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GAS CHROMATOGRAPHIC EVIDENCE FOR PHASE TRANSITIONS IN VERY COMPACT OCTADECYL BONDED SILICAS

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SUMMARY

Evidence has been found for fusion-like transitions in either the bonded material alone or the composite phase obtained after coating with heptadecane upon gas chromatography of a volatile solute using very compact C_{18}-bonded silicas as stationary phases near room temperature. Such phenomena may be important for the interpretation of the frequently observed irreproducibilities of properties of materials used in liquid chromatography.

INTRODUCTION

In spite of the success of C_{18}-bonded silicas in liquid chromatography, the irreproducibility of the capacity factors and selectivities obtained by using these materials as stationary phases makes it impossible to identify significant compounds on the basis of the published chromatographic data[1,2].

An enormous amount of work[3–14] has been carried out in an attempt to explain the influence of structure and texture parameters of silicas as well as of the nature of the bonding reagent on chromatographic retention data. In the accompanying discussion on the nature of chromatographic retention, adsorption[4,5,10], solubility[12,14] or mixed[8,13] mechanisms have been invoked.

Confusion in the field of bonded silicas has arisen from the use of too many parameters in some studies. We have tried to simplify the problem as follows:

(1) By using gas chromatography (GC) we eliminate the influence of the solvent on the physical state of the fatty chains. However, unlike other authors[7] who chose this type of chromatography, we do not carry out any secondary treatment after the high efficiency bonding of the C_{18} chains. Most of the test solutes employed are alkanes.

(2) Our bonding reagent is monofunctional. The use of di- or trifunctional reagents, as is general, may result in the formation of polymers if there is the slightest trace of water. In addition, polyfunctional reagents are not advantageous for eliminating silanol groups, and may in fact create other such groups and lead to chemisorbed materials, the structure of which is irreproducible.

(3) Wide pore silicas are used in order to eliminate the influence of pore

curvature on the structure of the chemisorbed layer, and the resistance to access of the bonding reagent and the chromatographic solute. However, we also use a series of less macroporous silicas, which allows a study of the influence of pore size.

Preparation of very densely covered C_{18}-bonded silicas by Kováts' techniques[15] and application of the methods elaborated in our laboratory for studying phase transitions of physisorbed monolayers[16,17] allow us to study transformations of the bonded layer recently evidenced by contact angle measurements[18].

Taking advantage of the above simplified conditions we have observed the existence of phase transitions concerning either the bonded material alone or the bonded material coated with heptadecane as stationary phase.

Use is made of the so-called "inverse gas chromatography" in which the retention volume of a more or less arbitrarily chosen test solute is studied as a function of physical parameters, particularly temperature.

EXPERIMENTAL

Substrates

Spherosil beads (Rhône Poulenc, Paris, France) (100–200 μm diameter) and untreated Chromosorb P granules (180–250 μm) (Johns-Manville, Denver, CO, U.S.A) were used. The specific surface areas of the substrates were measured in this laboratory by a BET nitrogen adsorption method[19]. These values and the mean pore diameters given by the suppliers are reported in Table I.

TABLE I

PHYSICAL DATA FOR THE BONDED MATERIALS AND THEIR SUBSTRATES

	Chromosorb P	Spherosils				
		XOC 005	XOB 015	XOB 015*	XOB 030	XOA 200
Specific surface area	4.06	13.55	27.7	27.7	55.3	174
Mean pore diameter (nm)	1000	300	125	125	60	15
Bonded C (%)	0.45	1.32	2.77	2.74	5.56	14.13
Percentage $C_{18}H_{37}(\tau)$	0.48	1.42	3.03	2.99	6.32	18.23
Molecular area (nm²)	0.36	0.40	0.38	0.39	0.37	0.40

Bonding process

The bonding reagent is octadecyldimethyl(dimethylamino)silane (II). First octadecyldimethylchlorosilane (I) was prepared by hydrosilylation of 1-octadecene using dimethylchlorosilane in presence of chloroplatinic acid[20]. The reagents were Fluka (Buchs, Switzerland) products. This reaction was carried out under a flow of dry nitrogen (quality U, L'Air Liquide, Paris, France). The cooler was swept by a stream of isopropanol at $-10°C$ for the reagent volatility. After 18 h infrared spectroscopy showed that all of the octadecene had disappeared. The resulting product was distilled at 155–160°C and $5 \cdot 10^{-3}$ Torr.

Compound I was then treated with dimethylamine in redistilled hexane (kept over sodium), according to Kováts[15]. The resulting reagent (II) was distilled at 143–145°C and $2 \cdot 10^{-3} - 3 \cdot 10^{-3}$ Torr. Its composition was controlled by acidimetry.

The bonding process has been described by Kováts[15]. It involves drying the

silica at 140°C under vacuum for 24 h, coating the substrate in hexane as solvent in the absence of water and treatment at 140°C under dry nitrogen for 18 h. Excess of reagent is eliminated by washing with ether. The silanizing treatment is repeated at least once.

The percentages of bonded carbon were determined by the Service d'Analyse du CNRS, and converted into mass of octadecyl radical per unit mass of substrate, τ (Table I). The contribution of the two methyl groups directly bonded to silicon was subtracted.

Gas chromatography

Most of the apparatus has been described previously[16,17]. In addition a platinum resistance thermometer with digital readout (A.O.I.P) was used for measurement of column temperature, and a flame ionization detector (GIRDEL) which allows the use of sample sizes of 10–100 ng. Such small samples do not modify the physical state of the bonded material used as stationary phase (2–3 g).

The solutes were "pure" commercial products, with the exception of the fluorocarbons kindly supplied by Produits Chimiques Ugine Kuhlmann, Pierre Benîte, France. The columns were of 4 mm I.D. and 30 cm length. Flow-rates were measured with a thermostated soap-bubble flow-meter after disconnecting the detector, or by interpolation.

RESULTS AND DISCUSSION

C_{18}-bonded uncoated silica columns

Figs. 1 and 2 show the logarithm of the absolute retention volume of hexane per unit mass of substrate, V_s, as a function of the reciprocal of the temperature, $1/T$, for four silicas and a Chromosorb.

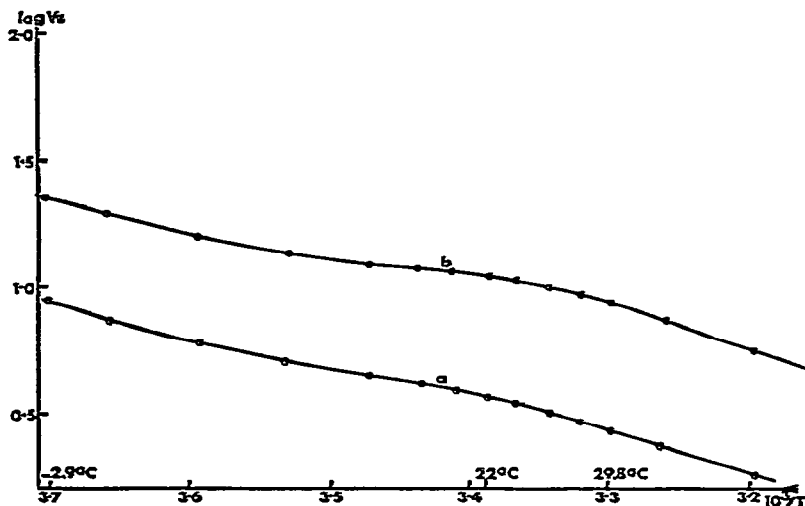Between about 7 and 27°C the diagrams deviate from the normal linear

Fig. 1. Variation of log V_s with $1/T$ for n-hexane as solute on a C_{18}-bonded Chromosorb P (a) and a C_{18}-bonded Spherosil XOC 005 (b).
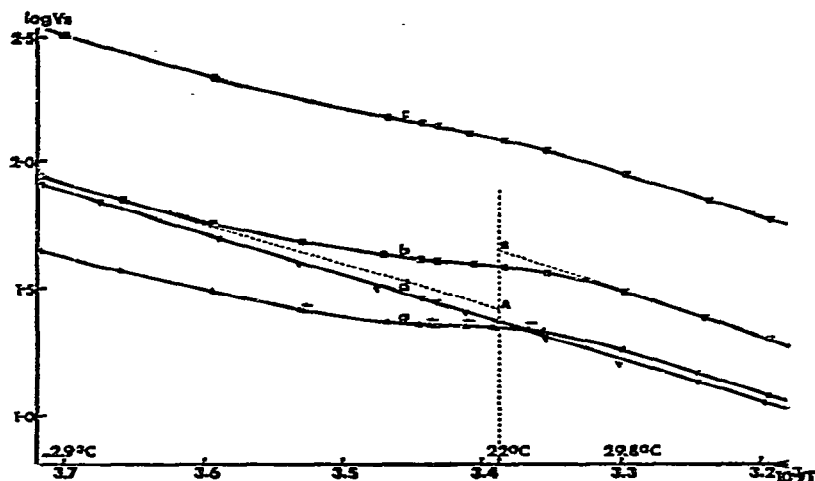
Fig. 2. Variation of log V_s with $1/T$ for n-hexane as solute and C_{18}-bonded Spherosils: a, XOB 015 (normal sample); b, XOB 030; c, XOA 200; d, XOB 015 (aberrant sample).

decrease found in both gas–solid and gas–liquid chromatography, except when a stationary phase transformation modifies the number and nature of the retention sites. An example of such a deviation from linearity is given by the monolayers of long-chain n-paraffins and fatty alcohols at the surface of hydroxylated substrates such as silicas[16,17] (Fig. 3). In this case we demonstrated unambiguously that the curve deviation corresponds to a transition of a monolayer from a condensed state of 0.21 nm² molecular area to a "liquid expanded" state of 0.27 nm² molecular area, 4–40°C above the ordinary three-dimensional melting point of the deposited compound. These transitions are clearly brought out by differential thermal analysis (DTA)[21]. In the case of films on the surface of the water used as chromatographic substrate[22], these transitions take place exactly at the temperatures known from experiments with the film balance. In addition the molecular areas are the same.
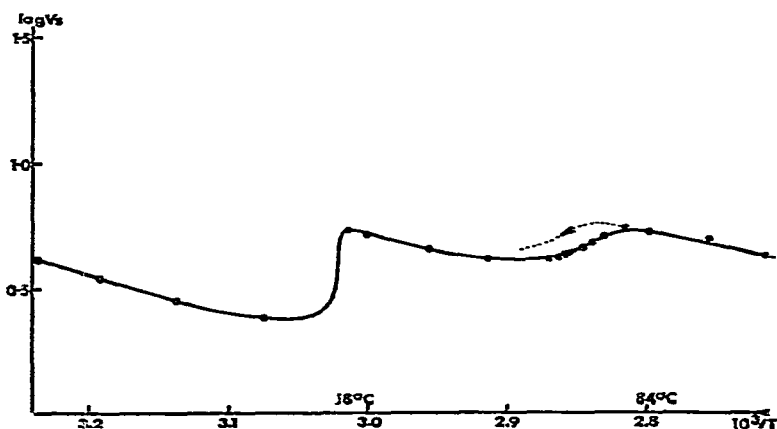

Fig. 3. Variation of log V_s with $1/T$ for n-heptane as solute and 7.53% of octadecanol on Spherosil XOB 015.

It is known that, for reasons of molecular structure[23], alkylsilanes as bonding reagents do not allow the formation of as compact layers as monofunctional fatty compounds at the surface of water or silica. Our results confirm this (Table I). However the area that we obtain (0.36–0.40 nm^2) is very low for C_{18}-bonded silicas, and corresponds to the bonding of 4.13–4.63 μmoles/m^2.

In spite of these differences it is not possible to interpret the increasing retentions in Figs. 1 and 2 differently than for fatty alcohol films: on heating a phase transition gives the solute access to new retention sites. Analogy with the physically adsorbed fatty layers suggests that the phenomenon is related to the fatty radicals and is a type of melting. Kováts' experiments by DTA support this interpretation[24]. However, chromatography throws some light on the real nature of the phenomenon:

(1) The perfect reversibility of the transition is shown in Fig. 2a, where the points obtained on decreasing the temperature have been marked by an arrow. Although a little hysteresis effect has been observed with physisorbed fatty compounds films[25], in this case the irreversibility may be explained quite normally by a capillary effect: melting of the film results in an increase of the molecular area and consequently an ejection of bulk material into the pores.

The impossibility of such a capillary loss accounts for the perfect reversibility observed in the case of bonded layers. This reversibility invalidates any explanation of the transition based on a modification of the silica surface.

(2) Dividing absolute retention volume by the mass of the bonded chain (each per unit mass of substrate) gives the specific retention volume of the chemisorbed layer:

$$V_g = V_s/\tau$$

Values of V_g from which the contribution of the underlying substrate is not excluded are reported in Table II for two temperatures, -2.9 and $29.8°C$, respectively below and above the transition.

TABLE II

SPECIFIC RETENTION VOLUMES (cm^3/g) OF HEXANE IN C_{18}-BONDED LAYERS AND OCTADECANE

| | Chromo-sorb P | Spherosils | | | | | V_g in octadecane |
		XOC 005	XOB 015	XOB 015*	XOB 030	XOA 200	
$V_s/\tau_{C_{18}H_{37}}$ at $-2.9°C$	1851	1569	1430	2525	1316	1730	1860
$V_s/\tau_{C_{18}H_{37}}$ at 29.8°C	560	595	596	540	492	512	400
$(\Delta V_s)_t/\tau_{C_{18}H_{37}}$ at 22°C	322	361	373	0	267	251	560

It appears that at the higher temperature all the V_g values are higher than the specific retention volume of the solute (hexane) in octadecane (last column). On the other hand, at $-2.9°C$ they are all more or less lower (except for the sample marked by a star, see below). This observation supports the occurrence of an adsorption at the

extremities of the chains below the transition, and the insertion of the solute between the fatty chains above the transition.

However, this type of "solubility" in a "melted" film need not be similar to that in a bulk liquid. In compact liquid-expanded films of fatty alcohols, the retention volumes of alkanes are lower than V_g in a bulk liquid[26], but may be much larger in a non-compact film[22].

This situation would seem to be similar to that of the bonded chains as a consequence of the relatively large area occupied by each alkyl radical. However, it should not be forgotten that "solubility" in a fatty monolayer depends to a large extent on the compactness of the chains, even in the absence of a residual influence of the substrate.

(3) The occurrence of the transition is not necessarily linked to the use of an alkane as solute: Fig. 4 shows a similar phenomenon with toluene and tetrachloroethylene as solutes on a bonded Chromosorb P. However, it is worth noting the inversion of the solute order in the chromatogram across the phase transition. But the perfluorodecane retention volume exhibits little deviation from the linear relationship (log V_s, $1/T$), in accordance with the low miscibility of hydrocarbons and fluorocarbons.
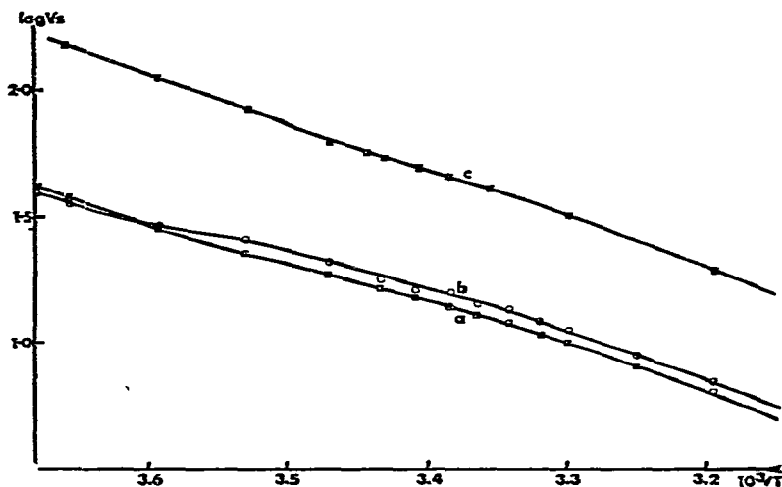

Fig. 4. Variation of log V_s with $1/T$ for toluene (a) and tetrachloroethylene (b) as solute on C_{18}-bonded Chromosorb P and for perfluorooctane (c) as solute on C_{18}-bonded Spherosil XOB 030.

All these observations support the existence of a type of crystallized state of the chemisorbed radicals at low temperatures, resulting from a marked tilting of the chains toward the surface. This state of the organic material is not very different from the model of aggregates proposed by Löchmuller and Wilder[13], as a result of the solvophobic interaction in reversed-phase liquid chromatography. However, because of the analogy with physisorbed phases, we prefer a more regular model of tilted chains.

(4) As shown by Figs. 1 and 2, for Spherosils of decreasing pore size, the transition becomes less marked. In the last line of Table II the values of $(\Delta V_s)_t/\tau$ support this observation: $(\Delta V_s)_t$ (= antilog B — antilog A) is the increase of the retention volume across the transition, calculated by extrapolation of the linear parts of Fig. 2b at 22°C[16]. $(\Delta V_s)_t/\tau$ is the retention volume corresponding to the sites created by the transition. It decreases continuously from the macroporous XOC 005 to the mesoporous XOA 200. The large curvature of the small pores would seem to impede crystallization of the chains: most of the layer remains in the "liquid" state at low temperature.

This is probably the explanation for the solution–dominated retention of most of the commercial alkyl-bonded silicas, prepared from high surface area substrates for high-performance liquid chromatography (HPLC), except when the hydrophobic action of the solvent results in aggregation of the chains.

Columns made from C_{18}-bonded silica coated with heptadecane

The C_{17} n-alkane was chosen as the coating stationary phase because of the impeding effect of the two methyl groups bonded per octadecyl chain.

Fig. 5 shows log V_s as a function of $1/T$ for heptane as solute and different percentages of heptadecane on C_{18}-bonded Spherosil XOB 015. Two new transitions can be seen. These are appreciably more abrupt than the preceding one (without heptadecane) and extend over about 5°C ending in a steeper increase at a temperature which we will use to designate the phenomenon. The transition at 22°C, the melting point of heptadecane, is easily explained by melting of a part of the deposited alkane which has remained in the three-dimensional state in the pores. The transition at 51°C, like the preceding one, cannot be interpreted other than by a phenomenon giving the solute access to new retention sites. Occurring at a much higher temperature than the melting point of heptadecane in bulk, this phenomenon is necessarily connected with the transformation of a film. Similarly, physisorbed films of octadecanol
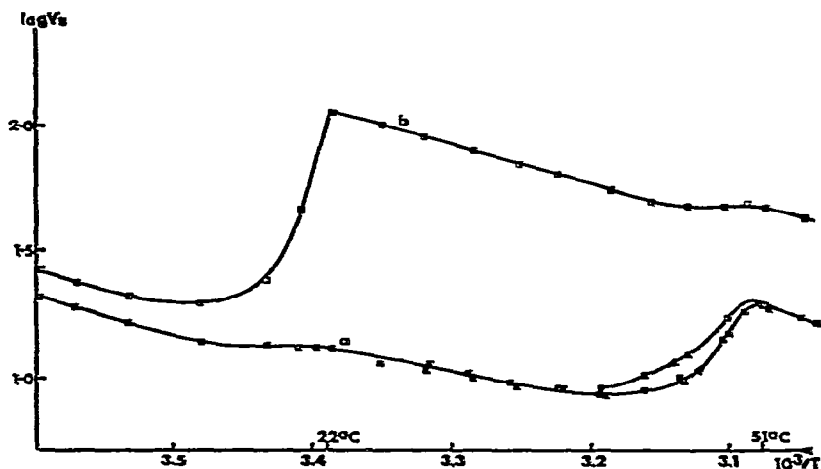

Fig. 5. Variation of log V_s with $1/T$ for n-heptane as solute and 3.78% (a) and 7.75% (b) of hepta decane on C_{18}-bonded Spherosil XOB 015 (normal sample).

or docosane melt at appreciably higher temperatures than the corresponding bulk materials[16].

Riedo et al.[18] studied contact angles of n-paraffins with alkyl-bonded glass capillaries, and demonstrated the penetration of the longest bonded chains by the long-chain alkanes and the melting of a "soaked" phase, a mixed phase physisorbed and chemisorbed at the same time. We have no reason to doubt that we are confronted with the same phenomenon in gas chromatography, in spite of the slightly higher temperature of the transition in our experiments with a somewhat different substrate.

However, GC makes it possible to go further in the analysis of this phenomenon.

(1) It is easy to evaluate the proportion of heptadecane inserted in the chains (per unit mass of bare silica) and consequently to determine the molecular area of all of the fatty chains (physisorbed and chemisorbed). We start by evaluating the proportion (or percentage), τ_{trld}, of heptadecane in bulk, from the amplitude of the transition at 22°C (see preceding paragraph and ref. 16)

$$\tau_{trld} = (\Delta V_s)_t / V_g$$

where V_g is the specific retention volume of the solute in heptadecane at 22°C (determined independently).

If the proportion of deposited heptadecane, τ (in mass per unit mass of non-bonded silica) is known, it is easy to calculate by difference the proportion of heptadecane inserted in the chemisorbed chains:

$$\tau_{film} = \tau - \tau_{trld}$$

If the loading of octadecyl radicals is also known (by carbon measurement and calculation, taking into account the two bonded methyls which do not belong to the chains), it is possible to sum the masses of all the fatty chains in the mixed phase per gram of substrate. If the specific surface area of the silica is also known, we can calculate the molecular area of the "soaked" phase. We find 0.21 nm² per chain.

This is typically the molecular area of a compact condensed phase, and has been known for a long time for monofunctional fatty compounds at the surface of water. Thus, the transition at 51°C represents the melting of a very solid mixed phase, that is to say its transformation into a liquid-expanded phase of higher molecular area (see 2 below). As has already been said, this must result in the ejection of bulk heptadecane and consequently in a hysteresis effect. We did observe such an effect (Fig. 5a).

(2) Chromatography allows the study of "undersoaked" phases, i.e., those with a heptadecane deficiency (Fig. 6). For very small heptadecane loadings (Fig. 6b) the wide transition observed at low temperature with the bonded phase alone (see Fig. 2 or Fig. 6a) is only shifted towards higher temperatures. This observation provides some support for our interpretation of the experiments without heptadecane.

However, for slightly higher percentages of heptadecane (Fig. 6c) a further transition appears very clearly at 51°C. But there is no transition at 22°C that could reveal the presence of bulk heptadecane. The limiting loading between these two situations corresponds approximately to the percentage of alkane in Fig. 6b, i.e., to an area of 0.30 nm² per molecule. This is typically the molecular area of a liquid-expanded fatty two-dimensional phase.
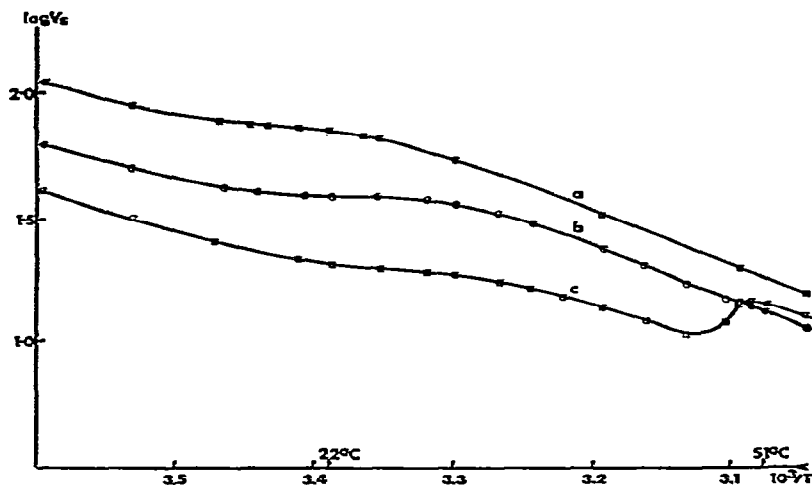
Fig. 6. Variation of log V_s with $1/T$ for n-heptane as solute and uncoated C_{18}-bonded Spherosil XOB 015 (a) (normal sample, *cf.*, Fig. 2a), 0.58% (b) and 1.24% (c) of heptadecane on C_{18}-bonded Spherosil XOB 015 (normal sample).

The case of an aberrant bonded silica

Our bonding method appears reliable. Only occasionally does it lead to materials with properties differing from those described above. But examination of such an abnormal sample is by no means uninteresting. The sample described below is a Spherosil XOB 015 that was C_{18}-bonded at a somewhat higher temperature (180°C).

(1) The percentage of carbon in the aberrant bonded silica is hardly lower than for a normal sample of the same substrate (Table I, sample marked by star).

(2) No GC transition appears in the uncoated stationary phase (Fig. 2d). However, the specific retention volume of the organic layer above the transition temperature for this sample and for a normally bonded one may be compared. At −2.9°C the retention volume is abnormally high. It is even higher than the retention volume in normal octadecane at this temperature: an aberrant bonded material is an uncrystallizable one.

(3) If the sample is coated with heptadecane, there is no transition at 51°C. Only the melting of bulk heptadecane at 22°C can be seen. However, the evaluation of the percentage of heptadecane responsible for this transition shows that a significant quantity of alkane is inserted in a layer, but that it is insufficient to form a compact monolayer.

Our purpose is not to discuss the cause of the disorder in the bonded layer, which seems to be the origin of the inability of this sample to "crystallize". But we suggest that the curve (log V_s, $1/T$) could be used to control the regularity of the bonding reaction.

CONCLUSIONS

(1) Gas-phase chromatography of a test solute shows a phase transition for densely covered octadecylsilylated silica.

(2) It also shows other transitions for the mixed physisorbed and chemisorbed phase obtained by coating the C_{18}-bonded material with heptadecane.

In this manner we have confirmed and added further precision to Kováts' observations using other techniques, emphasizing analogies and differences between these phenomena and the transitions of physisorbed phases.

(3) These observations suggest that the irreproducibilities of retention data and selectivities observed from one sample to another may for a large part be linked with changes in the physical state of the chemisorbed phase under the influence of temperature, curvature of the pores or the "hydrophobic" effect of the solvent. A recent observation by Little et al.[27] on the rather different properties of C_{18} and C_{22} alkyl-bonded materials could substantiate our point of view. We are pursuing our work with the aim of verifying this interpretation.

(4) Near room temperature, chromatography on a C_{18}-bonded material is probably never a pure adsorption phenomenon. But sorption in a liquid-expanded monolayer is not to be confused with the solubility in a bulk liquid.

(5) We suggest that curve (log V_s, $1/T$) be used to characterize the quality of a long-chain alkyl-bonded silica.

ACKNOWLEDGEMENTS

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