

CHROM. 5969

GAS CHROMATOGRAPHIC STUDY OF THE EXISTENCE AND THE PHYSICAL STATE OF MONOMOLECULAR FILMS OF STATIONARY PHASES IN CONTACT WITH SILICEOUS SUPPORTS

THE APPARENT INCREASE OF THE MELTING POINT OF THE FILM

J. SERPINET

Laboratoire de Chimie Industrielle et Analytique, Institut National des Sciences Appliquées, 20, Avenue A. Einstein, 69, Villeurbanne (France)

(Received December 15th, 1971; revised manuscript received February 7th, 1972)

SUMMARY

The relation between the logarithm of the retention volume of hydrocarbons and fluorocarbons on paraffins and fatty esters, as stationary phases, against the reciprocal of the absolute temperature has been studied. It indicates an apparent increase of the melting point of the film in contact with the support. The influence of the support, of the stationary phase, and of the proportion of the support present, on this phenomenon is discussed.

The results give some information on the wetting of the support and on the physical state of a liquid in a dispersed medium. They indicate that the liquid's properties cannot be correlated with those of a normal liquid.

INTRODUCTION

The melting point of the stationary phase presents a limit for its practical use at low temperatures. The effect on the retention properties of solutes of crossing the transition temperature has been observed by many workers¹. Some confusion arises from the qualitative character of much of this work, as the commercial equipment used is rarely suitable for this type of work. Also, the poorly defined stationary phases with no sharp melting points which have been generally used for analysis are not always beneficial.

According to most authors, if the liquid produced is not mesomorphic, melting is characterized by a rather sharp variation of the retention of the solute. The transition from adsorption to solubility phenomena allows molecules deep in the stationary phase to participate in the retention, the diffusion of the solute in the solid state being much too slow a phenomenon to allow complete equilibrium in a gas chromatographic (GC) column.

A linear relationship exists between the logarithm of specific retention volume and the reciprocal of the absolute temperature in the region of adsorption, as well as of the solubility. Therefore, for a given solute and a chemically well defined station-

ary phase, the graph of $\log V_g$ vs. $1/T$ (temperature increasing towards the right in the figures) would be made up of two straight lines separated by a sharp transition.

Much more complex phenomena are seen when working with a column of Chromosorb P lightly loaded (1%) with docosane, $C_{22}H_{46}$, and with either a very soluble solute, *n*-heptane, or a slightly soluble and very adsorbable one, perfluorododecane, $C_{12}F_{26}$ (Fig. 1). The retention increases at the melting point of docosane, but a second sharp increase of retention, which reaches its maximum 4.7° above the melting point of docosane, must be associated with a new phenomenon^{2,3}. An important hysteresis effect, extending over two degrees, may be observed by cooling. The retention, however, decreases much above the stationary-phase melting point (evaluated in the chromatographic bath itself), so the phenomenon cannot be ascribed to a delay in the temperature of the bath reaching equilibrium.

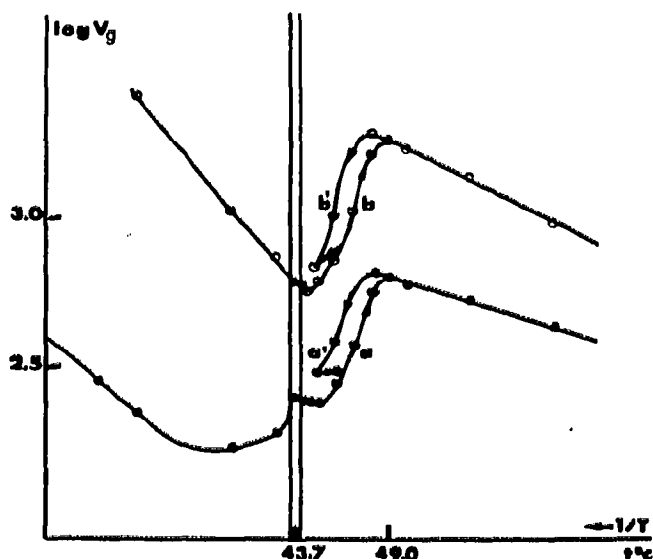


Fig. 1. Variation of $\log V_g$ with $1/T$ for 1% of docosane on Chromosorb P; V_g (cm^3). (a) With *n*-heptane as solute; (b) with perfluorododecane as solute. a' and b' refer to measurements at decreasing temperatures.

In this paper the influence on these transitions of most experimental parameters, changing either the stationary phase or the siliceous support or the percentage of stationary phase on the support, is studied. A first interpretation of the phenomena is proposed. We consider also some of the consequences of these experiments for analysis and for the determination of physical constants by GC.

EXPERIMENTAL

Apparatus

All the experiments were performed with a classical chromatograph (Intersmat) equipped with a catharometer, in which the air-bath had been replaced by a standard $1/10^\circ$ laboratory liquid bath (Prolabo). The bath reaches equilibrium immediately.

Stationary phases

Most stationary phases are commercial products for laboratory use: the esters are laboratory-made compounds obtained from octadecanol (puriss. Fluka) by

reaction with the corresponding acid chlorides. Polar impurities originating from the reagents were separated by liquid-phase chromatography on a silicic acid column.

Solutes

The hydrocarbons used were laboratory reagent grade. Fluorocarbons and amphiphathic compounds such as $C_6F_{13}-C_2H_6$ were experimental products kindly supplied by Ugine-Kuhlmann.

Supports

Chromosorbs used were all 60-80 mesh commercial products from Johns-Manville. Chromosorb P NAW, which is generally used, is characterized by a specific surface area of $4.1 \text{ m}^2/\text{g}$, according to our BET measurements with nitrogen. It is an essentially macroporous product, the mean pore diameter of which is 0.6μ (ref. 4). Other Chromosorbs are still more macroporous. We are grateful to Pechiney-St. Gobain for the samples of "Spherosils". They are made of very pure adsorbing silica in beads of diameter 100-200 Å. Their specific surface area and mean pore diameters are: XOC 005, $10 \text{ m}^2/\text{g}$ and 3000 Å, XOB 015, $25 \text{ m}^2/\text{g}$ and 1250 Å, XOB 075, $100 \text{ m}^2/\text{g}$ and 300 Å.

Coating the support

A solution of the stationary phase in a volatile and very pure solvent was evaporated, using standard procedures. The solvent was chosen so that it could be evaporated above the melting point of stationary phase. There was then no danger of precipitation of crystals outside the support.

Injections

Except for perfluorododecane, introduced in the liquid state as a solution in perfluoromethylcyclohexane, all the solutes were injected individually in the gas phase by a head-space sampling technique, the volume of sample gas being a few tenths of a microlitre.

Bath temperature

The temperature was changed by 0.5° or 1.0° increments.

Calculations

Specific retention volumes V_g were calculated according to the method of LITTLEWOOD⁵.

RESULTS AND DISCUSSION

Surface nature of the "shifted" transition phenomenon

According to most authors, in a lightly loaded GC column, at least a part of the stationary phase is dispersed as a thin film over all the accessible surface of the support. The excess would be in the smallest pores due to capillary condensation (Fig. 2). The relative importance of this excess would increase for increasingly loaded columns. GIDDINGS⁶ gives an approximative theory for the equilibrium between both phases which results in a formula giving the thickness of the film as a function of the radius of the largest filled pores.

Immediately after our first results on the "shifted" melting transition for docosane we suggested that the "normal" one at 43.7° is connected with the capillary liquid, and that the second one, at 48.4° is a property of the film.

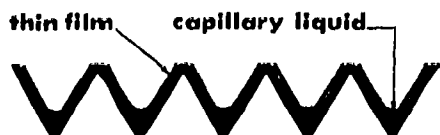


Fig. 2. GIDDINGS' model for lightly loaded packings.

The results of our latest experiments can be summarised as follows:

(1) Fig. 3* indicates "shifts" for different percentages of docosane as solvent on untreated Chromosorb P as support. With less than 1% docosane the shifted transition is the only one observed, whatever the solute. These results correspond rather well with the ideas of GIDDINGS on the formation of a film at low percentages of stationary phase, if it is accepted that the transformation at 48.8° and 4.7° above the bulk melting point of docosane is related to the film.

(2) No "shifted" transition is observed, even for very lightly loaded columns, in the case of silanized Chromosorb P (Fig. 4). The occurrence of a "normal" transition in its place immediately suggests the absence of a thin film of docosane on this support.

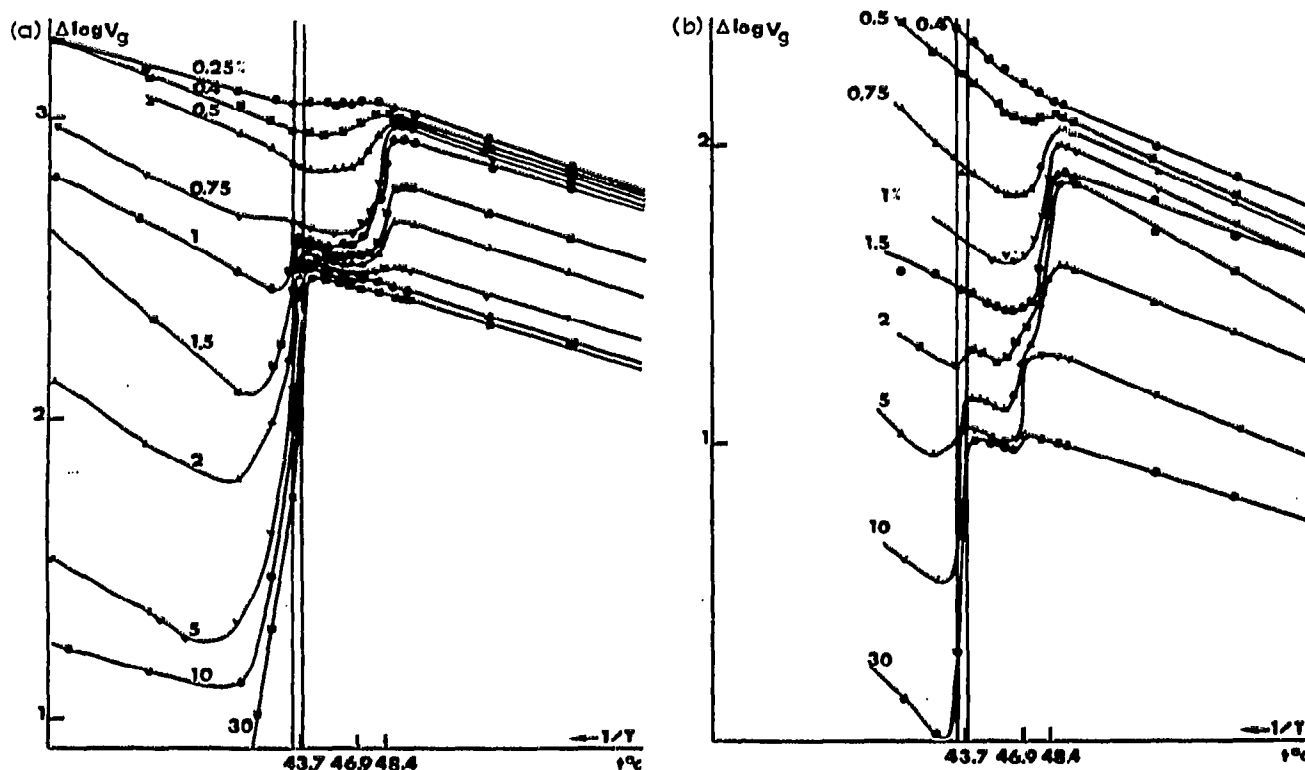


Fig. 3. (a) Variation of $\log V_0$ with $1/T$ for different percentages of docosane on Chromosorb P NAW, with *n*-heptane as solute; (b) variation of $\log V_0$ with $1/T$ for different percentages of docosane on Chromosorb P NAW, with perfluorododecane as solute.

* For greater clarity curves have been displaced along the $\log V_0$ axis. The amplitude of transitions is characterized by an arbitrary logarithmic scale.

Precisely this hypothesis had been suggested by the present author⁷ as a result of a study of the retention volume as a function of the mass of stationary phase on these supports.

(3) The interest of fluorocarbons as "solutes" arises from their very low solubility in paraffins and most organic solvents. A strong retention of such "solutes" must be merely a surface phenomenon. It may take place either at the liquid-gas interface, where the fluorinated compound lowers the surface tension according to the GIBBS equation, or at one of the solid-gas or solid-liquid interfaces, where they are strongly adsorbed.

If, as we think, an untreated Chromosorb coated with a paraffin contains a film and a capillary-condensed liquid, melting of this liquid would not be evidenced by any important change of the retention volume of a fluorocarbon, as long as the percentage of stationary phase in the column is not too high.

This is precisely what was observed, both with a hydrocarbon (Figs. 1 and 3)

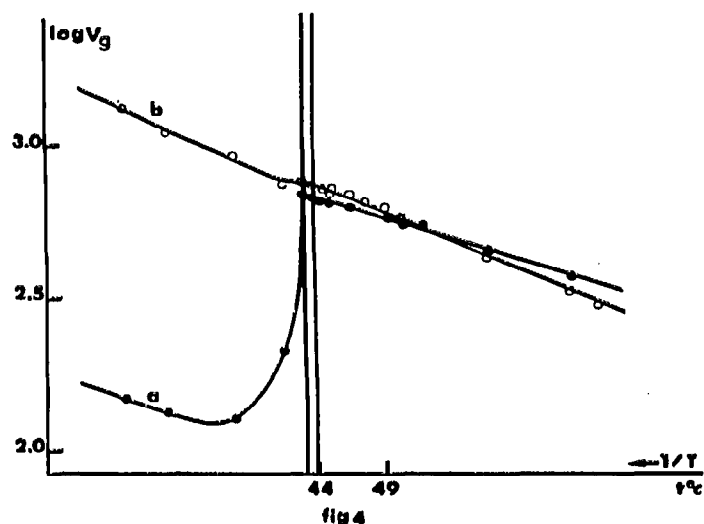


Fig. 4. Variation of $\log V_g$ with $1/T$ for 1% of docosane on Chromosorb P DMCS treated. (a) With *n*-heptane as solute; (b) with perfluorododecane as solute.

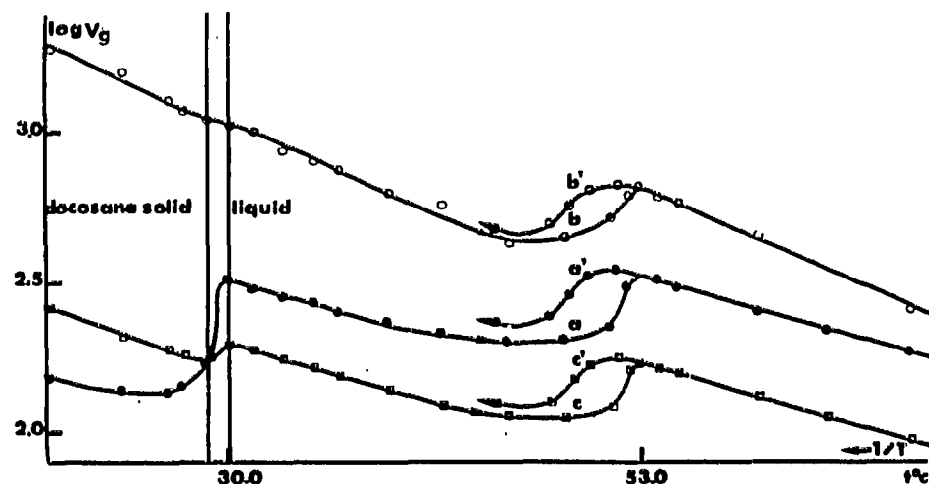


Fig. 5. Variation of $\log V_g$ with $1/T$ for 1% of octadecyl acetate as solvent on Chromosorb P NAW. With *n*-heptane as solute; (b) with perfluorododecane as solute; (c) with $C_6F_{13}-C_2H_6$ as solute. a', b' and c' refer to measurements at decreasing temperatures.

and with an ester (Fig. 5) as solvent, so long as the load does not surpass 5 % (Fig. 3). Conversely a "shifted" transition in the retention of fluorocarbons was observed, even with the lowest percentages of stationary phase (Figs. 3 and 5). If the retention is an essentially surface phenomenon and if the extent of the organic surface is not modified* by melting, we must conclude that the nature of the surface accessible to the solute is itself changed. This observation fits in well with the concept of the "shifted" melting of the film, giving access for fluorocarbons to the liquid-solid interface on which they are strongly adsorbed by the silanol groups.

In fact, the solubility of perfluorododecane in docosane is not strictly negligible. This situation seems to be responsible for the "normal" transition observed with fluorocarbon solutes, when the column load is greater than 2-5 % of docosane. But even at 30 % it is not sufficiently high to eradicate the transition connected with the residual film in the logarithmic curve.

It is noteworthy that amphipathic compounds such as $C_6F_{13}-C_2H_5$ give a curve (see Fig. 5) with a slight "normal" transition and a marked shifted transition. This situation is very logical for these compounds, which behave as intermediates between fluorocarbons and hydrocarbons. The usual polar or polarisable compounds such as ethyl ether, acetone, chloroform and carbon tetrachloride, do not behave very differently from heptane.

(4) The objective character of the observed transitions as a property of both the solvent and the support has been confirmed in the absence of solutes by thermal analyses⁹. A thermogram enhances supplementary peaks, which can easily be related to transformations in the solid state of the capillary-condensed liquid and the film. These transformations would perhaps be difficult to observe by chromatographic studies. However, the occurrence of two important thermal peaks, coinciding within a few tenths of a degree with the chromatographic transitions confirms the physical significance of the phenomenon.

Resolution of the transitions by means of thermal properties is even better than by chromatography. Solutes, even when injected in very small quantities, must modify the solvent melting temperature. This results is a sort of "cryoscopic effect", responsible for the long tail observed on the solid-state side of the normal transition. The superiority of chromatography lies in its ability to supply us with information about the arrangements of phases.

(5) By extrapolating the straight lines in Fig. 3 it is relatively easy to separate the retention originating from the melted film and the retention to be attributed to the capillary-condensed liquid at a temperature above the two transitions.

If we plot the absolute retention volume attributed to the capillary liquid (liquid-in-bulk state), V_{Nb} , against the percentage of stationary phase, t_f , we observe an almost linear decrease for increasingly low percentages of docosane (Fig. 6, curve a). Extrapolating this line to the t_f axis leads us to suppose that capillary liquid is absent at concentrations below 0.75 % of stationary phase.

Taking into account the 4.1 m²/g surface area of the uncoated support (untreated Chromosorb P), this critical percentage corresponds to an area of 28Å² per

* Melting cannot occur, in fact, without affecting the area available to the gas. Nevertheless, BET surface area measurements made by KREJCI⁸ on supports coated with different percentages of stationary phases seem to show that measurements made in liquid nitrogen give a sound estimate of the organic liquid surface.

molecule of docosane in the film. It is noteworthy that this value corresponds within 1 or 2 Å² to the numerical estimates given by many authors¹⁰ for the molecular area of fatty acids, alcohols or esters spread over water in the so-called "superficial mesomorphic" state. Therefore, the film of which we are studying transformations by GC seems to be a monolayer in which molecules are in an elongated configuration, the chains being directed towards the surface of the support, even if they are not strictly perpendicular to it.

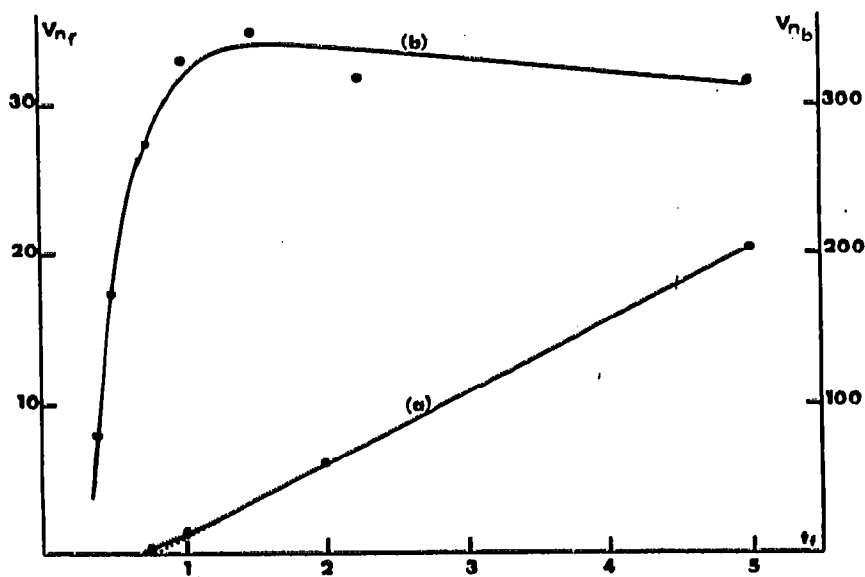


Fig. 6. (a) Absolute retention volume attributed to the capillary condensed liquid, V_{N_b} , versus the percentage of docosane, t_f , for *n*-heptane as solute and Chromosorb P NAW as support; V_N (cm³); (b) absolute retention volume originating from the melted film, V_{N_r} , versus the percentage of docosane, t_f , for *n*-heptane as solute and Chromosorb P NAW as support.

Study of the transformation of the film

We are led to connect the transition observed at 48.4° for docosane with the transformation from the well ordered "mesomorphic" state to a disordered, so-called "liquid expanded" state, according to the observations of TRAPEZNIKOV¹¹ on aqueous films of fatty alcohols. This transformation, above the normal melting point of the alcohol, has been shown by methods such as viscosimetry and surface pressure or energy measurements which would have been unpractical with our solid substrates. The same author has also recently¹² demonstrated the existence of a shifted transition in the case of thick films of fatty alcohols on water, but at lower temperature, due to the different properties of the films at the air-water and the alcohol-water interfaces.

It seems that we are observing similar transformations in the case of a silanol-covered solid support. Curve 3 indicates film transformation even with high percentages of docosane, but the temperature of transition is significantly lowered in such conditions (46.9° instead of 48.4° at low percentages of the phase). For intermediate values of the load, from 5-10 %, the curves indicate the transformation of the residual monolayer in the less curved parts of the support and at the same time the transformation at the solid-liquid interface of the film, resulting from the immersion of the film in the filled pores (Figs. 2 and 7).

It seems that our film behaves as an isolated layer of a smectic liquid. By analogy, it is known that chromatographic retention in liquid crystals as solvents, undergoes less change by melting than by the transformation of the liquid crystal into an isotropic liquid¹³.

However, it is worthy of note that we observed compact films with paraffins, which are reputed not to spread over water¹⁴.

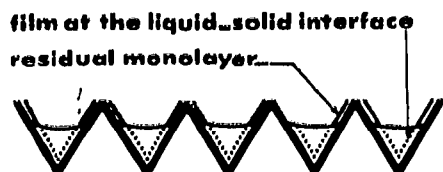


Fig. 7. Disposition of the stationary liquid in almost-filled pores.

Films of esters

If the phenomenon we observe with other paraffins, such as dotriacontane, as the stationary phase is exactly the same as that with docosane, a little larger shift is observed with an olefin, such as 1-octadecene.

However, the phenomenon is especially interesting with fatty acid esters as the stationary phases. With compounds such as methyl stearate (Fig. 8, curve a) or octadecyl acetate (Fig. 8, curve b), the shift exceeds 20°. The shift decreases steadily from octadecyl acetate to propionate and hexanoate (Fig. 8, curves b, d and c). These curves bring out, at least qualitatively, the influence of molecular interactions by hydrogen bonding at the solid-liquid interface. The difference between the two temperatures of transition decreases steadily in inverse proportion to the distance between the carboxyl group and the solid surface.

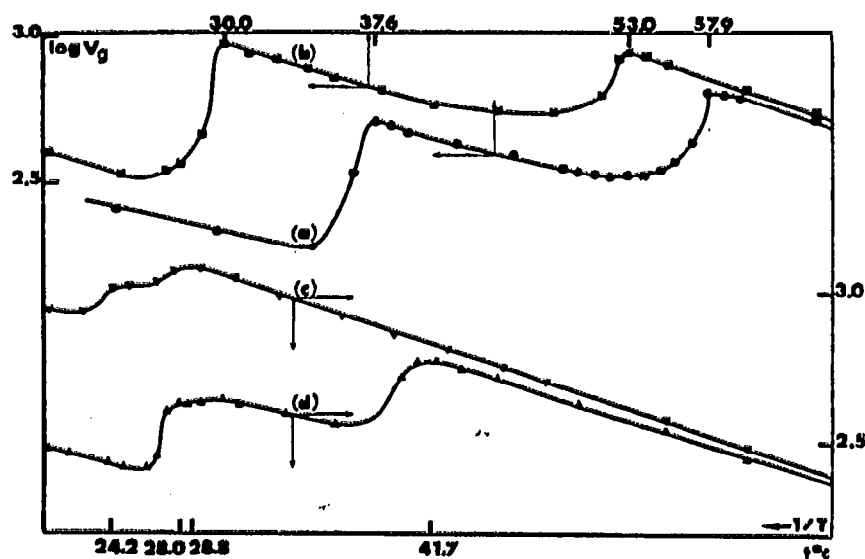


Fig. 8. Variation of $\log V_D$ with $1/T$ for 1% of different esters on Chromosorb P NAW. (a) Methyl stearate (puriss.) as solvent and *n*-octane as solute; (b) octadecyl acetate as solvent and *n*-octane as solute; (d) octadecyl propionate as solvent and *n*-heptane as solute; (c) octadecyl hexanoate as solvent and *n*-heptane as solute.

Microporous supports

Results obtained with "spherosils" indicate the influence of the pore radius on the formation of the adsorbed film itself. XOC 005, which is similar in texture to Chromosorb P, behaves in a similar manner, if a percentage of docosane, suitable for its surface area, is used.

The "shifted" transition is already reduced in amplitude for XOB 015 (more microporous), even when it is covered with a suitable percentage of stationary phase.

The shifted transition is not observed with XOB 075 except perhaps for very high loads (75 %), which are disproportionate with its surface area.

The explanation must lie in the small pores (300 Å) of this support: as the vapour pressure in equilibrium with a capillary liquid is reduced, according to KEELVIN'S formula, the surface pressure of a film in equilibrium with a meniscus undergoes a similar reduction.

The lack of wetting of microporous solids due to this sort of capillary suction has baffled many authors. This is probably the reason why they did not observe shifted transitions as we did, since adsorption is generally studied on microporous solids except in GC work¹⁵.

A short comment is appropriate on the lowering of the melting point, or, more exactly, freezing point, of a pure compound in very small pores. This homomolecular effect is described by the formula derived by KUBELKA¹⁶ which has often been verified and involves only the surface tension of the liquid as a physical constant. As already discussed⁹, the proportion of the porous volume of the Chromosorb which is contained in pores of less than 0.1 μ is completely negligible. Therefore, the lowering of the freezing point of the capillary liquid is much too small to be shown in our experiments.

Consequences for gas chromatography

(1) Studying phase transitions by GC should be a test of the existence of a film on a surface, in other words a test of the wettability of the support. This information could lead to a more realistic description of mass-transfer phenomenon in packed columns.

In our work on docosane and Chromosorb P the curve V_{Nf} against t_f , giving the retention volume created by melting the film, illustrates the occurrence of a complete monomolecular film for 0.75 % docosane. But, in addition, it can be seen that the area of the film remains almost unchanged up to about 5 % of stationary phase (Fig. 6, curve b). It does not appear that the film thickens when the macropores are progressively filled, but that the internal surface is merely immersed for high percentages of stationary phase. The occurrence of the transition at 46.9° would be characteristic of that immersion.

(2) The temperature interval in which the paraffin film remains compact is narrow above its normal bulk melting point (4 to 5°). This interval is larger for esters (10 to 20°). It should be still more extended for much polar compounds. Comparison of the present work on silicas with similar studies made in this laboratory on films spread on glycerol¹⁷ tends to suggest this. In this compactness interval there is no simple relationship between absolute retention volume V_N and the mass of stationary phase in a given column.

We have shown that the liquid dispersed in a column no longer keeps the prop-

erties of a normal liquid. The so-called "solid support effect" often appears to be a modification of the stationary liquid itself.

(3) Without contesting the possibility of GC determinations of thermodynamic constants, requiring many corrections, it appears that GC, a dynamic technique, operating in a dispersed medium, is primarily a method for studying interfaces. Transformations of surface phases certainly offer a very large field of applications to the method.

ACKNOWLEDGEMENTS

We are grateful to Mr. R. DIEMIASZONEK for his careful technical cooperation in performing the first experimental part of this work. The author expresses his appreciation to the technicians of Institut de Recherches sur la Catalyse for their assistance in specific surface measurements.

The author would also like to express his thanks to Professor GUIOCHON (École Polytechnique Paris), for a very fruitful discussion during this work and many interesting suggestions.

REFERENCES

- 1 W. FIDDLER AND R. C. DOERR, *J. Chromatogr.*, 21 (1966) 481.
- 2 J. SERPINET AND J. ROBIN, *C.R. Acad. Sci. Paris, Ser. C*, 272 (1971) 1765.
- 3 J. SERPINET, *Nature (Phys. Sci.)*, 232 (1971) 42.
- 4 W. J. BAKER, E. H. LEE AND R. F. WALL, in H. J. NOEBELS, R. F. WALL AND N. BRENNER (Editors), *Gas Chromatography*, Academic Press, New York, 1961, p. 21.
- 5 A. B. LITTLEWOOD, *Gas Chromatography*, Academic Press, New York, 1962, p. 32.
- 6 J. C. GIDDINGS, *Anal. Chem.*, 34 (1962) 458.
- 7 J. SERPINET AND J. ROBIN, *C.R. Acad. Sci. Paris, Ser. C*, 272 (1971) 768.
- 8 M. KREJCI, *Coll. Czech. Chem. Commun.*, 32 (1967) 1152.
- 9 J. SERPINET, C. DANEVROLLE, M. TROCAZ AND C. EYRAUD, *C.R. Acad. Sci. Paris, Ser. C*, 273 (1971) 1290.
- 10 D. DERVICHIAN, *J. Phys. Radium*, 10 (1939) 333.
- 11 A. A. TRAPEZNIKOV, *Acta Physicochim. URSS*, 19 (1944) 554.
- 12 A. A. TRAPEZNIKOV AND E. S. DOKUKINA, *Russ. J. Phys. Chem.*, 45 (1971) 401.
- 13 E. M. BARRALL II, R. S. PORTER AND J. F. JOHNSON, *J. Chromatogr.*, 21 (1966) 392.
- 14 G. L. GAINES, *Insoluble Monolayers at Liquid-Gas Interfaces*, Interscience, New York, 1966, p. 209.
- 15 G. BLANDENET AND J. ROBIN, *J. Gas Chromatogr.*, 4 (1966) 288.
- 16 P. KUBELKA, *Z. Electrochem.*, 38 (1932) 611.
- 17 G. UNTZ AND J. SERPINET, *C.R. Acad. Sci. Paris, Ser. C*, 273 (1971) 1424.