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ADSORPTION IN GAS CHROMATOGRAPHY WITH LIQUID AND SOLID STATIONARY PHASES

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SUMMARY

The peculiar features and the mechanism of ageing of sorbents containing a non-polar and a polar liquid as the stationary phase coated on a polar support are discussed. Procedures for ageing sorbents in order to improve the reproducibility of retention values have been developed. It is shown that the retention values for a polar sorbate–non-polar stationary phase–polar support system depend substantially on the degree of drying of both the carrier gas (in the chromatographic run) and of the stream of gas used in the ageing treatment.

The roles played by the different components of retention have been estimated on the basis of a study of the dependence of the specific retention of *n*-propanol on the percentage of squalane coated on Celite.

Static measurements of adsorption at the liquid–solid support interface have been made for two systems. In addition, for the *n*-propanol–squalane system static measurements of the partition coefficient have been carried out. The results of static measurements of adsorption at the liquid–solid support interface have confirmed the conclusions on the significant role of adsorption on this surface that have been drawn from the results of chromatographic measurements carried out with sorbents subjected to ageing.

The possibilities of using the effects of adsorption at the phase interfaces of sorbents containing liquid and solid stationary phases are considered.

A linear dependence of the retention volume or the reciprocal of the percentage of stationary phase is shown to exist when solid stationary phases are used. The height equivalent to a theoretical plate (HETP) is considerably lower when a solid than when a liquid stationary phase is used, owing to a decrease in the resistance to internal diffusion. The HETP decreases sharply if helium is substituted for nitrogen as the carrier gas.

INTRODUCTION

The adsorption at the phase interface plays an essential role in retention when there is a difference in the polarities of the stationary phase and the sorbate. While a large number of workers have dealt with the problem[1-6], experimental data are less reliable, and the theoretical conclusions are less decisive than those concerning solutions.

The contribution of adsorption to the retention results in some peculiar features of the retention data. The specific retention volume depends, in this case, on the percentage of the stationary phase coated on the support and on the concentration of sorbate in the gas phase. Some peculiar features occur, however, due to the fact that the area of the phase interface and hence the contribution of adsorption to the retention volume depends on the distribution pattern of the stationary phase in the support pores. The process of redistribution of the stationary phase is slow, particularly when the support surface is poorly wetted by the stationary phase, which should result in poor reproducibility of retention data and make them dependent on the time of storage ("ageing") of the sorbent. In addition, unlike solutions, the contribution of sorption at all phase interfaces varies substantially, depending on the presence of trace amounts of impurities (modifiers)[7,8], such as water. The participation of adsorption in retention should therefore cause a strong dependence of retention values on the moisture content. These effects should be most clearly manifested in a polar support–non-polar stationary phase–polar solute system, because in this case there is a poor wettability of the support surface by the stationary phase, and a strong effect of the moisture content is to be expected.

It seemed important to establish the role played by different components of retention from the results of chromatographic and static measurements.

Adsorption in gas–liquid chromatography not only introduces the above features in measuring retention values, but also opens useful possibilities for solving three problems, *viz.*, (1) increasing the selectivity, (2) increasing the efficiency and (3) measuring static adsorption values.

The objects of the present work were:

(1) to investigate the above specific features of retention (ageing, effect of moisture content);

(2) to establish the role played by the different partial components of retention, and

(3) to investigate the selectivity and efficiency of sorbents, particularly those containing a solid phase, taking into consideration adsorption of sorbents at the phase interfaces.

STUDY OF AGEING

We studied the variation in retention volumes in the *n*-propanol–squalane–Celite 545 (60–80 mesh) system when adsorption of sorbates takes place. Two distinguishing features of the procedure for measuring specific retention volumes should be noted. The experiments were made at very low solute concentrations (C) in the gas phase, corresponding to the linear part of the adsorption isotherms ($C \approx 10^{-5}$ vol. %). A flame ionization detector was used. With increasing concentration, the part played by adsorption processes decreases as the adsorption isotherms are convex. The sorbents were prepared with the application of a vacuum[8,9].

Experimental results for the above system are shown in Fig. 1. The specific

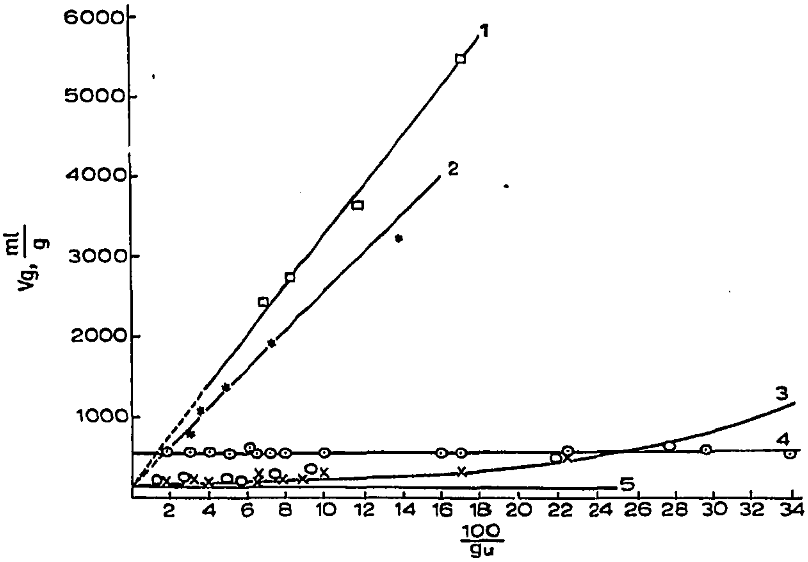

Fig. 1. Dependence of specific retention volumes, V_g, of *n*-propanol and *n*-hexane on $100/g_u$. Stationary phase: squalane. Column temperature: 19°. Curves 1 and 2 correspond to freshly prepared sorbents; sorbate, *n*-propanol. Curve 3 corresponds to sorbents subjected to ageing by different methods; sorbate, *n*-propanol. Curve 4 shows the dependence of V_g of *n*-hexane on $100/g_u$, and curve 5 the contribution of solution to the retention volume of *n*-propanol.

retention volume, V_g, calculated per gram of stationary phase, is plotted against $100/g_u$ (refs. 4 and 10) (g_u is the weight percent of the stationary phase, the support weight being taken as 100%). Curves 1 and 2 correspond to freshly prepared samples and show poor reproducibility of the retention values. The ageing operation (keeping the sorbent at 110° in a stream of nitrogen for 35 h) produces a sharp decrease in retention volume. The lowest retention volumes obtained are shown by curve 3. The time required to obtain the retention values shown by curve 3 can be decreased by using special intensive ageing procedures. In one of these procedures (the retention data are shown by crosses on the plot), the sample was subjected to vacuum treatment ($P \approx 10^{-1}$ torr) at 180°. The amount of squalane that remained after such a treatment was determined by measuring the retention volume of *n*-hexane. In the second procedure, a squalane solution in *n*-hexane containing the support was boiled under vacuum with a gradually increasing temperature, after which the sorbent was kept under vacuum for 2–3 h at 50°. The values obtained by this procedure of sorbent preparation are indicated on curve 3 by circles, while those obtained by simple ageing are indicated by points. A non-polar sorbate (*n*-hexane) is characterized by the absence of a dependence of retention volume on g_u and the retention volume is reproducible and unaffected by ageing (curve 4). This fact suggests that, in the case considered, ageing is not related either to chemical conversions or to bleeding of the stationary phase.

The effect of moisture content on retention data for the same system is illustrated in Fig. 2. Curve 1 corresponds to curve 3 in Fig. 1. If the silica gel (MCM grade) used as drying agent in measuring the retention volumes (the values of which are given in Fig. 1) is replaced by molecular sieve 5Å, the retention volumes increase sharply (Fig. 2, curve 2). This is true not only of the aged but also of the freshly pre-

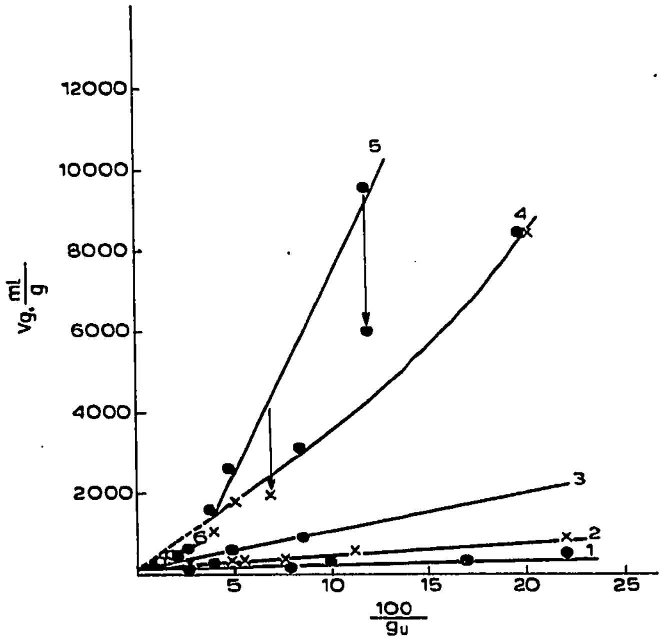

Fig. 2. Effect of moisture content on the retention volume of *n*-propanol. Stationary phase: squalane. Column temperature: 19°.

pared sorbent. Retention values obtained with silica gel as the drying agent are given by curve 3, while those obtained with molecular sieves are shown by curves 4 and 5. Examination of the graph shows clearly that the reproducibility of the data is very poor (curves 4 and 5).

It was of interest to obtain retention values for samples with very high percentages of stationary phase after prolonged storage. Data obtained under these conditions are presented in Fig. 2, curve 6. As the drying agent, molecular sieve 5Å was used.

Ageing carried out under the same conditions as those described above (35 h at 110°) with a nitrogen stream dried with molecular sieves was markedly slower, as shown by the data indicated by crosses in Figs. 4 and 5. The sample illustrated by curve 4 was virtually unaffected by the ageing treatment. This was to be expected, as the addition of water would decrease the polarity of the support and hence improve its wettability with a non-polar phase. It is interesting to note that chromatographic measurements offer the possibility of investigating the kinetics of the processes of spreading of the liquid over a solid surface. It should be noted that the phenomena described above are not observed in a system consisting of a non-polar sorbate, a polar stationary phase and a polar support. Fig. 3 shows the retention data obtained for *n*-decane and *n*-nonane on Celite coated with polyethylene glycol (PEG) 400 as the liquid phase. Examination of the graph reveals the essential role of adsorption in this system. Consistent data, however, were obtained after storage of sorbents at room temperature for only a few hours, and the magnitude of the change in retention volume with time, indicated by arrows, was small.

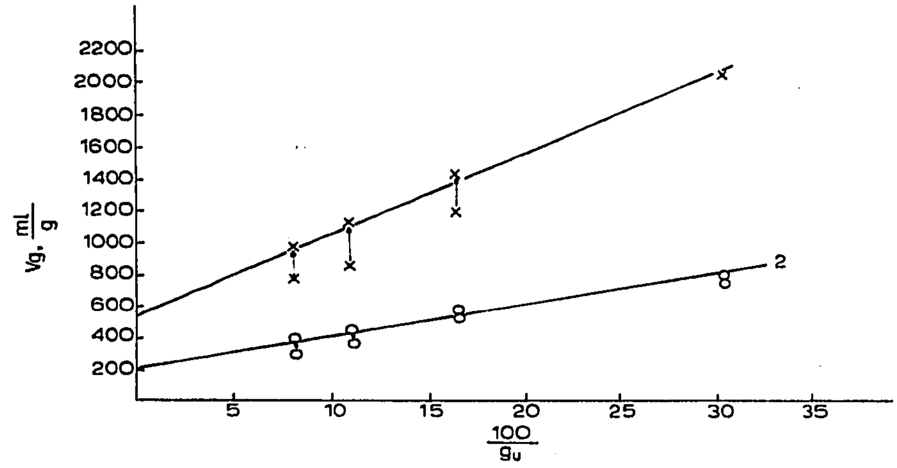

Fig. 3. Dependence of V_g values of *n*-nonane and *n*-decane on $100/g_u$. Stationary phase: PEG 400. Column temperature: 19°.

The phenomenon observed illustrates the risks that arise when measuring retention values for systems containing a polar support. Measuring thermodynamic properties of such solutions without the use of modifiers seems to be very difficult. This also applies to the measurement of adsorption isotherms at the phase interface and to the use of retention volumes for identification.

The basic physical mechanism underlying the phenomenon of ageing is a redistribution of the stationary phase, consisting in its passage from wide to narrow pores. This passage is accompanied by a removal of air bubbles and a decrease in the area of the gas–liquid interface.

STUDY OF THE CONTRIBUTION OF DIFFERENT TYPES OF RETENTION

We investigated the range of percentages of liquid phase from 3 to 90%. It seems that the contribution of adsorption at the gas–solid interface is small in comparison with the total retention volume. This is shown by the curves in Fig. 1. Let us consider the interpretation of the relation $V_g = f(100/g_u)$, permitting an estimation to be made of the contribution of adsorption at the gas–liquid and liquid–solid interfaces. Fig. 4 shows curve 3 on a larger scale. The tangent of the angle of slope of the straight portion describes adsorption at the liquid–solid interface. The part played by solution is illustrated by the part of the ordinate between the origin and the point of intersection of the straight line.

The calculation of the contributions made by the different components of the retention volume (η_i) was made by the following equations

$$\left.\begin{aligned}\eta_{\text{sol.}} &= \frac{a}{a+b+c}\\ \eta_{\text{ads. at g–l interface}} &= \frac{b}{a+b+c}\\ \eta_{\text{ads. at l–s interface}} &= \frac{c}{a+b+c}\end{aligned}\right\} \qquad (1)$$

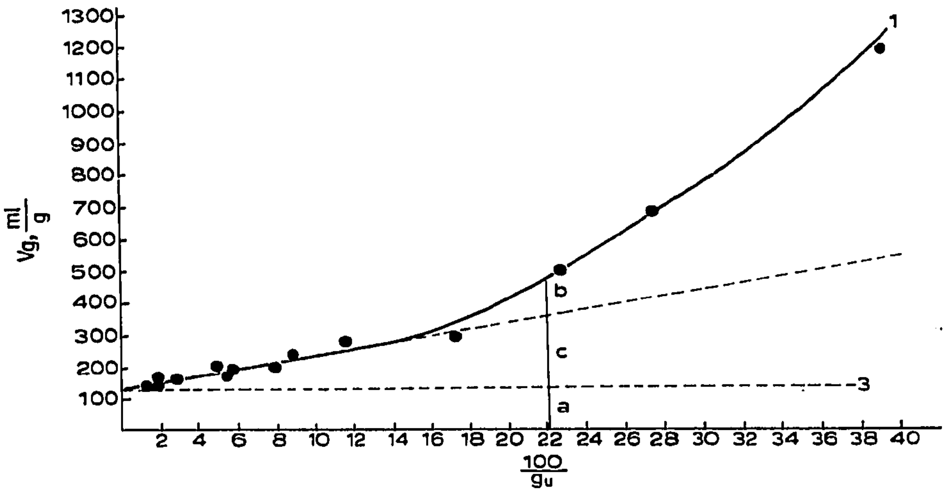

Fig. 4. Curve 3 in Fig. 1 on enlarged scale.

The meaning of a, b, c can be seeen in Fig. 4.

Fig. 5 illustrates the dependence of the contributions of the different components of the retention volume (η_i) on the value of $100/g_u$ for the curve shown in Fig. 4. It can be seen that with large values of g_u, the total adsorption effect is due to the liquid–solid interface, while with low percentages of stationary phase the contribution

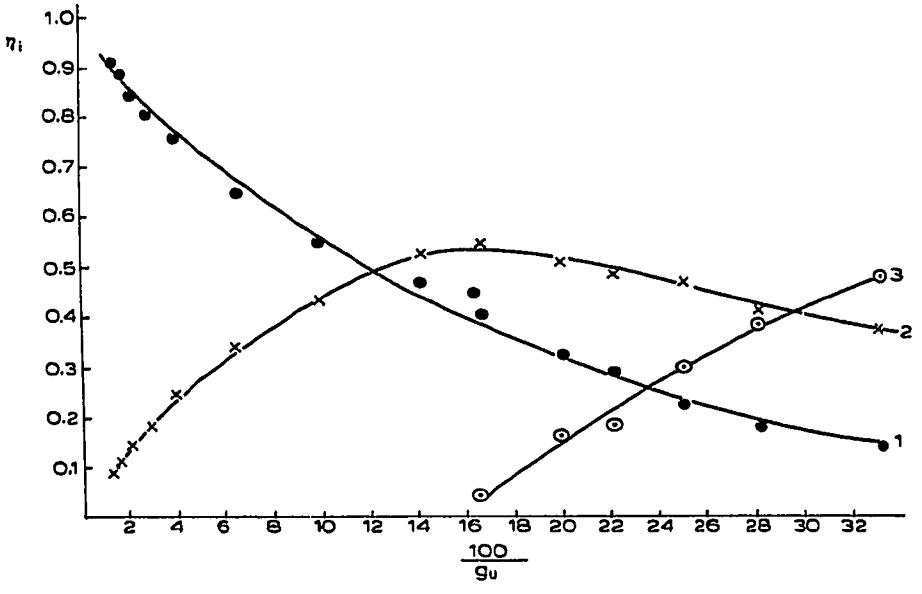

Fig. 5. Dependence of contributions of the different components of retention on $100/g_u$. Curve 1: contribution of solution to the total retention of *n*-propanol. Curve 2: contribution of adsorption at the liquid–solid interface to the total retention of *n*-propanol. Curve 3: contribution of adsorption at the gas–liquid interface to the total retention of *n*-propanol.

of this quantity to the total adsorption approximates to 0.44 at $g_u = 3\%$ when silica gel is used as the drying agent.

The reliability of these data would be improved if static measurements of the contributions of adsorption at different interfaces were used directly. Data on measurements of adsorption mainly at the gas–liquid interface are available in the literature[1,3,11,12]. We carried out static measurements of the amount of the substance adsorbed at the liquid–solid interface and of the partition coefficient, K_p.

Measurement of adsorption at the liquid–solid interface was based on chromatographic measurement of concentration[13]. A weighed sample of the support (0.3–2 g) was placed in a phase containing a sufficient volume of a solution of the sorbate to be investigated in the stationary phase (about 6 ml). Equilibrium was established in 4–5 h. In order to measure the concentration of the initial and final solution, a small portion of each was injected with a microsyringe on to a 3 cm × 4 mm I.D. column packed with the pure support. The dissolved substance was transferred by the carrier gas to a polyethylene glycol ($g_u = 20\%$) column and then to a flame ionization detector. The amount of the substance adsorbed (a) was calculated by the equation

$$a = \frac{\Delta C \cdot V}{g} \tag{2}$$

where ΔC is the change in concentration of the *n*-propanol solution, V is the volume of solution and g the weight of the sample of support.

Fig. 6 shows the adsorption isotherm of *n*-propanol at the *n*-hexadecane–Aprelevka firebrick interface. The results of five runs are shown. Neglecting the data

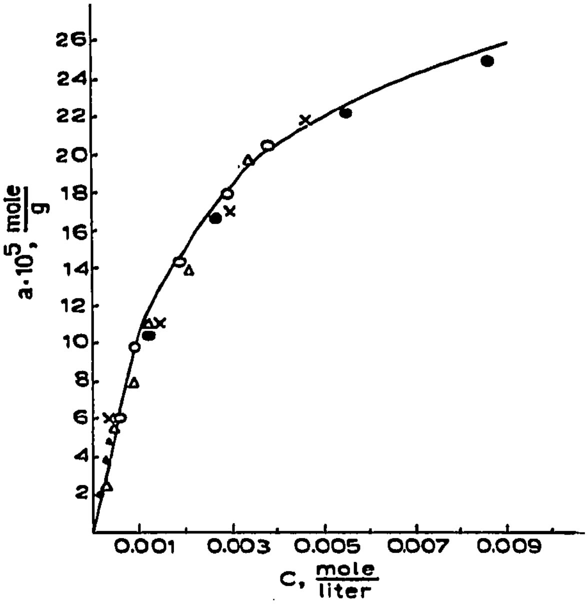

Fig. 6. Adsorption isotherm of *n*-propanol at the *n*-hexadecane–Aprelevka firebrick interface obtained by the static method.

corresponding to low concentrations ($C < 5 \cdot 10^{-4}$ mole/l), the mean quadratic deviation of the points from the smooth curve shown in the graph is 4.2%.

Fig. 7 shows the adsorption isotherms of *n*-propanol at the squalane–Celite interface.

It is very difficult to ensure identical conditions in static and chromatographic runs, particularly the moisture content. Moreover, in order to eliminate adsorption at the gas–liquid interface in static experiments, no gas bubbles in the pores of the support should be present.

Curve 2, Fig. 7, represents a support added directly to the solution; hence in this case a certain contribution of the gas–liquid interface is not completely excluded. Curve 1 describes the adsorption on samples subjected to ageing which had been prepared under vacuum conditions and contained 60–90% of squalane and were subsequently placed in a solution of *n*-propanol in squalane. In order to determine the initial concentration of *n*-propanol in squalane, *n*-hexane was added to the solution and the change in the initial concentration of *n*-propanol produced by the addition of the phase introduced simultaneously with the support was measured by the chromatographic method from the ratio of *n*-hexane peak areas. The data thus obtained coincided (within experimental error) with the results of direct calculation.

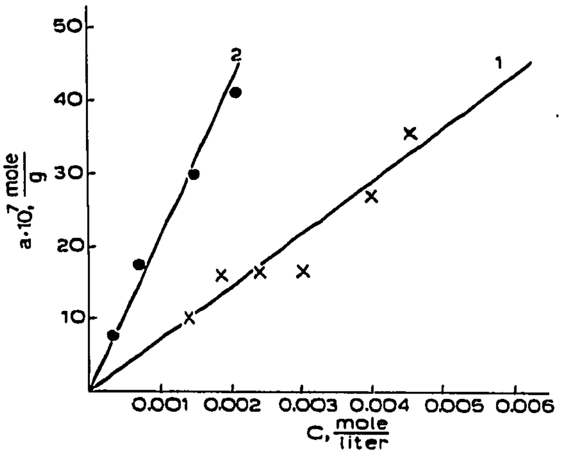

Fig. 7. Adsorption isotherm of *n*-propanol at the squalane–Celite interface obtained by the static method.

Examination of Fig. 7 reveals that adsorption on a sample prepared by the second method is substantially less than with direct addition of the support to the solution. This difference can be attributed both to the presence of a gas–liquid interface in one of these experiments, and to a possible difference in the moisture content of the samples of support used. It would therefore be difficult to expect any precise agreement between the coefficients characterizing adsorption at the liquid–solid interface obtained by the chromatographic and the static methods.

Henry's coefficient, $\Gamma^{l}_{ads.}$, describing adsorption from the liquid, is calculated as the tangent of the angle of slope directly from the adsorption isotherms presented in Fig. 7. It is not difficult to show that $\Gamma^{\mathrm{g}}_{\mathrm{ads.}}$, describing adsorption from the gas phase at the liquid–solid interface, is related to this quantity in a simple way by the equation

$$\Gamma^{\mathrm{g}}_{\mathrm{ads.}} = \Gamma^{\mathrm{l}}_{\mathrm{ads.}} \cdot K_p \tag{3}$$

where K_p is the partition coefficient.

Calculations according to eqn. 3 give a value of $\Gamma^{\mathrm{g}}_{\mathrm{ads.}}$ of 17 ml/ml for curve 1, Fig. 7, and 48 ml/ml for curve 2. The values of $\Gamma^{\mathrm{g}}_{\mathrm{ads.}}$ determined by chromatographic methods differ considerably, depending on the drying agent used and on the ageing treatment. Thus, for an aged sample with silica gel (MCM grade) as drying agent, $\Gamma^{\mathrm{g}}_{\mathrm{ads.}} = 2.4$ ml/ml (curve 1, Fig. 2). For aged samples with 5 Å molecular sieves as the drying agent (curve 2, Fig. 2), $\Gamma^{\mathrm{g}}_{\mathrm{ads.}} = 7.2$ ml/ml. For samples that were not subjected to thermal treatment, $\Gamma^{\mathrm{g}}_{\mathrm{ads.}}$ reaches very high values when molecular sieves are used as drying agents. For example, for curve 6 in Fig. 2, $\Gamma^{\mathrm{g}}_{\mathrm{ads.}} = 38$ ml/ml. It can be seen that the value of Henry's coefficient determined by the static method with the support added directly to the solution approaches the value obtained for samples not subjected to thermal treatment, molecular sieves being used as the drying agent in the chromatographic run (curve 6, Fig. 2). The value of Henry's coefficient obtained by the static method when aged sorbents are used is more than twice the coefficient obtained for an aged sample with the same drying agent. This fact may be accounted for either by incomplete removal of the gas–liquid interface in static runs or by better drying under conditions of a static run. In addition, the error in measuring the $\Gamma^{\mathrm{g}}_{\mathrm{ads.}}$ values by the static method is large when aged sorbents are used, because in this case the adsorption effect is small.

In order to determine K_p, the following technique was developed. The solution to be investigated (3–4 ml) was placed in a syringe (volume 10 ml). After 24 h, the needle of the syringe, in a vertical position, was introduced into a stopper connected directly to the inner channel of a four-way stopcock. The volume of the inner channel had been measured by weighing distilled water filling the inner channel of the stopcock.

By pressing the piston, the inner channel was swept with the vapour phase, the volume of which was many times that of the inner channel. The carrier gas subsequently carried the vapour phase from the inner channel to a Celite–PEG 300 chromatographic column, and the peak S_2 area was measured. The concentration of the solution was determined by the same method as that used to measure adsorption on the basis of an S_1 peak area measurement. The partition coefficient, K_p, was calculated by the equation,

$$K_p = \frac{S_1}{S_2} \cdot m \tag{4}$$

where m is the ratio of the inner channel volume to the liquid sample volume used to determine the S_1 area.

The value of K_p obtained ($K_p = 105$) agrees satisfactorily with the data obtained from chromatographic and static measurements[3]. The *a posteriori* error of the above method is close to 6%.

EFFECT OF ADSORPTION ON SELECTIVITY AND EFFICIENCY

The possibility of increasing selectivity by making use of adsorption phenomena has been indicated in the literature[14].

Fig. 8 shows the dependence of the specific retention volumes of dioxane (curve 1) and ethyl acetate (curve 2) on $100/g_u$ with C22 firebrick coated with PEG 300.

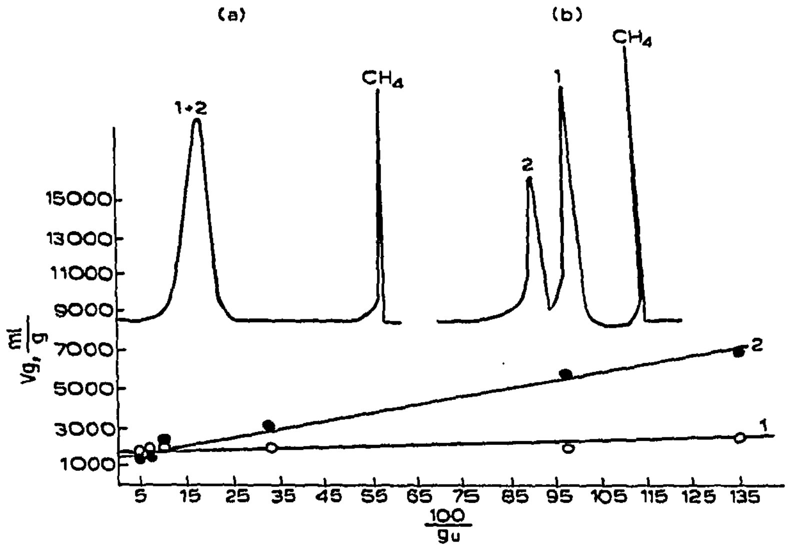

Fig. 8. Dependence of specific retention volumes of dioxane (curve 1) and ethyl acetate (curve 2) on the reciprocal of the percentage of PEG 300 on C22 firebrick. Chromatograms of a binary mixture of dioxane (1) and ethyl acetate (2): (a) $g_u = 20\%$; (b) $g_u = 3\%$. Column length: 36 cm. Column temperature: 22°.

Examination of the graphs reveals that the partition coefficients of the two substances are almost identical, and hence there is no resolution at large values of g_u. This is illustrated by the unresolved peak in chromatogram a, corresponding to $g_u = 20\%$. The adsorption of ethyl acetate is substantially greater than that of dioxane, and with $g_u = 3\%$ good resolution is obtained (chromatogram b).

In their pure form, adsorption effects are displayed when solid stationary phases are used[15-19].

We have used two procedures for solid stationary phase coating: (1) by heating a mechanical mixture of the ground stationary phase with the solid support to a temperature above the melting point, under vacuum with continuous stirring, and (2) by coating a liquid solution with subsequent evaporation of the solvent. After the stationary phase had been coated, the samples were subjected to ageing at a temperature above the melting point in a stream of helium for 5 h.

Our experiments showed that the dependence of retention on the amount of the solid phase coated is also expressed by a linear plot of V_g *versus* $100/g_u$. Fig. 9 illustrates this for isooctane (curve 1) and *n*-heptane (curve 2) on two solid phases, mannitol (a) and *n*-tetracosane (b). This result may be interpreted with the aid of a

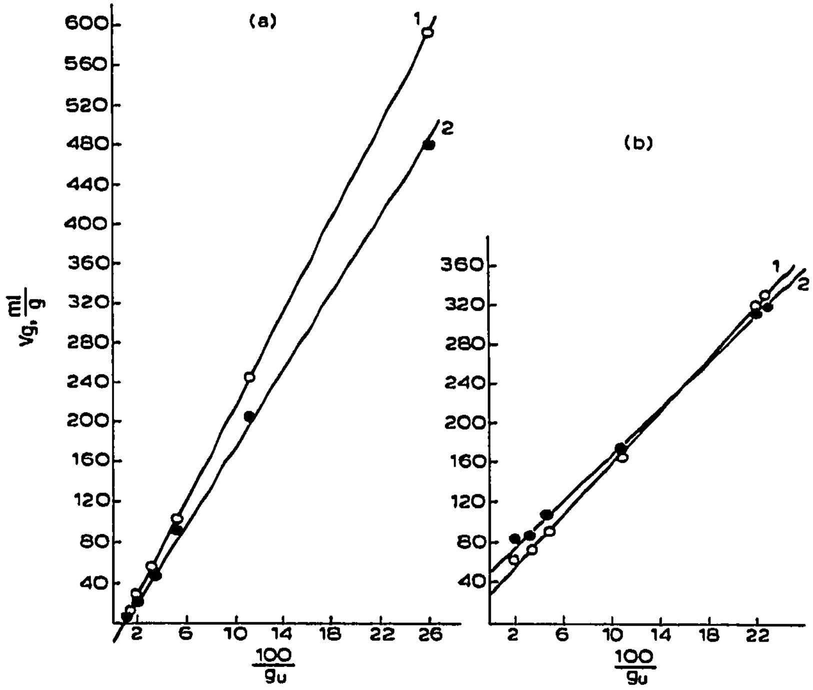

Fig. 9. Dependence of specific retention volume of isooctane (curve 1) and *n*-heptane (curve 2) on the reciprocal of the percentage of stationary phase on C22 firebrick. Column temperature: 22°. Stationary phase: (a) mannitol; (b) *n*-tetracosane.

model of "spots" of equal thickness which decrease the gas–support interface and produce a gas–solid stationary phase interface. In this case, the retention volume can be represented by the equation

$$V_N = M\,(S - Lg) + Ng \qquad (5)$$

where S is the surface area of the solid support and M is the retention volume due to adsorption per unit area of the gas–support interface. The term Lg (g is the weight of stationary phase in the column) describes a decrease in the surface of the solid support due to the presence of the stationary phase; the term Ng describes the retention value due to adsorption at the gas–stationary phase interface. In the general case, L and M can be dependent on g. If, however, instead of a model based on a continuous film of stationary phase we use a model assuming the presence of distinct "spots" of equal thickness (portions coated by the stationary phase), L and N should be constant. The linearity of the relationship presented in Fig. 9 is an argument in favour of the validity of this model.

Eqn. 5 can be represented by the equation

$$V_g = \frac{V_N}{g} = b + \frac{A'}{g} \qquad (6)$$

where $A' = MS$ and $b = N - LM$.

Eqn. 6 can be represented by the equation

$$V_g = b + \frac{100\,A}{g_u} \tag{7}$$

where A is retention due to adsorption at the gas–support interface per gram of solid support.

If the model discussed is correct, the value of A (angle of slope in the V_g *versus* $100/g_u$ plot) should depend only to a small extent on the nature of the stationary phase with the same sorbate and the same support. The values of A for different systems are given in Table I.

TABLE I

VALUES OF A FOR *n*-HEPTANE AND ISOOCTANE WITH DIFFERENT STATIONARY PHASES

Column temperature 12°.

Stationary phase	*Sorbate*	
	n-Heptane	*Isooctane*
Polyethylene glycol 1000	13.7	15.8
Mannitol	19.3	23.7
n-Tetracosane	11.7	13.1

The data given in Table I show that in the case of polyethylene glycol and *n*-tetracosane, A is slightly dependent on the nature of the stationary phase, while for mannitol a marked deviation is observed.

If the "spots of equal thickness" model is correct, the temperature dependence of A would permit the heat of adsorption of the sorbate on the solid support to be calculated. The coefficient b can have a different sign, as suggested by eqn. 6 and by examination of Fig. 9. As b is the difference between two exponential functions, the logarithm of b must not strictly be a linear function of $1/T$.

Fig. 10 presents a plot of log V_g *versus* $1/T$ for *n*-heptane and isooctane on a solid support (C22 firebrick) without a stationary phase, as well as plots of log A *versus* $1/T$ on a support containing PEG 1000 and of log $|b|$ *versus* $1/T$ for the latter system. The heats of adsorption of *n*-heptane and isooctane on a support without a stationary phase were found to be 8.1 and 8.2 kcal/mole, respectively. In the case of a sorbent containing PEG 1000, the heats of adsorption of *n*-heptane and isooctane corresponding to the pure support are 9.6 and 10.1 kcal/mole, respectively. In spite of the comparatively rough nature of the model used, these values are, in our opinion, reasonable. As Fig. 10 shows, it is only for low temperatures that the dependence of log $|b|$ upon $1/T$ is linear.

Examination of Fig. 9 shows that isooctane is more strongly sorbed than *n*-heptane on the solid support, while on the *n*-tetracosane surface the relationship is reversed. For every temperature of the run there is therefore a certain value of g_u at which the sorption of components is similar, and they are not resolved from each other. At g_u values below that indicated above it is isooctane, and at higher values *n*-

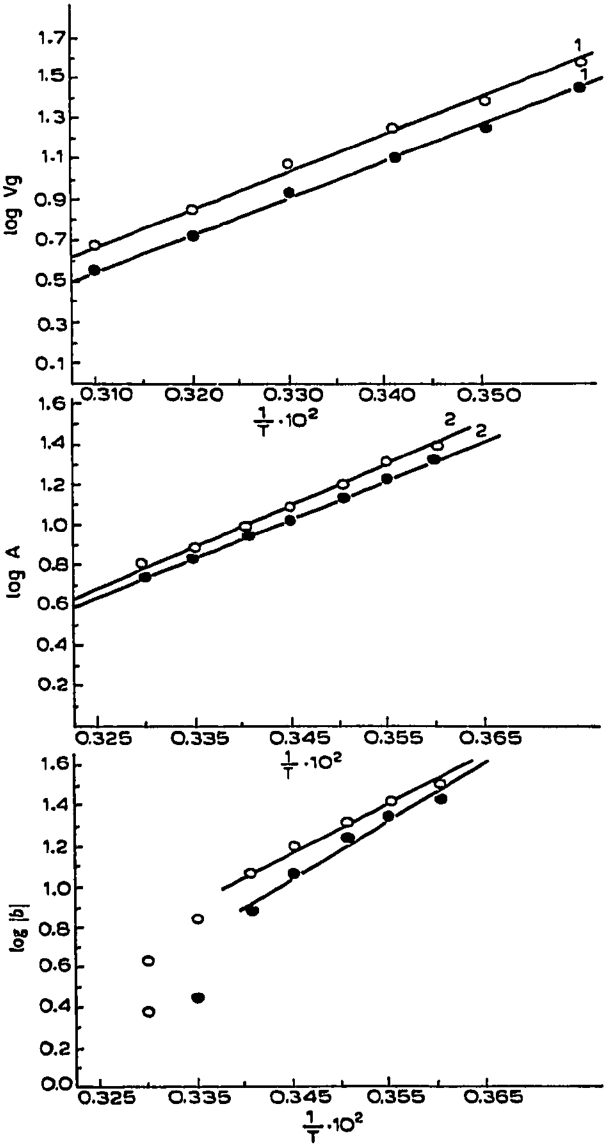

Fig. 10. Dependence of log V_g, log A and log $|b|$ on the reciprocal of column absolute temperature ($1/T$). (1) C22 firebrick without stationary phase; (2) C22 firebrick coated with PEG 1000. ●, *n*-Heptane; ○, isooctane.

heptane, that is more strongly sorbed. In those cases when PEG 1000 and mannitol are used as stationary phases, adsorption of the sorbates occurs mainly on the gas–support interface at almost all g_u values, while with *n*-tetracosane, this is true only for $g_u < 6\%$. The values of b accordingly have opposite signs when *n*-tetracosane or polyethylene glycol and mannitol are used as stationary phases.

Fig. 11 shows the dependence of log V_g on $1/T$ for different values of g_u. An increase in the retention value that takes place after a certain temperature has been reached is accounted for by the melting of the stationary phase. The range of melting is rather wide (about 20°) with the solid phase coated on the support, according to the literature, while when the support is not coated with the phase this range is from 37° to 40°. At low g_u values, the melting range is weakly displayed on the graph because the contribution of solution to the retention value is small. Examination of Fig. 11 also reveals that the sequence of solubility values is similar to that for adsorption values on the surface of solid stationary phases.

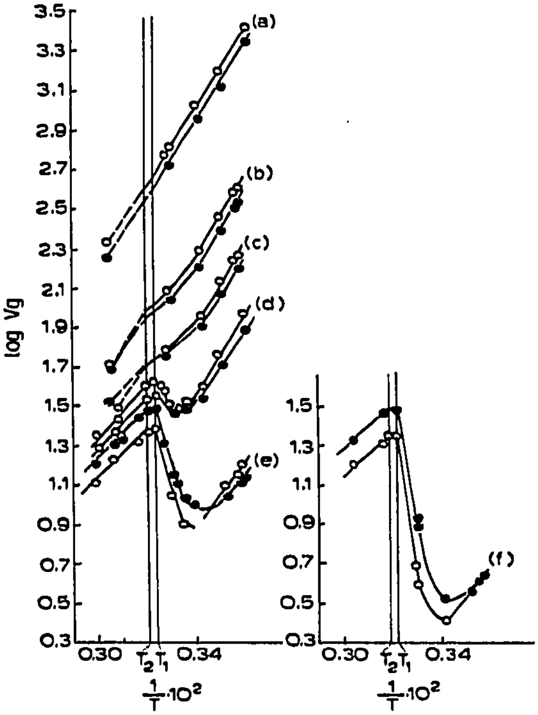

Fig. 11. Dependence of the logarithm of specific retention volume on the reciprocal of absolute column temperature ($1/T$). g_u: (a) 1%; (b) 5%; (c) 10%; (d) 20%; (e) 50%; (f) 79%. $T_1 = 310$°K; $T_2 = 313$°K. ●, *n*-Heptane; ○, isooctane. Stationary phase: PEG 1000.

It is to be expected that the efficiency of separation caused by adsorption processes will be greater than it is in the case of solution because of an absence of resistance to internal diffusion. In this case, the effect of the nature of carrier gas will be more strongly displayed than with liquid stationary phases. Fig. 12 shows the dependence of the height equivalent to a theoretical plate (HETP) on linear carrier gas velocity (α) for isooctane on C22 firebrick coated with 20% PEG 400 or 1000. In the former case, the stationary phase is liquid, and with a large value of g_u the contribution of adsorption is small. In the latter case, retention is due only to adsorption on the gas–solid support and the gas–solid stationary phase interfaces. It is evident from the graph that, in accordance with the above discussion, the HETP values are close to each other with the two carrier gases (helium and nitrogen) only at small values of α, and the plate height is significantly less when solid stationary phases

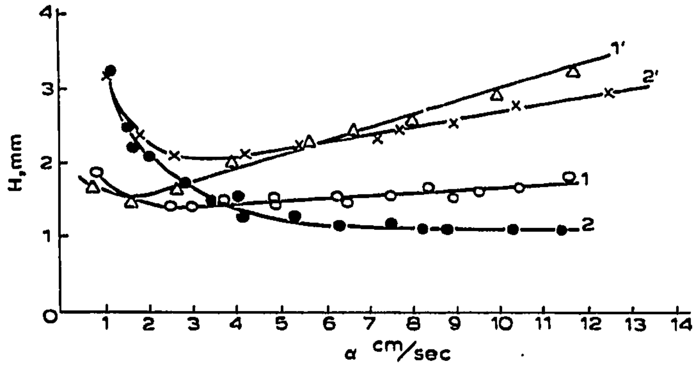

Fig. 12. Dependence of the height equivalent to a theoretical plate on linear velocity of the carrier gas. Carrier gas: curves 1 and 1', nitrogen; curves 2 and 2', helium. ●, ○, stationary phase PEG 1000; ×, △, stationary phase PEG 400. Sorbate: isooctane.

are used than with liquid phases. When a solid stationary phase is employed, the angle of slope of the curve representing resistance to internal diffusion is small with nitrogen as carrier gas and almost zero with helium. This fact suggests that the application of solid stationary phases is promising for rapid gas chromatographic techniques and for the analysis of high-boiling substances.

CONCLUSIONS

Adsorption at the phase interface of a sorbent in the case of a polar support, a polar sorbate and a non-polar stationary phase leads to a lack of reproducibility in the retention values, to a sharp decrease in these values upon ageing and to a strong influence of the moisture content of the sorbents upon retention data.

Experimental studies have shown that these phenomena are distinctly exhibited in the *n*-propanol–squalane–Celite 545 system and are not observed in the *n*-nonane–polyethylene glycol 400–Celite 545 and the *n*-decane–polyethylene 400–Celite 545 systems.

A number of procedures have been proposed, the application of which secures greater stability and better reproducibility of specific retention values.

An interpretation of the ageing phenomenon is suggested based upon a consideration of the process of stationary phase redistribution, modification of adsorption sites with water, and acceleration of the process of stationary phase redistribution as influenced by the moisture content.

Examination of the results obtained in this study concerning the relationship between specific retention volume and percentage of stationary phase for the *n*-propanol–squalane–Celite system has permitted an estimation to be made of the contribution of the solution and the adsorption process on two (gas–liquid and liquid–solid) interfaces.

Static measurements made with the aid of procedures either developed or improved by the authors (determination of adsorption values at the liquid–solid interface, as well as the determination of partition coefficients) have, in general, confirmed the results of chromatographic measurements carried out on aged sorbents and particularly the significant role of adsorption at the liquid–solid interface.

Using as an example the gas chromatographic analysis on a column packed with PEG 300 (as the stationary phase) coated on C22 firebrick, it has been shown for the ethyl acetate–dioxane system that adsorption at the phase interfaces changes the selectivity compared with that caused by solution, and can substantially improve resolution.

For these solid stationary phases (PEG 1000, *n*-tetracosane and mannitol) coated on C22 firebrick and for two sorbates (*n*-heptane and isooctane), the relationship between specific retention volume and the percentage of stationary phase has been investigated. It has been shown that in accordance with the "spots of equal thickness" model, the data can be well represented by a linear plot of V_g *versus* $100/g_u$

The HETP is considerably lower when a solid stationary phase is used and sharply decreases if helium is used instead of nitrogen as the carrier gas.

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