LONG-CHAIN ALKYL GRAFTS AND MIXED ALKYL–ALKANE LAYERS AT THE SURFACE OF MACROPOROUS SILICAS

THEIR GAS CHROMATOGRAPHIC PROPERTIES BELOW AND ABOVE THE PHASE TRANSITION

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SUMMARY

Macroporous silicas have been used to prepare well defined docosyl grafts of various bonding densities from the corresponding monofunctional (dimethylamino)-silane as bonding reagent without any effect of curvature and diffusion. Heneicosane molecules have been inserted between the alkyl radicals in order to form a sort of two-dimensional mixed crystal of very high surface density (8 μmol/m^2). The phase transitions observed upon increasing the temperature for both the pure and mixed layers have been studied. The retentions of various test solutes, below and above these transition temperatures, have been examined and interpreted with the help of differential scanning calorimetry and some wide-band NMR experiments. The perfect dissimulation of the residual silanols in the mixed layers indicates promising applications of those materials.

INTRODUCTION

As early as 1971[1–3], using gas chromatography (GC) of a test solute (so-called "inverse gas chromatography"), we demonstrated the existence and the phase transitions of brush-like films of pure normal paraffins at the surface of various materials, solids and liquids when covered by "free" hydroxyl groups, not involved in mutual hydrogen bonds[4] (Fig. 1a). In spite of the lack of a polar group in the molecule these films exist, as was further confirmed by calorimetry[2]. Interpretation of the GC results was made easier by a similar study of films of well known amphiphilic compounds such as fatty alcohols[5].
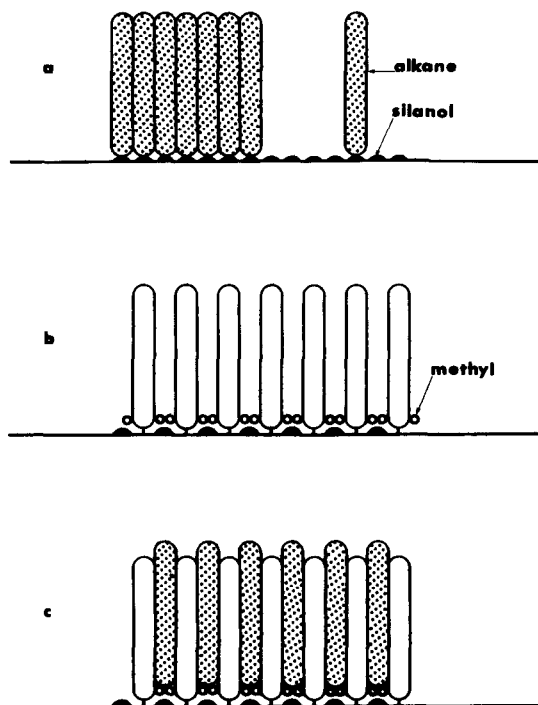
Fig. 1. Sketch of three types of alkyl layer in their low temperature state at the surface of silica: a, pure physisorbed monolayer; b, alkyldimethylsiloxy bonded layer; c, alkyl–alkane mixed layer.

More recently[6], with help of new inverse GC experiments, we discovered rather similar phase transitions for very dense C_{18} and C_{22} alkyl monolayers at the surface of silica. Similar experiments with test solute molecules of various shapes and weights and with water–methanol mobile phases (from 0 to 100%) confirmed the existence of this new phenomenon and indicated its influence upon retention and selectivity in reversed-phase high-performance liquid chromatography (RP-HPLC)[7] (Fig. 1b).

Nevertheless, for steric reasons[8], the surface density of these bonded silicas cannot surpass 4.2 μmol/m², but coating this material by free normal paraffins of similar chain lengths, which insert themselves between the bonded chains, leads to a much denser mixed layer, as Riedo *et al.*[9] were the first to show, by contact-angle measurements in capillaries (Fig. 1c). By inverse GC[6], we showed that, at low temperatures, these films have the same limiting surface density of fatty chains, namely 8 μmol/m² (0.21 nm² per molecule), as the films of fatty acids formed at the surface of the Langmuir trough, in their solid two-dimensional state. The mixed layer undergoes a phase transition at a temperature markedly higher than both the transition temperature of the chemisorbed layer and the melting point of the paraffin. This transformation has recently been studied by André[10] by means of differential scanning calorimetry (DSC).

The significance of these phenomena in chromatography, at least for the purely chemisorbed layers, is well recognized now and many recent papers are devoted to these phase transitions[11–13]. However, most of the transitions are characterized by an

increase in the absolute retention volume, V_N, with increasing temperature, whereas log V_N is normally a linear function of $1/T$. Characterized by an endothermic peak in DSC, this phenomenon appears as a sort of two-dimensional "melting" which gives the solute access to new retention sites in the inner part of the thick two-dimensional layer. Therefore, as far as the chromatographic process is concerned, there is a transition from a more or less pure adsorption phenomenon to solubility in a rather special two-dimensional solvent.

In contrast, Gilpin and co-workers[14-16] and recently Hammers and Verschoor[17] describe transitions in which there is an abnormal decrease in retention over a limited temperature range. This phenomenon, observed in HPLC, results from a change of the mobile phase. We have also observed it recently in GC as a consequence of the trapping of coating solvent molecules in the fatty layer[18]. However, we shall not deal here with this completely different sort of transition.

This paper aims to investigate the real nature of the "melting-like" transitions of the purely bonded and mixed monolayers, in order better to understand the structure of the high and low temperature films and the retention by these stationary phases. In spite of the wide use of bonded phases in liquid chromatography and of our promising attempt[19] to use the mixed alkyl–alkane phases in RP-HPLC, we chose to study first the GC retention data, in order to eliminate the influence of the mobile phase on the alkyl chains and to simplify the interpretation. In addition, contrary to most work done on bonded silicas, we used macroporous substrates, in order to eliminate the diffusion and curvature effects*, and (dimethylamino)silane monofunctional reagents to obtain well defined film structures. Thus, the results cannot be obscured by many secondary phenomena.

Several series of docosyl-bonded silicas of surface density from 0 to 4 μmol/m^2 were prepared according to the same technique, and then coated with various percentages of heneicosane. The GC retention measurements were completed by mass-transfer coefficient determinations, DSC experiments and wide-band NMR measurements.

EXPERIMENTAL

Preparation of bonded materials

The preparation of very densely covered alkylsilicas (4–4.2 μmol/m^2) by means of (dimethylamino)silanes has been described[6]; the use of these bonding agents was suggested first by Kováts and co-workers[21]. The choice of the C$_{22}$ graft instead of the more usual C$_{18}$ was made chiefly because of a more favourable temperature range for the observation of the transitions. However, some experiments on octadecyl-bonded silica at around room temperature gave rise to the same phenomena[6].

Docosyldimethylchlorosilane and docosyldimethyl(dimethylamino)silane were distilled at 185°C at $5 \cdot 10^{-3}$ and $3 \cdot 10^{-3}$ Torr, respectively.

Grafts of lower surface density were obtained by decreasing the quantity of the reagent, without modifying the physisorption process at -30°C. In a first attempt to ensure the homogeneous coverage of the surface, we diluted the reagent in a nor-

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* There are no transitions in microporous bonded silicas. This situation explains the contradictory results obtained by certain authors[20].

mal paraffin of about the same chain length (heneicosane) in a suitable proportion so as to form a complete, mixed physisorbed monolayer (8 μmol/m^2) before bonding. However, no change in the graft's properties resulting from the addition of the diluent was observed. Accordingly, we suppressed the paraffin in ensuing preparations.

Exceptionally, a few silica samples were bonded by means of the chlorosilane according to the same process.

For the above-mentioned reasons, we made use of three large-pore silicas: Spherosil XOB 075 (Rhône Poulenc, Paris, France) of mean pore diameter 35 nm, particle size 100–200 μm and surface area 114 m^2/g (from our own BET measurements on the non-bonded substrate); Spherosil XOB 015 of mean pore diameter 125 nm, particle size 100–200 μm and surface area 28 m^2/g; and Spherosil XOC 005 of mean pore diameter 300 nm, particle size 100–200 μm and surface area 13.6 m^2/g. Our previous experiments[7] led us to suppose that these three silicas are representative of two sorts of surfaces, chiefly covered by hydrogen-bonded silanols (XOB 075) and free silanols (XOB 015) and XOC 005. Only the last silica may be covered by a brush-like dense normal paraffin monolayer (molecular area 0.21 nm^2 or surface density 7.9 μmol/m^2), characterized by a phase transition 7° above the melting point of the bulk paraffin.

A few similar grafts were prepared at the surface of Chromosorb P (Johns-Manville, Denver, CO, U.S.A.), a diatomite of surface area 4.1 m^2/g and pore diameter 1 μm.

The density was monitored by carbon analysis (Service d'Analyse du C.N.R.S., Solaize, France) and by hydrofluoric acid (40%) attack and GC of the fluorosilane[22]. The latter method has proven to be more precise than the former for low surface areas and less densely bonded materials.

Gas chromatography

The classical home-made chromatograph, equipped with a catharometer, has already been described[6]. It allows precise control of the column temperature, T, the inlet pressure and the carrier gas flow-rate, for the calculation of V_s, the absolute retention volume per gram of silica substrate.

Differential scanning calorimetry

DSC was effected with a Mettler TA 2000 B apparatus which operates from −170 to 550°C and allows a quantitative interpretation of the observed phenomena. The weighed sample (10–20 mg) is placed in an aluminium crucible, which is subsequently sealed. The sweeping gas is argon Nertal (L'Air Liquide, Paris, France) containing 0.1% of oxygen. All the described experiments were carried out at a heating rate of 3.5°C/min.

The quantitative exploitation of the thermal effect requires the processing of the calorimetric signal and standardization of the microcalorimeter[23].

Nuclear magnetic resonance spectroscopy

NMR experiments were effected at the Centre d'Etudes Nucléaires de Grenoble (France) with a Brücker CXP 200 spectrometer by observing the proton magnetic resonance at 200 MHz. In order to improve the signal-to-noise ratio, a Fourier transform was effected after the accumulation of 20 successive free precession signals.

Accordingly, during the 40–60 sec of observation of the NMR signal, the temperature of the circulating nitrogen gas may have changed by 1–2°C, which results in a slight uncertainty in the sample temperature.
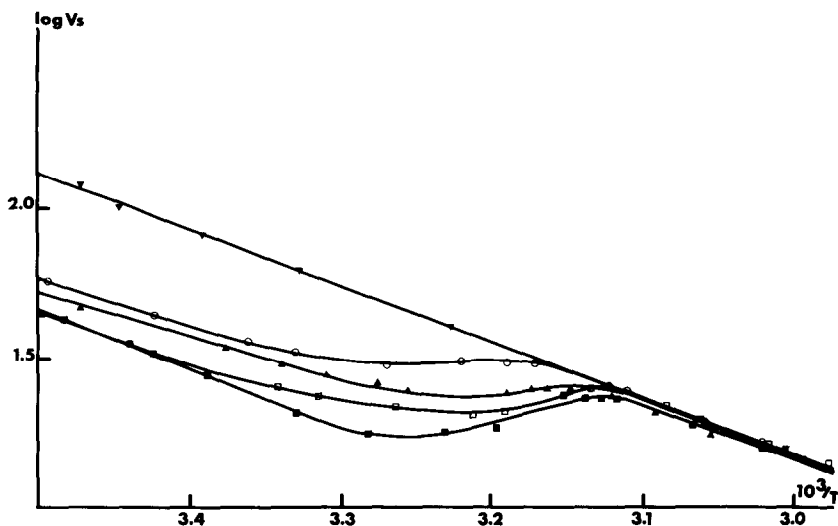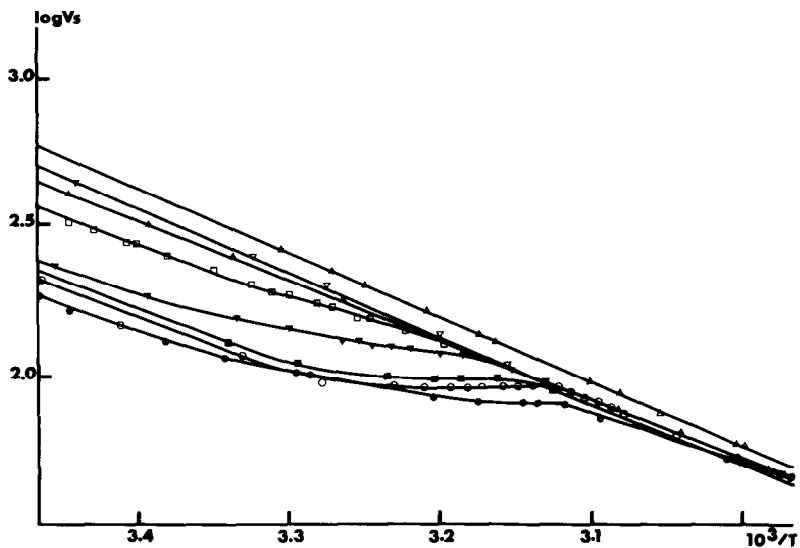

Fig. 2. Variation of log V_s with $1/T$ for n-heptane as solute on C_{22}-bonded Spherosils XOB 015 of different densities: ■, 4.40; □, 4.35; ▲, 4.30; ○, 4.04; ▼, 2.90 μmol/m^2.

Fig. 3. Variation of log V_s with $1/T$ for n-heptane as solute on C_{22}-bonded Spherosils XOB 075 of different densities: ●, 4.40; ○, 4.30; ■, 3.90; ▼, 3.80; □, 2.80; ▲, 2.0; ▽, 0.66 μmol/m^2; △, raw silica.
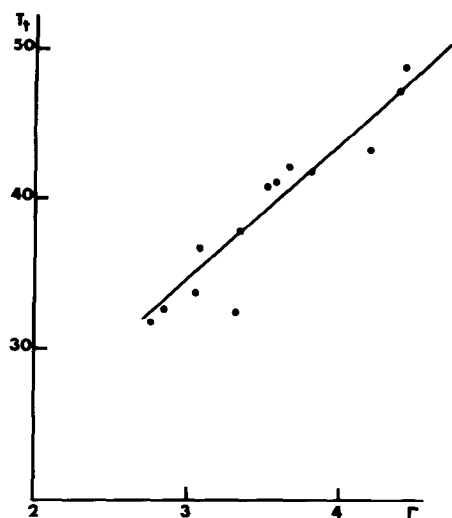
Fig. 4. Variation of the end-transition temperature, T_t, with the bonding density, Γ, for C_{22}-bonded Spherosils XOB 075.

RESULTS AND DISCUSSION

Non-coated alkyl grafts: influence of the bonding density on some physical and chromatographic properties of the monolayer near the phase transition

   The phase transition of the layer
   Inverse GC. The phase transition previously described for very densely bonded silicas ($\Gamma > 4$ μmol/m^2) may also be observed in GC of a test solute on less densely grafted substrates, Figs. 2 and 3 illustrate this for normal heptane as solute and Spherosils XOB 015 and 075 as substrates, respectively. However, this transition disappears at densities less than 2.6 μmol/m^2. Between 2.6 and 4 μmol/m^2, the end-

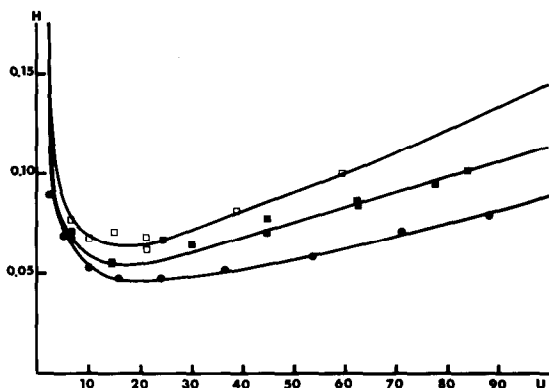Fig. 5. Curves of H (HEPT in cm) *versus* U (gas flow-rate in cm/sec) for *n*-hexane as solute and a C_{22}-bonded Spherosil XOC 005 (13.6 m^2/g, 3.9 μmol/m^2) as stationary phase, at 23°C (■), 34°C (□) and 80°C (●).

TABLE I

CONTRIBUTIONS OF THE DIFFERENT TERMS OF THE KINETIC EQUATION, TO THE HETP AT THREE DIFFERENT TEMPERATURES BELOW THE TRANSITION, IN THE TRANSITION RANGE AND ABOVE THE TRANSITION

Stationary phase: C_{22}-bonded Spherosil XOC 005 (13.6 m^2/g, 3.9 $\mu mol/m^2$). The kinetic contributions (cm) refer to eddy diffusion, h_A, gas phase diffusion, h_B, liquid and gas phase mass-transfer resistances, h_{Cl} and h_{Cg} respectively. Solute: n-hexane. $U = 75$ cm/sec.

$t (^\circ C)$	h_A	h_B	h_{Cl}	h_{Cg}	h_{total}
25	0.0165	0.0030	0.0673	0.0078	0.0946
34	0.0054	0.0038	0.1218	−0.0347	0.0963
80	0.0165	0.0025	0.0505	0.0024	0.0719

temperature of the transition is a decreasing and approximately linear function of the bonding density (Fig. 4).

The concept of inverse GC may be utilized in a very different way by studying not the retention time, but the height equivalent to a theoretical plate (HETP), related to the second moment of the peak, as a function of temperature. A plot of HETP *versus* flow-rate at three temperatures for a C_{22}-bonded Spherosil XOC 005 reveals a decrease in efficiency over the temperature range of the transition, particularly at high rates[24]. Above the phase transition, the efficiency is still higher than at low temperature (Fig. 5).

In the intermediate temperature range, the mobility of the alkyl chains appears to be limited and the solute diffusion rather slow. Calculation of the gas and liquid mass-transfer contributions, h_{Cg} and h_{Cl}, by use of the non-coupled four coefficients Giddings equation[25]* leads to values which confirm this interpretation rather well (Table I): h_{Cg} is not significant; h_{Cl} is higher in the transition range.

DSC curves and calorimetric measurements. The transition temperatures observed by DSC are in good agreement with those from the inverse GC experiments, if the temperature at the peak maximum is adopted (Table II). It is difficult to determine the enthalpy changes because of the problem in appraising the beginning of

TABLE II

COMPARISON OF THE CHROMATOGRAPHIC END-TRANSITION TEMPERATURE AND THE CORRESPONDING DSC PEAK MAXIMUM TEMPERATURE FOR VARIOUS C_{22}-BONDED SPHEROSILS XOB 075 OF BONDING DENSITY, Γ ($\mu mol/m^2$)

Γ	t_{DSC}	$t_{chromato}$
4.3	48	47
3.7	40	40
3.13	35	35
3.07	27	35
2.91	21	33
1.78	19	★

★ No chromatographic transition.

* Basic principles and calculation methods are developed in refs. 26 and 27.
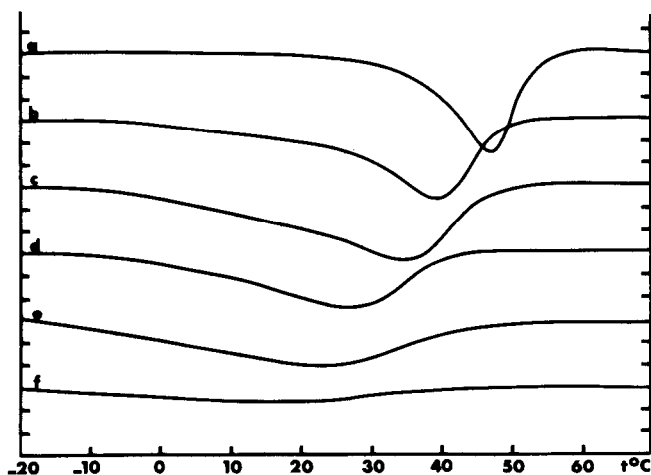
Fig. 6. DSC curves for variously grafted Spherosils XOB 075: a, 4.3; b, 3.7; c, 3.1; d, 3.0; e, 2.9; f, 1.78 μmol/m^2. The vertical scale divisions correspond to 0.1 mW.

the transition, as Fig. 6 shows for variously bonded Spherosil XOB 075. Conse-quently, it is rather difficult to obtain a well defined correlation between the enthalpy and the percentage of bonded organic material. Nevertheless, the DSC curves exhibit a very regular trend: for the less densely bonded materials, the phase transition begins at much lower temperatures.

However, as far as dense grafts are concerned (about 4 μmol/m^2), the transition enthalpies per gram of film for the two macroporous silicas are in fair agreement: 40.6 and 44.6 J/g for XOB 015 and 075 respectively. This indicates the good repro-ducibility of dense grafts obtained from (dimethylamino)silanes. On the contrary, André[10] in his study of very different silicas reports transition enthalpies which are strongly dependent on the pore size. These observations reveal extreme difficulty of preparating reproducible long-chain grafts on the small-pore silicas used in RP-HPLC, which are much more microporous than Spherosil XOB 075. In addition, as we have already shown, there are no transitions for pore diameters < 5 nm[6], even for the densest grafts possible. These experiments explain the non-observation of the transition by certain authors[20].

However, two further observations are worthy of note. Even for the more macroporous substrate, our experiments lead to transition enthalpies of about 28% that for melting of the docosane (158 J/g)[10], the paraffin having the same chain length*. If it is supposed that the change in the layer corresponds to the acquisition of a certain mobility by the chains, *i.e.*, to a "melting-like" phenomenon, these results can be considered as foreseeable, at least qualitatively. A bonded radical is able to acquire only partially the degrees of freedom possessed by a molecule in the liquid state.

We did not observe any transition phenomena in the cryogenic temperature range (from − 130°C), as did Kessaissia *et al.*[28] for silicic esters of macroporous silicas. In any case, the tentative interpretation proposed by these authors of the

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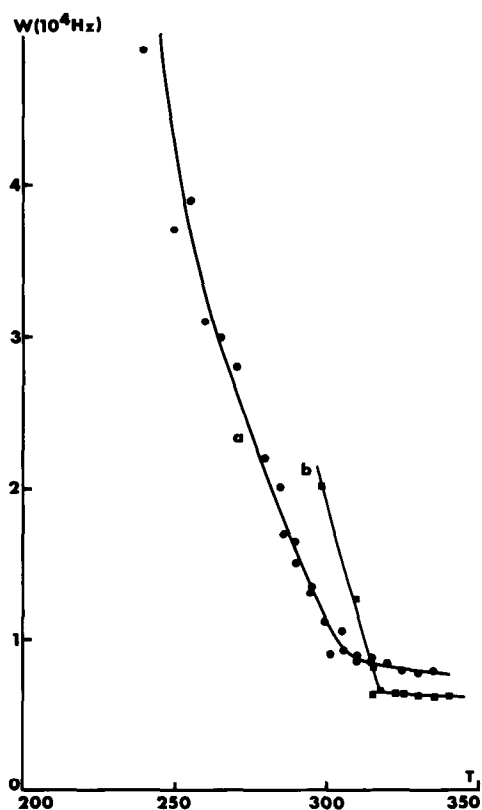* The values given by André[10] are somewhat higher (75% of the heat of melting).

Fig. 7. Variation of the proton NMR band width at a quarter of the peak height with the temperature
(°K): a, C_{18}-bonded Spherosil XOB 075 (4.15 μmol/m²); b, C_{22}-bonded Spherosil XOB 075 (4.4 μmol/m²).

occurrence of rotational movements in the bonded radical cannot be transposed sim-
ply to our Si–C grafts.

   Wide-band NMR measurements. Fig. 7 shows the proton NMR band width at
a quarter of the peak height for a C_{18} and a C_{22} densely bonded silica, as a function
of the temperature. In both cases, a very rapid narrowing of the band may be seen
upon increasing the temperature to 30 and 50°C for the C_{18} and C_{22} silica, respec-
tively. At higher temperatures, the band width is constant and reproducible, even
after several weeks.

   It is as if the mobility of the alkyl chains were to reach a limit, at approximately
the end temperature of the transition observed by GC.

   In brief, the low value of the transition enthalpy could perhaps be attributed
to a mere configurational transformation of the chain, as is accepted for the so-called
"rotational transition" of the paraffins[29,30]. However, not only the retention mea-
surements, but also the mass-transfer coefficient determinations and the NMR ex-
periments substantiate the "melting-like" model in which the transformation of the
graft gives the solute access to new retention sites in the inner part of the layer and
possibly on the remaining active centres of the substrate.

GC properties of the two kinds of films for grafts of various densities

Below the transition temperature. At below 30°C, on densely bonded C_{22} silicas, heptane appears to be slightly retained, as could be foreseen for a gas–solid retention process at the surface of bulky not very strongly adsorbing CH_3 groups. However, a thorough examination of the dependence of the logarithm of the retention time *versus* the number of carbon atoms for an alkane solute reveals a somewhat more complex behaviour. If the linear dependence usually observed in gas–solid or gas–liquid chromatography to a high degree of approximation is obeyed, the ratio of the retention times of two consecutive homologues, t_{Rn}/t_{Rn-1}, should be independent of the length of the chain. As Fig. 8 shows, this is the case at 50 and 75°C (above the phase transition temperature, see below), but not at 30°C (before the commencement of the transition). The retention of normal alkane solutes is not an adsorption but an insertion process, at least for alkanes having more than seven carbon atoms, and is very likely related to the strong adsorption of long-chain normal alkane stationary phases.

Besides, as Fig. 9 shows, the absolute retention volume per mass of substrate, V_s, is exactly proportional to the surface area of the underlying siliceous material over the range from 4 m²/g (Chromosorb P) to 400 m²/g (mesoporous silica of mean pore diameter *ca.* 8 nm). For all these (relatively) large-pore silicas, the retention is a well defined surface process, not influenced by the texture of the substrate, *i.e.*, by diffusion and curvature phenomena influencing the structure of the graft.

The less densely bonded silicas have stronger retention properties (Figs. 2 and 3). However, it is worth noting that for the less densely bonded silicas, as for more
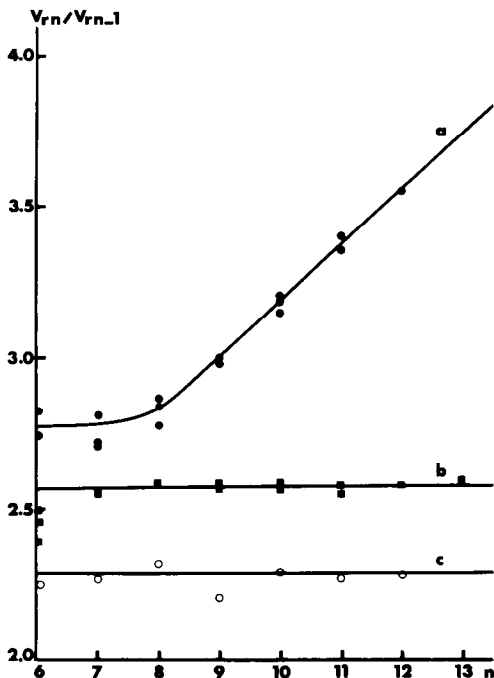

Fig. 8. Ratio of the retention volumes of two consecutive *n*-alkane homologues *versus* the number of carbon atoms on C_{22}-bonded Spherosil XOB 015 (4.3 μmol/m²) at 29.5 (a), 50 (b) and 75°C (c).
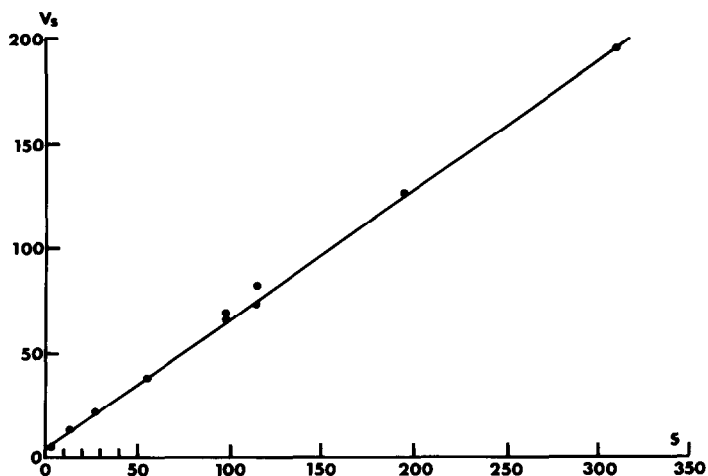
Fig. 9. Absolute retention volume of normal heptane per mass unit of solid substrate, V_s, *versus* the surface area, S, of the substrate for various densely grafted Spherosils at 49.4°C.

microporous substrates (not studied here), as well as for most of the grafts prepared from the classical chlorosilanes, the "liquid-like" state occurs at any temperature.

Above the transition temperature. Returning to Figs. 2 and 3 for the apolar solute heptane, it is possible to see the unexpected and striking independence of the absolute retention volume per mass of substrate, V_s, of the bonding density, at any temperature above the transition, even for very low densities. This is hardly consistent with the description of the high temperature film as a simple "immobilized" liquid stationary phase.

Indeed, GLC retention volumes are rarely proportional to the percentage of stationary phase coated as a monolayer on the support[5,31,32]. The retention normally increases with the percentage of stationary phase or decreases with the progressive deactivation of the support and, in this case, it exhibits a minimum value for higher percentage coatings. However, it never remains constant, as the percentage of coating is multiplied by a factor as large as 100. In addition this constant value is near the retention volume of the silica itself, as Fig. 3 shows.

It is as if the chromatographic process takes place at the silica surface, as soon as the thermal agitation has given a sufficient mobility to the chains to give the solute access to the inorganic material. Apparently the graft plays little part in the retention of an apolar solute even if the silica is covered by 4 μmol/m^2 of docosyldimethylsiloxy groups, *i.e.*, by 14% (w/w) of organic material.

Several experiments have allowed us to test this hypothesis.

(1) If we take a "polar" solute such as benzene, chloroform or even perfluorooctane, the retention is no longer independent of the percentage of the graft, as could be foreseen. The retention decreases with increasing bonding density, as a consequence of the progressive deactivation of the most polar adsorbing sites of the silica (Fig. 10). On the contrary, the retention of the apolar solute heptane is scarcely influenced by the elimination of a few specifically adsorbing groups at the surface of the silica.

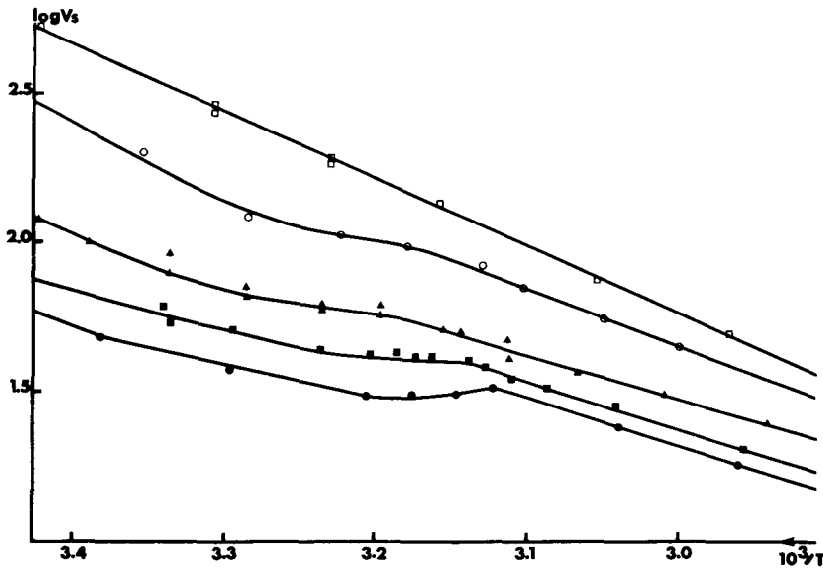(2) If we modify the substrate by trimethylsilylation by means of trimethyl-

Fig. 10. Variation of log V_s with $1/T$ for benzene as solute on C_{22}-bonded Spherosils XOB 075 of various surface densities: ●, 4.4; ■, 3.9; ▲, 3.5; ○, 2.8; □, 1.96 $\mu mol/m^2$.

(dimethylamino)silane ("end-capping"), the retention of benzene (or chloroform) no longer varies significantly with the bonding density (Fig. 11), except on materials of very low densities.

(3) However, the retention of normal heptane on a dense C_8 graft is markedly lower than that on either C_{18} or C_{22} grafts (Fig. 12).

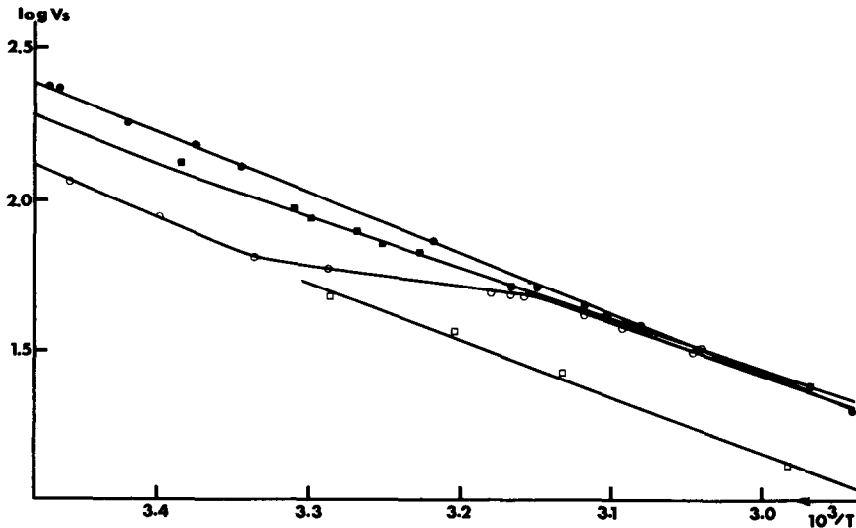Since it is difficult to accept that 14% of the chains bonded to the silica do not

Fig. 11. Variation of log V_s with $1/T$ for benzene as solute on end-capped C_{22}-bonded Spherosils XOB 075 of various surface densities: ○, 3.5; ■, 2.8; ●, 1.96; □, 0.17 $\mu mol/m^2$. Trimethylsiloxy densities are 0.09, 0.52, 1.41 and 3.81 $\mu mol/m^2$ respectively.
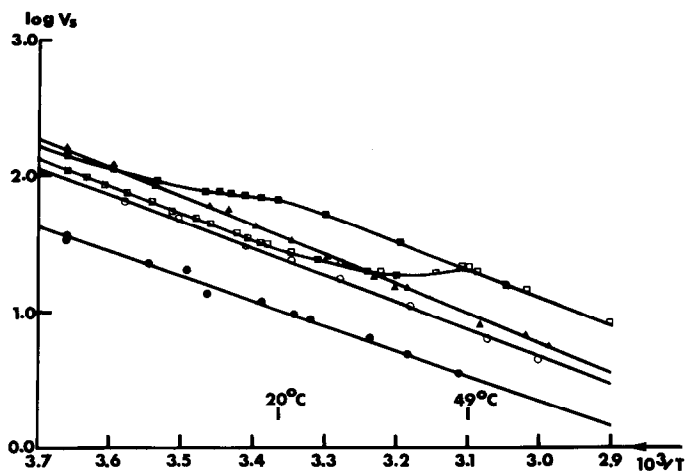
Fig. 12. Variation of log V_s with $1/T$ for normal heptane as solute on Spherosil XOB 015 densely bonded with various alkyldimethyl radicals: ●, trimethyl; ○, propyldimethyl; ▲, octyldimethyl; ■, octadecyldimethyl; □, docosyldimethyl.

participate in the retention of organic molecules, we propose a tentative interpretation of the experimental results, as follows. As for the melting of the normal paraffins themselves[29,30], the transition of the graft leads to the formation of non-planar configurations of the chains. Bent chains are attracted by the substrate and cover the silica with a layer made up of CH_2 groups, the nature of this surface being not strongly dependent on the bonding density. In addition, it is possible that the non-specific interactions of the methylene and siloxane groups are not very different.

Nevertheless, as Snyder et al.[30] pointed out that for paraffins, a linear configuration of short alkyl chains is much more probable. This results in a completely different structure of the layer and a completely different GC retention process.

However, the chromatographic retention on a C_{22}-bonded silica above the transition temperature is a perfectly regular process. A linear relationship between log V_s and n_c is observed (Fig. 8). The retention volume, V_s, is proportional to the surface area of the substrate between 4 and 400 m²/g (Fig. 9).

Finally, these properties may be observed at any temperature (Figs. 2 and 3), if the low density of bonding or the microporosity of the substrate hinders the formation of a dense monolayer characterized by a phase transition. Obviously these conclusions are true only for real monolayers obtained from monofunctional bonding reagents, i.e., for a small proportion of the commercial C_{18} silica packings.

Heneicosane-coated C_{22} alkyl grafts: influence of the bonding density on the properties of the mixed layer

The film at low temperature. All of the above-described grafts, even the less dense ones, when coated by an excess of heneicosane (n-C_{21} paraffin) undergo a characteristic phase transition revealed not only by DSC but by "inverse gas chromatography". For the highest bonding densities (4.0–4.2 mol/m²), this transformation terminates at about 68°C, much higher than the transition of bonded silica at 48°C which disappears, and higher than the melting point of the paraffin at 40°C[6].

In addition, the DSC curves reveal a secondary transition about 6° below the principal peak. As for purely physisorbed paraffin films at the surface of silica[4,5], this secondary transition has been ascribed to the transformation of the part of the monolayer covered by the excess of bulk material in the pores[33].

The existence of a solid film at low temperature is revealed by a phase transition, even for very low bonding densities, if a sufficient quantity of normal alkane has been deposited at the surface of the graft. The borderline case is merely the
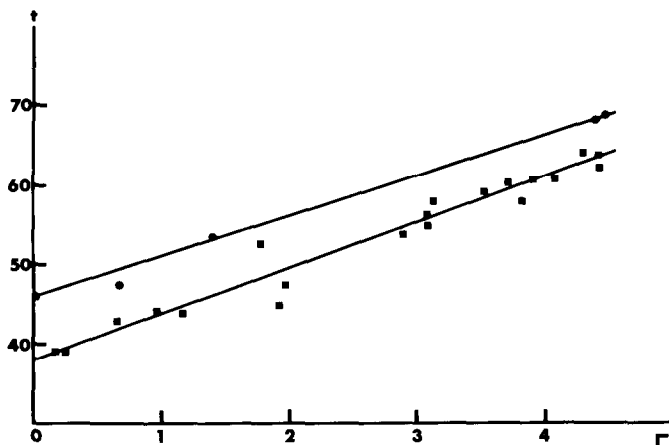
Fig. 13. End-transition temperature, $t(°C)$, *versus* docosyl radical bonding density, Γ, for heneicosane-coated grafted silicas; ●, Spherosil XOB 015; ■, Spherosil XOB 075.

brush-like film of the pure normal paraffin at the surface of the macroporous silica gel, as has been noted in the introduction.

As Fig. 13 shows, for grafts of decreasing density, the end-temperature of the mixed film transition decreases.

In order to measure the molecular area at low temperatures for mixed films obtained from grafts of various densities, we used a method which has proven to be of high precision for films of physisorbed fatty compounds. As explained in ref. 34 (p. 486), we start from the measurement of the amplitude, ΔV_s, of the chromatographic transition corresponding to melting of the small three-dimensional excess of heneicosane (deliberately added) in order to calculate the percentage of heneicosane in the film, τ_f (τ_c in ref. 34). If the molecular area is expressed in nm², the specific surface area of the substrate in m²/g is given by

$$S = N\tau_f A/M_f$$

where M_f is the molecular weight of the inserted paraffin and N is Avogadro's number. As the surface area, S, is known from BET measurements on the non-bonded silica, the same formula allows the determination of the molecular area, A, of the paraffin in the film. However, in the present case, the bonded alkyl chains have to be taken into account for the measurement of the global "molecular" area of all the alkyl chains.

Fig. 14 shows the molecular area of heneicosane-saturated mixed layers as a function of the C_{22} bonding density. All the dense grafts have the characteristic 0.21
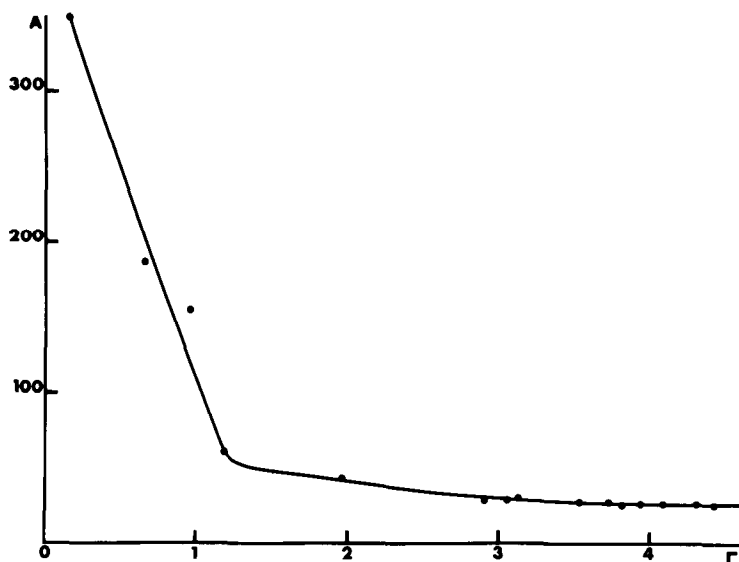
Fig. 14. Molecular area, A, of heneicosane-saturated mixed layers *versus* the C_{22} bonding density for Spherosil XOB 075 as substrate.

nm^2 area of the solid two-dimensional phases of polar fatty compounds, which corresponds to the highest possible compactness of the fatty chains (about 8 μmol/m^2). However, as soon as the density of the bonded layer falls below 2 μmol/m^2, the molecular area of the mixed layer increases considerably.

It is difficult to imagine that a homogeneous film, less dense than a laid out, flat monolayer of heneicosane (about 160 nm^2 from published data for normal octane[35]), could undergo a phase transition. Therefore it must be admitted that the film is not continuous and that it comprises a few aggregates of heneicosane around the broadly scattered C_{22} grafts (Fig. 15). This may be compared with the existence of phase transitions for submonolayer films of normal paraffins at the surface of non-bonded siliceous supports[4].

End-capped C_{22}-bonded silicas do not lead to different mixed films, as regards the thermal and chromatographic properties. This reflects the crucial rôle played by the interactions between the chains in the stability of the films. In addition, even in the absence of a trimethylsilylation, the silanols of the silica are perfectly dissimulated to the solute by the (8 μmol/m^2) bonded layer. This situation permits interesting applications in liquid chromatography, as we have shown elsewhere[19].

Contrary to the grafted alkyl films, the transition enthalpies of the mixed layers
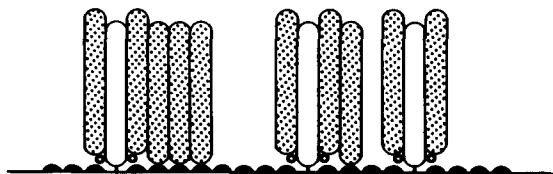

Fig. 15. Sketch of a mixed layer comprising aggregates of alkane molecules around broadly scattered alkyl grafts (see Fig. 1).

TABLE III

TRANSITION ENTHALPIES OF HENEICOSANE-COATED C_{22}-BONDED SILICA MIXED LAYERS

No excess of bulk material and hence no secondary transition

C_{22}-silica	Pore diameter (nm)	Enthalpy (J/g)
XOB 075	30	148
XOB 015	125	174
Free heneicosane (incl. polymorphic transition)		217

are not too different from the enthalpy of melting of heneicosane (Table III). However, even for our two large-pore silicas, the heat of transformation appears to be slightly affected by the surface curvature of the substrate, in agreement with the recent measurements of André[10].

In addition, since the transition of the C_{22}-chemisorbed layer disappears upon coating, the participation of the bonded chains in the transition of the mixed layer is obvious. Therefore, the above-mentioned estimations of the enthalpies obtained by dividing the experimental heat by the mass of heneicosane in the film are questionable. Lastly, molecular area measurements on the "melted" film have revealed the complexity of the mixed-film transition as we shall now show.

The mixed layer in the transition temperature range and above the transition temperature: the nature of the transition. The method of determination of the film's molecular area used below the transition temperature is inapplicable, because there is no means of distinguishing the monolayer and the bulk phase directly, starting from their retentions.

Following the same method as for purely physisorbed films[4], we coated the same densely bonded C_{22}-silica (4 μmol/m^2) with various percentages, τ, of heneicosane (in g of paraffin per g of raw substrate). The linear function $V_s/\tau = f(1/\tau)$ is normally used in GC to determine the true specific retention volume, V_g, free from adsorption effects, by extrapolating to τ_∞[36]. However, this function is also characterized by changes in slope which may reveal the existence of different monolayers, their retention volumes and their molecular areas[5].

Fig. 16 shows this function for Spherosil XOB 015, coated with various percentages of heneicosane at 40 and 68°C. It is seen that there are angular points corresponding to pure monolayers having limited molecular areas (compact monolayers) separated by segments representing an equilibrium between these layers. At the melting point of heneicosane (40°C), two sorts of film appear, having molecular areas of 0.30 and 0.21 nm^2, respectively (Fig. 16). They are in equilibrium in the absence of a three-dimensional excess.

Examination of the log V_s, *vs.* $1/T$ curves for grafts differently loaded with heneicosane sheds some light on the nature of these phenomena. Starting from a pure bonded silica (transition at 48°C), if the paraffin is progressively added, the initially deposited molecules insert themselves into the graft, gradually modifying its properties. This results in a shift of the transition of the bonded silica (Fig. 17a) to higher temperatures (curves b and c). When the chains have a molecular area of 0.30 nm^2,
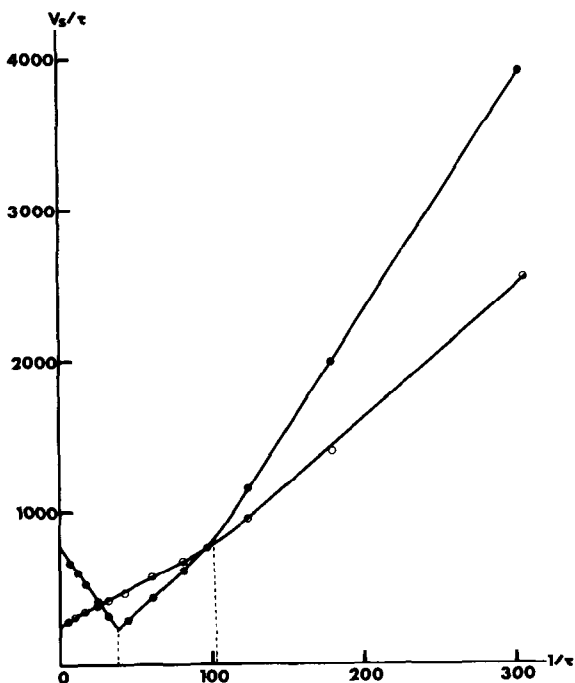
Fig. 16. Plots of V_s/τ versus $1/\tau$ for the C_{22}-bonded Spherosil XOB 015 (4.4 $\mu mol/m^2$) at 40°C (●) and 68°C (○). The solute is n-heptane. τ is expressed in g of heneicosane per g of grafted silica. The values of the abscissa at the angular points enable the calculation of the molecular areas of the monolayers; the corresponding values of the ordinate give the retention volumes. The intercepts with the V_s/τ axis yield the classical (three-dimensional) specific retention volume, V_g.
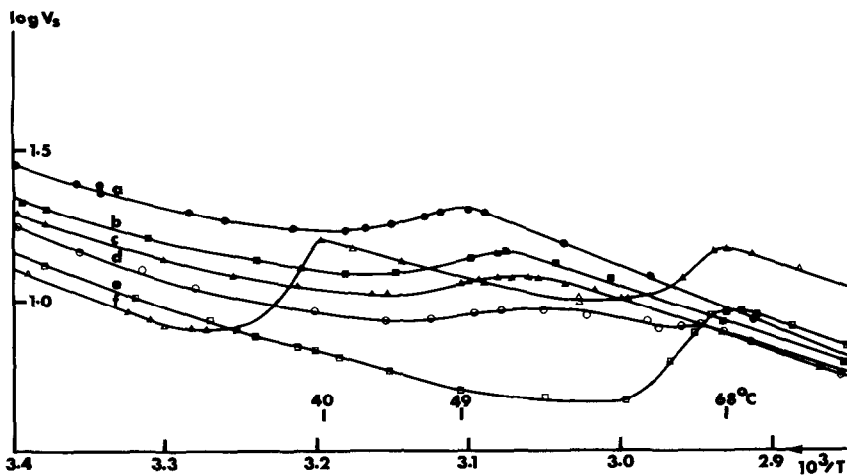

Fig. 17. Variation of log V_s with $1/T$ for n-heptane as solute on C_{22}-bonded (4.4 $\mu mol/m^2$) Spherosil XOB 015 for pure bonded silica (a) and for bonded silica coated with various percentages of heneisocane; 0.33 (b), 0.56 (c), 0.80 (d), 1.64 (e) and 2.03% (f).

this trend ceases. Another transition appears at 68°C (curve d) and gradually becomes dominant. When the global molecular area is 0.21 nm², there is no other film transition. If a further quantity of heneicosane is added, it appears on the curves as a three-dimensional excess, characterized by a melting transition at 40°C (curve e).

At 68°C, the transition temperature of the dense mixed film, there is only one break in the linear plot of V_s/τ *vs.* $1/\tau$) (Fig. 16). This corresponds to a chain molecular area of 0.30 nm². As the area below the transition temperature is 0.21 nm², we may conclude that, as for physisorbed layers[4], the phase transition results in the ejection of part of the inserted paraffin in the pores as a capillary condensate.

The observed phenomena are not so sharp with the smaller pore substrate XOB 075 (curves not shown). The curvature of the pores as well as the nature of the silanols lead to the formation of less dense films. The transition ends 4° lower than it does on Spherosil XOB 015, and the molecular area measured at low temperature is 0.24 instead of 0.21 nm². One may suppose that the low temperature film is inhomogeneous. The regular solid film (area 0.21 nm²) is interrupted by liquid-like areas, where the curvature of the substrate is too pronounced to allow the formation of a regular layer.

Nevertheless, the molecular area of the film above 64°C remains 0.30 nm². Consequently, the transition again results in the ejection of a (smaller) part of the heneicosane in the pores.

CONCLUSIONS

The long-chain alkyl phases bonded at the surface of silicas and diatomites are often considered as simple "immobilized" stationary phases. In reality, as far as the well defined layers obtained from monofunctional reagents are concerned, they have very unusual gas chromatographic properties. Above the phase transition, for all of the solutes, the specific or non-specific adsorption properties of the underlying, partially deactivated, substrate play a significant part in the retention.

Below the phase transition, retention is a complex process in which the adsorption on the layer or the insertion in the layer dominates according to the solute. However, for normal alkane solutes, the usual laws of gas chromatography are not obeyed.

Most of the commercial materials have narrow pores and "liquid-like" films at any temperature. For real monomeric films, on macroporous materials which undergo a phase transition, our experiments using various techniques show that this concept is valid. However, this "liquid" is a bonded liquid having very special solvent properties.

In practice, the influence of the phase transition is more important in HPLC, because, with the C_{18}-bonded silicas, this phenomenon takes place at the usual room temperatures[6].

The alkane-treated alkyl-bonded phases have very special properties, but their shifted phase transition is more similar to a melting phenomenon, and the GC retention at their surface is more like a regular adsorption or a solubility retention process. Nevertheless, the transition is a complex phenomenon which is accompanied by the ejection of about half the paraffin as bulk material in the pores. In addition, a secondary transition reveals the existence of two kinds of films in heavily loaded grafted silicas.

These new materials with extremely dense and regular monolayers (8 μmol/m^2), have promising applications[19]. Below the transition temperature, they will be the first modified silicas for which access of a solute to the underlying silanols is absolutely impossible at the low temperatures in normally employed HPLC.

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