volume of the solute, λ is a proportionality factor by which v_S is multiplied to give the molecular volume v_S of the complex composed of the ligand and the solute, and ΔA is the contact surface area of the associated species given by

$$A_{LS} = A_S + A_L - \Delta A \tag{9}$$

where A_S is the molecular surface area of the solute, A_L that of the ligand and A_{LS} that of the complex. The presentation of experimental data in terms of eqn. 8 is possible but rather difficult, particularly because the three terms on the right-hand side of

eqn. 8 are not independent. In order to simplify the treatment, we looked for the dependence of the capacity factor of a given solute on the following three molecular properties of the ligand and solute: the total hydrocarbonaceous surface area of the ligand (TSA_L, nm^2 per group), calculated according the method of Bondi[17], the total hydrocarbonaceous surface area of the solute (TSA_S, nm^2 per molecule)[17] and the molecular dipole moment of the solute (μ_S), taken from the literature[18].

For a graphical presentation, the logarithm of the capacity factor of a given solute normalized to unit surface area of the corresponding reversed-phase packing is plotted against TSA_L, TSA_S and μ_S. The normalization to unit surface is considered to be necessary because (i) the S_{BET} values of the packings are still relativily high and hence may substantially affect the retention of solutes, and (ii) the S_{BET} values of the packings are not constant but decrease with the chain length (see Table III). Contrary to this, it may be argued that S_{BET} is obtained from nitrogen sorption measurements at $77°$ K and these conditions are different from those applying to the surface of the packing, which exists at room temperature in solvent-filled pores. Nevertheless, this is only one approach.

As shown for a series of substituted benzenes as representative solutes, the plot of log k'/S_{BET} against TSA_L can be approximated fairly well by a straight line for BDMCS-, ODMCS-, DDMCS- and HDMCS-silica (Fig. 2). This indicates that the whole chain is accessible for solute–ligand interactions. Exceptional behaviour is
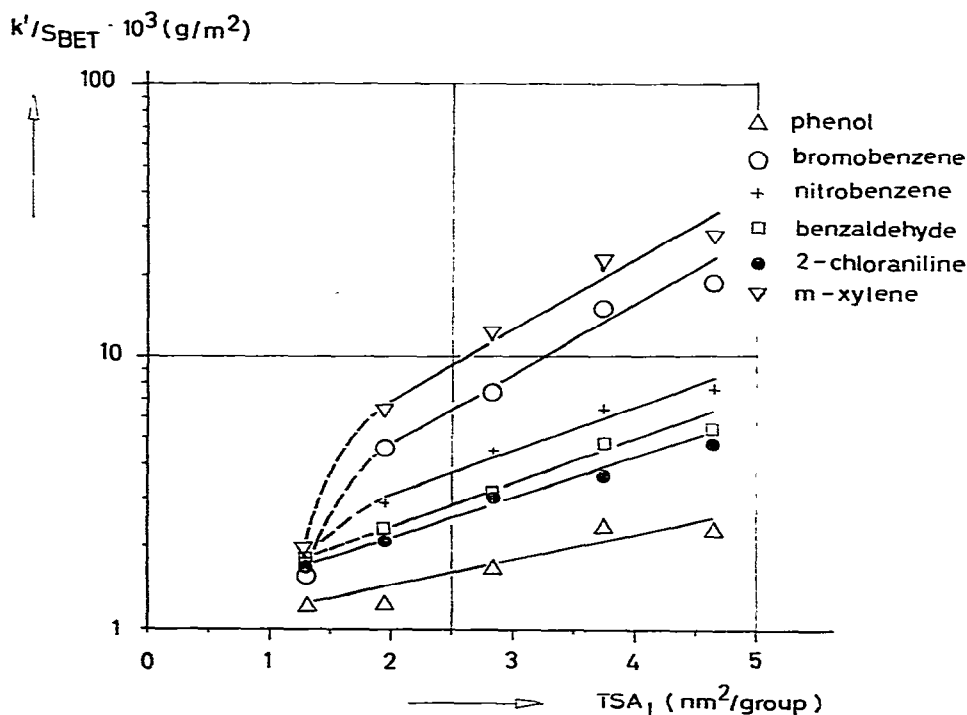

Fig. 2. Plot of k'/S_{BET} for selected solutes *versus* the TSA_L of the *n*-alkyldimethylsilyl group. Eluent, methanol–water (65:35, v/v); column temperature, $323°$ K. △, Phenol; ○, bromobenzene; +, nitrobenzene; □, benzaldehyde; ●, 2-chloraniline; ▽, *m*-xylene.

observed for TMCS-silica, which does not show this linear relationship. In a compara-
tive study of reversed-phase packings Knox and Pryde[3] also concluded that the elu-
tion behaviour of short-chain silica is different from that of long-chain silica. This
anomaly of TMCS-silica might be caused by its special surface structure: the bonded
TMCS layer extends in thickness only to about 0.3 nm from the original surface
boundary. Further, both the surface hydroxyl groups and the siloxane groups of the
silica matrix are in close vicinity to the trimethylsilyl groups. As a result, the force
field of the surface layer may be perturbed by the siloxane matrix.

Assuming that the total n-alkyl chain is accessible for interactions, the plot of
log k'/S_{BET} against TSA_S for selected solutes should also give a straight line for a
given packing. This is demonstrated in Fig. 3 for some homologous n-alkanols. The
parallel course of the three upper curves for BDMCS-, ODMCS- and HDMCS-
silica suggest a similar selectivity behaviour with respect to methylene groups. The
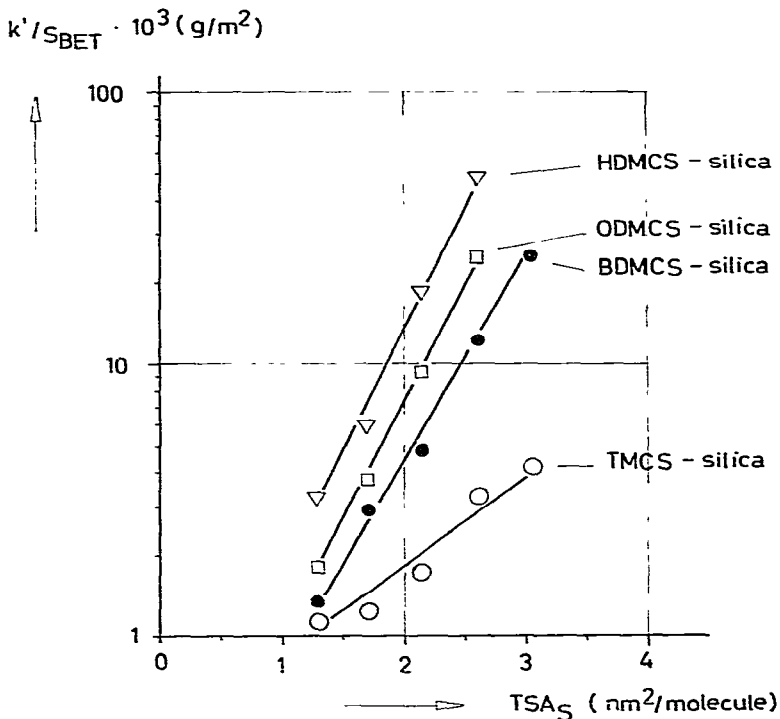TMCS silica again exhibits exceptional behaviour.

Fig. 3. Plot of k'/S_{BET} for n-alkanols (n-pentanol, n-hexanol, n-octanol, n-decanol and n-dodecanol)
versus their TSA_S values for four n-alkyl silicas. Eluent, methanol–water (65:35, v/v); column tem-
perature, 323° K. ▽, HDMCS-silica; □, ODMCS-silica; ●, BDMCS-silica; ○, TMCS-silica.

It is interesting to investigate the influence of the polarity of solute molecules
on their retention on the n-alkyl packings. For comparative purposes, two sets of
solutes were chosen that have a total hydrocarbonaceous surface area (TSA_S) of the
same order of magnitude but that differ considerably in their dipole moments (see

TABLE IV

CHARACTERISTIC MOLECULAR PARAMETERS OF TWO SETS OF SELECTED SOLUTES

Set	Solute	Total hydrocarbonaceous surface area, TSA_S (nm^2 per molecule)	Molecular dipole moment, μ_s (D)
I	Bromobenzene	1.31	1.52
	Chlorobenzene	1.18	1.57
	3-Chloroaniline	1.46	2.71
	Benzaldehyde	1.32	2.86
	4-Chloroaniline	1.46	3.04
II	n-Hexylamine	1.76	1.46
	1-Bromonaphthalene	1.63	1.48
	2-Bromonaphthalene	1.63	1.71
	1-Bromohexane	1.81	2.01
	Hexanone-2	1.73	2.64

Table IV). The deviation of the mean value of TSA_S is about $\pm 15\%$; the dipole moment varies between 1.4 and 3.0 Debye.

As an example, Fig. 4 shows the dependence of log k'/S_{BET} of solutes of set II on the dipole moment for four n-alkyl packings. For a given packing the normalized
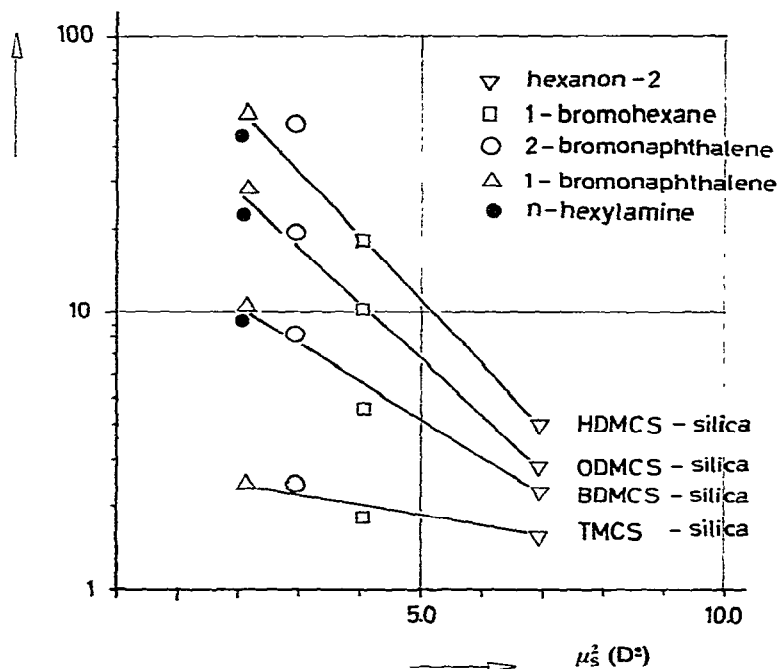

Fig. 4. Plot of k'/S_{BET} for selected solutes (see set II in Table IV) *versus* their molecular dipole moments squared, μ_s^2. Eluent, methanol–water (65:35, v/v); column temperature, 323 °K. △, Hexanone-2; □, 1-bromohexane; ○, 2-bromonaphthalene; △, 1-bromonaphthalene; ●, n-hexylamine.

capacity factor of solute decreases linearly with μ_s^2. The slopes of the straight line increase in the sequence HDMCS-silica > ODMCS-silica > BDMCS-silica > TMCS-silica. A similar dependence is obtained for solutes of set I (not shown here).

The main conclusions of this part of the work are as follows.

(i) Provided that there is a maximal surface concentration of bonded *n*-alkyldimethylsilyl groups, the normalized capacity factor of a solute increases linearly with the chain length of the bonded support expressed in terms of the total hydrocarbonaceous surface area (TSA_L). Exceptional behaviour is shown by TMCS-silica.

(ii) For homologous series of solutes, the normalized capacity factors increase linearly with the total hydrocarbonaceous surface area of the solute (TSA_S) for a given type of *n*-alkyl packing.

(iii) At nearly constant TSA_S the normalized capacity factors of selected solutes fall linearly with the square of the molecular dipole moment of solute, μ_S, at a given type of packing.

NOTE ADDED IN PROOF

Scott and Kucera[19] published a paper entitled "Examination of five commercially available liquid chromatographic reversed phases (including the nature of the solute–solvent–stationary phase interactions associated with them)". In order to compare their findings with our results one has firstly to state that the packings being examined in both studies are not identical. While Scott and Kucera employed commercial reversed-phase packings with bonded methyl-, *n*-octyl- and *n*-octadecyl groups, differing in the degree of derivatisation, we used home-made preparations of graduated *n*-alkyl chain length in which the bonded moiety covered the parent surface in a complete monolayer. It has to be further added that the term "bulk modified" used by Scott and Kucera on p. 217 is reserved exclusively for packings which are synthesized by co-hydrolysis and co-condensation, *i.e.* porous polybenzylsiloxanes (see ref. 7) of which the organofunctional groups are constituents of the silica bulk phase as well as of the surface.

In agreement with the results presented in Fig. 2 by Scott and Kucera we also could not establish a linear relationship between the capacity factor of solute and the carbon content of packing under a fixed set of conditions. (The plot k' *vs.* carbon content is not included in our paper). The effect of incomplete surface coverage after silanization on retention in forward-phase chromatography given in Fig. 5 of Scott's paper was also demonstrated by us previously (ref. 20, Fig. 5).

As a variety of packing-surface properties, such as mode of modification (monolayer, polymer layer), functionality of silanizing reagent, chain length of reagent, degree of silanization, surface area of modified product etc. seem to influence the retention of solutes we tried to minimize these effects by employing the same parent silica in all modifications, exclusively monochloroalkylsilanes as modifier, and

conditions that permit a complete monolayer coverage. Accepting these presuppositions it was possible to derive some conclusions regarding the solute and the packing properties. One result was that short-chain silica being silanized with trimethylchlorosilane behaves quite differently in retention when compared with long-chain silica, as was also found by Knox and Pryde[3].

We did not include a discussion about selectivity of packings in our study because a general and conclusive judgement could not be derived utilizing some dozen solutes. This subject needs more careful study.

It seems quite interesting to apply the method for estimation of wetting behaviour proposed by Scott and Kucera, to our products.

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