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## GAS CHROMATOGRAPHIC STUDY OF THIN FILMS OF PARAFFINS ON GRAPHITE SUPPORTS

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### SUMMARY

Studies of the retention volume of hydrocarbons and fluorocarbons in a normal paraffin coated on a graphite surface revealed the complex character of the melting of the multilayers of the stationary phase.

As on hydroxylated supports, the film melts at a much higher temperature than the bulk material, but the progressive nature of the chromatographic results shows the different arrangements of the molecules in the thin layer on the graphite.

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### INTRODUCTION

The retention of a solute in the inner part of a stationary phase is strongly dependent upon the accessibility of this bulk material to the solute molecules across the interfaces. Nevertheless, gas chromatography has been scarcely used in studies of the transformations of surface phases. Most studies deal with transitions of bulk materials, for instance, with liquid crystal transitions or polymer transformations by gas-solid chromatography.

As we showed recently<sup>1,2</sup>, plots of the logarithm of the specific retention volume against the reciprocal of the absolute temperature in the region of the melting of a paraffin used as a stationary phase on a siliceous support show at least one transition of the film at about 4° above the usual melting point of the bulk material.

The study of this transformation in terms of the percentage of stationary phase in the column for different hydrocarbons and fluorocarbons as solutes reveals the existence of a monolayer in which the molecules are oriented perpendicularly to the surface or make a small angle to the perpendicular.

The planar character of the surface of graphite and the better defined structure of this material suggested a similar study with this support and with the same normal paraffins as stationary phases. The stretched molecules of these paraffins are assumed to lie horizontally on the graphite surface, in which position they fit very well the

surface of the support<sup>3</sup>. Studies by different physical methods<sup>4,5</sup> reveal that the thermodynamic properties of these compounds are modified when they are disposed in a thin layer of a few molecular diameters thickness on carbon supports. Apparently the first multilayers are compressed close to the surface, as ASH AND FINDEREGG<sup>6</sup> discovered recently by direct density measurements.

This paper describes a study of the variation of the specific retention volumes of hydrocarbons and fluorocarbons with temperature for different percentages of docosane as stationary phase on a very pure industrial graphite support. The results indicate the continuous variation of the permeability of the thin film to the molecules of volatile solutes, thus confirming the variation of the rigidity of this film with temperature. In addition, they indicate new and rather well defined transitions at temperatures above and below the normal melting point of the stationary phase, for which we propose a tentative interpretation.

## EXPERIMENTAL

### *Apparatus*

All of the experiments were performed with a laboratory-made chromatograph in which the classical air bath was replaced with a standard 1/10° laboratory liquid bath.

### *Products*

The stationary phases were commercial products at 98–99% purity for laboratory use. The purification of docosane by liquid chromatography on a silica gel column so as to eliminate trace amounts of polar compounds does not affect the results. The fluorinated solutes were experimental products kindly supplied by Société des Produits Chimiques Ugine-Kuhlmann. The graphite PZ 77 of particle diameter 0.200–0.250 mm was a Pechiney product. It is a very pure industrial graphite, already used by JEQUIER<sup>7</sup> in this laboratory. It was reduced by us at 1100° under hydrogen so as to eliminate the surface oxides for the purpose of obtaining a better defined material<sup>8</sup>. This treatment modifies the thermodynamic properties of the adsorbent but it does not change the general form of the phenomena described in this paper. The surface area of the graphite is 0.94 m<sup>2</sup>/g after reduction, according to classical B.E.T. measurements.

### *Coating the support*

The support was coated by means of a solution of docosane in methylene chloride. The replacement of this solvent by *n*-hexane purified over silica gel had no influence on the results of the experiments. The evaporation was completed above the melting point of the stationary phase.

### *Injections*

Most solutes were introduced in minute amounts of gas by a head-space sampling technique, the volume of sample gas being about 1  $\mu$ l. Perfluorododecane was introduced in the liquid state as a few tenths of a microlitre of solution in perfluoromethylcyclohexane.

### Calculations

Specific retention volumes,  $V_G$ , were calculated according to the usual method<sup>9</sup>. Most results of this work were interpreted more clearly in terms of specific retention volumes per gram of support,  $V_G$ . If  $\tau$  is the mass percentage of stationary phase per gram of support, then

$$V_G = \frac{\tau}{100} \cdot V_D$$

Corrections for the non-ideality of the gas phase were not taken into account, as such a correction would have been small with hydrogen as carrier gas. Also, our purpose was to compare the retention volumes of different columns at different temperatures and not to effect absolute determinations.

### RESULTS

#### Octane as solute

The first 0.01% of paraffin on the graphite results in a large deactivation of the surface without modifying the linearity of the relationship between  $\log V_G$  and  $1/T$  (Fig. 1a)\*. For 0.036% of stationary phase, a decrease of the slope appears well above the melting temperature of the stationary phase,  $T_f$  ( $43.7 + 273.2$ ) (Fig. 1b). This temperature of transition decreases to a value lower than  $T_f$  for a concentration of stationary phase of 0.075% (Fig. 1c), at which temperature a new break in the curve appears at a temperature higher than  $T_f$ .

This double break leads to a single, rounded transition enclosing the melting point for  $\tau = 0.125\%$  (Fig. 1d). It is worth noting that the increase in the retention continues well beyond  $T_f$ . For 0.4% (Fig. 1e), this transition represents a typical

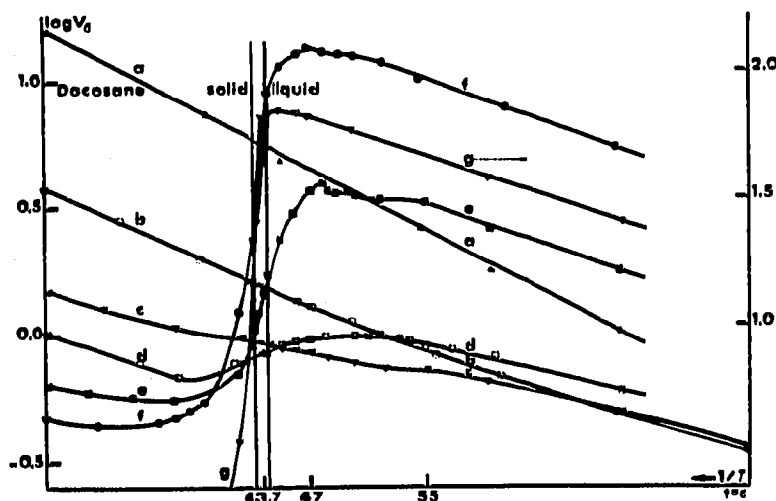


Fig. 1. Variation of  $\log V_G$  with  $1/T$  for *n*-octane as solute and different percentages of docosane on graphite: (a) 0.03%; (b) 0.036%; (c) 0.075%; (d) 0.125%; (e) 0.4%; (f) 1.2%; (g) 5.0%.

\* The temperature increases towards the right in all of the graphs.

example in which the increase beyond  $T_f$  is terminated by a sharp peak at  $47^\circ$  followed by a slowly inclined plateau that extends to about  $55^\circ$  followed by the normal linear decrease that is common in gas-liquid chromatography. The increase begins a little below  $T_f$ , and in the normal melting interval of docosane becomes larger and larger for higher percentages of stationary phase (1.2%, Fig. 1f). However, the increase in the retention volume above  $T_f$  remains significant even for 5% of docosane (Fig. 1g), in spite of the shape of the logarithmic graph and in spite of the relatively high load on this support of low surface area.

### Perfluorinated solutes

The solubility in the paraffins of partially fluorinated compounds ( $C_8F_{17} \cdot C_2H_5$ ) is low, and the solubility of fluorocarbons ( $C_{12}F_{12}$ ) is almost nil. The curves obtained for these "solutes" do not differ from the preceding ones in their general shape, but in the relative importance of the different transitions (Figs. 2 and 3). For intermediate

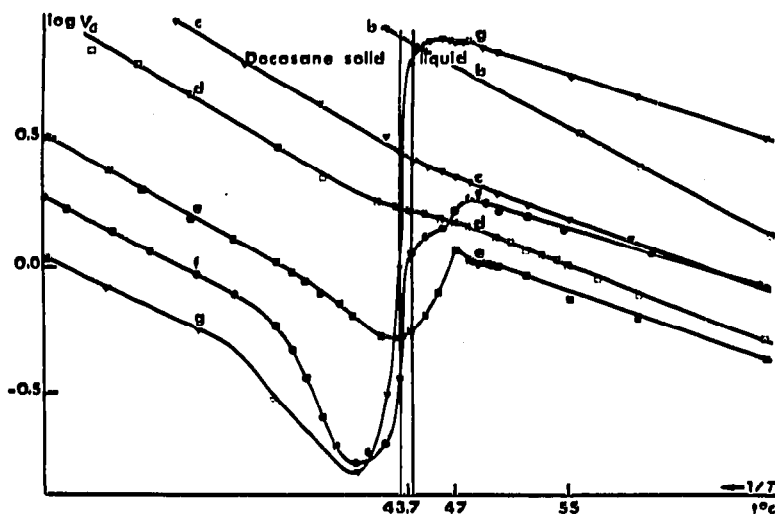


Fig. 2. Variation of  $\log V_G$  with  $1/T$  for  $C_8F_{17} \cdot C_2H_5$  as solute and different percentages of docosane on graphite: (b) 0.036%; (c) 0.075%; (d) 0.125%; (e) 0.4%; (f) 1.2%; (g) 5.0%.

loads (0.4%, Figs. 2e and 3a), the increase in the retention volume is small or nil below and at about the melting temperature of docosane. The increase is very significant, however, beyond  $T_f$  and the peak at  $47^\circ$  is rather sharp. In addition, for all of these perfluorinated "solutes" and above a load of 0.4%, a large decrease in the retention volume is observed a few degrees under the normal melting point of docosane.

### Reversibility of the phenomenon

By decreasing the temperature, a significant hysteresis effect can be observed for the shifted chromatographic transition, which takes place above the normal melting point of the stationary phase. Nevertheless, as with Chromosorb, the decrease in the retention, which characterizes the inverse transition, is observed well above the normal crystallisation temperature of docosane (Fig. 4a). The apparent

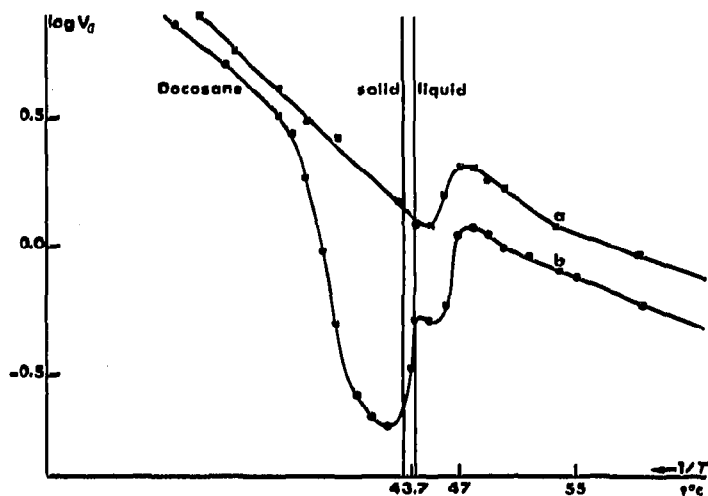


Fig. 3. Variation of  $\log V_G$  with  $1/T$  for  $C_{19}F_{20}$  as "solute" and different percentages of docosane on graphite: (a) 0.4%; (b) 1.2%.

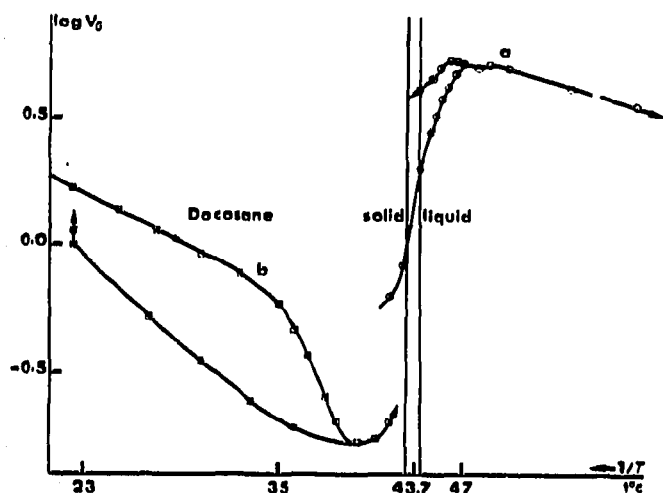


Fig. 4. Variation of  $\log V_G$  with  $1/T$  with increasing and decreasing temperatures (in the direction of the arrows): (a) for *n*-octane as solute and 0.54% of docosane on graphite; (b) for  $C_8F_{17} \cdot C_8H_8$  as solute and 1.2% of docosane on graphite.

shift of the melting point cannot be merely ascribed to a delay in the temperature of the bath reaching equilibrium.

The decrease in the retention volume of perfluorinated "solutes" a few degrees under the normal melting point of the stationary phase also gives rise to a hysteresis effect, which is larger and extends over about  $20^\circ$  (Fig. 4b). The return to the equilibrium curve is a function of time.

## DISCUSSION

The continuous increase in the retention volume above the melting point of the stationary phase suggests that at these temperatures the progressive melting of a film of paraffin that remains partly rigid near the carbon surface occurs. Heating the column permits an increasing proportion of the stationary phase to participate in the chromatographic process. This interpretation is in good agreement with our experiments on silica supports and with the observations by several workers<sup>4-6</sup> of the modifications of the properties of normal paraffins on contact with graphite surfaces.

The progressive nature of the variation in retention with increasing temperature, contrasting with the abrupt transition observed with silica supports, can be interpreted rather well in terms of the different arrangements of the molecules of the film. Instead of the thick, compact, single monolayer that paraffin molecules form on macroporous hydroxylated silicas<sup>1,2</sup>, their horizontal position on the surface of graphite leads to thicker multilayers of the stationary phase. It is easily conceivable why such multilayers progressively approach the mobility of a normal liquid, beginning with the layer farthest from the graphite surface.

The interest of chromatography with perfluorinated solutes lies in the fact that it gives a sensitive test of small variations in the rigidity of surface layers, even if the layers are very thin and if the support has a small surface area. Hence, in addition to the continuous phenomenon already observed on graphite by other methods, we found two breaks in the curve characterized by a peak at 47° and a plateau from 50 to 55°. We consider that these effects are connected with the "melting" of the last monolayers of docosane in contact with the graphite. This hypothesis is in agreement with our observation of these breaks for concentrations of stationary phase as low as 0.075%, at which level the layer is only a few molecular diameters thick, according to the molecular cross-sectional area estimations of GROSZEK<sup>3</sup> for dotriacontane and KISELEV<sup>10</sup> for lower hydrocarbons. In addition, as for the transformation of monolayers on Chromosorbs<sup>11</sup>, we have confirmed recently by thermal analysis the physical reality of some of these transitions<sup>12</sup>.

The blunt character of the transitions for this low coating of the surface agrees well with the fact that the melting of a mono- or bimolecular layer cannot be merely considered as a co-operative phenomenon, as is the case with the melting of a crystal or the transition of a thick monolayer. The large amplitude of the transitions of the retention volumes for fluorinated solutes confirms that they are connected with a progressive modification of the interfaces, which are the only positions where these compounds are appreciably retained.

On the contrary, however, the retentions of the fluorocarbons do not increase below and at about the melting point of docosane and the large increase in retention observed in this temperature range for hydrocarbon solutes must be ascribed to the cryoscopic effect of a very soluble solute.

*Retention by the film and by the "bulk solvent"*

Extrapolation of the straight lines of the graph of  $\log V_G$  against  $1/T$  at the temperature of melting ( $T_f = 43.7 + 273.2$ ) divides the retention volume into three parts (Fig. 5);  $V_{Ga}$ , corresponding to the pure adsorption at the gas-organic layer interface, which is generally low;  $V_{GB}$ , the retention volume in the bulk sta-

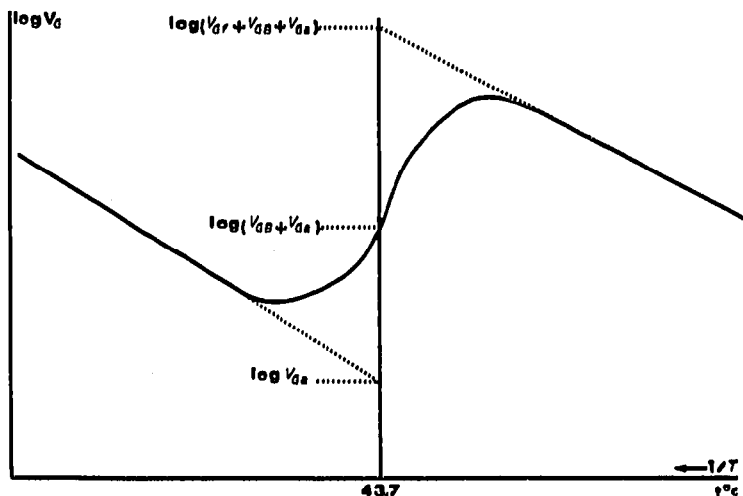


Fig. 5. Definition of  $V_{GB}$  and  $V_{Gf}$ .

tionary phase; and  $V_{Gf}$ , the retention volume extrapolated at the temperature  $T_f$  in the "melted" multilayer.

These definitions are justified experimentally by the linearity of the variation of  $V_{GB}$  with  $\tau$ , the percentage of docosane, for the high values of this parameter according to the normal laws of gas-liquid chromatography (Fig. 6). However, the extrapolated straight line intercepts the  $\tau$  axis at 0.9% of stationary phase. The effect is as if under this load of organic material there would not be any real bulk material in the column. Below 0.9%, the  $V_{GB}$  values measured for octane must be connected with a pre-melting or a "cryoscopic" effect of the solute. In agreement with these ideas,  $V_{Gf}$  increases with  $\tau$  and reaches a constant value for about 1% of stationary phase.

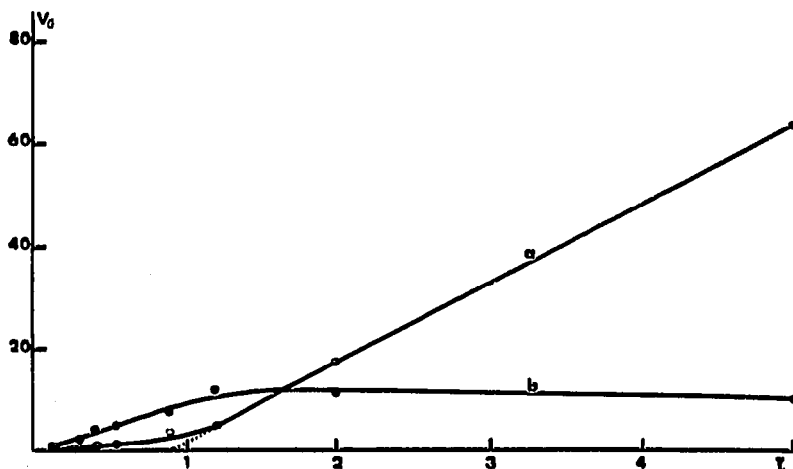


Fig. 6. (a) Specific retention volume attributed to the capillary condensed liquid,  $V_{GB}$  ( $\text{cm}^3$  per gram of support), versus the percentage of docosane on graphite,  $\tau$ , for *n*-octane as solute. (b) Specific retention volume originating from the melted film,  $V_{Gf}$ , versus the percentage of docosane on graphite,  $\tau$ , for *n*-octane as solute.

Hence, according to the above-quoted molecular cross-sectional areas for normal paraffins, it appears that there is no docosane in the normal bulk liquid state at its melting point unless it forms at least 30 layers of molecules in a horizontal position on the graphite surface.

*Retention by the successive layers of solvent*

With the aim of characterizing quantitatively the permeability of the successive layers of docosane to a hydrocarbon solute, we defined the "differential specific retention volume",  $v_g$ , as

$$v_g = 100 \frac{dV_G}{d\tau} \approx 100 \frac{\Delta V_G}{\Delta \tau}$$

and we studied its variation with  $\bar{\tau} = \frac{\tau_n + \tau_{n+1}}{2}$  for two columns with loads  $\tau_n$  and  $\tau_{n+1}$

This study was carried out for three temperatures:

$\theta_1 = \theta_f = 43.7^\circ$ , the melting point of docosane

$\theta_2 = 49.4^\circ$  in the "melting" range of the first layers near the graphite

$\theta_3 = 71.6^\circ$  in the terminal linear part of the graph of  $\log V_G$  against  $1/T$ .

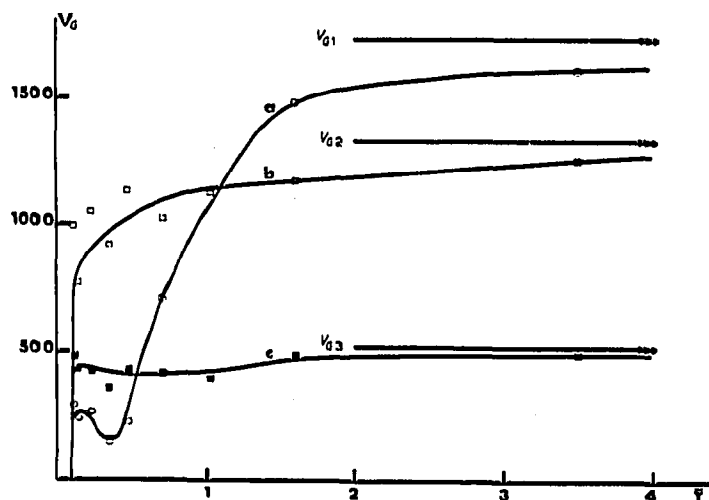


Fig. 7. Differential specific retention volume per gram of docosane,  $v_g$ , for *n*-octane as solute versus the percentage of stationary phase at different temperatures: (a)  $\theta_1 = \theta_f = 43.7^\circ$ ; (b)  $\theta_2 = 49.4^\circ$ ; (c)  $\theta_3 = 71.6^\circ$ .

Although the small spacing of the low values of  $\tau$  renders very imprecise the determination of  $v_g$  for lightly loaded columns, a clear increase in the retention volume can be observed for thicker layers (Fig. 7). Although the additional layers modify the physical properties of the underlying layers, the increase in  $v_g$  with  $\tau$  reflects the state of the external layers becoming more and more normal.

The classical specific retention volume of octane in docosane was determined by separate experiments with two differently loaded columns of DMCS-treated



Chromosorb P. The results of these determinations were in agreement to within a few tenths of 1%.

For the three temperatures used, the  $v_g$  values tend towards these specific retention volumes asymptotically. As shown in Fig. 7 and Table I, the difference between  $v_g$  and the limiting value remains very large at the normal melting temperature of docosane, even for  $\bar{r} = 3.5\%$  of stationary phase. Hence, docosane does not have normal solvent properties even in the external part of a very thick multilayer at the normal melting temperature.

At 49.4° and 71.6°, the asymptotic values are more nearly reached for highly loaded columns. Nevertheless, it is worth noting that in spite of the perfect linearity of the graph of  $\log V_g$  versus  $1/T$  above 55° at all loads, docosane never possesses normal solvent properties on graphite, even in thick layers.

TABLE I

SPECIFIC RETENTION VOLUME,  $V_g$  (cm<sup>3</sup>/g), AND DIFFERENTIAL VOLUME,  $v_g$ , OF OCTANE IN DOCOSANE

Temperature	$V_g$ , 5% on DMCS-treated Chromosorb P	$V_g$ , 10% on DMCS-treated Chromosorb P	$v_g$ , 3.5% on graphite
43.7	1730	1727	1605
49.4	1331	1329	1255
71.6	514	512	484

Hence, the thickness of the abnormal layer of a paraffin on graphite appears to be much more extended than after other physical measurements.

The decrease in the retention volume for perfluorinated "solutes" a few degrees below the melting point of the solvent is an objective property of the stationary phase, as shown by the hysteresis effect observed.

For a tentative interpretation, we compare this phenomenon with the continuous variation of many properties of normal paraffins preceding the solid-solid transformation in these compounds one or two degrees below their melting point. This transformation is a change in the crystalline structure connected with the possibility of the stretched molecules rotating more or less freely around their elongated axis<sup>13</sup>.

If such a transformation exists in multilayers, it may lead to a change in the nature of the surface CH<sub>3</sub> or CH<sub>2</sub> groups, on which the adsorption of fluorocarbons is very sensitive. However, this transformation may be hindered by the underlying surface under a determined thickness of the layer, which was confirmed experimentally. In addition, it is worth noting that the results of a few experiments carried out with hexatriacontane instead of docosane indicated a higher limiting thickness at which the decrease occurred corresponding to a concentration of 0.66% instead of 0.40%. This effect is as if the arrangement of molecules changes from a horizontal to a vertical position.

These experiments confirmed the ability of gas chromatography to supply information about the state of surface phases. In addition, they have shown the impossibility of carrying out gas chromatographic determinations of the usual solvent properties of paraffins over a large temperature range when graphite is used as the support. Hence this restriction, encountered with hydroxylated silicas and many stationary phases following our recent studies, must now be extended to other chro-

matographic systems. Finally we point out the lack of significance of the simple concept of specific retention volume when paraffins are used as solvents on a support that is being more commonly used for analytical purposes. In addition to the "support effect", the influence of the support on the physical state of the stationary phase must be taken into account.

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