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ADSORPTION IN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

The equilibrium theory for relation values in gas–liquid chromatography was considered taking into account both the absorption of chromatography-volatile substances and adsorption at the stationary liquid phase/solid or stationary liquid phase/gas interfaces.

The methods of simultaneous determination of absorption and adsorption on the stationary liquid phase surface were suggested from experimental dependence of relation volume upon surface. Experimental data agree satisfactorily with obtained equations. It is necessary to take into consideration the adsorption at the stationary liquid phase/solid and stationary liquid phase/gas interfaces in order to perform the analytical and physico-chemical measurements.

During the last ten years some works have been published which were devoted to the processes occurring at the stationary liquid phase (SLP)/solid or SLP/gas interfaces in gas–liquid chromatography (GLC)[1–5]. This paper describes an attempt to consider the problem of absorption effect in general.

GLC has been intensively developed during the last twenty years, and at present it is the main technique used for the analysis of complex mixtures of volatile organic compounds. However, "pure" GLC, in which the chromatographic characteristics of the separated substances are determined by the properties of the SLP only, is seldom used in practice, since reversible (or irreversible) adsorption of the separated compound and that of the components of the mixture can occur at the SLP/solid support interface. These phenomena may cause large errors in the interpretation of the analytical and physicochemical experimental results. Therefore, development of GLC requires extensive study of the processes occurring at the SLP/solid or SLP/gas interfaces. It should be mentioned that the classical GLC theory does not take into account the multiphase nature of the real sorbents.

With an adequate amount of SLP on a solid support (Fig. 1), the sorbent in GLC can be regarded approximately as a combination of at least three phases capable of adsorption and absorption: (1) the SLP/gas surface, (2) the SLP/solid surface, and (3) the SLP. In general, the retention volume observed should be determined by a contribution from all three of these phases.

For the sorbent model being discussed the system of equations describing the equilibrium during chromatography of a single component, under the action of
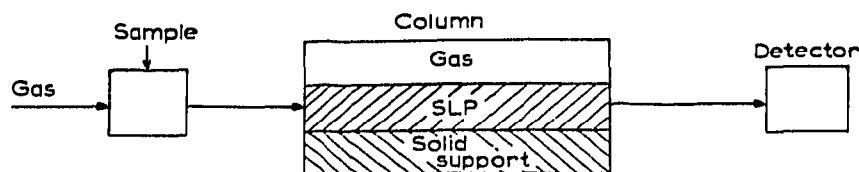
Fig. 1. Scheme of chromatographic device for gas–liquid chromatography.

longitudinal erosion factors, accounting for absorption in SLP and adsorption at the interface, can be written as:

$$u \frac{\partial c}{\partial x} + \varrho_g \frac{\partial c}{\partial t} + \varrho_{gl} \frac{\partial a_l}{\partial t} + \varrho_l \frac{\partial \alpha}{\partial t} + \varrho_{ls} \frac{\partial a_s}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

$$a_l = f_{gl}(c) \qquad (2)$$

$$\alpha = f_l(c) \qquad (3)$$

$$a_s = f l_s(a) \qquad (4)$$

where

u = the linear velocity of the carrier gas;
x = the coordinate;
t = the time;
c = the bulk concentration of the compound in the gas phase;
α = the bulk concentration of the substance in SLP;
a_l = the surface concentration of the compound at the SLP/gas interface;
a_s = the surface concentration of the compound at the SLP/solid support interface;
ϱ_g = the fraction of gas phase in the cross-section of the column;
ϱ_l = the SLP portion in the cross-section of the column;
ϱ_{gl} = the ratio of the surface of SLP/solid support interface to the sorbent volume;
ϱ_{ls} = the ratio of the surface of SLP/solid support interface to sorbent volume;
D_x = the effective coefficient of longitudinal diffusion.

Eqns. 2 and 4 are the adsorption isotherms on the SLP and solid support surfaces, eqn. 3 is the dissolution isotherm in SLP. It differs from the ordinary equation (see for example ref. 6) by the presence of third and fifth terms, which account for the adsorption at the SLP/gas and SLP/solid support interfaces. An equation similar to eqn. 1 has been solved earlier[7].

The rate of motion of a peak of a chromatographic zone and consequently the retention volume, V_N, can be determined by solving eqns. 2 and 4.

$$V_N = f_l' V_l + f_{gl}' S_l + f_l \cdot f_{ls}' \cdot S_s \qquad (5)$$

$$f_{gl}' = \frac{da_l}{dc}; \quad f_{ls}' = \frac{da_s}{da}; \quad f_l' = \frac{da}{dc}$$

where V_l is the volume of SLP in the column; S_l and S_s are respectively the SLP/gas and SLP/solid support interfaces in the column. Eqn. 5 is a general expression for

the model considered, where the whole surface of a support is covered with a macro-layer of the SLP. It takes into account the dissolution in SLP and adsorption at its interface boundaries.

If the adsorption and sorption isotherms are linear (*i.e.*, $f_{gl}' = K_{gl}$; $f_{ls}' = K_s$; $f_l = K_l$), then the retention volume equation should be:

$$V_N = K_l V_l + K_{gl} S_l + K_l K_s S_s \qquad (6)$$

From eqn. 6 K_l, K_{gl} and K_s can be found using the experimental relationships:

$$V_N = \psi(V_l) \qquad (7)$$

$$S_l = \varphi(V_l) \qquad (8)$$

The function 8 is non-linear.

For a graphical determination of the distribution factor it is expedient to use the equations:

$$\frac{V_N - \nabla_N}{V_l - \nabla_l} = K_{gl} \frac{S_l - \bar{S}_l}{V_l - \nabla_l} + K_l \qquad (9)$$

$$V_N - K_{gl} S_l = K_l V_l + K_l K_s S_s \qquad (10)$$

where $V_N = \nabla_N$ (V_l, S_l) is some reference point chosen in the low SLP content region.

Our experimental results and those reported elsewhere[8,9] are fitted well by eqns. 9 and 10.

Let us consider some conclusions resulting from eqns. 9 and 10 and use of the latter for analysing the experimental data.

Firstly the contribution of adsorption on the SLP interfaces to the retention volume can be considered. For example, Fig. 2 shows the relation of all three absorption processes in the SLP and adsorption at its interfaces for the system: the chromatographed compound–ethyl acetate; SLP–thiodipropionitrile; solid support–firebrick.
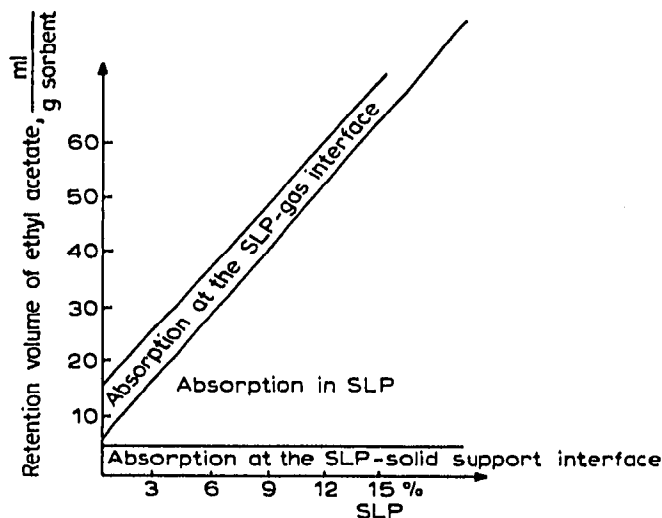

Fig. 2. Contribution of adsorption—at interface boundaries—to the retention volume for ethylene on β,β'-thiodipropionitrile.

TABLE I

CONTRIBUTION OF SOLID SUPPORT TO RETENTION VOLUME
Support, Chromosorb P.

Substance	K_l	K_{gl}	K_s	15% stearic acid on Chromosorb P						
				V_N	$K_l V_l$	$K_{gl} S_l$	$K_l K_s S_s$	$\dfrac{K_l V_l \cdot 100}{V_N}$	$\dfrac{K_{gl} S_l \cdot 100}{V_N}$	$\dfrac{K_l K_s S_s \cdot 100}{V_N}$
Benzene	150	2.5	0.025	187	157	9.9	20.1	84.0	5.3	10.7
Ethyl acetate	89.0	0.7	0.052	121	93.0	2.7	25.0	77.0	2.3	20.7
Hexyne-1	112.5	1.0	0.062	160	118	3.9	38.1	73.6	2.4	24.0

Table I shows the experimental data which also show the importance of the adsorption process on a solid support. It can be seen that adsorption on the surface of Chromosorb P may contribute (up to 24%) to the retention volume.

TABLE II

COMPARISON OF V_g VALUES USED FOR CALCULATION OF PHYSICAL AND CHEMICAL CHARACTERISTICS IN GLC FOR DIFFERENT COMPOUNDS ON β,β'-THIODIPROPIONITRILE

Compounds	Firebrick		Chromosorb W	
	V_g Our method	V_g Usual method	V_g Our method	V_g Usual method
n-Butyl ethyl ether	66	185	76	113
Propionic aldehyde	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
Cyclohexane	69	99	76	89

We have shown[10] that if adsorption is not taken into account the error in determining the physical and chemical characteristics of an SLP/gas system by a chromatographic method can be as much as 30–50% (see Table II).

TABLE III

HEATS OF SOLUTION AND ADSORPTION OF ALKANES AND ALKYNES ON APIEZON K COATED ON INZ-600

Substance	ΔH of solution (kcal/mole)	ΔH of adsorption (kcal/mole)	Heat of solution on squalane (kcal/mole) (literature data[12])
n-Hexane	5.8	4.55	6.21
Hexyne-1	5.2	10.9	—
n-Heptane	6.6	7.6	7.37
Heptyne-2	8.6	17.8	—

TABLE IV

COMPARISON OF CHROMATOGRAPHIC CHARACTERISTICS OF POLAR AND NON-POLAR COMPOUNDS ON ON DIFFERENT SUPPORTS UNDER GLC CONDITIONS (CONCENTRATION OF SQUALANE 10.65%)

Compounds	Sterchamol (j = 0.91)			Chromosorb W (j = 0.84)			Chromosorb G (j = 0.90)			Porcelain[a] (j = 0.93)			Sodium chloride[b] (j = 0.91)		
	Relative retention volume	A	$V_g°$	Relative retention volume	A	$V_g°$	Relative retention volume	A	$V_g°$	Relative retention volume	A	$V_g°$	Relative retention volume	A	$V_g°$
Cyclohexane	0.69	0.8	325	0.68	0.0	318	0.68	0.8	324	0.68	0.5	318	0.65	0.0	258
Isooctane	0.91	2.4	423	0.90	0.4	421	0.89	0.0	432	0.89	1.5	410	0.89	0.0	368
n-Hexane	0.37	0.8	176	0.37	0.0	168	0.37	0.0	171	0.37	0.6	163	0.35	0.0	147
Benzene	0.61	8.2	234	0.55	0.6	231	0.55	0.0	243	0.58	3.5	229	0.53	0.0	219
n-Heptane	1.00	2.6	475	1.00	0.4	485	1.00	0.0	477	1.00	1.5	473	1.00	0.0	410
Diethyl ether	0.75	—	—	0.20	3.1	78	0.12	0.0	58	0.80	—	—	0.10	0.0	41

[a] Concentration of squalane 5.65%.
[b] Concentration of squalane 1.00%.

Secondly, the possibility of new physico-chemical applications of gas chromatography follows from these three equations, namely measuring the adsorption of volatile compounds dissolved in SLP on the solid surface (for example, by determination of K_s). This possibility can be easily realised experimentally. The heats of solution of hydrocarbons in Apiezon K and adsorption on an Apiezon K–INZ-600 interface are shown in Table III. Thus it can be seen that for hydrocarbons the heats of adsorption considerably exceed those of solution.

Thirdly, eqns. 9 and 10 permit quantitative interpretation of such phenomena in GLC as zone asymmetry, irreproducibility of retention values, and in particular, their dependence upon the sample volumes.

Asymmetry of chromatographic zones is usually due to the solid support used. If for the compound analysed the adsorption isotherm at the SLP/solid support interface is non-linear and obeys the Freundlich equation

$$a_s = \alpha a^\beta \ (\beta < 1, \alpha = \text{constant}) \tag{11}$$

then the equation for the retention volume can be given in the following form (assuming that $K_{gl} \approx 0$)

$$V_N = K_l V_l + \frac{K_l S_s \alpha \beta}{c^{1-\beta}} \tag{12}$$

It follows from this equation that the retention volume increases with decreasing compound concentration in the gaseous phase, which explains a diffuse tail to the zone. Asymmetry of the latter is enhanced with increase in the value of $(1-\beta)$.

Eqn. 12 can be used also to interpret the empirical dependence of the retention volume on the sample volume q.

The equation for the relative volume, $V_{N(o)}$ describing this dependence (at $V_{N(st)} = K_{l(st)} \cdot V_l$) can be written as follows:

$$V_{N(o)} = \frac{K_l}{K_{l(st)}} \left[1 + \frac{\varepsilon}{V_l^\beta} \left(\frac{K_{l(st)}}{K_l} \right)^{1-\beta} \left(\frac{V_{N(o)}}{q} \right)^{1-\beta} \right] \tag{13}$$

where ε is a constant. The literature and our experimental data[8] are quantitatively described by eqn. 13.

Fourthly, eqns. 9 and 10 can be used to quantitatively estimate the adsorption properties of the solid supports under conditions of GLC and consequently the efficiency of the modified methods. It is expedient to characterise the adsorption properties of the solid supports by their retention volumes as the adsorption of the chromatographed compound on the surface per gram of the support covered with SLP[11].

As an example the contribution from adsorption of chromatographed compounds to the retention volume at the squalane–solid support interface for different support are given in Table IV.

Thus, adsorption phenomena are of great importance in the GLC and they should be taken into account in analytical, physical and chemical measurements.

Adsorption on the solid support surface can play a positive role by providing better separation of compounds with similar properties (for example, the organic mineral clays).

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