

## ADSORPTION PHENOMENA IN GAS-LIQUID CHROMATOGRAPHY

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## SUMMARY

The problem of adsorption in gas-liquid chromatography is briefly considered. Based on a derived generalized equation for retention volumes that is valid for real sorbents, methods of calculation of adsorption and absorption constants are developed. The ideas proposed are used to interpret experimental data.

## THEORETICAL

The principal equilibrium chromatographic characteristic of a substance in gas chromatography (GC) is the retention volume. On the basis of relative or absolute values of the retention volumes of chromatographed compounds, both the qualitative composition of analysed mixtures and the various equilibrium physico-chemical characteristics of the compounds (partition coefficient, heat of solution, activity coefficient, etc.) are determined.

In gas-liquid chromatography (GLC) (see, for instance, refs. 1 and 2), in accordance with the chromatographic separation theory<sup>3</sup>, the relationship between the pure retention volume ( $V_N$ ) and the partition coefficient ( $K_e$ ) is expressed by the equation

$$V_N = K_e \cdot V_e \quad (1)$$

where  $V_e$  is the volume of the stationary liquid phase (SLP) in the column.

PORTER *et al.*<sup>4</sup> and ANDERSON AND NAPIER<sup>5</sup> showed the validity of this relationship for a number of specific systems by comparing the values of the partition coefficients determined by the chromatographic and classical statistical methods. It follows from eqn. 1 that the value of the pure retention volume depends only on the partition coefficient of the chromatographed compound between the liquid and the gaseous phases and the volume of the stationary liquid phase in the column.

It is interesting to note, however, that in their first work on GLC, JAMES AND MARTIN<sup>6</sup> mentioned the phenomenon of adsorption of chromatographed substances. To reduce the adsorption of polar compounds (organic acids) on the surface of the solid support, they modified it by using phosphoric acid on kieselguhr as support and

TABLE I

VARIATION IN RELATIVE RETENTION VOLUMES AS A FUNCTION OF SLP CONTENT AND THE TYPE OF SOLID SUPPORT FOR DIFFERENT COMPOUNDS ON THIODIPROPIONITRILE AT 25°

Compound	Relative retention volume					
	Content of SLP on Chromosorb W (%)			Content of SLP on firebrick (%)		
	1	6	14	1	6	12
<i>n</i> -Hexane	1.00	1.00	1.00	1.00	1.00	1.00
<i>n</i> -Heptane	2.96	2.61	2.39	2.87	2.85	2.84
Benzene	7.64	—	37.6	3.72	12.7	21.4
Cyclohexane	2.34	5.43	7.82	1.53	3.25	5.15
2,2,4-Trimethylpentane	3.70	2.61	2.18	3.5	3.3	3.1
Propionic aldehyde	4.9	14.8	—	2.97	8.07	13.5
Ethyl acetate	10.3	27.4	—	9.32	17.0	24.8
Methyl ethyl ketone	15.3	45.5	—	11.5	25.9	41.0

introducing stearic acid (10%) into silicone oil. In further work, a number of investigators<sup>7-13</sup> showed that the absolute and relative retention values, and also the shapes of the chromatographic zones, are determined not only by the properties of the SLP, but also by the type of the solid support used and, consequently, by the amount of the SLP on the solid support. As an example, Table I lists the relative retention values for certain compounds calculated by us from the data given in ref. 14. The tabulated data indicate that the relative retention values (including retention indices) depend on the content of SLP on the solid support, which is contrary to eqn. 1. Thus, "pure" GLC in which the retention values and other chromatographic characteristics of compounds are determined only by the properties of the SLP is often not realized in practice as it does not take into account the multi-phase (heterogeneous) nature of a real sorbent, which, in addition to the SLP, has at least two interfaces (gas phase-SLP and SLP-solid support) capable of adsorption (and hence retention) of chromatographed compounds. One of the simplest models of such a sorbent is shown in Fig. 1.

The non-reproducibility of experimental results and their dependence on the type of solid support used and the amount of SLP on the support, and other similar phenomena, which point to a limited range of applicability of eqn. 1, were at first explained qualitatively by the adsorption of chromatographed compounds on the surface of the solid support<sup>3,7-12,15</sup>. Special effective methods were developed to reduce the adsorption activity of solid supports in GC such as the use of small addi-

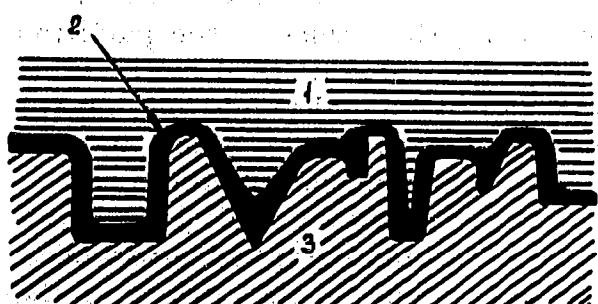


Fig. 1. Simplified sorbent model; 1 = carrier gas; 2 = stationary liquid phase; 3 = solid support.

tions of polar compounds (modifiers), processing with active silicone compounds in order to transform the surface hydroxyl groups into non-active groups and coating the surface of the support with a film of an inert solid compound (see, for instance, refs. 3 and 15).

MARTIN<sup>16,17</sup> was the first to demonstrate theoretically and experimentally the necessity of supplementing eqn. 1 with a term that takes into account the adsorption of chromatographed compounds on the gas-SLP interface. He also showed that there is agreement between the adsorption coefficients of chromatographed compounds on the surface of the SLP as measured by the chromatographic method and by the classical method according to the Gibbs equation. The pure retention volume per unit weight of the sorbent,  $V_{N_0}$ , is described, according to MARTIN<sup>16</sup>, by the equation

$$V_{N_0} = K_e V_{er} + K_{ge} S_{er} \quad (2)$$

where  $V_{er}$  and  $S_{er}$  are, respectively, the volume of the liquid phase and the area of the gas-SLP interface in the column referred to 1 g of the sorbent, and  $K_{ge}$  is the partition coefficient of the chromatographed substance in the system gas-SLP surface. For the pure retention volume, MARTIN's equation can be represented by

$$V_N = K_e V_e + K_{ge} S_e \quad (3)$$

where  $S_e$  is the total area of the gas-SLP interface of the sorbent in the column.

The next step in the development of the retention theory was made by KELLER AND STEWART<sup>18,19</sup>, who proposed an equation that took into account the adsorption of the chromatographed substance on the surface of the solid support. In the terms used by us, the KELLER-STEWART equation can be written as:

$$V_N = K_e V_e + K_s S_s \quad (4)$$

where  $K_s$  is the partition coefficient of the gas-SLP surface on the boundary with the solid support and  $S_s$  is the surface area of the solid support covered with a layer of SLP. It should be emphasized that in their work KELLER AND STEWART<sup>18,19</sup> noticed that the retention volume equation may be supplemented by a term that takes into account the adsorption on the gas-SLP interface according to MARTIN.

A qualitative analysis of experimental data which took into consideration, in addition to dissolution in the SLP, also the adsorption of the chromatographed substance on the SLP-solid support interface, was first carried out by BEREZKIN and coworkers<sup>20,21</sup>. These authors also showed the significance of multi-term retention-value equations for determining the physico-chemical properties of solutions from GC data.

In the general case, retention is determined both by dissolution in the SLP and by adsorption on its interfaces with the gas and the solid support.

If the retention volume is an additive function of the retention on the separate phases of a real sorbent, then the following equation<sup>22</sup> is valid:

$$V_N = \sum \frac{\partial V_N}{\partial V_i'} V_i' + \sum \frac{\partial V_N}{\partial S_j} S_j = \sum K_i V_i' + \sum K_j S_j \quad (5)$$

where  $V_N$  is the pure retention volume of the chromatographed compound,

$K_i = \frac{\partial V_N}{\partial V_i'}$  the coefficient of partition of the compound in a system gas-SLP of the

*i*-type (for instance SLP in a macrolayer, SLP in a microlayer and SLP in fine capillaries),  $V_i'$  is the volume of an *i*-type SLP in the column,  $K_j = \frac{\partial V_N}{\partial S_j}$  is the partition coefficient in a system gas-surface of the *j*-type (for instance, gas-pure solid support interface, gas-monomolecular layer of SLP on the support interface and gas-macrolayer of SLP interface), and  $S_j$  is the area of the *j*-type surface in the column. Eqn. 5 appears to be sufficiently general, and the following particular cases can be obtained from it: a retention-volume equation for classical GLC (see eqn. 1), MARTIN's equation (see eqns. 2 and 3), the KELLER AND STEWART equation (see eqn. 4), and also KISELEV's equation<sup>23</sup> for gas-adsorption chromatography:

$$V_N = K_T \cdot S_T \quad (6)$$

where  $K_T$  is the partition constant in the gas-solid system, and  $S_T$  is the surface area of the solid. Unfortunately, the practical utilization of eqn. 5 in the general case is rather complicated, since it requires additional data on the phase characteristics of the sorbent.

With a sufficient amount of SLP on the solid support, when complete coverage of the surface by a liquid macrofilm is achieved (see Fig. 1), eqn. 5 is simplified and converted into the following three-term retention-volume equation:

$$V_N = K_e V_e + K_{ge} S_{ge} + K_s \cdot K_s \cdot S_s \quad (7)$$

Eqn. 7 takes into account the dissolution of the chromatographed compound in the SLP and its adsorption on the interfaces of the SLP with the gas and the solid support. For the case of linear isotherms of dissolution and adsorption, partition constants are independent of concentration.

A special investigation into the nature of the coverage of a solid support by an SLP film for a number of real systems by the method of solid-surface markers showed that, for stationary phases effectively wetting the support surface and with a content of SLP exceeding 1-3%, complete coverage of the solid support by the liquid film is attained<sup>24</sup>. For this sorbent model (see Fig. 1), the system of equations for the case of equilibrium elution chromatography of a substance with the action of longitudinal wash-out factors, with allowance for adsorption in the SLP and adsorption on the SLP interfaces, may be written as follows:

$$U \frac{\partial c}{\partial x} + \varrho_a \frac{\partial c}{\partial t} + \varrho_{ge} \frac{\partial a_e}{\partial t} + \varrho_{es} \frac{\partial a_s}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2} \quad (8)$$

$$a_e = f_{ge}(c) \quad (9)$$

$$a_s = f_{es}(c) \quad (10)$$

$$a_s = f_{es}(a) \quad (11)$$

where  $U$  is the linear velocity of the carrier gas,  $x$  is a coordinate,  $t$  is the time,  $C$  is the volume concentration of the chromatographed substance in the gaseous phase,  $a$  is the volume concentration of the substance in the SLP,  $a_e$  is the surface concentration of the substance on the gas-SLP interface,  $a_s$  is the surface concentration of the substance on the SLP-solid support interface,  $\varrho_g$  is the fraction of the gaseous phase throughout the column section,  $\varrho_e$  is the fraction of SLP throughout the column

section,  $\rho_{ge}$  is the ratio of the area of the SLP-solid support to the sorbent volume,  $\rho_{es}$  is the ratio of the area of the SLP-solid support interface to the sorbent volume and  $D^*$  is the effective coefficient of longitudinal diffusion.

Eqn. 9 and 11 are equations of the adsorption isotherm of the chromatographed substance on the gas-SLP and SLP-solid support interfaces, and eqn. 10 is the equation of the isotherm of adsorption (dissolution) in the SLP. Eqn. 10 differs from the usual type of equation (see, for instance, ref. 25) by the presence of two additional terms—the third and the fifth. The introduction of these terms deals with adsorption on the interfaces of the SLP with the carrier gas and the solid support. In a similar manner it is also possible to take into account the other types of retention considered above. The solution of an equation of the type of eqn. 8 has already been described in the literature (see, for example, ref. 26).

By solving eqns. 8-11, it is possible to determine the rate of motion of the peak of the chromatographic zone and, consequently, the value of the pure retention volume,  $V_N$ :

$$V_N = f'e V'e + f'ge S_e + f'e \cdot f'_{es} \cdot S_s \quad (12)$$

where

$$f'e' = \frac{da}{dc}; f'ge' = \frac{da_e}{dc}; \text{ and } f'_{es}' = \frac{da_s}{da}.$$

Eqn. 12 establishes a relationship between the retention volume and the characteristics of the sorbent used when the entire surface of the support is covered with a macrolayer of SLP. It makes allowance for dissolution in the SLP and adsorption on its interfaces.

Using an analogous method, one can obtain the general eqn. 5 as well. For the three-phase sorbent model under review, if the adsorption and sorption isotherms are linear (i.e.,  $f'ge = K_{ge}$ ;  $f'_{es} = K_s$ ;  $f'e = K_e$ ), the retention-volume equation can be represented as follows<sup>22</sup>:

$$V_N = K_e V_e + K_{ge} S_e + K_e K_s S_s \quad (7)$$

A similar equation was used by CONDER *et al.*<sup>28</sup> in analysing the role of adsorption phenomena in GLC. A method for determining all three constants in eqn. 7 characterizing dissolution and adsorption on separate phases of the sorbent has been described<sup>22</sup>. The method is based on the use of the experimentally obtained dependences

$$V_{Ns} = \Psi(V_{es}) \quad (13)$$

$$S_{es} = \Phi(V_{es}) \quad (14)$$

where  $V_{Ns}$ ,  $S_{es}$  and  $V_{es}$  are, respectively, the pure retention volume, the gas-SLP interface area and the volume of SLP referred to 1 g. of the solid support. In these terms, eqn. 7 should be given thus:

$$V_{Ns} = K_e V_{es} + K_{ge} S_{es} + K_e K_s S_{ss} \quad (15)$$

where  $S_{ss}$  is the specific surface area of the solid support. It should be emphasized that the dependence in eqn. 14 is generally non-linear<sup>14,16,21,27</sup>.

In the graphical determination of partition coefficients, it is advisable to use the following relationships obtained from eqn. 15:

$$\frac{V_{Ns} - \bar{V}_{Ns}}{V_{es} - \bar{V}_{es}} = K_e + K_{ge} \cdot \frac{S_{es} - \bar{S}_{es}}{V_{es} - \bar{V}_{es}} \quad (16)$$

$$V_{Ns} - K_{ge} S_{es} = K_e V_{es} + K_e \cdot K_g \cdot S_{ss} \quad (17)$$

where  $\bar{V}_{Ns} = f(\bar{V}_{es}, \bar{S}_{es})$  is a certain arbitrary reference point, *i.e.*, the value of the

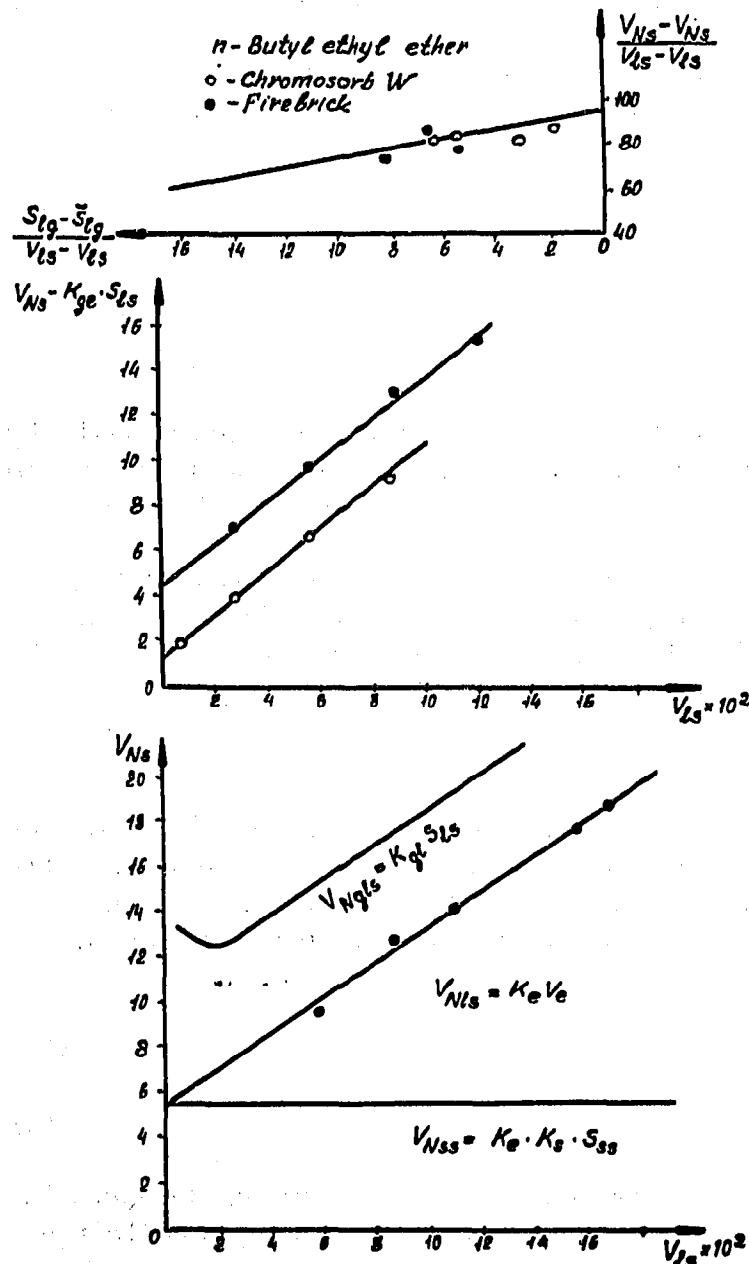


Fig. 2. Graphical determination of absorption and adsorption constants of *n*-butyl ethyl ether and dependence of contributions of absorption and adsorption to retention volume on content of thiadipropionitrile on firebrick.

TABLE II

CONTRIBUTION OF ADSORPTION ON THE THIODIPROPIONITRILE INTERPHASE TO THE RETENTION VOLUME

Substance	Solid support	$K_e$	$K_{ge}$	$K_s$	Contribution of adsorption on the interphase (%) (8.8% SLP on the solid support)	
					Gas-SLP	SLP-solid support
Ethyl acetate	Firebrick,	439	3.3	0.000323	15.1	10.6
	Chromosorb W	456	3.3	0.00327	5.6	3.35
Acetone	Firebrick,	430	0.85	0.00274	4.5	10.3
	Chromosorb W	437	0.85	0.00235	1.53	3.61
2,2,4-Trimethyl-pentane	Firebrick,	14.0	2.4	0.0043	79.4	2.71
	Chromosorb W	15.0	2.4	0.0019	57.1	1.27
Cyclohexane	Firebrick,	32.8	0.47	0.0027	25.7	8.00
	Chromosorb W	33.6	0.47	0.0019	10.3	2.72

pure retention volume at definite constant values of  $V_{es}$  and  $S_{es}$ . The reference point is evidently best selected in the range of large values of  $V_{es}$ , where reproducibility is higher.

As an example, Fig. 2 shows the graphical determination of absorption and adsorption constants and their respective contributions for *n*-butyl ethyl ether on thiodipropionitrile carried out by us on the basis of the experimental data in ref. 14.

In Table II are listed absorption and adsorption constants for certain chromatographed compounds as calculated by us from the data in ref. 14. It follows from Table II that the contribution of adsorption on the SLP interfaces is considerable, reaching in some cases 46% of the retention volume.

Certain important conclusions that follow from taking into account adsorption phenomena in GLC are now considered.

#### STUDY OF THE INTERACTION OF A DISSOLVED SUBSTANCE WITH THE STATIONARY LIQUID PHASE UNDER CONDITIONS FOR WHICH THE CHROMATOGRAPHED SUBSTANCES ARE ADSORBED ON STATIONARY LIQUID PHASE INTERFACES

The application of well-known GLC methods in studying the interaction of a dissolved substance with a non-volatile SLP and the identification of the analysed components requires, in general, the isolation from the entire retention volume of the portion due solely to the dissolution of the chromatographed substances in the SLP. The explanation lies in the fact that, as indicated above, adsorption on interfaces can make a considerable contribution to the value of the retention volume.

In the light of available data on the contribution of adsorption to retention values, it is necessary to refine the methods previously used for determining the specific retention volume for the SLP and the partition constant (see, for instance, ref. 3). In determining these values, it is impossible, in general, to proceed directly from an experimentally obtained value of the pure retention volume; the contribution associated only with dissolution in the SLP should be isolated:

$$V_g = \frac{V_{Nse} \cdot 273}{W_e \cdot T} \quad (18)$$

where  $V_{Ns}$  is the portion of the pure retention value due only to dissolution in the SLP,  $T$  is the absolute temperature of the column and  $W_e$  is the weight of SLP in the column.

To determine the partition constant of volatile substances in the gas-SLP system, it is possible to use eqn. 16 or the similar eqn. 19:

$$\frac{\partial V_{Ns}}{\partial V_{es}} = K_e + K_{ge} \frac{dS_{es}}{dV_{es}} \quad (19)$$

However, owing to the fact that the use of eqns. 16, 17 and 19 requires, in general, the measurement of both the retention volume and the gas-SLP interface as a function of the SLP content (see eqns. 13 and 14), simplified methods were proposed for determining the partition constant of volatile compounds in the gas-SLP system based solely on the dependence of the retention volume on the SLP content. If both parts of eqn. 15 are divided by  $V_{es}$ , the second term on the right-hand side of the equation will tend to zero at high SLP contents and, hence, extrapolating the dependence

$$\frac{V_N}{V_{es}} = f\left(\frac{1}{V_{es}}\right) \propto \frac{1}{V_{es}} \rightarrow 0$$

it is possible to determine  $K_e$ :

$$\frac{V_{Ns}}{V_{es}} = K_e + \frac{K_{ge}S_{es} + K_e \cdot K_s S_{ss}}{V_{es}}$$

$$K_e = \lim_{\frac{1}{V_{es}} \rightarrow 0} \frac{V_{Ns}}{V_{es}} \quad (21)$$

This method was developed by CONDER *et al.*<sup>28</sup>. A similar technique can be applied in determining  $K_e$  from eqn. 16 if one of the points at a moderate content of SLP on the solid support is chosen as the reference point:

$$\lim_{\frac{1}{V_{es} - \bar{V}_{es}} \rightarrow 0} \frac{V_{Ns} - \bar{V}_{Ns}}{V_{es} - \bar{V}_{es}} = K_e \quad (22)$$

The published<sup>14, 16, 21, 27</sup> dependences of the area of the gas-SLP interface on the volume of SLP per 1 g of the support in the range of SLP contents exceeding 2–5% can be expressed approximately by the equation

$$S_{es} = A + B \frac{1}{V_{es}} \quad (23)$$

In this case, eqn. 16 can be represented only as a function of  $V_{es}$ :

$$\frac{V_{Ns} - \bar{V}_{Ns}}{V_{es} - \bar{V}_{es}} = K_e - \frac{K_{ge} \cdot B}{V_e} \cdot \frac{1}{V_{es}} \quad (24)$$

Eqn. 24 can also be used for determining  $K_e$ .

Fig. 3 illustrates the graphical determination of the partition constant of cyclohexane on thiadpropionitrile by various methods (eqns. 2, 22 and 24) from the experimental data in ref. 14. The different methods yield almost identical values of  $K_e$ .

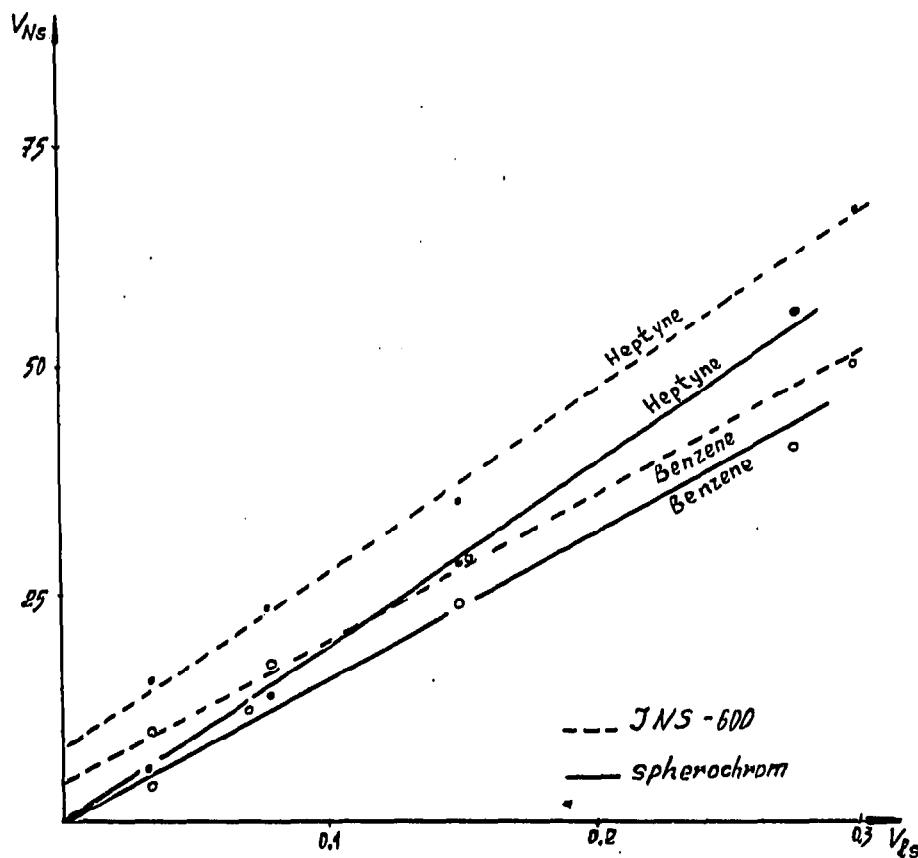


Fig. 3. Graphical determination of partition constant of cyclohexene on thiodipropionitrile applied to firebrick and Chromosorb W according to eqns. 21, 22 and 24.

If adsorption on the gas-SLP interface is low compared with dissolution of the SLP, i.e.,  $K_{se} \frac{dS_{es}}{dV_{es}} \ll K_e$  (see eqn. 19), then the dependence of the retention volume on the content of SLP on the solid support is expressed as a straight line, which is in fact often observed in practice, in particular for capillary fibres<sup>20</sup>. In this case, the retention volume equation may be as follows:

$$V_{Ns} = K_e V_{es} + K_e \cdot K_s \cdot S_{ss} \quad (25)$$

and this is used for determining the values of  $K_e$  and  $K_s$ . Fig. 4 shows the dependences of  $V_{Ns}$  on  $V_{es}$  for two solid supports as measured by us, for inert spherochrome and for adsorption-active "INZ-600". For a sorbent with inert spherochrome and  $K_s \approx 0$ , the straight line  $V_{Ns} = f(V_{es})$  passes through the origin. For a sorbent with "INZ-600", the dependence of the retention volume on the volume of SLP on a solid support is described by eqn. 25; the slope of the lines describing the dependence  $V_{Ns} = f(V_{es})$  is almost identical for both supports.

#### STUDY OF THE ADSORPTION INTERACTIONS OF VOLATILE COMPOUNDS ON STATIONARY LIQUID PHASE INTERFACES WITH SOLID SUPPORT AND CARRIER GAS

MARTIN<sup>30</sup> stated in 1956 that "the method of gas chromatography is probably the easiest of all the existing methods for studying the thermodynamics of interaction

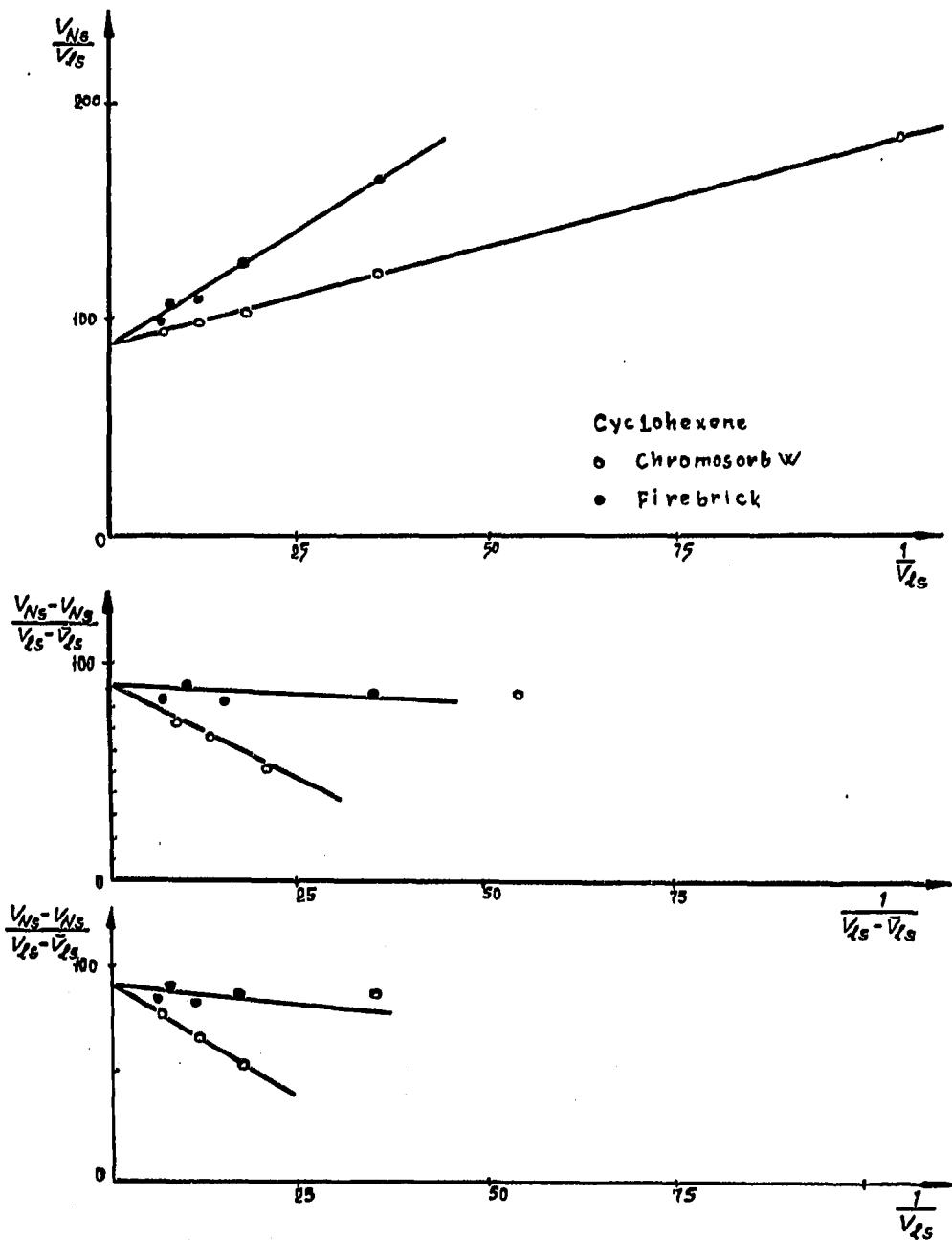


Fig. 4. Dependence of retention volumes  $VN_8$  of heptyne-2 and benzene on content of Apiezon K on two supports: INZ-600 and spherochrome.

of a volatile dissolved substance with a non-volatile solvent, and its potential value as a method for obtaining the relevant quantitative data is extremely high". The development of GLC since then has corroborated this forecast.

Later, it was shown that GC can also be used for the study of thermodynamic parameters of interactions of chromatographed compounds with the gas-stationary liquid phase interface<sup>16</sup> and the SLP-solid support (solid body) interface<sup>21,31</sup>. Some investigators also indicated the possibility of determining other interactions that make a definite contribution to the value of the retention volume<sup>31</sup>.

From eqn. 16, 17 and 19, there arises the possibility of measuring the adsorp-

TABLE III

HEATS OF SOLUTION AND ADSORPTION ON THE SURFACE OF SOLID SUPPORT OF ALKANES AND ALKYNES IN THE SYSTEM APIEZON K-INZ-600

Component	Heat of solution (kcal/mole)	Heat of adsorption (kcal/mole)
<i>n</i> -Hexane	5.8	4.55
Hexyne-1	5.2	10.9
<i>n</i> -Heptane	6.6	7.6
Heptyne-2	8.6	17.8

tion of volatile compounds from solutions in an SLP on a solid surface (for instance, by determining the coefficients  $K_s$ ). This possibility can easily be realized experimentally. Table III gives the heats of solution and adsorption of some hydrocarbons on Apiezon K and on the interface Apiezon K-INZ-600 solid support. It can be seen that the heats of adsorption of alkynes are considerably higher than their heats of solution. If adsorption on the surface of the solid support is taken into account, it will be possible to obtain more precise values for the constant of adsorption on the gas-SLP interface. Thus, the values of the Gibbs adsorption constant obtained from chromatographic data with the use of eqn. 13 are, for all compounds, much closer to the Gibbs adsorption constants calculated from the data on the concentration dependence of surface tension (see Table IV).

TABLE IV

COMPARISON OF GIBBS COEFFICIENTS OF ADSORPTION OF CERTAIN COMPOUNDS ON THE SURFACE OF CHLORONAPHTHALENE DETERMINED FROM THE GIBBS EQUATION AND BY THE CHROMATOGRAPHIC METHOD WITH AND WITHOUT ALLOWANCE FOR ADSORPTION ON THE SURFACE OF THE SOLID SUPPORT

Compounds	Gibbs adsorption coefficient $\times 10^{11}$		
	From chromatographic data without allowance for adsorption on support <sup>16</sup>	From Gibbs equation <sup>17</sup>	From chromatographic data with allowance for adsorption on support <sup>16</sup>
<i>n</i> -Pentane	6.5	4.8	5.1
Hexane-1	5.8	4.9	4.7
2-Methylpentane-2	5.1	4.4	4.8
Benzene	2.6	2.4	2.3
3-Methylpentane	6.8	5.7	5.7
Methylcyclohexane	3.7	3.2	3.4

Adsorption of chromatographed compounds on the surface of solid supports, with certain exceptions, usually produces an adverse effect on chromatographic separation. In this connection, it is of practical and theoretical interest to estimate the adsorption properties of supports used in GC with a view to selecting the best solid supports and also to evaluating the efficiency of the various methods of their modification. In this connection, it is necessary to emphasize that the evaluation should be carried out only under specific conditions. As a rule, it is of interest to study adsorption on the SLP-solid support interface rather than in the gas-solid support

TABLE V

VALUE OF THE RETENTION VOLUME OF BENZENE DUE TO ADSORPTION ON THE SQUALANE-SOLID SUPPORT INTERFACE FOR VARIOUS SOLID SUPPORTS

Solid support	Adsorption retention volume (cm <sup>3</sup> /g of support)
Sterchemol	8.2
Sterchemol modified with 1% triethylene glycol	1.9
Porcelain	3.5
Chromosorb G	0.0
Sodium chloride	0.0
Chromosorb W	0.6

system. It is well known that the adsorption properties of the adsorbing surface are determined by a set of properties of the solid support and of the SLP. The quantitative characteristic of the adsorption properties of the SLP-solid support interface is the value of the retention volume due to the adsorption of the chromatographed compounds on the surface of 1 g of support covered with SLP:

$$V_{Nss} = K_e \cdot K_s \cdot S_{ss} \quad (26)$$

where  $S_{ss}$  is the specific surface area of the solid support. The value of  $S_{ss}$  decreases with increasing "inertness" of the support. Table V lists the values of the adsorption retention volume of benzene for various solid supports impregnated with squalane. The results obtained agree with the qualitative conceptions of the inertness of solid supports. It is interesting to note that modification of the surface of a solid support with small additions of polar compounds (for instance, triethylene glycol) reduces the adsorption of benzene by a factor of more than 4.

#### USE OF THE CONCEPT OF ADSORPTION OF CHROMATOGRAPHIC COMPOUNDS ON STATIONARY LIQUID PHASE INTERFACES FOR THE INTERPRETATION OF CERTAIN COMMON PHENOMENA IN GAS-LIQUID CHROMATOGRAPHY

The concept of adsorption on SLP interfaces developed by a number of investigators makes it possible to interpret quantitatively common phenomena in GLC such as the asymmetry of chromatographic zones, the non-reproducibility of retention values, and the dependence of retention values on the volume of the analysed sample. It is usually correctly assumed that the asymmetry of chromatographic zones is due to the adsorption of the analysed compounds on the surface of the solid support<sup>3,9,32</sup>. The formation of asymmetric zones of the chromatographed substances follows from an analysis of eqn. 12 if the adsorption isotherm is non-linear. For instance, if the adsorption isotherm of a substance on the SLP-solid support interface is expressed by the Freundlich equation:

$$a_s = \alpha \cdot a^\beta \quad (27)$$

where  $a_s$  and  $a$  are the concentration of the substance on the surface and in the bulk of SLP, respectively, and  $\alpha$  and  $\beta$  are constants ( $\beta < 1$ ). In this case, the retention volume equation may be written as follows:

$$\begin{aligned}
 V_N &= K_e V_e + K_{ge} S_e + \frac{K_e \alpha \beta S_s}{\alpha^{1-\beta}} \\
 &= K_e V_e + K_{ge} S_e + \frac{K_e \beta \alpha \cdot \beta \cdot S_s}{c^{1-\beta}}
 \end{aligned} \tag{28}$$

From this equation, it follows that the value of the retention volume increases with decreasing concentration of the substance in the gaseous phase, which explains the formation of a different tail to the zone. The asymmetry of the zone increases with an increase in  $(\alpha - \beta)$ . At  $\beta = 1$ , the Freundlich isotherm transforms into the Henry equation and the chromatographic zone is symmetrical. In this connection, it should be pointed out that the formation of symmetrical zones does not indicate the absence of adsorption on the surface of the solid support; it only indicates the absence of non-linear adsorption. Equations of the type of eqns. 5, 12 and 28 may be taken as a basis for determining the parameters of the adsorption isotherm (of Freundlich, Langmuir, etc.)<sup>33,34</sup>.

Eqn. 12 can be used for the quantitative explanation of the dependence of the retention value on the sample size<sup>33,34</sup>. If the retention volume of a standard compound is determined only by dissolution in the SLP, i.e.

$$V_{Nst} = K_{e st} \cdot V_e \tag{29}$$

then the dependence of the relative volume of the substance,  $V_{Nr}$ , on the size of the analysed sample,  $g$ , is expressed by the equation:

$$V_{Nr} = \frac{K_e}{K_{e st}} \left[ 1 + \frac{\Sigma}{V_e^\beta} \left( \frac{K_{e st}}{K_e} \right)^{1-\beta} \left( \frac{V_{Nr}}{g} \right)^{1-\beta} \right] \tag{30}$$

where  $\Sigma$  is a constant. The data of ref. 8 and our experimental data<sup>34</sup> are described well by eqn. 30.

In connection with the considerable contribution of adsorption interactions to the value of the retention volume and with their effect (especially that of adsorption on the SLP-solid support interface) on the specific efficiency value, it would be expedient to refine the currently accepted classification of chromatographic methods. In particular, it would be advisable to introduce the definition of gas (liquid-solid)-phase chromatography, because the chromatographic process is often determined both by the properties of the SLP and by those of the solid support. A more detailed classification should reflect the participation of volume phases as well as of surface phases.

Adsorption phenomena thus play an important role in GLC and they should be taken into account in carrying out analytical and physico-chemical measurements.

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