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ADSORPTION IN GAS–LIQUID CHROMATOGRAPHY

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CONTENTS

1. INTRODUCTION

Advances in chromatography are associated with the use of adsorption and the development of our concepts of the role of adsorption in chromatographic processes. The first chromatographic technique, invented by Tswett in 1903, was liquid–solid chromatography. Separation in this technique is based on the difference in the adsorption of the substances being separated on the surface of a solid. Tswett wrote[1], "On the basis of all previous studies it becomes possible to develop a new method of physical separation of various substances in organic liquids. The method resides in the ability of dissolved substances to form adsorption compounds with most diverse mineral and organic solids".

The next important stage in the development of chromatography was the introduction by Martin and Synge, in 1941, of partition chromatography based on the different partition (absorption) of the substances being separated between two phases: the mobile phase (gas, liquid) and the stationary phase (liquid)[2]. In their conclusions, Martin and Synge proposed a new type of chromatography, based not on adsorption on the solid phase, but on partition of the dissolved substances between two liquid phases[2]. In the same work they also proposed another new technique of partition chromatography, namely gas–liquid chromatography (GLC). The first experimental work on GLC was published in 1952 by James and Martin[3]. It is interesting that even in this first work asymmetric peaks (with trailing edges and steep fronts) were observed when lower fatty acids (formic and acetic) were separated, which was explained by adsorption of the acids separated on the surface of diatomite. It was shown that the adsorption could be reduced by introducing orthophosphoric acid into the stationary liquid phase (SLP) or by applying it on the surface of diatomite. Thus, even in their first work on GLC, James and Martin had to take into account the adsorption of the substances separated on the solid support and to take special measures to minimize it.

At present, one of the most widely employed techniques in analytical organic chemistry is gas chromatography[4].

Over the past 15 years, we have learned a good deal about the mechanism of separation in GLC, and our concepts of the nature and role of the individual processes that occur have undergone substantial changes. It is not an exaggeration to say that owing to the extensive work by scientists in many countries our concepts of the mechanism of the retention of compounds of interest in GLC have been revolutionized insofar as adsorption phenomena are concerned, especially as their essential role in most chromatographic systems of practical importance has been established. Unfortunately, however, most analytical and physico-chemical studies are conducted, in practice, without a quantitative evaluation of adsorption and retention, and their role is ignored. Such a situation seems to result from the universally adopted, simplified notion of the phase state of the sorbent in GLC, which is regarded only as an SLP.

Investigations of a wide range of analytical samples (particularly high-boiling and polar compounds) and special studies have shown that adsorption phenomena play an important role in GLC, and the classical notion of GLC as a chromatographic technique involving a single stationary phase (liquid) holds only if it is considered as an extreme (particular) case.

To interpret experimental results in classical GLC[5], extensive use has been made of the following relationship between the true retention volume (V_N) and the partition coefficient ($K_l = c_l/c_g$):

$$V_N = K_l v_l \tag{1}$$

where v_l is the volume of SLP in the column and c_l and c_g are the sorbate concentrations in the liquid and gas phases, respectively. In quantitative analyses aimed at identifying chromatographic zones, relative retention volumes have been widely used:

$$r_i = V_{Ni}/V_{Nst} = K_{li}/K_{lst} \tag{2}$$

where the subscript *st* relates to the substances selected as a standard, or retention indices, I_i, (refs. 6 and 7) which are a function of the corresponding relative retention volumes:

$$I_i = 100z + 100\log \cdot \frac{r_{i,z}}{r_{z+1,z}} \tag{3}$$

where $r_{i,z}$ is the relative retention volume of the *i*th compound (standard: *n*-alkane with *z* carbon atoms) and $r_{z+1,z}$ is the relative retention volume of an alkane containing $z + 1$ carbon atoms, $1 \leqslant r_{i,z} < r_{z+1,z}$.

As can be inferred from eqns. 1–3, the relative retention volumes and retention indices in the case when the retention of the sorbate in a chromatographic column is determined only by the dissolution of the sorbate in the SLP are independent of the content of the latter and of the properties of the solid support, while the true retention volume is determined only by the partition coefficient of the compound being analysed and the volume of the SLP in the column. Van de Graats[8] showed that the relative retention volumes are invariant with respect to certain conditions of a chromatographic experiment, while Porter *et al.*[9] and Anderson and Napier[10] corroborated the validity of eqn. 1 for some specific systems by comparing the values of partition coefficients defined chromatographically and statically. For example, the partition coefficient of *n*-heptane in the gas–diisodecyl phthalate system at 105° was found to be 55 ± 3 by GLC, which does not differ markedly from the value of 57.1 ± 1 determined statically. For 2-propanol in the same system, satisfactory agreement between the values found chromatographically (28 ± 3) and statically (25 ± 1) was obtained.

Many studies described in the literature were aimed at determining another equilibrium value, the activity coefficient, j, at infinite dilution, which is representative of the degree of deviation of the behaviour of a real solution from that of the ideal solution. The basic static characteristic used for calculating the value of j was the specific retention volume (V_g^T) calculated per gram of the SLP[11–14]:

$$j = RT/V_g^T M p^\circ \tag{4}$$

where R is the universal gas constant, T is the absolute temperature, p° is the vapour pressure of the sorbate at temperature T and M is the molecular weight of the SLP.

As was shown by Kwantes and Rijnders[14], the activity coefficient of *n*-hexane in 1,2,4-trichlorobenzene determined by GLC is 2.90, which agrees well with the value of 2.93 determined statically. Good agreement between the activity coefficients determined by various methods has also been pointed out in a number of other publications for different systems[15–18].

According to Kwantes and Rijnders[14], different results are obtained with systems that include a polar dissolved compound and a non-polar stationary liquid, *e.g.*, alcohols, aldehydes, ketones or esters in a hydrocarbon solvent, particularly hexadecane. The peaks obtained in these instances were sloping with pronounced tailing, while the retention time was strongly dependent on the sample size, being short with large samples and *vice versa*. This is indicative of residual adsorption of the polar dissolved compound on the support. All inorganic supports in current use produce the same results. Some improvement was achieved if the minerals were treated with dimethyldichlorosilane, but even then the results were not reliable.

These difficulties have been overcome by using very fine metal spirals as the support, the stationary liquid being introduced into the column after it has been packed with metal spirals. The amount of liquid present was calculated on the basis of the retention volume (of *n*-pentane) for which the coefficient of partition between the liquid and gas phases was known.

As a result of a subsequent study of the role of adsorption on the support surface in GLC, Bohemen *et al.*[19] showed that the adsorption of polar compounds is essential even for a sorbent that contains a large amount of a non-polar liquid phase. For example, the retention time of acetone is halved on a sorbent containing 20% of squalane after the surface of the solid support used (Sil-O-Cel) has been modified with hexamethyldisilazane; at the same time, the symmetry of the acetone peak is improved.

TABLE 1

EFFECT OF SOLID SUPPORT ON RETENTION INDICES OF COMPOUNDS BEING SEPARATED
100°; column 150 × 0.4 cm.

Solid support	*SLP*	*Compound being separated*					
		2-Hexanone	*Chloro-benzene*	*1-Pentanol*	*2-Methyl-heptanol*	*Benzo-nitrile*	*Nitro-benzene*
Chromosorb W	10% of squalane	774.0	825.7	800.0	939.5	918.6	1016.9
Celite		747.2	826.0	763.5	902.3	904.2	1009.7
Anachrom		733.3	826.8	714.9	885.2	896.5	1005.2
Chromosorb G		732.6	826.9	714.4	885.3	896.6	1005.4
Gas-Chrom Q		730.9	826.8	703.9	883.2	893.1	1004.3
Silanized							
Chromosorb G		728.7	826.5	694.9	883.9	1005.1	
Chromosorb W	10% of polyethylene glycol 400	1147.1	1252.9	1347.2	1377.0	1644.0	1745.0
Celite		1170.0	1275.0	1369.4	1397.9	1675.8	1779.4
Anachrom		1177.9	1283.5	1384.2	1408.8	1696.8	1801.2
Chromosorb G		1179.0	1284.2	1381.2	1409.2	1693.3	1798.2
Gas-Chrom Q		1181.8	1287.6	1414.9	1702.3	1810.5	
Silanized							
Chromosorb G		1186.4	1293.0	1390.7	1419.1	1709.0	1817.0

Bohemen *et al.* concluded that, as a result of adsorption on the support, the retention volumes of the compounds being analysed are not directly proportional to the volume of SLP in the column, which is at variance with eqn. 1.

In the first work on GLC by James and Martin[3], mention was made of adsorption on the solid support surface of the compounds being analysed, and to minimize that adsorption (of organic acids) the solid support was modified by applying orthophosphoric acid on diatomite and introducing stearic acid (10%) and silicone oil; prior to analysing amines, the support was pre-treated with an alkali. In subsequent work, adsorption on the solid support was shown to play an important role in GLC[20–31]; in particular, the type of solid support used and the content of SLP on the latter were shown to influence the absolute and relative retention volumes, and also the shape of the chromatographic zones. Table 1 gives, as an example of the effect of the solid support on retention volumes, the retention indices of some polar compounds on polar and non-polar phases, depending on the type of the solid support used.

These data were obtained by Evans and Smith[30] in their evaluation of GLC as a quantitative analytical technique. It can be seen that the retention indices of some compounds depend, to a considerable extent, on the type of solid support used for preparing the sorbent for GLC. Pecsok *et al.*[32] have shown that the specific retention volume of hydrocarbons depends strongly on the content of the polar SLP (β,β'-thiodipropionitrile). In this instance the values of V_g^T are not constant even if the β,β'-thiodipropionitrile content is 20%. According to Vigdergauz and Pomazanov[33], the specific retention volumes of polar sorbates continue to decrease until the content of the non-polar SLP (squalane) applied on Chromosorb W reaches 40%. Bonastre *et al.*[34,35] examined the dependence of the specific retention volumes of various classes of organic compounds on the amounts of polyethylene glycol 20000 and β,β'-thiodipropionitrile. A pronounced dependence of these values on the SLP content was observed with non-polar sorbates for a wide range of SLP contents on the support (up to 30–40%).

The dependence of retention volumes on the type of solid support and SLP content on the solid support makes it difficult to use the tabulated retention values for identifying chromatographic peaks and is inconsistent with eqn. 2. Thus, the development of GLC has shown that eqns. 1 and 2, and hence eqn. 3, are far from valid in all instances. Moshier and Sievers[31] pointed out with good reason that, theoretically, the role of the solid support in GLC is to maintain the SLP in such a state as to enable the flow of gas to pass through it. In fact, the solid support often affects the elution characteristics (*e.g.*, peak shape, retention time, tailing) of volatile components. A similar viewpoint was shared by Dal Nogare and Juvet[5], who stated that adsorption on the active surface of a solid support is responsible for tailing. Although diatomite supports are weak adsorbents in comparison with alumina, silica gel, etc., their activity is usually sufficient for the above-mentioned effect of adsorption to become apparent with polar substances, for instance, alcohols, water, ketones and esters. Adsorption on firebrick is more pronounced than on Celite. It is less obvious with non-polar substances, large relative amounts of the liquid phase and polar liquid phases saturating active portions of the adsorbent's surface.

"Pure" GLC, in which retention volumes and other chromatographic characteristics of compounds are determined only by the properties of the SLP, is almost never realized in practice. The limited area of application of eqns. 1 and 2 is, in our opinion, accounted for by the fact that they have been derived by using an extremely idealized model of the sorbent, in which the polyphase nature (heterogeneity) of the latter is ignored. According to this simplified model, no adsorption takes place at the interphases (*e.g.*, gas–SLP, SLP–solid support), and sorption occurs only in the SLP film whose properties are similar to those of a pure SLP taken in a large amount. Therefore, to account quantitatively for the regularities of variations in retention value on a sorbent containing an SLP, one should consider a more realistic model of this sorbent, with particular emphasis on the distribution of the SLP on the surface of the solid support.

In the early 1960s, the adsorption of compounds on the SLP–solid support interphase was an experimentally well established fact. However, the experimental data on the adsorption of separated substances in GLC were inconsistent both with the then prevailing notion of GLC being a purely partition chromatographic technique involving not only adsorption but also adsorption processes and with the then popular theory of retention of compounds being separated in the SLP. Emphasizing the importance of experimental results in considering the role of adsorption in GLC, starting with the first work by James and Martin, it may be appropriate to cite the following statement made by the Russian organic chemist A. M. Butlerov (1828–1886): "Facts that cannot be explained in terms of existing theories are particularly precious for science; finding the right answers will pave the way to its progress in the near future".

2. SORBENT MODEL

When considering the chromatographic process in GLC, one should use the model of a real sorbent in GLC, which cannot be regarded merely as an SLP. A real sorbent is a polyphase, a simple model of which is shown in Fig. 1. The SLP covers the surface of a solid sorbent as a continuous film of irregular thickness. In spite of its simplicity, this model illustrates the basic features of the retention of volatiles on a real sorbent. Indeed, one should distinguish three phases in a sorbent rather than one (the SLP), namely: (1) the SLP, which adsorbs the substances being separated; (2) the gas–SLP interphase, which adsorbs the substances; and (3) the SLP–solid support interphase, which also adsorbs the substances being separated.

The manner in which the SLP is distributed over the surface of the solid support is determined by the nature of its interaction with the solid support, by its content, by

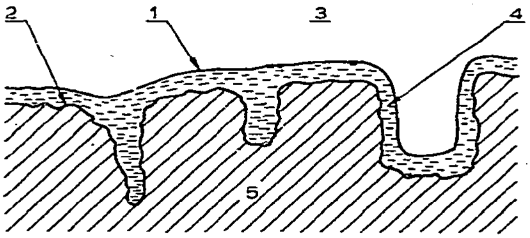

Fig. 1. Simplified model of a polyphase sorbent in gas–liquid chromatography. 1 = Mobile phase–SLP interphase; 2 = liquid–solid (support) interphase; 3 = mobile phase; 4 = stationary liquid phase (SLP); 5 = solid support.

the technique used to prepare the sorbent and its subsequent treatment[22,26,36–41]. In this section, we consider possible models of the distribution of SLP on a solid support, based on experimental data on (1) mass transfer, (2) a porosimetric study of sorbents, (3) variations in the surface area of the sorbent with increasing content of SLP on the solid support and (4) variations in the vapour pressure of the SLP with increasing concentration of the SLP.

Different opinions have been expressed on the distribution of the SLP on the solid support surface. The SLP film may, in general, cover the solid support surface completely or partially, forming separate areas. It may have a uniform thickness (even distribution) or the thickness may vary from one microportion to another (uneven distribution).

According to Zhukhovitskii and Turkel'taub[42], the film concept offers a poorer description of a phenomenon (broadening) than that involving a plurality of microdrops of the stationary phase on the support. This point of view seems to hold in the case of poor wettability of the support surface with the stationary phase.

In their work on the theory of chromatographic zone broadening in GLC, Van Deemter *et al.*[43] made two assumptions regarding the possible distribution of the SLP on the solid support: (1) the SLP forms a continuous film of uniform thickness on the solid thickness, and (2) the SLP forms a film of irregular thickness on the solid support surface, filling mainly smaller pores. The effective SLP film thickness calculated on the basis of the relationship between the height equivalent to a theoretical plate (HETP) and the carrier gas flow-rate, in accordance with the Van Deemter equation for a sorbent obtained by applying 30% of vacuum grease on Celite or Sterchamol, is 9–10 μm. At the same time, the mean thickness of the SLP film, calculated on the assumption that the liquid phase uniformly covers the entire solid support surface, is only about 0.1 μm. The much greater (100-fold) effective thickness of the SLP film found from kinetic measurements using the Van Deemter equation seems to corroborate the fact that a major portion of the SLP fills smaller pores. Such a distribution results in a sharp increase in the effective film thickness, and hence a greater HETP. This concept is shared by Keulemans[120], who considers that the liquid accumulates in the smallest pores and holes under the effect of capillary forces. As the amount of the liquid increases, larger pores start to be filled. In the liquid phase, the distance to be covered by a diffusing molecule equals the average length of a capillary filled with the liquid.

The filling of the smaller pores of a solid support first with the SLP was demonstrated experimentally for the first time by Baker *et al.*[44], who conducted a porosimetric study of an unimpregnated solid support (of the Chromosorb P type) and a support after impregnation with different amounts of the SLP (5–33%). The results indicated that fine pores are filled first. The SLP also seems to fill fine pores inhomogeneously and to form a thin film over the remainder of the surface of the solid support.

The equilibrium theory of the distribution of the SLP on a solid support was elaborated by Giddings[45] and Saha and Giddings[46,47]. According to their theory, the SLP forms a continuous film over the solid support surface; part of it is in capillaries "capillary" liquid), while the remainder coats the walls of larger pores with a continuous thin layer ("adsorbed" liquid). With an equilibrium distribution of the SLP on the solid support, the chemical potential for all types of SLP (adsorbed, capillary, etc.) is constant and equal for all phases. Giddings and co-workers showed that with an equilibrium of the capillary and adsorbed SLP between the layer thickness (d_s) of the adsorbed SLP and the radius of a filled capillary (r), the following relationship applies:

$$d_s = \left(\frac{\Delta E}{2\sigma N_A}\right)^{1/3} = J_a r^{1/3} \tag{5}$$

where ΔE is the difference in the energies of liquid–solid and liquid–liquid interactions, σ is the surface tension and N_A is Avogadro's number. The coefficient J_a is, according to Giddings and co-workers, equal to 10^{-5} cm$^{2/3}$ (ΔE was assumed to be about 1 kcal/mmole and $\sigma = 30$ erg/cm^2). Therefore

$$d_s = 10^{-5} r^{1/3} \tag{6}$$

Using eqn. 6, let us determine the parameters of the adsorbed and capillary SLP for the diatomite supports most frequently used in gas chromatography. The average pore diameter in diatomite supports normally varies from 10^{-4} to 10^{-3} cm. Hence, the adsorption film thickness calculated from eqn. 6 for solid supports varies from 40 to 80 Å. If sorbents are prepared by using a solid support with a specific surface area of 3 m^2/g and a density of 1 g/cm^3, with an even distribution of the SLP, the amount corresponding to the above layer thickness is only 2–4% of the SLP, relative to the weight of the solid support. Thus, the bulk of the SLP in a sorbent containing more than 10–15% of the SLP on a diatomite support must be in the fine pores of the support.

In other work[40,48,49], a similar model of the distribution of the SLP on the solid support was adopted for the case of good wettability, in which, after a monolayer has been formed on the surface of all pores in the support, a further increase in the SLP content results in its film becoming thicker and the gas–SLP surface area becoming smaller owing to fine capillaries being filled to a certain asymptotic value corresponding to the surface area of larger pores. With liquids that inadequately wet the sorbent, this picture is complicated by the appearance of separate drips on the surface of the support.

Consider now the dependence of variations in the surface area of the sorbent, in GLC, on the SLP content on the solid support, with a view to defining the distribution of the SLP[50]. Using the above notions of the manner in which the surface of the solid support is filled with the SLP, one can assume that the surface of the sorbent must change with an increase in the content of the SLP on the solid support as follows. Firstly, the SLP fills fine pores, which results in a sharp decrease in the surface area of the sorbent; then larger pores start to be filled, which also results in a decrease in the surface area, but to a lesser extent than when the fine pores were being filled; finally, the adsorbed liquid film becomes thicker with virtually no decrease in the total surface area of the sorbent. Fig. 2A represents one of the simplified models of a solid support surface being filled with the SLP, in accordance with existing concepts.

Fig. 2B gives experimental data on the dependence of the surface area of the sorbent on the SLP content for various supports (firebrick and Chromosorb W), as well as on the content of β,β'-thiodipropionitrile. These data were obtained by Pecsok *et al.*[32] in a study of the role of the adsorption by the gas–SLP interphase of substances being analysed; the distribution of the SLP on the solid support surface was not considered in their work. It can be inferred from the data that the surface area of the sor-

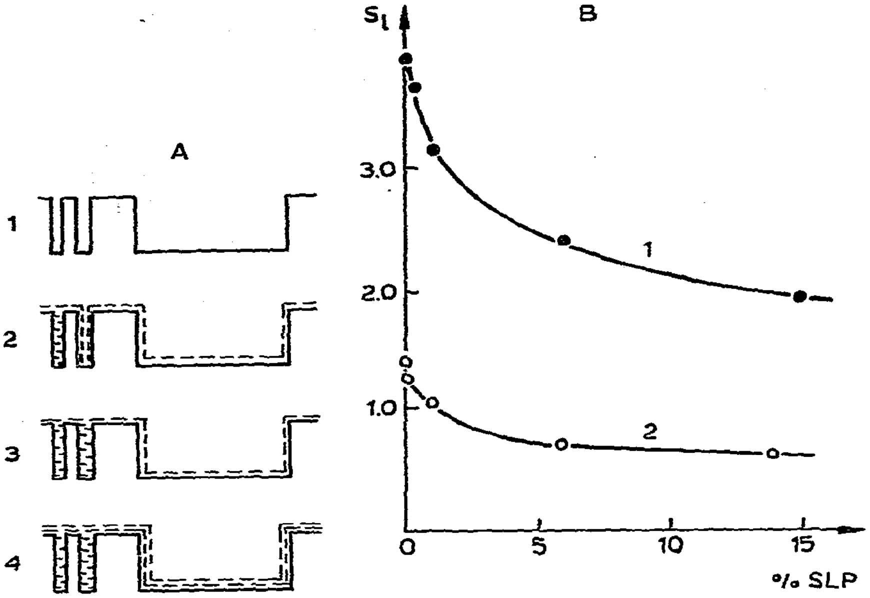

Fig. 2. Simplified model of coverage of the solid support with the SLP (A) and experimental relationship between the sorbent's specific surface area and the SLP content (β,β'-thiodipropionitrile, *n*-hexadecane) (B). (a) 1 = 0%; 2 = x%; 3 = y%; 4 = z%; $0 < x < y < z$. (b) 1 = Firebrick; 2 = Chromosorb W.

bent varies with increasing SLP content in accordance with the above model (see Fig. 2). Firstly, a sharp decrease in the surface area (as a result of fine pores being filled) is observed, then the diminution of the surface area slows down and, for supports with a small surface area, stops completely. Similar experimental results were obtained by Martin[51].

Berezkin *et al.*[52] considered variations in the surface area of the sorbent with increasing SLP content on a solid support with the following assumptions: (1) the pores in the support are filled consecutively, the SLP first filling the smallest pores and the diameter of the pores being filled then gradually increasing; (2) the outer surface area of the sorbent decreases in proportion to the surface area of the pores being filled; and (3) the volume of the pores being filled is equal to that of the SLP applied on the solid support. Variations in the surface area of the sorbent pores being filled are approximately described, with a linear relationship between the pore volume and pore diameter, by the equation

$$S_{lS} = S_0 - S_{S_p} = S_0 = 4\omega \ln\left(\frac{v_{lS}}{v} + 1\right) \qquad (7)$$

where S_0 is the specific surface area of the initial solid support, S_{S_p} is the surface area of the pores being filled, ω and v are constants and v_{lS} is the amount of the SLP per unit mass of the solid support. For a variation in the relative surface area, the following relationship applies:

$$\varrho_S = \frac{S_{lS}}{S_0} = 1 - \frac{4\omega}{S_0} \cdot \ln\left(\frac{v_{lS}}{v} + 1\right) \qquad (8)$$

For $v_{lS}/v \gg 1$, a variation in the surface area can be described as follows:

$$1 - \varrho_S = \frac{4\omega}{S_0} \cdot \ln v_{lS} - \frac{4\omega}{S_0} \cdot \ln v \qquad (9)$$

To check the validity of this equation, use was made of the experimental data in ref. 52. For most solid supports (Chromosorb P, Celite 545, Sterchamol, Resorb, Porolite) this equation holds in the region $v_{lS} > 0.1$ ml/g or even $v_{lS} > 0.05$ ml/g. Fig. 3 shows, as an example, experimental data (eqn. 9) for Resorb and Chromosorb W. It can be seen that this equation adequately describes the dependence of variations in the surface area of the sorbent on the concentration of SLP on a solid support over a wide range of concentrations.

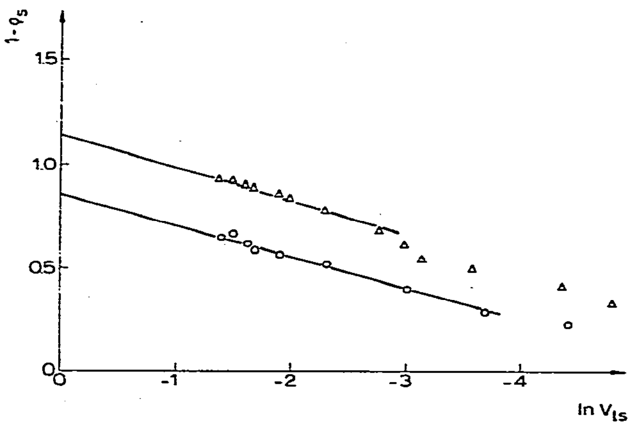

Fig. 3. Experimental verification of eqn. 9. △ = Resorb; ○ = Chromosorb W; SLP = squalane.

To establish the manner in which a solid support is covered by a film of SLP, experiments were carried out[53] using solid supports with lead acetate applied on their surface in advance. The solid supports were impregnated with 0.1–1% solutions of lead acetate, then dried. The SLP (solid at room temperature) was applied on the solid supports covered with lead acetate by using a conventional technique. The SLP was stearic acid (melting point 68–72°) and polyethylene glycol 1000 (melting point 38–40°). The sorbents obtained were loaded into a short glass column, through which a carrier gas with added hydrogen sulphide was passed. If the surface of the solid support were fully covered with the SLP, one would expect the sorbent to remain colourless, whereas if drops form on the surface (as well as partial coverage of the solid support with the SLP in the form of a loose monolayer), the sorbent would tend to become black, the shade representing the fraction of the surface not covered with the SLP (it is assumed that the lead acetate and solid support surfaces are wetted with the SLP to approximately the same extents).

Lead acetate was applied from an ethanol solution: 1% on Chromosorb P, 0.1% on Chromosorb W and 0.05% on sodium chloride. Then the SLP was applied on the treated support by a conventional technique from a solvent in which lead acetate was insoluble (diethyl ether or light petroleum).

This method was used for a quantitative study of the coverage of the surface of various solid supports with various SLPs. The results obtained (Table 2) suggest that both complete and drop-like coverage of a solid support with the SLP occur in practice. It should be noted that the introduction of a surfactant (*e.g.*, stearic acid) results in the drip-like coverage becoming complete. In this instance, the SLP–solid support interphase expands, with consequent complete coverage with the stationary phase. Hence, the wettability of the solid support surface with the SLP has an effect on the manner in which it is distributed over the solid support.

TABLE 2

SLP DISTRIBUTION ON THE SOLID SUPPORT[53]

*Solid support**	*SLP*	*SLP content (%)*	*Sorbent colour***	*Solid support coverage with SLP*
Chromosorb W	Stearic acid	10	White	Continuous film
		5	White	Continuous film
		1	Black	Drops
Chromosorb W	Neopentyl glycol succinate	10	Black	Drops
	PEG 1000	10	Black	Drops
Chromosorb W	PEG 100 + stearic acid	10 + 1	White	Continuous film
Chromosorb P	Stearic acid	25	Pink	Continuous film
		15	Pink	Continuous film
NaCl	Stearic acid	3	White	Continuous film
		1	White	Continuous film
		0.1	Black	Drops

* Treated with $Pb(CH_3COO)_2$.

** After treatment with hydrogen sulphide in the carrier gas flow at room temperature.

Zhukhovitskii and co-workers[38–41] and Keller *et al.*[54] studied the effect of the technique used for the preparation of the sorbent and the conditions applied in subsequent ageing (conditioning) of the sorbents on the SLP distribution pattern. When a vacuum is used in the course of sorbent preparation, the efficiency of chromatographic columns containing squalane or dinonyl phthalate as the SLP on Celite 545 tends to improve in comparison with columns packed with sorbents prepared in a conventional fashion[38,41]. This improved efficiency is indicative of a redistribution of the SLP under the influence of the vacuum, leading to a more even distribution of the SLP on the support surface. For example, for the *n*-hexane–dinonyl phthalate system in which the SLP content is 35%, the use of a vacuum halves the HETP as a result of the lower internal diffusion resistance of the SLP film.

In conclusion, the results of studies conducted using various methods are indicative of a complex SLP distribution pattern. Firstly, the SLP fills primarily fine pores in the solid support, then larger pores are filled, and the SLP film on the macropore walls becomes thicker. When the SLP content on the solid support exceeds a few per cent and the support is adequately wetted with the liquid phase, its surface seems to be coated with a continuous film of SLP: if the wettability is poor, the SLP is present on the surface in the form of drops (isolated areas). The distribution pattern is expected to be substantially affected by the wettability of the support with the SLP and its solution, by the technique of applying the SLP and by the conditions applied in subsequent column ageing. The distribution pattern data must be taken into account in examining the regularities of the retention of the substances being analysed on a real sorbent in GLC.

3. FUNDAMENTALS OF EQUILIBRIUM RETENTION THEORY

A real sorbent has a polyphase nature and, in a general case, the retention of the substances being analysed cannot be explained only in terms of their dissolution in the SLP; one should also take into account the retention by other phases.

Consider now the derivation of an equation for the retention volume of a model in which the SLP forms a continuous film covering the solid support surface, under conditions of ideal non-linear chromatography. Then, the system of equations for the case of ideal (equilibrium) non-linear elution chromatography of a substance, taking account of the adsorption of the substance by the SLP and its adsorption on the SLP interphases, can be written as

$$u \cdot \frac{\partial c_g}{\partial x} + \chi_g \cdot \frac{\partial c_g}{\partial t} + \chi_{gl} \cdot \frac{\partial c_{gl}}{\partial t} + \chi_l \cdot \frac{\partial c_l}{\partial t} + \chi_{lS} \cdot \frac{\partial c_S}{\partial t} = 0 \tag{10}$$

$$c_{gl} = \mathrm{f}_{gl}(c_g) \tag{11}$$

$$c_l = \mathrm{f}_l\,(c_g) \tag{12}$$

$$c_S = \mathrm{f}_{lS}\,(c_1) \tag{13}$$

where u is the linear velocity of the carrier gas, x is a coordinate, c_g is the volume concentration of the substance being analysed in the gas phase, c_l the volume concentration of the substance in the SLP, c_{gl} is the surface concentration of the substance on the gas–SLP interphase, c_S is the surface concentration of the substance on the SLP–solid support interphase, χ_g is the fraction of the gas phase across the column, χ_l is the ratio of the SLP–solid support interphase surface area to the sorbent volume and χ_{gl} is the ratio of the SLP–solid support interphase surface area to the sorbent volume.

Eqns. 11 and 13 are the isotherms of adsorption of the substance being analysed on the gas–SLP and SLP–solid support surface, respectively, eqn. 12 is the isotherm of adsorption (dissolution) in the SLP and eqn. 10 differs from a standard equation by the presence of two additional terms — the third and the fifth. The introduction of these terms has made it possible to take into account the adsorption on the SLP–carrier gas and SLP–solid support interphases.

Let us transform the above system of equations so as to exclude the variables c_{gl}, c_l and c_S. Using the equation for adsorption isotherms, we obtain the following expressions for the partial derivatives of c_{gl}, c_l and c_S with respect to time:

$$\frac{\partial c_{gl}}{\partial t} = \mathrm{f}'_{gl} \frac{\partial c_g}{\partial t} \tag{14}$$

where $\mathrm{f}'_{gl} = \dfrac{\mathrm{d}c_{gl}}{\mathrm{d}c_g}$

$$\frac{\partial c_l}{\partial t} = \mathrm{f}_l' \frac{\partial c_g}{\partial t} \tag{15}$$

where $\mathrm{f}_l' = \dfrac{\mathrm{d}c_l}{\mathrm{d}c_g}$ and

$$\frac{\partial c_S}{\partial t} = \mathrm{f}_{lS}' \frac{\partial c_l}{\partial t} = \mathrm{f}_l'\mathrm{f}_{lS}' \frac{\partial c_g}{\partial t} \tag{16}$$

where $\mathrm{f}_{lS}' = \dfrac{\mathrm{d}c_{lS}}{\mathrm{d}c_l}$

Substituting the derived expressions into eqn. 10, we obtain

$$U \cdot \frac{\partial c_g}{\partial x} + \chi_g \cdot \frac{\partial c_g}{\partial t} + \chi_{gl}\mathrm{f}_{gl}' \cdot \frac{\partial c_g}{\partial t} + \chi_l \mathrm{f}_l' \cdot \frac{\partial c_g}{\partial t} + \chi_{gS}\mathrm{f}_{lS}'\mathrm{f}_l' \cdot \frac{\partial c_g}{\partial t} = 0 \tag{17}$$

or

$$U \cdot \frac{\partial c_g}{\partial x} + (\chi_g + \chi_{gl}\mathrm{f}_{gl}' + \chi_l \mathrm{f}_l' + \chi_{lx}\mathrm{f}_{lS}'\mathrm{f}_l') \frac{\partial c_g}{\partial t} = 0 \tag{18}$$

or

$$V(c) \cdot \frac{\partial c_g}{\partial x} + \frac{\partial c_g}{\partial_c} = 0 \tag{19}$$

where

$$V(c) = \frac{U}{\chi_g + \chi_{gl}\mathrm{f}_l' + \chi_l \mathrm{f}_l' + \chi_{lS}\mathrm{f}_{lS}'\mathrm{f}_l'} \tag{20}$$

Consider now the physical meaning of $V(c)$. Concentration, $c = c_g$, is a function of two variables, x and t:

$$c = c(x,t) \tag{21}$$

Then, the following expressions hold:

$$\left(\frac{\partial c}{\partial t}\right)_x = -\left(\frac{\partial c}{\partial x}\right)_t \left(\frac{\partial x}{\partial t}\right)_c \tag{22}$$

$$\left(\frac{\partial x}{\partial t}\right)_c = -\frac{\left(\dfrac{\partial c}{\partial t}\right)_x}{\left(\dfrac{\partial c}{\partial x}\right)_t} \tag{23}$$

Taking into consideration eqn. 19, we obtain

$$\left(\frac{\partial x}{\partial t}\right)_c = -\frac{(\partial c/\partial t)_x}{(\partial c/\partial x)_t} = V(c) \tag{24}$$

The physical meaning of the derived equation is that the velocity of the content concentration point moving along the column is $V(c)$. It can also be shown that the solution of eqn. 19 is the function

$$c = c(Z) \tag{25}$$

where

$$Z = x - V(c)t \tag{26}$$

As the basic value to be determined in GC is the retention volume rather than the velocity of a chromatographic zone, let us transform eqn. 20 into an equation for the retention volume. In doing so, we shall assume that the pressure drop across the column is small and, consequently, no correction for the compressibility of the carrier gas need be introduced. In this instance, one can write for the volume of retention of a substance

$$\begin{aligned} V_R^\circ = Ft_R^\circ &= \frac{FL}{u}(\chi_g + \chi_{gl}f'_{gl} + \chi_{lS}f'_{lS}f'_l) \\ &= SL\,\chi_g\left(1 + \frac{\chi_{gl}}{\chi_g}\cdot f'_{gl} + \frac{\chi_l}{\chi_g}\cdot f'_l + \frac{\chi_{gl}}{\chi_g}\cdot f'_{lS}f'_l\right) \\ &= V_M\left(1 + \frac{S_l}{V_M}\cdot f'_{gl} + \frac{V_l}{V_M}\cdot f'_l + \frac{S_{lS}}{V_M}\cdot f'_{lS}f'_l\right) \end{aligned} \tag{27}$$

where F is the volumetric flow-rate of the carrier gas in the column, t_R^0 is the retention time, S is the column cross-section, L is the column length, V_M is the dead volume of the column, S_l is the gas–SLP interphase surface area, v_l is the SLP volume and S_{lS} is the SLP–solid support interphase surface area for the entire sorbent filling the column. In this model for the net retention volume, the following equation is valid:

$$V_N = V_R^\circ - V_M = f'_{gl}S_l + f'_l v_l + f'_{lS}f'_l S_S \tag{28}$$

Eqn. 28 establishes a relationship between the retention volume and the characteristics of the sorbent used; it takes into account the dissolution in the SLP and the adsorption on its interphases. Eqn. 28 suggests that the retention volume in equilibrium chromatography is an additive function of retention on different phases of a real sorbent.

The additivity equation for ideal non-linear chromatography may be derived in a different way, on the basis of the Vicke law, by using the adsorption isotherms for a real complex sorbent. In this instance, sorption consists of the adsorption on the SLP interphases and the dissolution in the SLP film.

Because, in a general case, a real sorbent may contain many more than three phases, each being capable of retaining substances of interest, the relationships derived above should preferably be generalized for the case of a large number of phases. In refs. 49, 54 and 55, in considering ideal non-linear chromatography (*i.e.*, assuming an instantaneous establishment of equilibrium and the absence of diffusion effects of broadening), it was shown that the net retention volume, V_N, on a real polyphase sorbent is the sum of partial retention volumes, V_{li} and V_{Sj}, determined, respectively, by the solution and adsorption of a substance being analysed on individual sorbent phases:

$$V_N = \sum_{i=1}^{m} V_{li} + \sum_{j=1}^{n} V_{Sj} \tag{29}$$

or

$$V_N = \sum_{i=1}^{m} K_{li} V_{li} + \sum_{j=1}^{n} K_{Sj} S_{Sj} \tag{30}$$

where K_{li} is the equilibrium constant of a substance distributed between the mobile and stationary liquid phases of type i, v_{li} is the i-type SLP volume in the chromatographic column (*e.g.*, macro- or microlayer of the liquid phase on the solid support surface, liquid phase in micropores, K_{Sj} is the equilibrium constant of the substance distributed between the stationary phase and the j-type interphase surface and S_{Sj} is the extent of the j-type surface in the column (*e.g.*, gas–solid support interphase, SLP–solid support interphase, gas–SLP interphase).

Eqns. 29 and 30 are sufficiently general, and it can be shown that the known retention volume equations are particular cases of these two equations.

The following relationships hold for the equilibrium constant:

$$K_{li} = \frac{V_N}{v_{li}} = \frac{dc_{li}}{dc} \tag{31}$$

$$K_{Sj} = \frac{V_N}{S_{Sj}} = \frac{dc_{Sj}}{dc} \tag{32}$$

where c_{li} and c_{Sj} are, respectively, the concentration of the substance in the stationary bulk phase of type i and the stationary surface phase of type j, and c is the concentration of the substance in the mobile phase. If the adsorption isotherm is described by a non-linear equation, in this instance eqns. 29 and 30 are valid only within the framework of ideal non-linear chromatography, which, of course, limits the area of their application. It should be noted, however, that elution chromatographic techniques for determining non-linear adsorption isotherms, developed on the basis of ideal non-linear chromatography, can be employed successfully in practice, and the results obtained are independent of the carrier gas flow-rate, sample size, etc. The adsorption isotherms in gas–solid chromatography, measured by the above-mentioned chromatographic and static methods, are in good agreement with one another[56,57]. Therefore, the area of application of eqns. 29 and 30, with non-linear isotherms, seems to us to be sufficiently wide. Clearly, in the future the development of more rigorous methods based on the non-equilibrium theory of chromatography[58–60] will permit the mechanism of the chromatographic process to become better understood and will lead to more accurate techniques for measuring the adsorption characteristics for polyphase sorbents.

The development of concepts relating to the role of adsorption in GLC and the equilibrium theory of retention has been associated with account being taken of the contribution of retention on individual bulk and surface phases of a real sorbent to the total retention volume. Important steps in the development of new concepts of the role of adsorption in GLC were newly derived retention equations and their experimental verification.

Martin was the first investigator to have theoretically corroborated the necessity of adding to eqn. 1 a term representing the adsorption of substances chromatographed on the gas–SLP interphase[51,61]. Martin's equation for the net retention volume can be written as

$$V_N = K_l V_l + K_{gl} S_l \tag{33}$$

where S_l is the total area of the gas–SLP surface in the column and K_{gl} is the coefficient of partition of the substance being analysed between the gas–SLP interphase and the gas phase. Martin was also first to verify eqn. 33 experimentally and to show that there is agreement between the adsorption coefficients measured by two independent methods: (i) gas chromatographic, using eqn. 33 and (ii) classical, from the dependence of the surface tension of the SLP solution on the concentration of the volatile substance.

The next step in the development of retention theory was made by Keller and Stewart[62,63], who proposed an equation that takes into account the adsorption of a substance on the solid support surface. The equation proposed by Keller and Stewart can be writen as follows, using the terms employed in their paper:

$$V_N = K_l V_l + K_s S_s \tag{34}$$

where K_s is the coefficient of partition of the substance being analysed between the SLP–solid support interphase and the gas phase and S_s is the area of the SLP–solid support interphase. An equation of this was verified experimentally for the first time by Berezkin *et al.*[50], while it was shown elsewhere[51,64,65] that the coefficients of adsorption of volatiles on the SLP–solid support interphase almost coincide when measured by two independent methods: (i) gas chromatographic, using equations similar to that derived by Keller and Stewart, and (ii) static, by measuring adsorption on a solid support from an SLP solution[64].

A three-term equation for the net retention volume, taking into account the dissolution and adsorption of a volatile substance on the SLP–gas and SLP–solid support interphases, was proposed for the first time by Berezkin *et al.*[49] (see eqn. 28):

$$V_N = K_l V_l + K_{gl} S_{gl} + K_l K_s S_s \tag{35}$$

where K_s is the adsorption coefficient of the volatile substance in the solid support–SLP system. With linear isotherms of dissolution and adsorption, the constants in eqn. 35 do not depend on concentration.

Berezkin *et al.*[49] also proposed methods for the simultaneous determination of all coefficients in eqn. 35, and it was shown that the equation adequately describes the experimental data obtained by different workers[32,37,76]. Conder *et al.*[48] also utilized eqn. 35.

Eqn. 35 was later used successfully in determining partition coefficients in the gas–SLP system, and also in the study of adsorption phenomena in GLC by several groups, for example Conder and co-workers[48,67], Karger *et al.*[68], Urone *et al.*[69], Gritchina and Dreving[70] and Liao and Martire[71].

Eqns. 30 and 35 are of a sufficiently general nature and it can be shown that the known equations for the retention volume are particular cases of these equations (see Table 3).

TABLE 3

SOME EQUATIONS FOLLOWING FROM EQN. 30

No.	*Values of parameters in eqn. 30*	*Equation at a given parameter value*	
1	$K_{ll} = 0$ at $i \geqslant 2$; $K_{sj} = 0$ at $j \geqslant 1$; $K_{ll} = 0$; $V_{ll} = V_l$	$V_N = K_l V_l$	(1)
2	$K_{ll} = 0$ at $i \geqslant 2$; $K_{sj} = 0$ at $j \geqslant 2$; $K_{sl} = K_{gl}$; $S_{sl} = S_l$	$V_N = K_l V_l + K_{gl} S_l$	(33)
3	$K_{ll} \times 0$ at $i \geqslant 2$; $K_{sj} = 0$ at $j \geqslant 3$ and $j = 1$; $K_{s2} = K_s$; $S_{s2} = S_s$	$V_N = K_l V_l + K_s S_s$	(34)
4	$K_{ll} = 0$ at $i \geqslant 2$; $K_{gj} = 0$ at $j \geqslant 3$; $K_{sl} = K_{gl}$; $S_{sl} = S_l$; $K_{s2} = K_s$; $S_{s2} = S_s$	$V_N = K_l V_l + K_{gl} S_l + K_s S_s$	(35)
5	$K_{ll} = 0$ at $i \geqslant 1$ $K_{sj} = 0$ at $2 \leqslant j \leqslant 4$ $K_{s3} = K_{gs}$; $S_{s2} = S_{gs}$	$V_N = K_{gs} S_{gs}$ (ref. 56)	(36)
6	$K_{ll} = 0$ at $i \geqslant 1$ $K_{sj} = 0$ at $j \geqslant 2$ $K_{sl} = K_{gl}$; $S_{s2} = S_l$	$V_N = K_{gl} S_l$ (ref. 68)	(37)
7	$K_{ll} = 0$ at $i \geqslant 2$ $K_{sj} = 0$ at $j \geqslant 6$ $K_{sl} = K_{gl}$; $S_{sl} = S_l$ $K_{s2} = K_s$; $S_{s2} = S_s$ $K_{s3} = K_{gs}$; $S_{s3} = S_{gs}$ $K_{s4} = K_{lA}$; $S_{s4} = S_{gA}$ $K_{s5} = K_{lA}$; $S_{s5} = S_{lA}$	$V_N = K_l V_l + K_{gl} S_l + K_s S_s +$ $+ K_{lA} S_{lA} + K_{gs} S_{gs} +$ $+ K_{gA} S_{gA}$ (ref. 72)	(38)

We consider below some of the most important conclusions that arise when adsorption phenomena are taken into account in GLC.

4. STUDY OF THE INTERACTION BETWEEN THE DISSOLVED SUBSTANCE AND THE STATIONARY PHASE WITH THE SUBSTANCE OF INTEREST BEING ADSORBED ON THE STATIONARY LIQUID PHASE INTERPHASES

As Martin stated in 1956[73], GC is the simplest means of studying the thermodynamics of interaction between the volatile dissolved substance and the non-volatile solvent, and the potential value of this technique as a method for obtaining quantitative data is extremely high.

Advances in GLC have proved the accuracy of this statement and, at present, GC is widely used in determining various thermodynamic characteristics of interaction between the volatiles being analysed and the SLP. However, the correct implementation of the adequately developed GC techniques for studying the interaction between the dissolved substance and the non-volatile SLP and also the identification of the components being analysed are possible in a general case, provided that one segregates the contribution to the SLP of only the dissolution of the substance being analysed from the total retention volume. This is explained by the fact that, as has been mentioned above, adsorption on interphases may contribute substantially to the retention volume. In the light of the available data on the contribution of adsorption to the retention volumes of substances being analysed, it becomes necessary to refine further the earlier adopted methods for determining the specific retention volume and partition coefficient (see, for example, ref. 4). In a general case, to determine these values as the initial one, it is impossible to make direct use of the experimentally found value of the true retention volume, but one should discriminate the contribution made only by the dissolution of the volatile substance in the SLP (V_{Nl}):

$$V_N = V_{Nl} + \sum_{i}^{n-1} V_{Ni} \tag{39}$$

$$V_g = V_{gl} \cdot \frac{273}{T} = \frac{V_{Nl}}{W_l} \cdot \frac{273}{T} = \frac{K_l}{d_l} \cdot \frac{273}{T} \tag{40}$$

where V_{Nl} is part of the total net retention volume, for which only the dissolution of the substance being analysed in the SLP macrolayer is responsible, V_{Ni} is part of the total net retention volume, for which the retention of the volatile substance by the ith phase of the sorbent (with the exception of the SLP macrolayer) is responsible, V_g is the specific retention volume, V_{gl} is the retention volume determined by dissolution of the volatile substance in 1 g of the SLP and measured at absolute temperature T, W_l is the mass of the SLP in the column, and d_l is the density of the WLP.

As it is difficult to determine directly all contributions to retention, rapid approximate methods of determining V_{Nl} have been proposed, based on the assumption that, as the SLP content increases, the second term in eqn. 10 becomes almost constant starting from a certain SLP content on the solid support.

Taking into consideration that $V_{Nl} = K_l V_l$ and dividing all terms of the equation by V_l, we obtain the following expression for determining K_l:

$$K_l = \frac{V_N}{V_l} + \frac{1}{V_l} \sum_{i=2}^{n} V_{Ni} \tag{41}$$

or

$$K_l = \lim_{1/V_l \to 0} \frac{V_N}{V_l} \tag{42}$$

This method of determining the value of the partition coefficient on the basis of the derived three-term equation was first proposed by Conder[48]. A similar equation may also be proposed for defining V_{gl}, which is the initial value in determining the specific retention volume:

$$V_{gl} = \frac{V_N}{W_l} + \frac{1}{W_l} \sum_{i=2}^{n} V_{Nl} \tag{43}$$

$$V_{gl} = \lim_{1/V_l \to 0} \frac{V_N}{W_l} \tag{44}$$

Table 4 summarizes the values of V_{gt} that we calculated [50] by using eqns. 43 and 44 and on the basis of the experimental data of Pecsok *et al.*[32]. Table 4 also includes values obtained by a conventional method, *i.e.*, by calculations using the equation $V_{gt} = V_N/W_l$ for sorbents containing 8.75% (solid support, firebrick) and 8.98% (solid support, Chromosorb W). It can be seen that the extrapolation method gives, as would be expected, stable, constant values of V_{gt} independent of the type of solid support. The results of calculating V_{gt} by the conventional method are dependent on the type of solid support, and also on the SLP content on the solid support.

TABLE 4

COMPARISON OF V_{gt} VALUES FOR β,β'-OXYDIPROPIONITRILE, CALCULATED BY DIFFERENT METHODS[50] ON THE BASIS OF THE EXPERIMENTAL DATA OF PECSOK *et al.*[32]

Compound	*Solid support*			
	Firebrick		*Chromosorb W*	
	By extrapolation, taking adsorption into account	*Traditional, without taking adsorption into account*	*By extrapolation, taking adsorption into account*	*Traditional, without taking adsorption into account*
Propionaldehyde	242	300	243	260
Benzene	384	425	372	389
Ethyl acetate	379	533	388	444
Acetone	393	450	400	414
Methyl ethyl ketone	718	849	714	753
1-Hexene	14	34	15	22
Cyclohexene	69	99	74	89

Veening and Huber[74] were the first to study in GLC the influence of adsorption phenomena on the retention of metal chelates [tris(trifluoroacetonato)chromium and tris(trifluoroacetylacetonato)ruthenium]. They investigated the influence of the treatment of the support and liquid loading on the retention behaviour of volatile metal fluoroacetylacetonates in GLC. The decrease in adsorption activity of the solid support due the silanization of the sorbent in the column was demonstrated (see (Fig. 4). Veening and Huber[74] determined the relative contributions of solution in the stationary liquid phase and adsorption on the solid support surface by investigating the retention of metal chelates on columns with different liquid loadings; they suggested that the adsorption retention volume is equal to the difference between the total retention volume and the solution retention volume. A graphical evaluation of the data showed that the retention of the investigated compounds at low liquid loading is governed essentially by adsorption. For more highly loaded columns (15–20% of SLP) the solution effect dominates, but adsorption on the surface of the solid support cannot be neglected. Therefore, retention data will be more meaningful and useful on highly loaded columns and sufficiently deactivated solid supports[74]. Later, Huber and Gerritse[75] proposed an equation that takes into account the heterogeneity of the stationary bed.

Thus, in conducting a quantitative study of the interaction between the dissolved substance and the SLP, one should take into account adsorption, for which

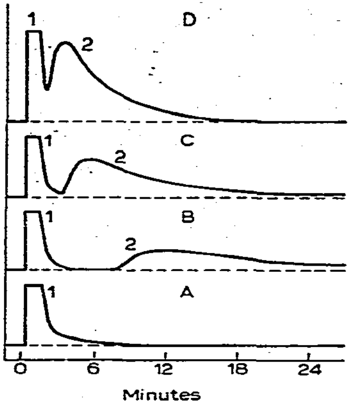

Fig. 4. Chromatograms for tris(trifluoroacetylacetonato)chromium(III) at various stages of silanization with dichlorodimethylsilane (DCDMS). Column: 3.4 g of Chromosorb W, no liquid loading. Temperature: 120°. Sample: 30 μg of eluate dissolved in 3 μl of solution. Carrier gas flow-rate: 4.0 cm/sec. 1 = Solvent; 2 = chelate. A, 0 μl of DCDMS; B, 30 μl of DCDMS; C, 100 μl of DCDMS; D, 500 μl of DCDMS.

purpose one can use the above calculation methods with due consideration of the adsorption of volatiles on the sorbent.

5. STUDY OF THE ADSORPTIVE INTERACTIONS OF VOLATILES ON THE STATIONARY LIQUID PHASE–SOLID SUPPORT AND STATIONARY LIQUID PHASE–CARRIER GAS INTERPHASES

The recognition of the important role of adsorption phenomena and the development of methods for their quantitative evaluation open up new possibilities for the use of GC to study and measure the adsorption of volatile substances, firstly on the gas–SLP interphase and secondly on the SLP–solid (support) interphase.

As has been mentioned above, the net retention volume on a polyphase sorbent is the sum of the partial retention volumes, V_{li} and V_{Sj}, determined, respectively, by the solution and adsorption of the substance being analysed on individual sorbent phases.

If the partial retention volumes are known in gas liquid–solid phase chromatography, by using eqns. 31 and 32, similar to those used in gas–solid chromatography, it is possible to calculate the adsorption or adsorption isotherm:

$$c_{li} = \frac{1}{v_{li}} \int_0^c v_{li}\,(c)\mathrm{d}c \tag{45}$$

$$c_{Sj} = \frac{1}{S_{Sj}} \int_0^c V_{Sj}\,(c)\mathrm{d}c \tag{46}$$

The derived relationships open up new possibilities for physico-chemical measurements in partition chromatography. Using these equations one can calculate not only the partition isotherms, but also the adsorption equations for compounds being analysed on interphases.

It should be noted that, in some instances, it is possible to determine the adsorption isotherm parameters directly, without an intermediate calculation of the isotherms using eqns. 45 and 46. Consider, as an example, a particular but practically important case where retention is determined only by the dissolution of a substance being analysed in the SLP and its adsorption on the SLP–solid support interphase.

In accordance with the general eqns. 29 and 32 for the net retention volume, in this instance

$$V_N = V_l + V_s = K_l V_l + \frac{dc_s}{dc} \cdot S_s \tag{47}$$

Division of both sides of the equation by the weight of the solid support in the column, with $c_s = f(c_l)$, gives

$$V_{NS} = K_l v_{lS} + \frac{dc_S}{dc_l} \cdot \frac{dc_l}{dc} \cdot S_{SS} \tag{48}$$

or

$$V_{NS} = K_l v_{lS} + K_l \cdot \frac{dc_{SS}}{dc_l} \tag{49}$$

where $c_{SS} = c_S S_{SS}$ is the concentration of the substance adsorbed on the liquid–solid interphase, calculated per unit weight of the solid, and V_{NS} and v_{lS} are the net retention volume and the SLP volume, respectively, both calculated per gram of the solid (support).

Consider a case where the adsorption isotherm is described by an equation of the Langmuir type[76]:

$$c_{SS} = \frac{a_m K c_l}{1 + K c_l} = \frac{a_m K K_l c}{1 + K K_l c} \tag{50}$$

where a_m and K are constants of the Langmuir equation. In this instance, the net retention volume depends on the concentration as follows[24]:

$$V_{NS}(c) = K_l v_{lS} + V_{SS} = K_l v_{lS} + \frac{a_m K K_l}{(1 + K K_l c)^2} \tag{51}$$

where

$$V_{SS} = \frac{a_m K K_l}{(1 + K K_l c)^2}$$

In order to determine the parameters of the Langmuir equation, several methods can be used. If the value of K_l is known from independent chromatographic or static measurements, the determination is carried out with a known SLP content using the equation

$$V_s(c) = V_N(c) - K_l v_l = \frac{K_l a_m K P_{SS}}{(1 + K K_l c)^2} \tag{52}$$

where P_{SS} is the weight of the solid (support). The calculation technique is similar to that used in gas–solid chromatography[56,57], except that the value $V_l = K_l v_l$ is used as

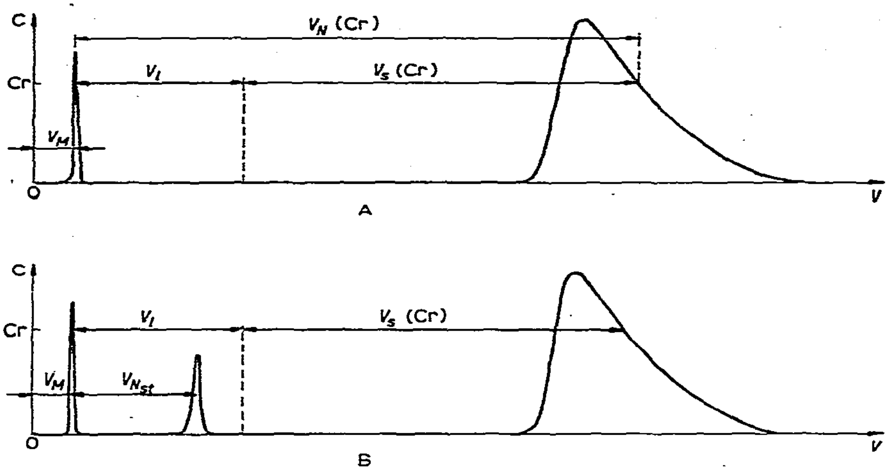

Fig. 5. Determination of the retention volume due to the adsorption on the SLP–solid interphase and to the dissolution of the substance being analysed in the SLP. (A) V_l determined by independent measurement; (B) V_l determined by the relative method using a standard substance whose adsorption in the system under consideration can be ignored.

the origin (Fig. 5). If one can select, for the system under examination, a compound for which the retention is determined only by the dissolution in the SLP, it is expedient to use the relative method for defining the value of the retention volume determined only by the dissolution of the substance in the SLP.

$$V_l = V_{Nst} \frac{K_l}{K_{lst}} \tag{53}$$

To calculate the parameters of the Langmuit isotherm using the relationship $V_{SS} = V_S/P = \psi(c)$, the following equation should be employed:

$$\frac{1}{\sqrt{V_{SS}(c)}} = \frac{1}{\sqrt{a_m K K_l}} + \sqrt{\frac{KK_l}{a_m}}\, c \tag{54}$$

The second variant of the method for determining the parameters of the adsorption isotherm is based on measuring the dependence of the retention volume on the SLP content at a fixed concentration of the substance being analysed:

$$V_{VS}(c_r) = K_l v_{lS} + V_{SS}(c_r) \tag{55}$$

where $c_r = c_1, c_2, \ldots, c_n$. This method of measurement is similar to that described elsewhere[49,56,77]. As a result of a calculation on the basis of the conducted measurements, one can determine K_l and the relationship $V_{SS} = V_{SS}(c)$, which serves as a basis for determining the parameters of the adsorption isotherm equation using eqn. 46 or 54.

Note that one can also use the following relationships to determine the parameters of the adsorption isotherm:

$$\frac{\mathrm{d}V_{NS}}{\mathrm{d}c} = \frac{\mathrm{d}V_{SS}}{\mathrm{d}c} = -\frac{2a_m K^2 K_l^2}{(1 + KK_l c)^3} \tag{56}$$

$$-\frac{1}{\sqrt[3]{\dfrac{\mathrm{d}V_{NS}}{\mathrm{d}c}}} = \frac{1}{\sqrt[3]{2a_m K^2 K_l^2}} + \frac{1}{\sqrt[3]{\dfrac{2a_m}{KK_l}}} \cdot c \tag{57a}$$

These methods were used for the experimental determination of the adsorption isotherm of *p*-xylene on a dimethyl dioctadecylammonium derivative of vermiculite, impregnated with diisooctyl sebacinate[64]. At the same time, the adsorption isotherm of *p*-xylene was studied by the static method, the adsorption being examined in glass ampoules, while the equilibrium concentration of *p*-xylene in the liquid phase was determined by GC[64]. Fig. 6 represents the adsorption isotherm (63°) of *p*-xylene, whose parameters were determined by processing GC data using eqn. 57, as well as the experimental points for the same system, obtained from static experiments. It can be seen that the results of the GC and static measurement agree well. As far as we know, this study provides the first independent verification of the chromatographic method of measuring non-linear SLP–solid adsorption isotherms. Specially conducted experiments have shown that the parameters of the adsorption isotherm determined by the chromatographic method are independent of the carrier gas flow-rate in the range 10–75ml/min, which indicates that the non-equilibrium of the process may be ignored. It should be noted that GC methods of determining the equilibrium constant (in the SLP–solid support system) for a linear isotherm have been developed earlier[49, 50,77]. When the coefficients K_{li} and K_{Sj} in eqns. 29–32 are constant and independent of concentration, the interpretation and determination of the sorption characteristics become much simpler, particularly in the SLP content range sufficient for complete coverage of the solid support with a continuous film of SLP[78]. The equation for the net retention volume in this instance is simplified and can be represented in a three-term form.

The methods for determining the sorption characteristics of this equation were proposed and elaborated by Berezkin and co-workers[49,66,79].

Eon *et al.*[80] critically assessed our suggested method of "reference point"[66] for the calculation of the contribution of the interphase adsorption value of the analysed compounds. Their views were substantiated by the analysis of results obtained from "chromatography on water" on Spherosil XOB-30. When they applied our method, large errors were obtained in estimating the contribution of liquid–solid adsorption to the general retention volume of the volatile compound being analysed. However, it should be noted that firstly, they applied the method where the surface area of the gas–liquid phase depends linearly on the amount of the SLP, *i.e.*, under circumstances where our theory cannot be applied; this point was especially stressed by us[66]. Secondly, they quoted our work incorrectly. In our work, the values of V_{NS}, V_{ls} and S_{ls} referred to 1 g of the solid support, but not to 1 g of the sorbent, [V_N^0 (retention

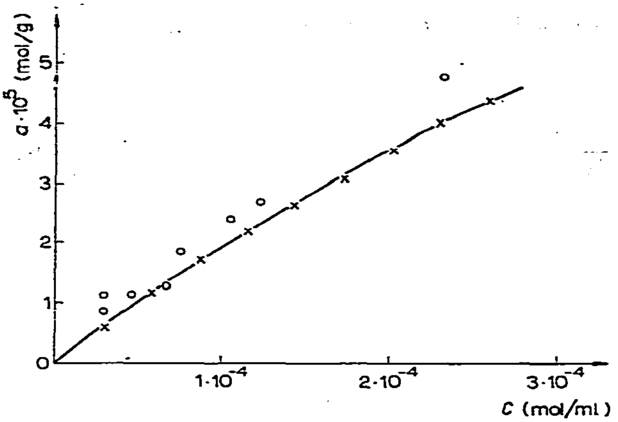

Fig. 6. Measurement of the adsorption of *p*-xylene on a dimethyl dioctadecylammonium derivative of vermiculite from solutions in diisooctyl sebacinate. Solid line, adsorption isotherm according to gas chromatographic data; ○, statically obtained data.

volume), A_l^0 (surface area of the gas–SLP interphase) and V_l^0 (volume of the SLP) referred to 1 g of the sorbent], which is why the equations in ref. 80 cannot be compared with those in refs. 49 and 66. If the units used in our work are retained, then the equation obtained[80]:

$$\frac{V_N^0 - \bar{V}_N^0}{V_l^0 - \bar{V}_l^0} = \bar{K}_{gl} \cdot \frac{A_l^0 - \bar{A}_l^0}{V_l^0 - \bar{V}_l^0} + \bar{K}_l \tag{57b}$$

does not correspond to the suggested equation[66]:

$$\frac{V_{Ns} - \bar{V}_{Ns}}{V_{ls} - \bar{V}_{ls}} = K_l + K_{gl} \cdot \frac{S_{ls} - \bar{S}_{ls}}{V_{ls} - \bar{V}_{ls}} \tag{57c}$$

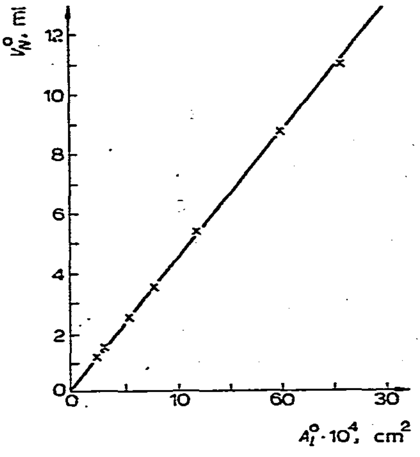

Fig. 7. Dependence of the retention volume of *n*-heptane on the area of the gas–SLP interphase in the system water–Spherosil XOB-30 at 10° (ref. 80).

in our method of "reference point". The character of the dependence $V_N^0 = f(A^\circ)$ is also different (Fig. 7); it is non-linear in our work and linear in ref. 80. Thirdly, they made only general conclusions, analysing the results concerning only one system (water–XOB-30). Hence the criticisms of Eon *et al.* are not valid.

Berezkin and Fateeva[81] demonstrated the possibility of determining the heat of adsorption on the SLP–solid support interphase on the basis of the temperature dependence of K_s. Table 5 gives, as an example, the heats of dissolution of hydrocarbons on Apiezon K and the heats of their adsorption on the Apiezon K–solid support interphase. The data indicate that the heats of adsorption for alkynes are much greater than the heats of their dissolution, whereas with *n*-alkanes these values are roughly the same. Taking the adsorption on the solid support surface into consideration one can obtain also more accurate values for the gas–SLP adsorption constant[79]. Original methods for determining the mechanism of retention in GLC have been proposed by Suprinowicz and co-workers[82,83].

TABLE 5

HEATS OF DISSOLUTION AND ADSORPTION (ON THE SOLID SUPPORT SURFACE) OF ALKANES AND ALKYNES IN THE APIEZON K–INZ-600 SYSTEM

Compound	*Heat of dissolution (kcal/mole)*	*Heat of adsorption (kcal/mole)*
n-Hexane	5.8	4.55
1-Hexyne	5.2	10.9
n-Heptane	6.6	7.6
2-Heptyne	8.6	17.8

A new and ingenious method for studying the distribution of volatiles in a gas–thin SLP film–solid support system was proposed by Belenky and co-workers[84,85].

In comparison with static methods, chromatographic methods have the following advantages: (1) rapidity of analysis, (2) the possibility of using small samples and (3) the possibility of measuring weak adsorption effects. The results obtained suggest that this approach is highly promising, particularly when adsorption-active substances are used as solid supports[86–88].

Huber and Gerritse[88] investigated adsorption phenomena in GLC, especially their influence on the reproducibility of retention data.

The precision of the measurements within one laboratory will be higher when only one instrument is used for obtaining identification parameters than when different instruments are used. The lowest reprodicibility may be expected when the results from different instruments in different laboratories are compared. This inter-laboratory precision is crucial to the usefulness of a collection of data compiled from different sources. The influence of the precision of the retention data must be standardized or reduced in order to achieve highly reproducible measurements. Standardization of all secondary parameters is in part not possible and in part not practical, and it is therefore important to establish all of the parameters that cannot be standardized and to reduce their influence as much as possible.

The inter-laboratory reproducibility of retention data has been tested several times[90–92] and the results were unsatisfactory, Some effects that decrease the precision of retention data in GC have been discussed in many papers. Huber and Gerritse[89] identified the significant sources of errors in the measurement of retention data in GLC, discussed the conditions for the reduction of the dominating statistical errors and estimated the limits of inter-laboratory precision. The samples and chromatographic systems investigated for adsorption effects[89] are given in Table 6.

TABLE 6

SOLUTION AND ADSORPTION DATA IN GAS–LIQUID–SOLID SYSTEMS AT CONSTANT TEMPERATURE (100°) AND CONSTANT PARTIAL PRESSURE (1 OR 10 mmHg AT 0°) OF THE SOLUTE

Solute	*Liquid**	*Solid***	r***	$a \pm s_a$ *(mole/g)* × 10^8 §		$b \pm s_b$ *(mole/g)* × 10^8 §		*Lower limit of linear range [% (w/w) liquid loading]*
Carbon tetrachloride	DNP	W	1.000	−1.3	1	27.5	0.2	0.5
		G	0.994	2.8	3	27.7	0.6	0.4
Acetone	SQ	W	0.986	167	11	5.1	0.6	4
		G	1.000	3.0	0.5	5.0	0.1	1
	PEG	W	0.999	−6	1.5	11.6	0.2	1
		G	0.996	−1	1.8	11.4	0.5	1
Ethanol	SQ	W	0.997	173	13	4.2	0.6	4
		G	0.996	2.5	0.4	3.3	0.1	1
	PEG	W	0.998	−11	3	20.1	0.4	1
		G	0.998	−3	3	22.7	0.6	1
Toluene	SQ	W	0.999	17	16	70.3	1.1	2
		G	1.000	−2	1.4	70.8	0.2	0.5
	PEG	W	0.999	−11	6	45.1	0.8	0.5
		G	0.995	−5	8	44.8	2.0	0.3
n-Heptane	SQ	W	0.999	−4	11	46.3	0.7	2
		G	1.000	1	3	46.3	0.4	0.5
	PEG	W	0.995	3	1.4	5.1	0.2	4
		G	0.993	1	1.1	5.2	0.3	1

* DNP = dinonyl phthalate; SQ = squalane; PEG = polyethylene glycol 20,000.

** W = Chromosorb W NAW; G = Chromosorb G DMCS.

*** r = correlation coefficient for linear regression

$$\frac{n_t}{m_s} = a + b \cdot \frac{m_\beta}{m_s} \cdot 100,$$

where n_t = number of moles of solute in total liquid–solid system, m_s = mass of solid s and m_β = mass of liquid β on the solid.

§ a and b = parameters of the linear regression; s_a and s_b = estimated standard deviations of a and b, respectively.

The distribution coefficients were determined as a function of the amount of the liquid phase on the solid support, assuming only liquid–gas distribution. The concentration in the liquid phase was given in moles per gram and the concentration in the gas phase in moles per millilitre; consequently, the liquid–gas partition coefficient was in millilitres per gram. The concentration of the sample in the mobile phase was kept constant. The measurements were carried out following the method described in an earlier paper[93]. The component of which the distribution was to be measured was mixed with an inert carrier gas and led through a tube containing the chromatographic system. After attainment of equilibrium, the contents of the tube were analysed on a gas chromatograph. In addition to the tube containing the chromatographic packing, a tube of known volume, filled with the gas mixture only, was used as reference in exactly the same way. In this manner, all of the parameters necessary for the calculation of distribution data could be obtained. The system [carbon tetrachloride (solute) and dinonyl phthalate] was chosen as data for a similar system were available from the literature[83], thus allowing a comparison of results. The type of solid support appeared to have no effect on the distribution data. The result suggested that only bulk solution is significant. At liquid loadings less than 0.5% (w/w), the relationship between the weight of SLP and the weight of solid support became non-linear and different results were obtained with differennt supports. This was attributed to the influence of adsorption effects, probably at the solid–liquid interphase.

Significant adsorption of carbon tetrachloride at the gas–liquid interphase of the system dinonyl phthalate–diatomite support is doubtful and the data can be satisfactorily described by assuming only distribution between the gas phase, the bulk liquid and the solid surface[89].

Adsorption effects can be identified[22,32,34,49,50] by representing the amount of solute contained in the liquid–solid system, including interphases, as a function of the mass of liquid coated on the solid. It was found that the data (see Table 6) could be described by a linear function at liquid loadings above about 1% (w/w) of liquid on solid G and 3% (w/w) on solid W, corresponding to about 0.03 g/m^2 in all instances.

The parameters a and b were calculated from the data by determining the linear regression. The corresponding correlation coefficient characterizing the degree of linearity was also calculated and the results are given in Table 6.

The results[89] show that the value of a is significantly different from zero in a number of instances. The magnitude of a corresponds to the amount of solute adsorbed at the gas–liquid and liquid–solid interphases at a given concentration in the gas phases. The linear relationship at higher liquid loadings shows that the adsorption is independent of the liquid loading, which suggests that the adsorption on the liquid–solid surface dominates, as this interfacial area is constant whereas the liquid–gas interfacial area decreases with increasing liquid loading on the solid. The magnitude of a was found to be especially large for ethanol and acetone with squalane as solvent coated on solid W, which is to be expected as this support is not silanized and a non-polar solvent such as squalane does not compete effectively with the solute for the adsorption sites on the solid surface. Even with the silanized solid support G, the value of a is not zero for this case. Weak adsorption effects can also be observed for acetone and ethanol with the polar solvent polyethylene glycol. It is interesting that in this instance the values of a are negative, suggesting negative adsorption.

The gas–liquid partition coefficient is independent of the nature of the solid support and the amount of liquid coated on the solid. When the liquid loading is decreased to below 0.03 g/m^2, the contribution of the adsorption given by the value of a is not constant, but changes with decreasing liquid loading from the combined value for gas–liquid and liquid–solid adsorption to the value for gas–solid adsorption in the case of an uncoated solid support. The concentrations of the adsorbates on the uncoated solid at 100° and 10 mmHg (at 0°) are given in Table 7[89] for the two solid supports studied. If positive adsorption effects occur, the apparent partition coefficient should decrease with increasing liquid loading. This is generally found. For ethanol and acetone in polyethylene glycol coated on solid W, however, a minimum value of the partition coefficient is observed, which suggests that a negative adsorption effect is involved, which could be due to the gas–liquid interphases. Another explanation can be given if it is assumed that the thin film of liquid (0.01 μm thick) on the solid surface has solvent properties that differ from those of the bulk liquid owing to the orienting influence of the solid surface. In particular, a thin film of a polar liquid, *e.g.*, tolyethylene glycol, may be structurally oriented by the solid surface[36] and should then be considered more as an adsorbed layer than as a liquid film.

TABLE 7

GAS–SOLID ADSORPTION OF DIFFERENT COMPOUNDS AT 100° AND CONSTANT PARTIAL PRESSURE OF 10 mmHg AT 0°

Relative standard deviation of the data = 10%.

Solid	*Adsorbate concentration on the solid surface (mole/g)* $\times 10^7$				
	Carbon tetrachloride	*Acetone*	*Ethanol*	*Toluene*	*n-Heptane*
Chromosorb W NAW	0.8	19.8	22.9	8.7	1.9
Chromosorb G DMCS	0.3	0.2	0.1	0.15	0.2

6. METHODS OF IDENTIFYING CHROMATOGRAPHIC ZONES IN GAS–LIQUID CHROMATOGRAPHY

Identification methods based on a comparison of experimentally found relative values of the retention of chromatographic zones of unknown compounds with corresponding values available in the literature have been widely used in GC, together with combined methods (chromatography–mass spectrometry, reaction chromatography, etc.)[94,95]. However, the simple comparison method developed early in the development of GLC unfortunately has the limitation of a poor inter-laboratory reproducibility, which seems to be due to the dissimilar properties of the sorbent prepared by different techniques using different solid supports. Little attention has been paid in the literature on chromatography to the difference in sorbent properties in GLC being responsible for the inadequate inter-laboratory reproducibility of retention values, although the advantages of the chromatographic technique reside mainly in its being widely applied in different laboratories. Advances in recent years in the development of the retention theory and studies of the properties of sorbents in GLC chromatography enable one to understand better the causes of the irreproducibility of the above values and to develop effective methods for identifying chromatographic zones.

Adsorption phenomena in partition chromatographic techniques, which have been studied by many investigators, give new insight into the problems of the identification of chromatographic zones. Until recently, it was generally assumed in chromatography that a relative retention value is determined only by the ratio of the partition coefficients of a given and standard compound and, consequently, is a chromatographic constant of the compound of interest. Therefore, the values of the relative retention volume served as a basis for identifying chromatographic zones, *i.e.*, for the qualitative chromatographic analysis of mixtures being separated[5,96].

The adsorption of the compounds being analysed on interphases in the course of chromatographic separation has the result that absolute and relative retention values are, in a general case, determined not only by the ratio of the partition coefficients of a given and standard compound, as was assumed earlier, but also by the adsorption properties of the solid support (see Table 1), the SLP content on the latter and the phase characteristics of the sorbent, which depend on the conditions of its preparation, etc.[49,66,97]. Fig. 8 shows, as an example, the relative retention volume *versus* the SLP content on the solid support, as calculated using the data of Pecsok *et al.*[32]. It can be seen that a relative retention value, in the presence of adsorption in the chromatographic process involving the gas–liquid–solid system, is not a chromatographic constant of the compound concerned.

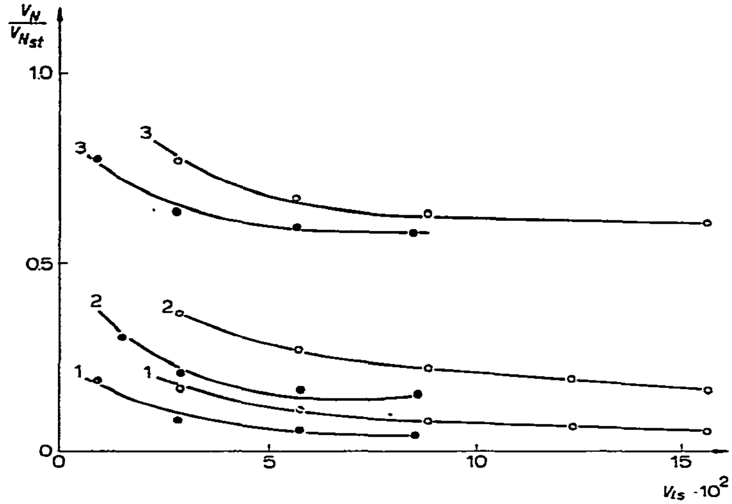

Fig. 8. Relative retention volume *versus* SLP content (per gram of solid support). Calculated according to ref. 32. 1 = *n*-Heptane; 2 = *n*-butyl ethyl ether; 3 = ethyl acetate. Experimental conditions: SLP, β,β'-thiodipropionitrile; temperature, 25°; solid support, Chromosorb W (●) and firebrick (○); standard, methyl ethyl ketone.

To derive a general equation for the relative retention volume that would take into account both dissolution and adsorption of compounds being analysed, let us use the reduced generalized eqn. 31 for the net retention volume of the compound and standard. In this instance, the following equation is obtained for the relative retention volume:

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} \cdot \frac{\left[1 + \left(\sum_{i=2}^{m} K_{li}v_{li} + \sum_{j=1}^{n} K_{S_j}S_{Sj}\right)\frac{1}{K_l v_l}\right]}{\left[1 + \left(\sum_{i=2}^{m} K_{list}v_{li} + \sum_{l=1}^{n} K_{Sjst}S_{Sj}\right)\frac{1}{K_{lst} v_l}\right]} \tag{58}$$

As follows from this equation, a relative retention value is not a constant of the substance being analysed, and therefore cannot be used for the identification of compounds on the basis of the data available in the literature. Note that despite the use of known techniques for modifying solid diatomite supports or the employment of polymer supports, the contribution of adsorption to a relative retention value more often than not is appreciable[69]. Adsorption phenomena become particularly manifest in the high-temperature chromatography of polar compounds. Therefore, in order to be able to use gas chromatography widely as a qualitative analytical technique, it became necessary to develop methods for determining partition coefficient ratios, K_l/K_{lst}, on the basis of the relative retention values of compounds being analysed[98,99].

If the retention volume is determined only by the dissolution of a substance being analysed in the SLP and by the linear isotherm of adsorption on the SLP–mobile phase and SLP–solid support interphases, eqn. 58 is simplified, and the relative retention volume can be expressed by the following equation:

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} \cdot \frac{1 + \dfrac{K_{gl}S_{lS} + K_l K_S S_{SS}}{K_l} \cdot \dfrac{1}{v_{lS}}}{1 + \dfrac{K_{glst}S_{lS} \times K_{lst}K_{Sst}S_{SS}}{K_{lst}} \cdot \dfrac{1}{v_{lS}}} \tag{59}$$

where v_{lS}, S_{lS} and S_{SS} are the SLP volume, the area of the gas–SLP interphase and the area of the SLP–solid support interphase, respectively, calculated per gram of the solid support. Expanding this equation into the Maclaurin series with respect to the variable $1/v_{lS}$, we derive the following linear equation for the reciprocal SLP content:

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} + \lambda_1 \cdot \frac{1}{v_{lS}} \tag{60}$$

where

$$\lambda_1 = \frac{(K_{gl}K_{lst} - K_{glst}K_l)S_{lS} + (K_S - K_{Sst})K_l K_{lst} S_{SS}}{K_{lst}^2} \tag{61}$$

Note that a similar relationship is derived when the more general eqn. 30 is considered, provided that an increase in the SLP content on the solid support is accompanied by an increase in the thickness of the SLP film whereas the content of other phases in the sorbent remains virtually the same. In Fig. 9, the experimental data from refs. 32 and 67 are represented in accordance with eqn. 60. It can be seen that the use of eqn. 60 permits the determination of the value of the partition coefficient ratio, which is independent of the experimental conditions.

The standard should preferably be a substance for which the retention is determined only by dissolution, *i.e.*

$$V_{Nst} = K_{lst}v_l \tag{62a}$$

$$\lambda_1 = \frac{K_{gl}S_{lS} + K_l K_S S_{SS}}{K_{lst}} \tag{62b}$$

In some instances, it is convenient to use the SLP content as characteristic of the percentage content of the SLP in the column. Then appropriate transformations give the following equation similar to eqn. 60:

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} + \frac{\lambda_2}{P_l} \tag{63}$$

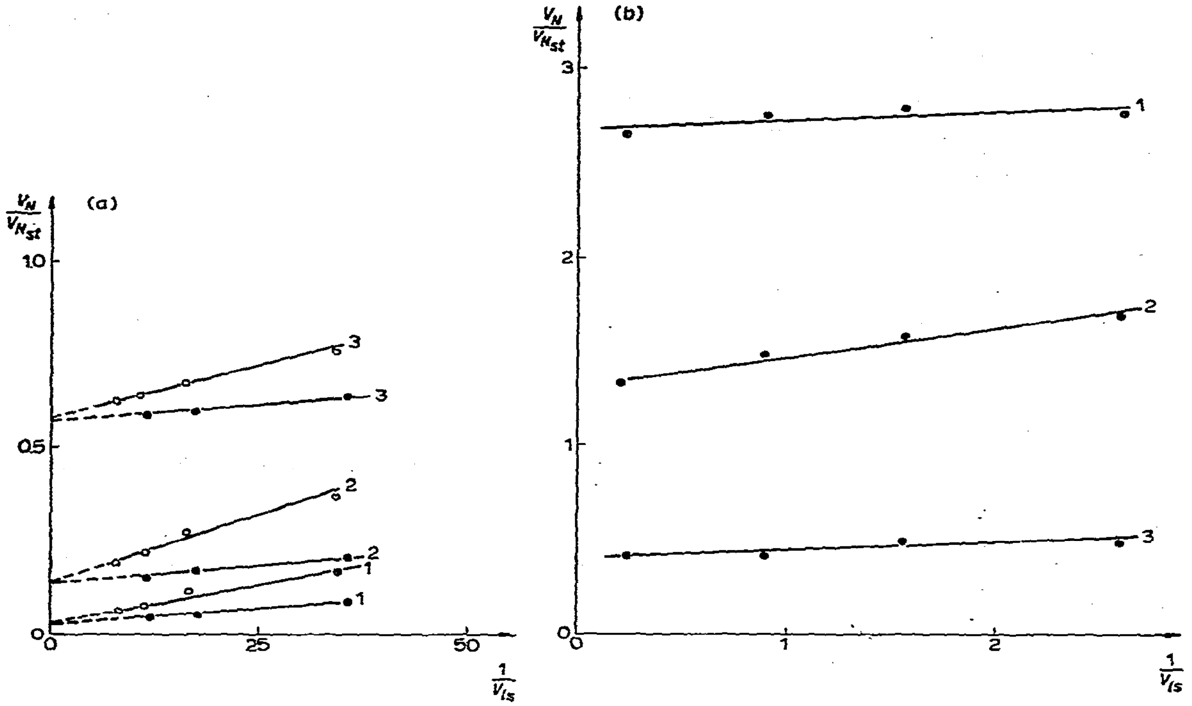

Fig. 9. Relative retention volume *versus* reciprocal of SLP content (per gram of solid support). Calculated according to (a) ref. 32 and (b) ref. 64. (a) Experimental conditions as in Fig. 8. (b) Experimental conditions: SLP, dinonyl phthalate; temperature, 86°; solid support, PTFE; standard, ethanol; 1 = *n*-butylamine; 2 = *n*-hexane; 3 = water.

where P_l is the percentage content of SLP on the solid support (the weight of solid support is taken as 100%).

Eqn. 63 can be used when difficulties arise in determining v_{lS} (*e.g.*, the SLP density is not known at the experimental temperature). Fig. 10 shows the relative retention volume *versus* the reciprocal of the percentage SLP content on the solid support. It can be seen that eqn. 63 agrees well with the experimental results. The proposed methods can be used in determining the partition coefficient ratio (thermodynamic characteristics of a substance), and also in identifying the substance on the basis of these characteristics. The values of K_l/K_{lst} obtained are independent of the SLP content and the type of solid support.

During identification, in gas chromatography, Kováts retention indices[6] (I) are widely used together with relative retention values:

$$I = 100z + 100 \cdot \frac{\log (V_N/V_{Nz})}{\log (V_{N(z+1)}/V_{Nz})} \tag{64}$$

where V_{Nz} is the net retention volume of an *n*-alkane whose molecule contains z carbon atoms, $V_{N(z+1)}$ is the net retention volume of an *n*-alkane whose molecule

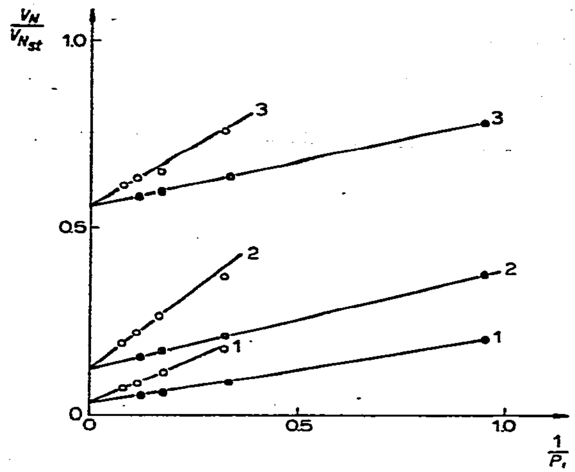

Fig. 10. Relative retention volume *versus* reciprocal of percentage content of the SLP. Calculated according to ref. 34.

contains $z+1$ carbon atoms and V_N is the net retention volume of the compound being analysed, $1/v_{lS}$:

$$V_{Nz} \leqslant V_N \leqslant V_{N(z+1)}$$

The standards should preferably be compounds for which the retention is determined only by dissolution in the SLP. In this instance, expanding the numerator of the second term of eqn. 64 into a Maclaurin series and restricting ourselves only to the first two terms, we obtain

$$\log\frac{V_N}{V_{Nz}} = \log\left(\frac{K_l}{K_{lz}} + \lambda_1 \cdot \frac{1}{v_{lS}}\right) = \log\frac{K_l}{K_{lz}} + 0.43\lambda_3 \cdot \frac{1}{v_l} \tag{65}$$

where λ_3 is a constant. Taking into consideration this derived equation, let us transform eqn. 64:

$$I = 100z + 100\frac{\log(K_l/K_{lz})}{\log\frac{K_{l(z+1)}}{K_{lz}}} + \frac{43\lambda_4}{\log\frac{K_{l(z+1)}}{K_{lz}}} \cdot \frac{1}{v_{lS}} \tag{66}$$

or

$$I = I_0 + \lambda_4 \cdot \frac{1}{v_{lS}} \tag{67}$$

where

$$I_0 = 100z + 100\log\frac{K_l}{K_{lz}}\Big/\log\frac{K_{l(z+1)}}{K_{lz}} \tag{68a}$$

$$\lambda_4 = \frac{43\lambda_3}{\log\frac{K_{l(z+1)}}{K_{lz}}} \tag{68b}$$

As has been mentioned above, the standards must be compounds whose retention is determined only by dissolution in the SLP. With non-polar phases and phases of medium polarity, this requirement is usually met by *n*-alkanes, but with polar SLPs the standards should preferably be polar compounds (*e.g.*, *n*-alcohols).

As an example, Fig. 11 shows determination of I_0, which is an invariate value relative to the experimental conditions, for methyl myristate and *n*-decanol. It can be seen that the use of sufficiently inert Chromosorb G as the solid support, acid washed and treated with dimethyldichlorosilane, does not guarantee the absence of adsorption effects in GLC.

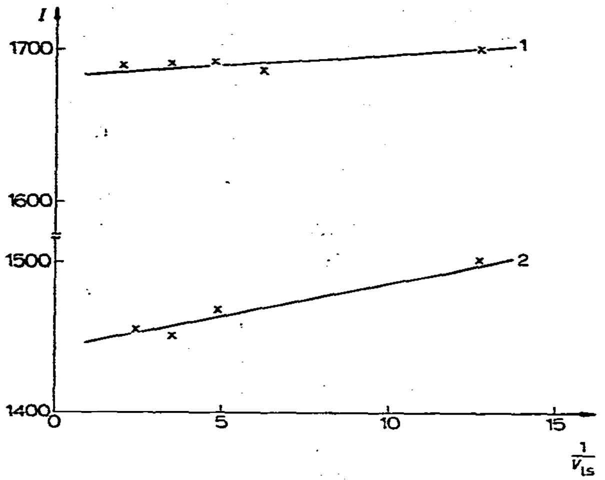

Fig. 11. Retention indices of methyl myristate (1) and *n*-dodecanol (2) *versus* reciprocal of SLP volume in the column. Experimental conditions: SLP, Apiezon L; temperature, 150°; solid support, Chromosorb W AW DMCS; column, 100 × 0.3 cm.

Thus, in partition (gas–liquid and, obviously, liquid–liquid) chromatography, there is a linear relationship between a relative retention value and the reciprocal of the SLP content on the solid support, which can be used successfully for determining the ratio of the partition coefficients of the compounds being analysed, thereby permitting a reliable identification of chromatographic zones even when adsorption is involved in the chromatographic process.

With the development in recent years of the concept of adsorption on interphases of sorbents, which normally manifests itself when the polarities of the compounds being analysed and the SLP are different, the theory and appropriate calculation methods permit the elaboration of new techniques for determining the adsorption characteristics and account quantitatively for such common phenomena in GLC as the asymmetry of chromatographic zones and the dependence of retention values on the sample size. Analysis of the derived equations has made it possible to explain the frequently observed irreproducibility of the absolute and relative retention values, which manifests itself in the dependence of the retention values on the type of solid support, the SLP content on the solid support, the moisture content, the techniques of sorbent preparation, ageing of sorbents, etc. All of these phenomena are associated with the adsorption of the volatile compounds being analysed on the SLP interphases, whose contribution to retention is described by the adsorption-related terms of the above equations. The values of these adsorption-related terms depend not only on the nature of the SLP and the solid support, but also on such sorbent characteristics as the interphase (gas–SLP, SLP–solid support) area determined by the pattern of distribution of the SLP on the support. These sorbent characteristics are determined by the properties of the solid support used, which vary from batch to batch, the SLP content and the sorbent preparation conditions, which also vary from one experiment to another. It is all of these factors that are responsible for the irreproducibility of the absolute and relative retention values.

To provide for reproducible retention values in gas–liquid and gas–liquid–solid chromatography, one should, in a general case, standardize not only the SLP, but also the solid supports used, as well as the techniques of preparation and subsequent treatment of the sorbents. When adsorption substantially affects the retention volume, GLC becomes gas–liquid–solid chromatography and loses one of its most important advantages ,namely, easy preparation of a sorbent with reproducible characteristics. It therefore seems justified when most investigators try, in their analytical work, to minimize the adsorption of compounds being analysed on the solid support or to carry out measurements under conditions in which the contribution of the adsorption to retention is small in comparison with that of the dissolution of the compounds being analysed in the SLP.

It should be emphasized that, unlike gas-adsorption chromatography, in gas–liquid–solid chromatography, one can take into account the irreproducibility of retention values, caused by adsorption using one of the above methods. These methods permit, with certain complication of the experiment, the determination of the absolute or relative partition coefficients of compounds being analysed in the gas–SLP system, *i.e.* measurement of values that are the thermodynamic characteristics of a compound. The partition coefficients found in this manner could be regarded as values that were measured directly on columns with a given sorbent if the adsorption of compounds on the SLP interphases had not taken place. Adsorption materially affects retention values in capillary chromatography also[100].

It is also of interest to make use of adsorption effects in improving the selectivity and efficiency of separations of gas mixtures, as well as the possibility of the chromatographic determination of adsorption characteristics. The proposed methods permit the measurement of truly invariate values of V_{R0} and I_0, determined only by the distribution of the compounds being analysed in the gas–SLP macro-layer system.

It has been impossible in this general review to discuss all important investigations that have been made an adsorption phenomena in GLC. However, there are many interesting and important papers that have not been discussed earlier in this review[10–119].

7. CLASSIFICATION OF CHROMATOGRAPHIC TECHNIQUES ON THE BASIS OF THE AGGREGATION STATE OF PHASES

The polyphase nature of the sorbent compels us to take a new view of the classification of chromatographic techniques. As one of the most important characteristics of a chromatographic process is the state of aggregation of the mobile and stationary phases (the definition of the mobile and stationary phases is often arbitrary because of the relativity of motion), various types of chromatography are usually defined on the basis of a different aggregation state of phases. The currently popular classification of gas chromatographic techniques includes two basic techniques: gas–liquid and gas-adsorption (or gas–solid) chromatography[4,6], which have been considered separately. It has been assumed that gas–liquid chromatography involves only processes of adsorption of substances being analysed by the SLP, while gas–solid chromatography involves only adsorption processes. However, even in adsorbtion (partition) types of chromatography, for instance, liquid–liquid and gas–liquid chromatographies, adsorption processes are involved together with dissolution. This is the result of the polyphase nature of various sorbents employed in standard techniques of partition chromatography. In gas–liquid or liquid–liquid chromatography, the sorbent has at least three phases rather than one, each being capable of retaining the substance of interest: firstly, the SLP, which absorbs the substances being separated; secondly, the mobile phase–SLP interphase, which adsorbs the substances; and thirdly, the SLP–solid (support) interphase, which also adsorbs the substances. Therefore, such techniques as gas–liquid or liquid–liquid chromatography should rather, in our opinion, be regarded as variants of gas–liquid–solid or liquid–liquid–solid techniques, respectively. For a more accurately defined classification of some widely used chromatographic techniques, see Table 8.

TABLE 8

PROPOSED CLASSIFICATION OF SOME WIDELY USED CHROMATOGRAPHIC TECHNIQUES, BASED ON THE AGGREGATION STATE OF THE MOBILE AND STATIONARY PHASES

Mobile phase	*Stationary phase*		
	Solid	*Liquid–solid*	
		Proposed terminology	*Traditional terminology*
Gas	Gas–[solid phase] chromatography	Gas [liquid–solid] phase chromatography	Gas [liquid] chromatography
Liquid	Liquid–[solid] phase chromatography	Liquid [liquid–solid] phase chromatography	Liquid–liquid chromatography

In conclusion, we should like to point that the development of concepts in chromatography is still in progress, and the current status of this development can be characterized in Einstein's words: "Science is not and never will be a completely written book. Each new success brings forth new problems. Every development reveals, in the course of time, ever more profound difficulties".

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9. SUMMARY

The development of the ideas concerning the adsorption of the compounds to be analysed chromatographically on the surface of gas–liquid and liquid–solid supports in gas–liquid chromatography is examined. The theory and new gas chromatographic techniques are described that allow one to measure the isotherms and heat adsorption of the compounds being analysed chromatographically on the interface of the stationary liquid phase (SLP) with the solid support and gas phase. The influence of adsorption phenomena on retention values, which are usually used for the identification of chromatographic peaks, is examined.

A new classification of chromatographic methods is suggested, based on taking into account the aggregate states of the phases that participate in chromatographic processes.

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