

CHROMSYMP. 1188

INFLUENCE OF THE CHAIN LENGTH ON THE PHYSICAL STATE OF SILICA SURFACES COVERED BY ALKYL DIMETHYLSILOXY LAYERS

D. MOREL, K. TABAR and J. SERPINET*

Laboratoire des Sciences Analytiques (U.A. 435 CNRS), Université Claude Bernard, Lyon I, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex (France)

and

P. CLAUDY and J. M. LETOFFE

Laboratoire de Thermochimie Minérale, Institut National des Sciences Appliquées, 20 Avenue A. Einstein, 69621 Villeurbanne Cedex (France)

SUMMARY

Adsorbents were prepared by heating silica with (R-dimethylsilyl)dimethylamine where R is a *n*-alkyl chain C_zH_{2z+1} with a carbon number, *z*, between 1 and 22. The silica covered with a dense monolayer was examined by inverse gas chromatography and differential scanning calorimetry. It was shown that surfaces covered with chains having $z = 16$ –22 exhibit a reversible phase transition around ambient temperature, which is characterized by an increase of the retention of molecular probes with increasing temperature. Surfaces with chains of 10–14 carbon atoms showed an irreversible transition, while shorter chains showed regular behaviour with temperature. On the basis of the observations presented, we conclude that silicas modified with hexadecyl chains are to be preferred over octadecyl silicas for analytical purposes.

INTRODUCTION

Results from this laboratory^{1–3} on dense octadecyldimethylsiloxyl and docosyldimethylsiloxyl covered layers suggested a possible analogy in behaviour of the ligands in gas chromatography with liquid chromatographic experiments using methanol–water mixtures as eluent. A phase transition was observed for such layers by gas as well as by liquid chromatography. In high-performance liquid chromatography (HPLC) peak reversals are observed across the transition. The reality of this phenomenon was confirmed by differential scanning calorimetry (DSC) and by nuclear magnetic resonance (NMR) spectroscopy³. The chromatographic properties of the two states of the adsorbed layers were thoroughly studied. In the case of polar solutes the role of the residual hydroxyl groups of the silica was demonstrated.

In wetting experiments Riedo *et al.*⁴ have observed anomalous contact angles below a given temperature if a non-branched alkane was used as wetting agent with a chain length similar to that of the chemically bonded alkyl group. It has been

proposed that a mixed crystalline layer was formed at the interface with non-branched wetting agents. This hypothesis has been confirmed by Körösi and Kováts⁵. Using C₁₈ and C₂₂ groups^{3,6} and various molecular probes, we made a thorough study of the resulting mixed layers by inverse gas chromatography (IGC). In these layers the global surface density of the ligand is 8 $\mu\text{mol}/\text{m}^2$ at low temperatures, which corresponds to 0.21 nm² per molecule at the surface of the silica, the same area as for "condensed" layers of fatty acid at the surface of water. However, upon heating this mixed layer undergoes a transition about 20°C above both the melting point of the alkane and the transition temperature of the bonded alkyl group. At the transition point about half of the adsorbed alkane molecules are expelled into the three dimensional space.

The choice of C₁₈ and C₈ ligands for the majority of everyday's analytical works is more or less arbitrary, because it has never been justified by scientific arguments.

The purpose of the present work is to extend the results of previous work^{3,4,6} to a series of ligands of various lengths between 1 and 22 carbon atoms, uncoated and coated with alkanes of similar chain length.

In order to simplify the study of the physical state of the ligand we choose

(a) a very macroporous silica in order to limit the effect of the curvature of the pores on the structure of the bonded layer and

(b) a monofunctional bonding reagent in order to obtain an unambiguously defined structure and

(c) a dimethylaminosilane reagent in order to obtain a very dense and regular bonded phase and

(d) a simple, volatile test solute (generally a volatile alkane).

EXPERIMENTAL

Bonded silicas

The substrate was a Spherosil XOB 015 (Rhône Poulenc, Paris, France) with a mean pore diameter of 130 nm and a specific surface area of 28 m²/g.

TABLE I

BOILING TEMPERATURES OF ALKYL DIMETHYL(DIMETHYLAMINO)SILANES

<i>Radical</i>	<i>Temperature (°C)</i>	<i>Pressure (Torr)</i>
Hexyl	95	23
Octyl	45	0.01
Decyl	77-82	0.02
Undecyl	92-97	5
Dodecyl	94-97	0.025
Tetradecyl	117	0.03
Hexadecyl	140-146	0.04
Heptadecyl	110-115	0.003
Octadecyl	145	0.003
Nonadecyl	152	0.003
Eicosyl	177	0.003
Docosyl	194	0.003

The alkyl(dimethyl(dimethylamino)silane bonding reagents were prepared in two steps by hydrosilylation of the corresponding 1-alkene with dimethylchlorosilane and subsequent reaction of the resulting chlorosilane with dimethylamine, as described previously^{1,7}. All bonding reagents were carefully distilled and kept in sealed ampoules. The distillation temperatures are given in Table I and the surface coverages of the alkyl-bonded silicas in Table II.

Differential scanning calorimetry

Thermograms were recorded between -100 and $+100^{\circ}\text{C}$ with a Mettler TA 2000 B differential scanning calorimeter, as described previously³. This apparatus enables the quantitative interpretation of the signal.

Gas chromatography

The apparatus was previously described¹. Solutes were "pure" commercial products, with the exception of perfluorocarbons, kindly supplied by Atochem (Pierre Bénite, France). Columns were 1/4-in. tubing of 15 cm length.

RESULTS AND DISCUSSION

Bonded alkyl groups of more than 16 carbon atoms

With a non-polar test solute, such as *n*-heptane, the curve representing the logarithm of the absolute retention volume per mass unit of substrate, $\log V_s$, as a function of $1/T$ exhibited an increase when the temperature was increased (Fig. 1).

Consequently, we are led to believe that the ligands with more than 16 carbon atoms undergo a phase transition as has been reported for the C_{18} and C_{22} chains. The phenomenon gives the solute access to new retention sites in the inner part of the layer and eventually at the surface of the silica. The transition temperature as

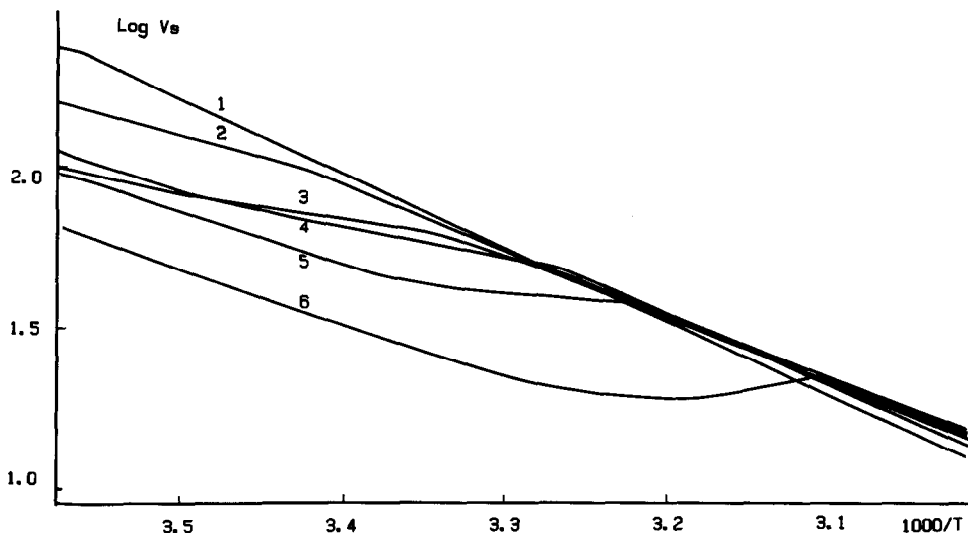


Fig. 1. $\log V_s$ versus $1/T$ for heptane on XOB 015 bonded by long alkyl chain. 1 = Hexadecyl; 2 = heptadecyl; 3 = octadecyl; 4 = nonadecyl; 5 = eicosyl; 6 = docosyl.

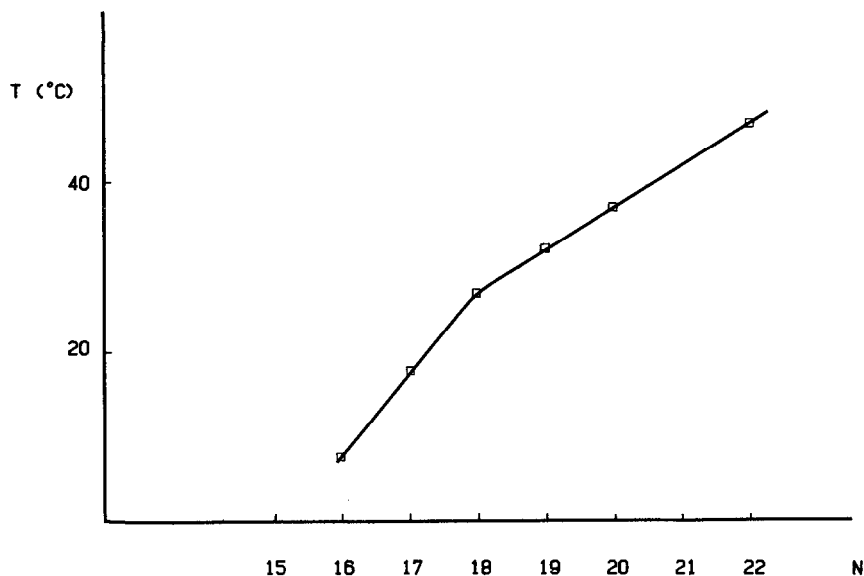


Fig. 2. End transition temperature *versus* carbon number of the bonded chain.

well as the amplitude of the phenomenon, increases with the length of the bonded chain. However, it must be noted that the retention of a non-polar solute is only slightly dependent on the length of the graft above the transition temperature.

A plot of the transition temperature as a function of the chain length, yields two linear segments which meet in a breaking point at about 18 carbon atoms. For more than 18 atoms, the transition temperature is of the same order of magnitude as the melting temperature of the corresponding alkane, but below 18 atoms the transition temperature is lower (Fig. 2). No significant odd-even alternation was observed in the transition temperature.

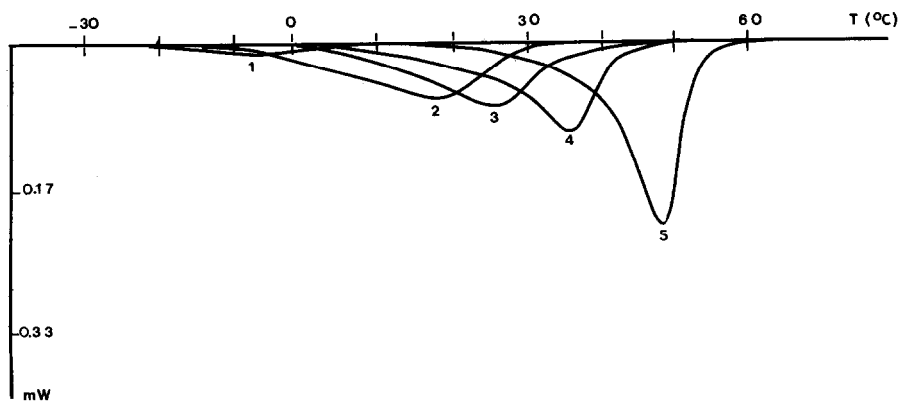


Fig. 3. DSC curves of densely bonded silicas. 1 = Heptadecyl; 2 = octadecyl; 3 = nonadecyl; 4 = eicosyl; 5 = docosyl.

TABLE II
SURFACE COVERAGE OF THE ALKYL SILICAS CHEMICALLY BONDED WITH ALKYL GROUPS OF VARIOUS CHAIN LENGTH

<i>Number of carbons in the chain</i>	<i>% C</i>	<i>Surface coverage ($\mu\text{mol}/\text{m}^2$)</i>
1	0.53	5.23*
6	1.17	4.36
8	1.43	4.28
10	1.66	4.16
11	2.02	4.6
12	2.09	4.5
14	2.37	4.48
16	2.65	4.47
17	2.63	4.26
18	2.69	4.13
19	2.85	4.13
20	3.13	4.34
22	3.46	4.4

* Aberrant result resulting from the poor precision of the analysis.

These phenomena were confirmed by DSC (Fig. 3). The temperatures of the maxima of the thermal peaks are very close to the end-transition temperatures observed by GC. The transition enthalpies (Table III) are much lower than the melting enthalpies of the corresponding normal alkanes. It is as if only a part of the bonded chain is participating in the transition phenomenon.

Medium-length bonded chains (10–14 carbon atoms)

For the dodecyl- and tetradecyl-bonded silicas, the chromatographic curve is completely different. The linear ($\log V_S$ vs. $1/T$) diagram was no longer interrupted by an increase in retention with increasing temperature (Fig. 4), but a new phenomenon was observed close to 20°C. Its amplitude increased with the surface coverage (Fig. 5). Its existence was confirmed with other test solutes, such as cyclohexane, perfluorocarbons, and chlorinated compounds (Fig. 6).

The decyl ligand presents only a break close to 40°C; the undecyl graft gives

TABLE III
TRANSITION ENTHALPIES OF BONDED SILICAS

<i>Number of carbons in the bonded chain</i>	<i>H/g support (J/g)</i>	<i>H/g chain (J/g)</i>	<i>H/g melting* (J/g)</i>
22	2.4660	66.48	248.4
20	1.8242	55.11	247.3
19	1.5345	51.01	227.4
18	1.6676	59.13	241.2
17	0.0489	1.58	218.9

* Melting enthalpy of the normal paraffin with the same number of carbons (measured with the same calorimeter).

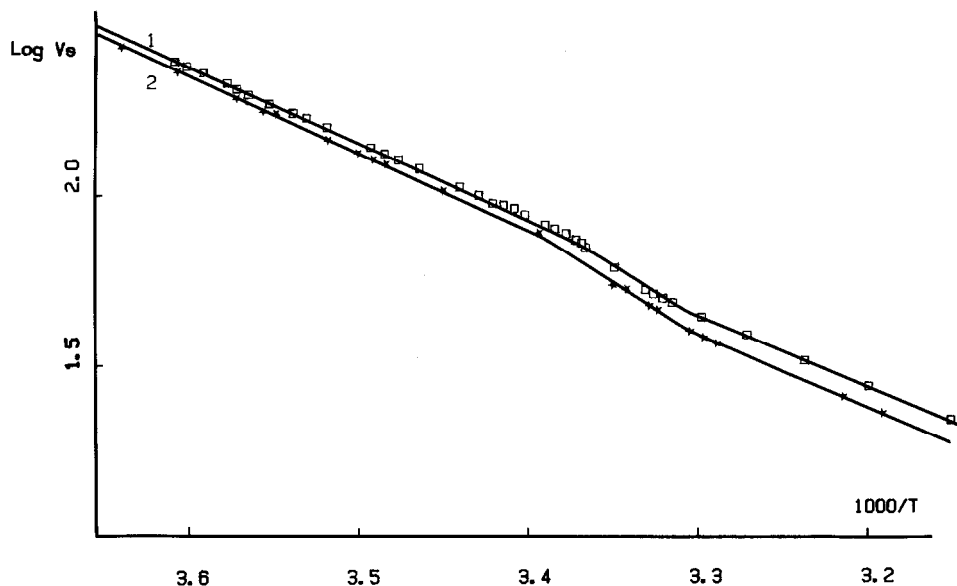


Fig. 4. $\text{Log } V_s$ versus $1/T$ diagram for heptane on (1) tetradecyl silica; (2) dodecyl silica.

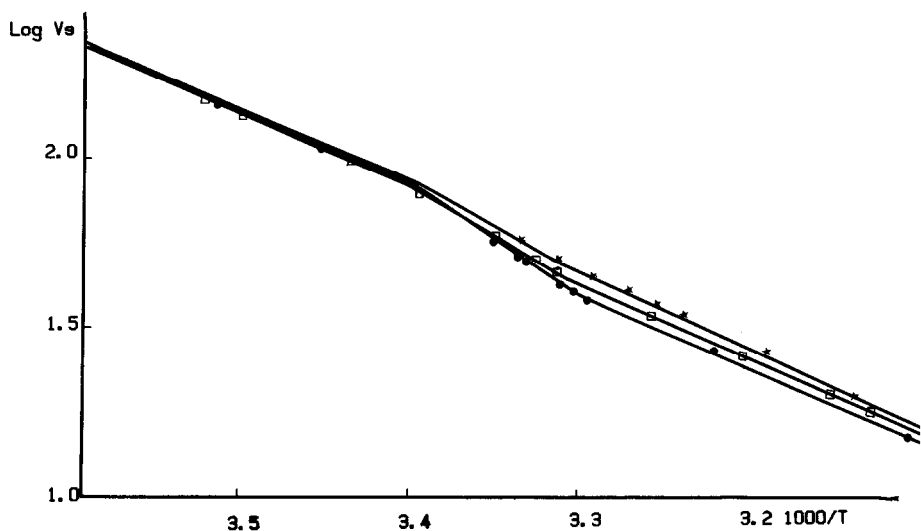


Fig. 5. $\text{Log } V_s$ versus $1/T$ curves for heptane on dodecyl bonded silicas. (●) $4.5 \mu\text{mol}/\text{m}^2$; (□) $4.4 \mu\text{mol}/\text{m}^2$; (★) $4.1 \mu\text{mol}/\text{m}^2$.

no transition. Contrary to the transition of the long chain grafts, the phenomenon observed with C_{12} and C_{14} chains shows a hysteresis effect (Fig. 7).

It is very interesting to note that the decrease in the retention is only observed if the column is first conditioned at about -30°C . If it is cooled only between 0 and 20°C , the experimental points remain on the same straight line at any temperature. No enthalpy effect was observed by DSC with or without conditioning the sample at -100°C . In a like manner, phase transitions of polymeric materials have only been

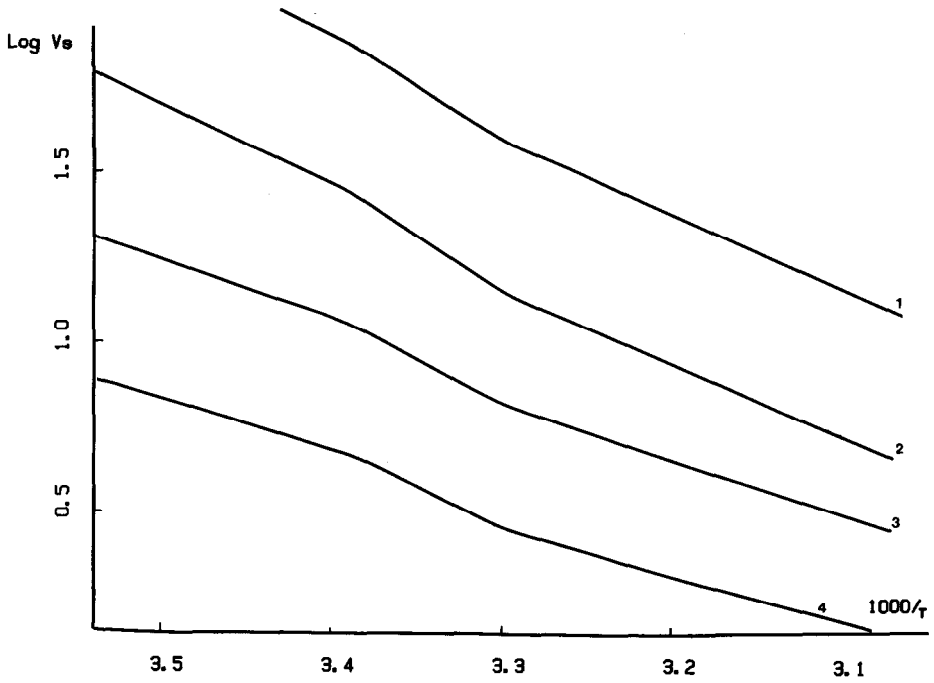


Fig. 6. $\log V_s$ versus $1/T$ curves on dodecyl-densely-bonded silica. 1 = Cyclooctane; 2 = perfluorooctane; 3 = chloroform; 4 = dichloromethane.

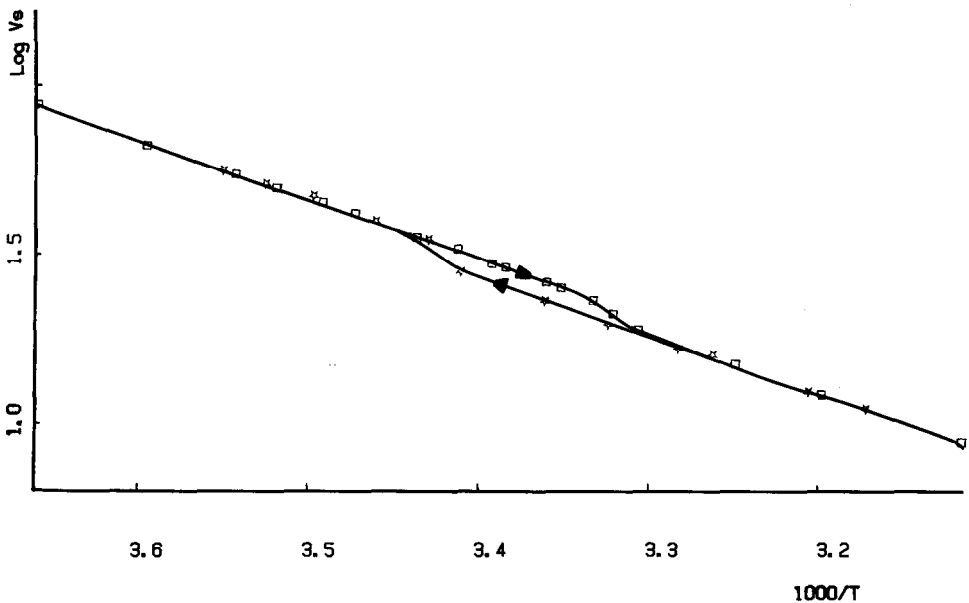


Fig. 7. Hysteresis in the diagram of $\log V_s$ versus $1/T$ obtained by increasing (\square) and thereafter decreasing (\star) the temperature. The support is tetradecyl silica and the solute cyclooctane.

observed by gas chromatography. This apparent disagreement demonstrate the sensitivity and the versatility of the inverse GC technique.

The curves obtained with GC may be compared with the rather similar diagrams, observed for HPLC by Gilpin and Gandoga in a very different way^{8,9}. These authors first conditioned medium-length grafts in an organic liquid before using a purely aqueous mobile phase. Upon increasing the temperature, they observed a decrease in the retention between two linear parts of the retention plot. The phenomenon was attributed to a change in the structure of the bonded layer, accompanied by the desorption of organic molecules trapped between the bonded chains. As far as our experiments are concerned, that interpretation can be ruled out, because our columns are conditioned at 110°C under inert gas flow before the experiments. Nevertheless, it is perfectly possible that the configurations of the chains could be the same in both types of experiments.

The weakness of the energetic effect leads us to suppose that these relatively short ligands are only able to interact slightly with the end parts of the chains. Nevertheless, these slight changes in the interactions are able to change the accessibility of the inner parts of the monolayer to the solute rather strongly.

Short-chain ligands

No transition is observed by either inverse GC or DSC. Nevertheless, it is worthwhile to note that the chromatographic retentions for the short grafts decrease with the length of the chains (Fig. 8).

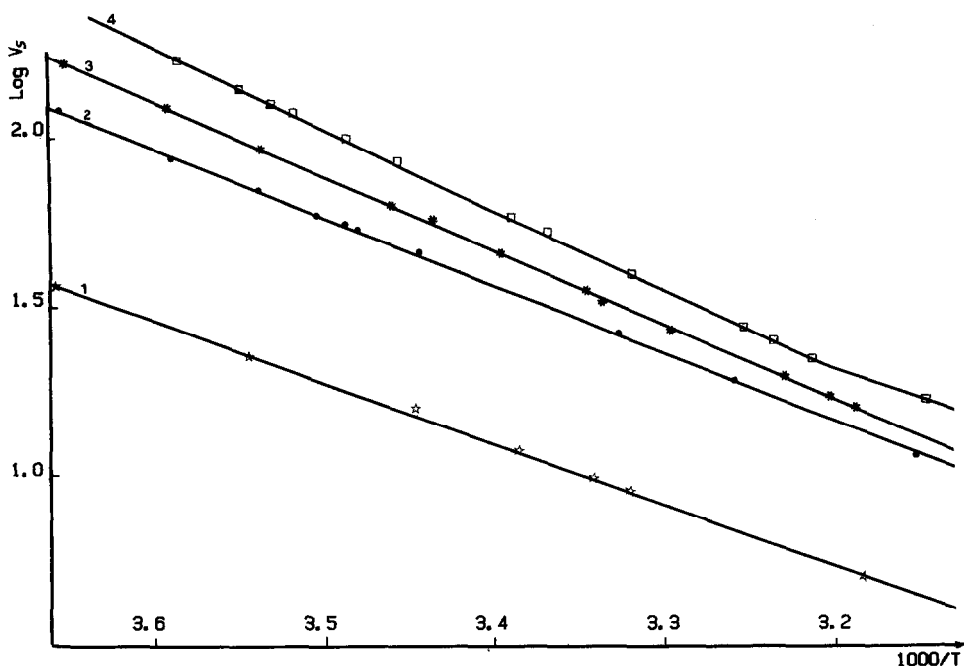


Fig. 8. $\log V_s$ versus $1/T$ curves for heptane on silicas, bonded to short alkyl chains. 1 = Methyl; 2 = hexyl; 3 = octyl; 4 = decyl.

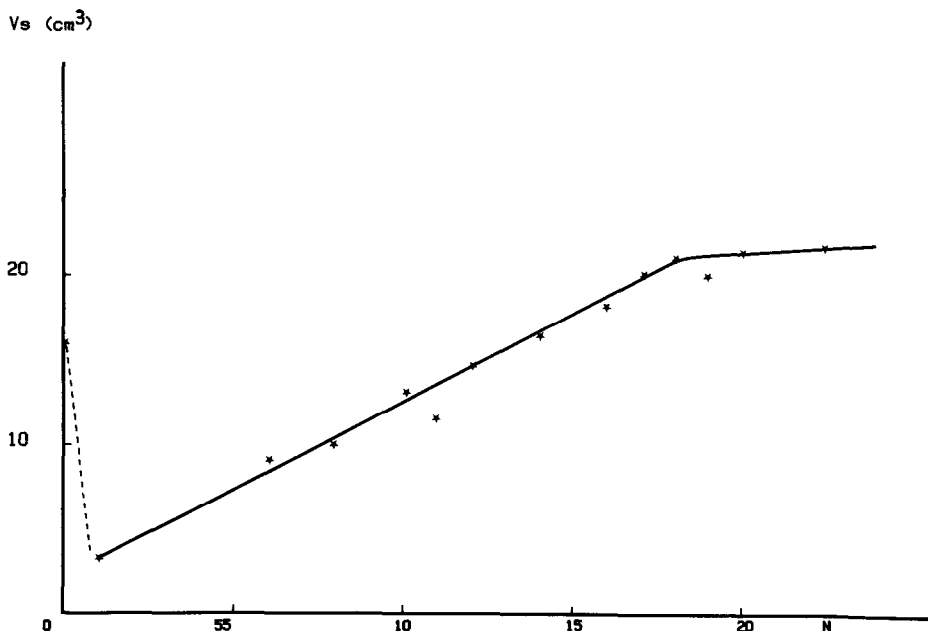


Fig. 9. Retention volume of heptane at 49.4°C versus carbon number of the bonded chain.

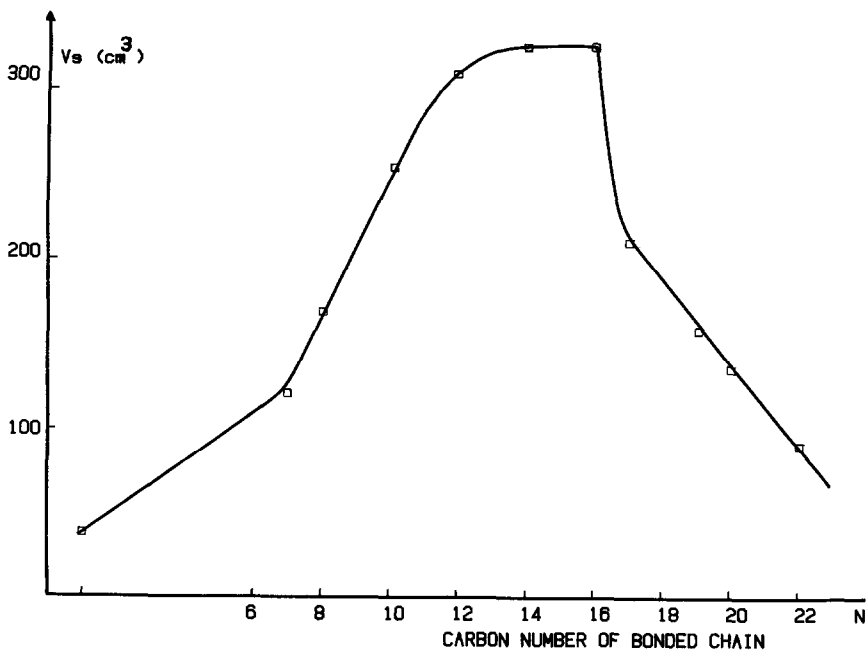


Fig. 10. Retention volume of heptane at 0°C versus carbon number of the bonded chain.

Variation of the chromatographic retention with the chain length

At 49.4°C, the temperature at which all the reported transitions are completed, the retention volume increases rapidly with increasing chain length up to about C₁₇ or C₁₈ and then increases only very slightly (Fig. 9). This last observation must be compared with the remarkable lack of variation in the retention on a non-polar solute

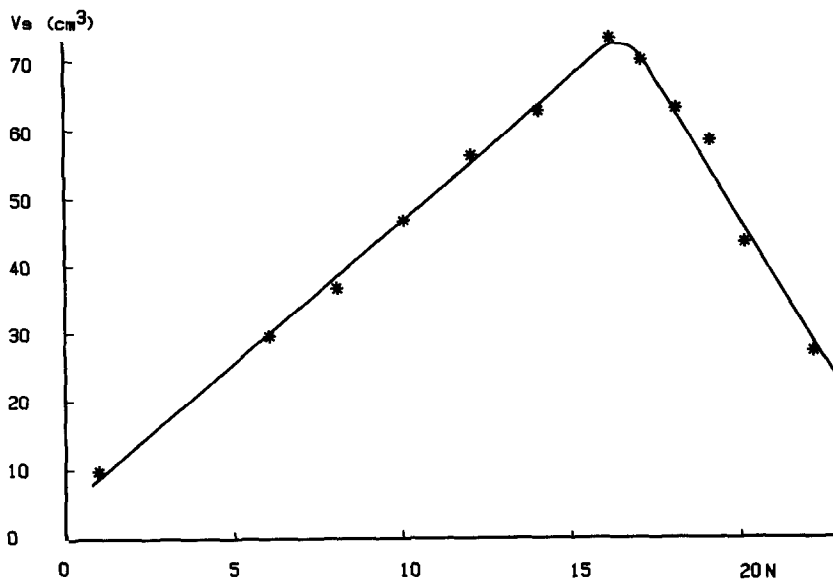


Fig. 11. Retention volume of heptane at 25°C versus carbon number of the bonded chain.

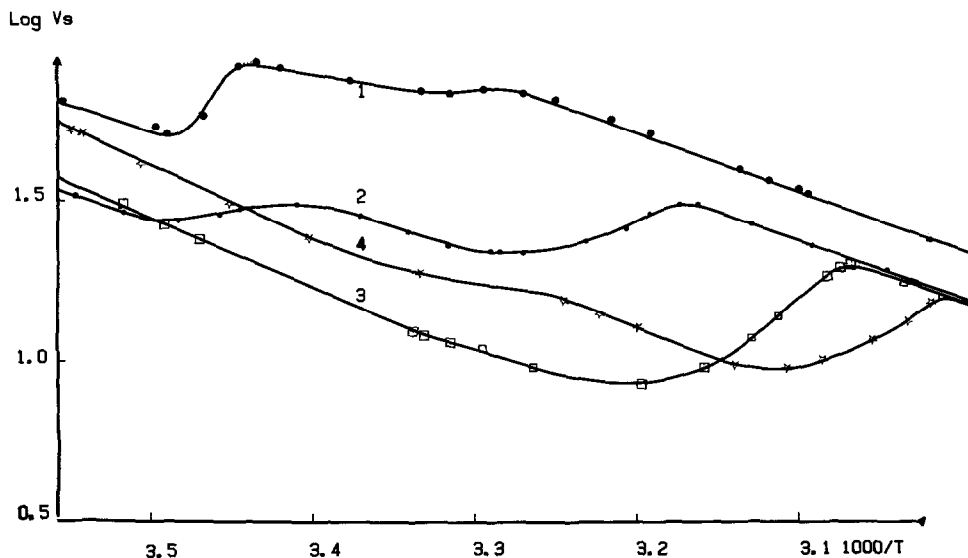


Fig. 12. Log V_s versus $1/T$ curves for heptane on densely bonded silicas, covered by alkanes of similar length. 1 = C₁₆ silica, covered by 3.6% of hexadecane; 2 = C₁₇ silica, covered by 2.94% of heptadecane; 3 = C₁₉ silica, covered by 2.32% of nonadecane; 4 = C₂₀ silica, covered by 2.35% eicosane.

with varying surface coverage between 0.1 and 4.2 $\mu\text{mol}/\text{m}^2$ for a C_{22} bonded phase¹⁰ above the transition temperature.

At low temperatures, for instance 0°C (Fig. 10), the curve is completely different. The retention volume first increases from 1 to 12 carbon atoms, but decreases

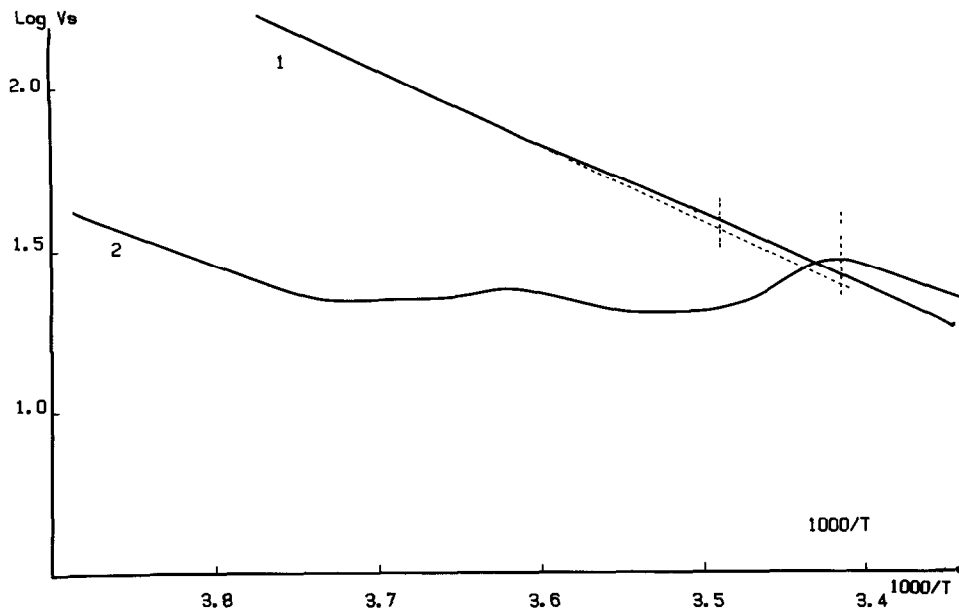


Fig. 13. $\text{Log } V_s$ versus $1/T$ curve of heptane on (1) C_{12} silica, covered by 2.00% of dodecane; (2) C_{14} silica, covered by 2.24% of tetradecane.

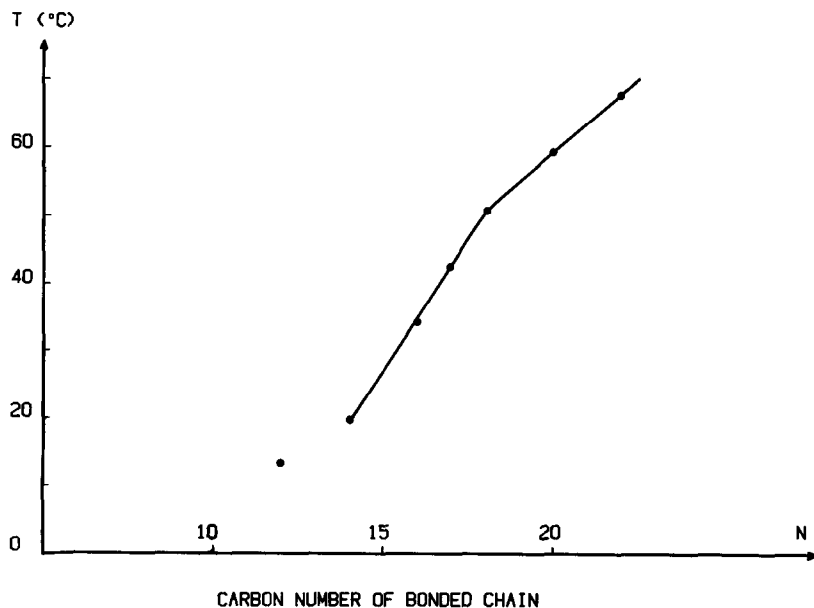


Fig. 14. End transition temperatures of mixed film versus carbon number in the bonded chain.

rapidly after C_{16} . At 25°C , near the laboratory temperature (Fig. 11), the retention volume increases regularly up to C_{16} and then decreases regularly. The differences observed between the two last plots confirm the existence of changes in the layers in the low-temperature range.

Extremely dense mixed monolayers, obtained by adsorption of alkane molecules

The inverse GC study of these materials revealed transitions (Fig. 12) rather similar to those previously observed in this laboratory for C_{18} and C_{22} phases. It must be pointed out that the C_{12} and C_{14} phases (Fig. 13) which do not exhibit regular transitions (see above) behave as regular mixed films after "densification" with a fitted alkane. This observation demonstrates the completely different nature of the two transition phenomena. Nevertheless, if we plot the transition temperature against the number of carbon atoms in the chain, we recognize the same break in the curve at 18 carbon atoms as for the uncovered bonded phases (Fig. 14).

CONCLUSIONS

The reported results demonstrate the great complexity of the physical properties of surfaces covered by bonded alkyl chains. They cannot merely be considered as immobilized alkanes as many people do. The structure of normal alkanes remains a very living field of research itself. However, the structure of bonded alkyl phases is even more complex. A precise study on quasi-planar surfaces or macroporous substrates is extremely difficult.

The global interpretation of our results will have to take into account the influence of other parameters, such as the surface coverage and the results of experiments by other physical methods, such as inelastic neutron diffusion experiments, which will be published in future papers.

The value of the transition enthalpies for the bare bonded layers leads to the hypothesis that only the end parts of the chains are involved in mutual interactions. In contrast, the mixed phase transition appears to be much more similar to the melting of an alkane.

As a conclusion we believe that the widespread choice of the C_{18} ligand for analytical purposes has probably been unfortunate. This phase undergoes a transition over the entire laboratory temperature range in GC as well as in contact with water-methanol mixtures. The choice of a C_{16} ligand would be much more advisable.

REFERENCES

- 1 D. Morel and J. Serpinet, *J. Chromatogr.*, 200 (1980) 95.
- 2 D. Morel and J. Serpinet, *J. Chromatogr.*, 214 (1981) 202.
- 3 P. Claudy, J. M. Letoffe, C. Gaget, D. Morel and J. Serpinet, *J. Chromatogr.*, 329 (1985) 331.
- 4 F. Riedo, M. Czencz, O. Liardon and E. sz. Kováts, *Helv. Chim. Acta*, 61 (1978) 1912.
- 5 G. Körösi and E. sz. Kováts, *Colloids and Surfaces*, 2 (1981) 315.
- 6 C. Gonnet, D. Morel, E. Ramamonjirinina, J. Serpinet, P. Claudy and J. M. Letoffe, *J. Chromatogr.*, 330 (1985) 227.
- 7 K. Szabo, N. Le Ha, P. Schneider, P. Zeltner and E. sz. Kováts, *Helv. Chim. Acta*, 67 (1984) 2128.
- 8 R. K. Gilpin and J. A. Squires, *J. Chromatogr. Sci.*, 19 (1981) 195.
- 9 R. K. Gilpin, M. E. Gangoda and A. E. Krishen, *J. Chromatogr. Sci.*, 20 (1982) 345.