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Note

Influence of the liquid chromatographic mobile phase on the phase transitions of alkyl-bonded silicas studied by gas chromatography

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Using gas chromatography of a test solute, we previously demonstrated a phase transition for a densely grafted C_{18} silica in the usual temperature range of separations by reversed-phase liquid chromatography[1]. More recently, Kessaissia *et al.* found a similar transition at cryogenic temperatures for alcohols chemisorbed at the surface of silica by the same method[2].

In the previous paper, we suggested that the hydrophobic pressure of the solvent could increase the transition temperature and that such a phenomenon would complicate the often discussed problem of retention by reversed-phase liquid chromatography. This paper supports this hypothesis by means of "inverse" gas chromatographic experiments in which the bonded material is covered with different stationary phases.

In addition, the use of a C_{22} alkyl chain in place of a C_{18} chain leads to more abrupt transitions and sheds some light on the critical influence of the chain length in the chromatographic applications of these materials.

EXPERIMENTAL

The preparation of densely covered alkyl-silicas by means of alkyldimethyl(dimethylamino)silanes according to Kováts' technique[3] has already been described[1]. The intermediate reagent docosyldimethylchlorosilane is distilled at 185°C and $5 \cdot 10^{-3}$ Torr. Docosyldimethyl(dimethylamino)silane is distilled at 185°C and $3 \cdot 10^{-3}$ Torr. The so-called "inverse" gas chromatographic technique using an auxiliary solute and a suitable chromatograph has also been described in earlier papers[1,4].

The stationary phases were commercial products: ethylene glycol (purissimum grade) and *n*-heneicosane (purum grade) from Fluka (Buchs, Switzerland), and glycerine (doubly distilled), triethylene glycol (for synthesis grade) and squalane (for gas chromatography grade) from Merck (Darmstadt, G.F.R.).

The silica substrate was Spherosil XOB 015 beads (100–200 μm diameter) from Rhône-Poulenc (Paris, France), with a specific surface area of 27.7 m^2/g (ref. 1). The percentage of bonded carbon was determined by the Service d'Analyse du CNRS (Solaise, France) and corresponded to the coverage of the surface by 4.35 $\mu mol/m^2$ of $C_{22}H_{45}$ radicals.

RESULTS AND DISCUSSION

C_{22} bonded uncoated silica column

Fig. 1a shows the logarithm of the absolute retention volume of heptane per unit mass of substrate (V_s) as a function of the reciprocal of the temperature ($1/T$) for the C_{22} bonded Spherosil. As for the C_{18}-bonded Spherosil (ref. 1 and Fig. 1b), the line deviates from the linearity usual in both gas–solid and gas–liquid chromatography, except when a stationary phase transformation modifies either the number or the nature of the retention sites.

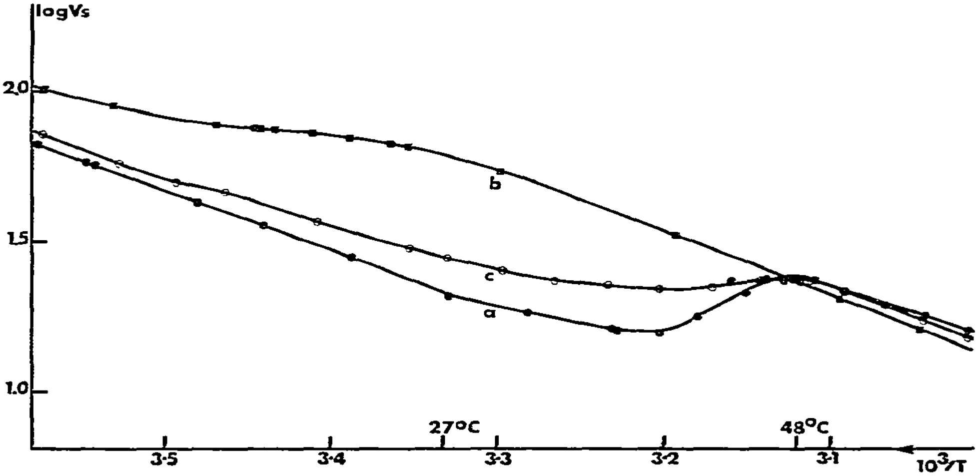

Fig. 1. Variation of log V_s with $1/T$ for *n*-heptane as solute: (a) on C_{22}-bonded (4.32 µmol/m^2) Spherosil XOB 015, (b) on C_{18}-bonded Spherosil XOB 015 (1) and (c) on a less densely (4.18 µmol/m^2) C_{22}-bonded Spherosil XOB 015.

However, for C_{22}-bonded silica the phenomenon is characterized by an overall increase in the retention volume in a limited range of temperature between 40 and 48°C, instead of the limited broad inflection of the curve between 7 and 27°C observed for the C_{18}-bonded material. Thus, better than the results with the C_{18} silica, the new experiments suggest an analogy of this transformation with the condensed phase–expanded phase monolayer transitions of fatty compounds physisorbed at the surface of polar substrates[4–6]. In both instances the increase in retention with increasing temperature is a consequence of a change which gives the solute access to the inner part of the alkyl layer.

These results substantiate the observations of Little *et al.*[7] of the different chromatographic properties of C_{18} and C_{22} alkyl-bonded materials. These differences may result from the physical state of the chains.

However, the marked character of the transition depends critically on the bonding density. If this density is reduced from 4.32 to 4.18 µmol/m^2, the amplitude of the gas chromatographic transition becomes much more limited (Fig. 1c).

Columns of C_{22} bonded silica covered with various liquids

Glycol stationary phases. As Fig. 2a shows for glycerine, the most striking

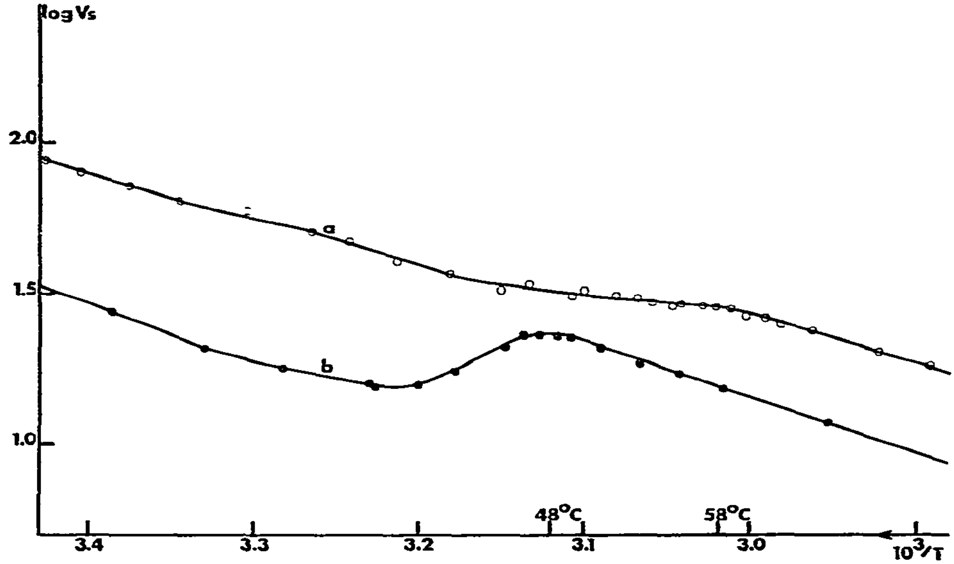

Fig. 2. Variation of log V_s with 1/T for *n*-heptane as solute and (a) 8.9% of glycerol on C_{22}-bonded Spherosil XOB 015 and (b) for uncoated C_{22}-bonded Spherosil XOB 015.

feature with these coated bonded phases is the marked increase in the end-temperature of the transition. In addition, this shift is only large for strongly associated stationary phases (end temperature of the transition: 58°C for glycerine, 57°C for ethylene glycol, 49°C for triethylene glycol). Changes in the ordinate of the curves could easily be ascribed to the retention by the coating stationary phases themselves.

Replacement of glycerine with a glycerine–water mixture does not result in an

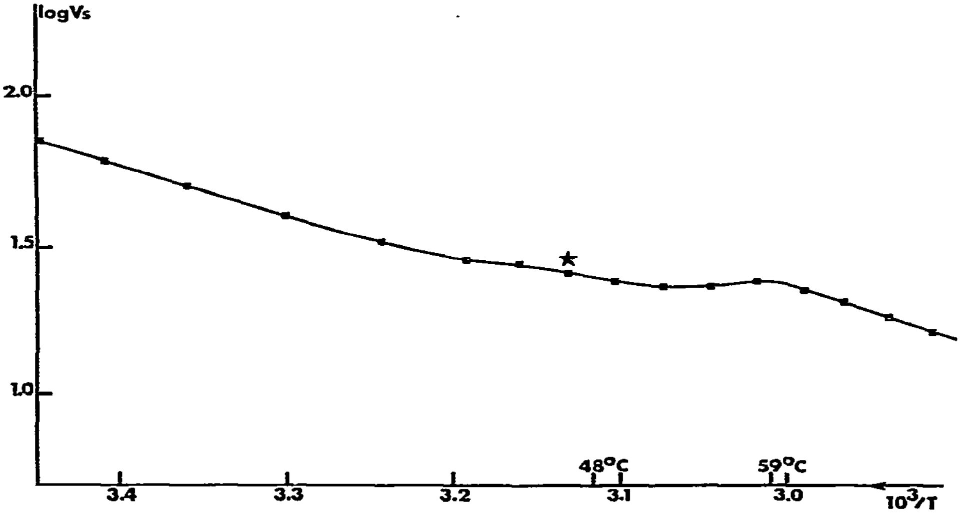

Fig. 3. Variation of log V_s with $1/T$ for *n*-heptane as solute on C_{22}-bonded Spherosil XOB 015 coated with 8.9% of glycerol and 9% of water.

additional shift of the end-temperature of the transition* (Fig. 3). However, a particularly sharp increase in V_s appears about 10°C above the transition temperature observed for the uncoated bonded silica.

It is worth noting the similarity of the experimental device in two kinds of experiments: first the previous experiments involving mixtures of water and strongly hydrophobic associated compounds and those inside a column in reversed-phase chromatography with water–methanol as the mobile phase. Therefore, it is logical to think that in this sort of chromatography the retention properties of the bonded silica may depend strongly on changes in a very narrow range of temperatures and that this range depends strongly on the composition of the mobile phase.

The only difference lies in the incomplete filling of the pores in the above-described experiments (Fig. 4). Part of the surface is not submitted to the effect of the hydrophilic solvent. This situation explains the appearance of a low secondary transition at the temperature marked by an asterisk in Fig. 3, which is the transition temperature in the absence of a coating stationary phase.

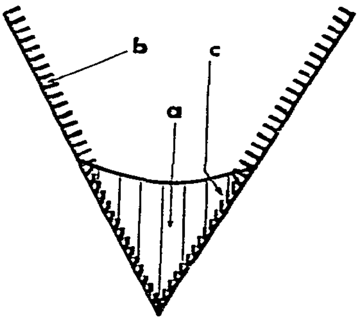

Fig. 4. Model of pore: (a) capillary condensate of liquid stationary phase; (b) bonded phase at the gas–solid interface; (c) bonded phase immersed in the liquid stationary phase.

These results on the influence of strongly hydrophilic liquids substantiate the recent comment of Scott and Simpson[8], after isothermal measurements of reversed-phase retention volumes with water as the mobile phase, that under the influence of water the hydrocarbon chains dispersively interact with themselves and that this interaction results in anomalously low retention volumes.

When polar test solutes are used in place of alkane (Figs. 5 and 6), the transitions are less abrupt, particularly with a coated substrate. However, it is worth noting that an inversion of the solute order may occur across the transition, as shown in Fig. 5 for methyl propyl ketone and dioxane on uncovered bonded silica.

Apolar stationary phases. Although it is unusual to use an non-polar mobile phase with bonded silica in liquid chromatography, replacing hydrophilic liquids with squalane is instructive (Fig. 7). The amplitude of the transition is reduced, but the end temperature of this transition is noticeably lowered (from 48 to 42°C) at the same time. It is as if there were a solution of squalane in the alkyl layer. In opposition to

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* With some reservations owing to the limited efficiency of the water-coated Chromosorb P column used as a saturator, when the temperature rises above 60°C.

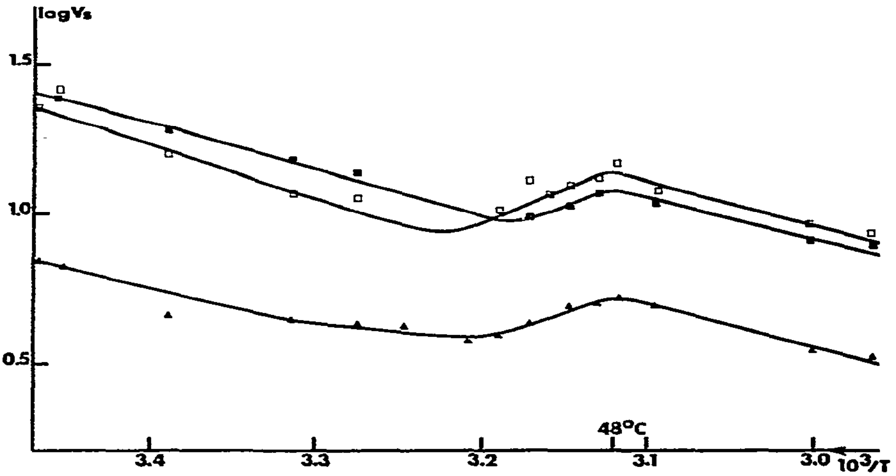

Fig. 5. Variation of log V_s with $1/T$ for uncovered C_{22}-bonded Spherosil XOB 015. Solutes: ■ = dioxane; □ = methyl propyl ketone; ▲ = chloroform.

hydrophilic liquids, squalane reduces the cohesion of the bonded chains and lowers their transition temperature as a result of a cryoscopic-like effect.

Coating the bonded silica with a long-chain *n*-alkane results in a very intriguing material, although it is of no practical use in liquid chromatography at present. At low temperature (in this instance under 60°C), the alkane chains have been inserted into the grafted alkyls to give a very compact mixed monolayer, physisorbed and chemisorbed at the same time. Riedo *et al.*[9] demonstrated such layers by contact angle measurements. We have previously published a study of these phases by inverse gas chromatography for C_{18}-bonded silica and heptadecane[1]. In the most compact

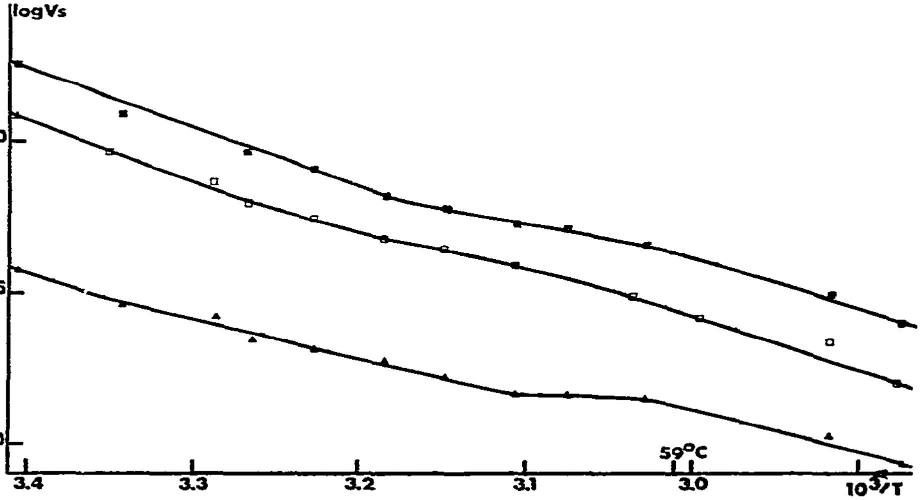

Fig. 6. Variation of log V_s with $1/T$ for 8.9% of glycerol on a C_{22}-bonded Spherosil XOB 015. Solutes: ■ = dioxane; □ = methyl propyl ketone; ▲ = chloroform.

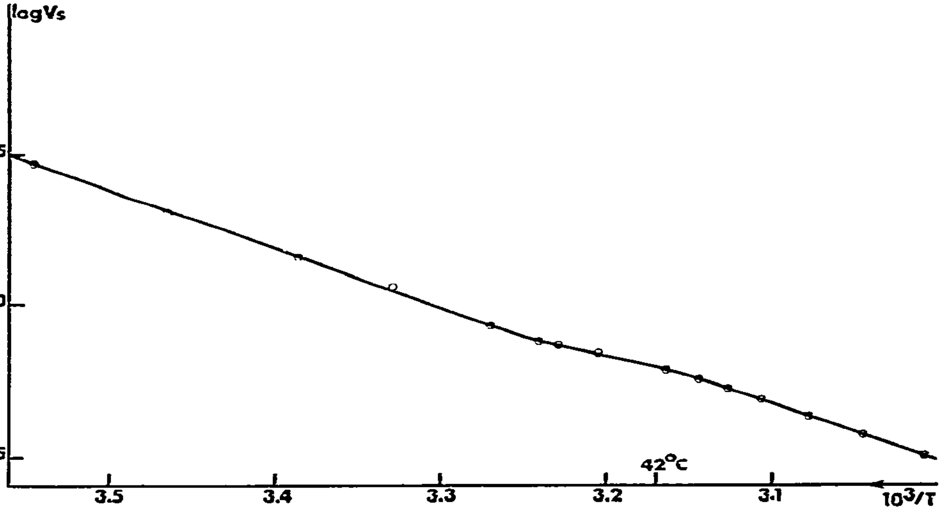

Fig. 7. Variation of log V_s with $1/T$ for *n*-heptane as solute on C_{22}-bonded Spherosil XOB 015 coated with 6.1 % of squalane.

layers, the area of substrate occupied for each chain is 0.21 nm^{2}, as in the classical condensed phases of polar fatty compounds at the surface of water. Such a two-dimensional phase undergoes a melting-like transition at 51°C.

Coating the C_{22} silica with *n*-heneicosane gives rise to very similar phenomena. As Fig. 8 shows, a transition may be observed between about 60 and 68°C, rather sharper at the end. However, it is worth noting that the phenomenon occurs at a much higher temperature than both the transition of the pure bonded silica (51°C) and the melting of heneicosane (40°C; the melting transition of an excess of bulk heneicosane can be seen in Fig. 8 at this temperature). In addition, such layers are not the exclusive property of alkanes and alkyl groups of exactly the same length, as we shall show in a future paper.

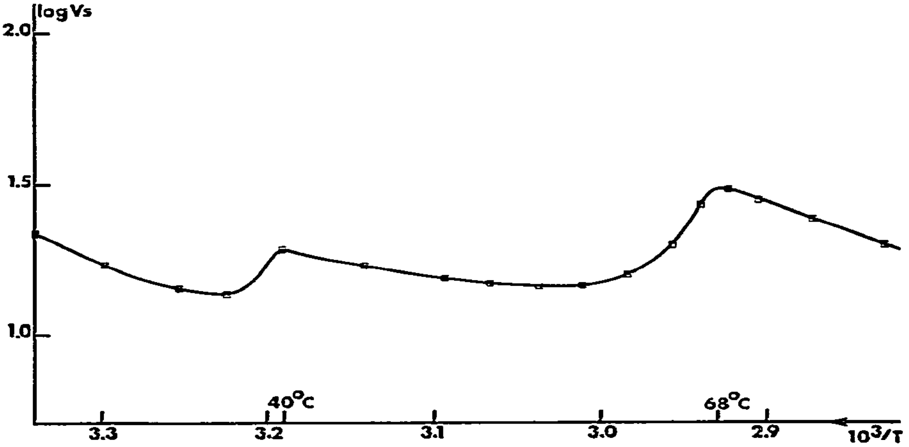

Fig. 8. Variation of log V_s with $1/T$ for *n*-octane as solute on C_{22}-bonded Spherosil XOB 015 coated with 3.1 % of *n*-heneicosane.

CONCLUSION

If long-chain alkyl-bonded silicas are immersed in various liquids, the physical state and the chromatographic properties of the bonded material depend very strongly on the temperature. This dependence is all the more critical if the alkyl chain is long ($>C_{18}$) and if the chain coverage is dense (>4 μmol/m^2). However, the temperature range of the transition is raised by a hydrophilic and lowered by a hydrophobic medium (inserted alkane phase excluded).

As the normal transition range of a C_{18}-bonded silica is near room temperature (7–27°C, ref. 1), it is obvious that the retention properties and selectivities of these materials may depend on the temperature and density of bonding in a very complex way. This situation could explain both the irreproducibility of analytical data[10,11] and many controversial points of view in the field of reversed-phase liquid chromatography.

Consequently, we suggest that the choice of C_{18} for economic and practical reasons has not been very good, and slightly shorter or longer chains could have given better results. In addition, it is not at all certain that densely covered silicas would give better analytical results.

REFERENCES

1 D. Morel and J. Serpinet, *J. Chromatogr.*, 200 (1980) 95.
2 Z. Kessaissia, E. Papirer and J. B. Donnet, *J. Colloid Interface Sci.*, 79 (1981) 257.
3 E. sz. Kováts, *Ger. Pat.*, DE 29 30 516 A1 (1979).
4 J. Serpinet, *Chromatographia*, 8 (1975) 18.
5 G. Untz and J. Serpinet, *J. Chim. Phys.*, 73 (1976) 912.
6 C. Daneyrolle, J. Serpinet, M. Troccaz and C. Eyraud, *C.R. Acad. Sci., Ser. C*, 276 (1973) 129.
7 C. J. Little, A. D. Dale and M. B. Evans, *J. Chromatogr.*, 153 (1978) 543.
8 R. P. W. Scott and C. F. Simpson, *J. Chromatogr.*, 197 (1980) 11.
9 F. Riedo, M. Czencz, O. Liardon and E. Sz. Kováts, *Helv. Chim. Acta*, 61 (1978) 1912.
10 K. Ogan and E. Katz, *J. Chromatogr.*, 188 (1980) 115.
11 E. C. Nice and M. J. O'Hare, *J. Chromatogr.*, 166 (1978) 263.