THE OBSTRUCTIVE COEFFICIENT AND STATIONARY PHASE DISTRIBUTION OVER SOLID SUPPORT SURFACES IN GAS CHROMATOGRAPHY

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SUMMARY

A relationship has been suggested for the explicit expression of the obstructive coefficient dependent on the basic characteristics of the supporting material and stationary liquid. In addition, the influence of support pore volume and the distribution of the support pores filled with various volumes of the stationary liquid on the value of the obstructive coefficient was investigated. The difference between the penetrability of material whose surface had been modified with trimethylchlorosilane and of that with an unmodified surface has been verified.

The distribution of the liquid on a solid support not only influences the mass transfer from the gaseous (mobile) to the liquid (stationary) phase and diffusion processes in the liquid phase, but also diffusion processes in the gaseous phase, due to the internal pore structure of the supporting material. The influence of the porous medium on such processes has been characterized by the obstructive coefficient, γ[1-3],

$$\gamma = CT^{-2} \tag{1}$$

where the influence of the constriction C and tortuosity T of the support channels on the longitudinal diffusion of sorbate in the gaseous phase are described. Attention has been given to various geometrical patterns of column packing[2], as well as to the influence of such an arrangement on the shape of channels in the packing material. A qualitative description of the role of the internal structure of material has also been made[4]. There is no doubt that the internal pore structure enhances the penetrability of loosely packed material[5] and, consequently, also the obstructive coefficient. It can be assumed[4] that the resulting obstructive coefficient corresponds to the sum of the obstructive coefficients representing the resistance against diffusional flow in interstitial space, γ_M, and that in the internal support pores, γ_V.

$$\gamma = \gamma_M + \gamma_V \tag{2}$$

The coefficient γ_M is unambiguously characterized by the shape and arrangement of the column packing. Thus, if the volume of coating liquid V_L does not exceed

the internal pore volume V_ε, the value of γ_M will not change with various volumes of the coating liquid.

We will therefore restrict ourselves to the dependence of γ_V on the volume of coating liquid.

THEORETICAL

Let us suppose that a major part of the solid support surface is constituted of its internal pores. This assumption holds for materials with surface areas of about $1 \ m^2 \cdot g^{-1}$, i.e. for the supports most widely used—diatomaceous supports (Chromosorb W) and firebrick supports (Sterchamol, Chromosorb P). Under these conditions, most of the coating liquid will collect in support pores[6,7].

Let us describe the distribution of pore radii, r, with respect to pore volume by the equation

$$dV = \alpha(r)dr \tag{3}$$

Since the relation[3] below holds true

$$S^+ \bar{r}/2 = V_\varepsilon \tag{4}$$

where S^+ is the dry surface area and $\bar{r}$ the mean value of pore radius relative to pore volume, we can write for the relative area[7]:

$$\rho = \frac{S}{S^+} = \frac{1}{V_\varepsilon} \int_{r_{min}}^{r_{max}} \alpha(r)dr \tag{5}$$

where S is the area of supporting material coated with liquid and r_{min} and r_{max} are the minimum and maximum radii of pores filled with liquid. The relative area does not depend on the absolute dry area of the support[8] and is a function of the distribution of support pore radii as well as of the volume of coating liquid. It can be derived[7] that

$$\rho = \frac{V_\varepsilon - V_L}{V_\varepsilon} \cdot \frac{\bar{r}}{\bar{r} + r(V_L)/\beta} \tag{6}$$

where β is a constant.

Let us further consider a single particle of the supporting material. The diffusional flow through this particle is proportional to the overall cross-section communicating from one side of the particle to the opposite one. Assuming that all of the pores are equal in length, then

$$\frac{d\gamma_V}{dV} = \frac{d\gamma_V}{dr} \frac{dr}{dV} = 0 \tag{7}$$

A change in the radius (cross-section) of pores r_i will be proportional to the change in the obstructive coefficient; thus

$$d\gamma_V = k\alpha(r)dr \tag{8}$$

where k is a constant. In respect to the number of pores in a particle of a particular radius

$$\gamma_V = \sum_1^n \gamma_{Vi} \tag{9}$$

For the sake of simplification, the total resistance of the system against diffusional flow can be represented by analogy to a system of parallel wire conductors of the same length and radius. The overall conductivity C of the system is given by the sum of reciprocal values of the resistors. If we select the system of resistors so that the distribution of their radii will correspond to the distribution function (3) (the radius of a wire resistor is denoted r'), we may write, in analogy to eqn. (9)

$$C = k_r \sum_1^n \frac{1}{r'_i} \tag{10}$$

where k_r is a constant.

With regard to eqns. (2), (7) and (8), the intraparticle obstructive coefficient can be written as

$$\gamma_V = k \int_{V_\varepsilon}^{V_\varepsilon - V_L} \mathrm{d}V = k \int_{r_{min}}^{r_{max}} \alpha(r)\mathrm{d}r \tag{11}$$

Combining eqns. (11) and (5) we obtain an explicit relation for the intraparticle obstructive coefficient as a function of the relative area and volume of the internal pores,

$$\gamma_V = k V_\varepsilon \rho \tag{12}$$

If the entire diffusion flow is confined to the internal structure of the pores of a single particle, then $k = 1$ and in accordance with presupposition (7) $\mathrm{d}\gamma_V/\mathrm{d}V = 0$ also.

The proportionality constant is $0 < k \leqslant 1$, and it indicates the part of the total diffusion flow of sorbate between two points in the column which will be confined to the diffusion through the particle and around the particle, i.e. through the interstitial space V_M.

Let us again illustrate the influence of the interstitial column space by analogy to electrical wiring (Fig. 1). The internal obstructive coefficient γ_V is analogous to the output voltage E_2 from the divider of input voltage E_1 (analogous to ρ). The resistors in the diagram represent the interstitial volume, V_M', and internal volume V_ε'. In analogy with eqn. (12) we may write

$$E_2 = \frac{V_\varepsilon'}{V_\varepsilon' + V_M'} E_1 \tag{13}$$

With regard to eqn. (13), eqn. (12) can be rewritten as

$$k = 1/(V_\varepsilon + V_M) \tag{14}$$

and in a final form

$$\gamma_V = \frac{V_\varepsilon}{V_\varepsilon + V_M} \rho \tag{15}$$
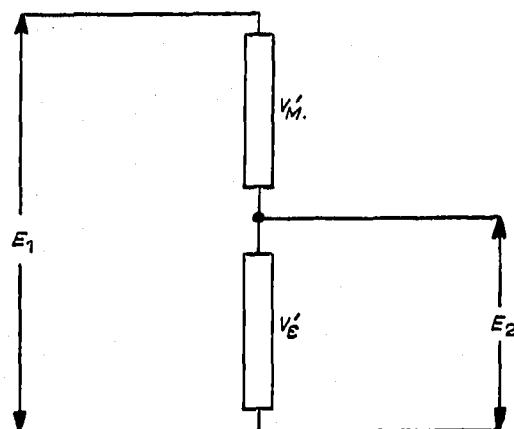
Fig. 1. Equivalent electrical circuit.

The limiting conditions are:

for $V_L = 0$, $\gamma_V = \dfrac{V_\varepsilon}{V_M + V_\varepsilon}$

for $V_L = V_\varepsilon$, $\gamma_V = 0$

for $V_M \to 0$, $\gamma_V \to \rho$

for $V_M \gg V_\varepsilon$, $\gamma_V \to 0$

With regard to eqn. (6), the internal obstructive coefficient can be expressed as a function of the volume of the internal pores, of the coating liquid, and of the distribution of support pore radii.

$$\gamma_V = \frac{1 - V_L/V_\varepsilon}{1 + V_M/V_\varepsilon} \; \frac{\gamma}{\gamma + r(V_L)/\beta} \tag{16}$$

By silanizing the support surface we obtained changes in the chemical character of the surface[8,10] and in the structure of internal support pores[11] which are reflected by a change of the dependence of the relative area on the volume of coating liquid[7] ($\rho = f(V_L)$). Structural (geometrical) changes of the surface indicate a closer (less penetrable) structure of silanized uncoated supports. For silanized supports, therefore, $(V_\varepsilon)_{sil} < (V_\varepsilon)$ and, consequently for $V_M = $ constant and according to eqn. (16) also $(\gamma_V)_{sil} < (\gamma_V)$.

The first addition of liquid onto a silanized support surface does not cause closure of the smallest pores and, consequently, γ_V will not decrease with the increasing volume of the liquid, in the same way as is the case with an unsilanized surface. Silanization of the surface will therefore decrease the $B = 2\gamma D_g$ term in the diffusion equation for small volumes applied, whereas with larger volumes of liquid, the term B will grow as compared with the same term for unsilanized materials.

EXPERIMENTAL

Materials

        Supports. Chromosorb P (Carlo Erba, Milan, Italy) particle size 0.25 mm–0.50

mm; Chromosorb P modified with trimethylchlorosilane, particle size 0.25–0.50 mm and 0.15–0.25 mm.

Liquid phase. Squalane (Carlo Erba, Milan, Italy).

Solvent. Ether.

Gases. Electrolytic hydrogen, nitrogen (Technoplyn, N. E., Ostrava), air, liquid nitrogen (Technoplyn, N. E., Komárov).

Methods

The diffusion coefficient and the obstructive coefficient were measured by the elution method[2]. Diffusion was measured in the system methane–hydrogen. At the temperature chosen (50°), methane was not sorbed on the supports used.

The surface areas of both activated and coated supports was measured by the dynamic desorption method[12]. A mixture of 20 % nitrogen and 80 % hydrogen (v/v) was used for the measurements.

Liquid nitrogen was used as coolant.

Apparatus

The obstructive coefficients were measured in the thermostat of an Argon-Pye instrument using a Vibron electrometer, model 33C (England), and a flame ionization detector constructed by the authors.
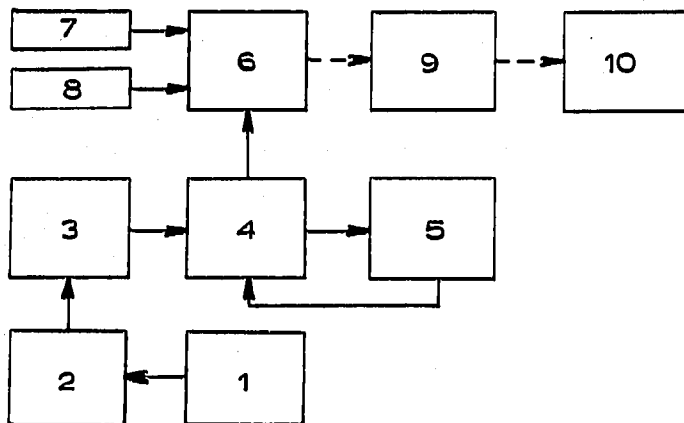

Fig. 2. Schematic representation of the apparatus.

Electrolytic hydrogen from a pressure cylinder (1) (Fig. 2) was passed *via* a pressure reducer (2), pressure gauge (3) and shut-off valve (4) into the column (5) and flame ionization detector (6). The sample was introduced directly into the column. A glass column was used (I.D. 3.6 mm, 740 mm long). In addition, a mixture of air (7) and hydrogen (8) was fed to the detector. The detector signal was transmitted by the electrometer (9) to a KBT recorder (10) (K. Marx Werke, Magdeburg, D.D.R.).

The specific area of the supports was measured with an instrument for dynamic desorption[13] measurements. The instrument was connected to a Pye integrator and a Honneywell-Brown recorder.

RESULTS AND DISCUSSION

The obstructive coefficients were calculated using the equation[2]

$$\frac{d\sigma_t^2}{dt} = 2\gamma D_g / u^2$$

where σ_t^2 is the standard deviation of the band of the diffusing material and u is linear velocity of the carrier gas. The diffusion coefficient D_g for the system hydrogen-methane was measured in an empty column ($D_g = 0.765$ cm²·sec⁻¹) at 50° and 1.08 atm and correlated with a tabulated value[14] corrected for the given temperature and pressure ($D_g = 0.760$ cm²·sec⁻¹). The value 0.76 cm²·sec⁻¹ was used for calculating the obstructive coefficient. The error of the measurement calculated from six measurements was $\vartheta = \pm 2.8$ %. The error involved in the determination of γ is higher because it is dependent on several geometrical factors (arrangements of packing material in column, accuracy of support sizing, abrasion of support during application of stationary phase and column packing).

The intraparticle obstructive coefficients were calculated from eqn. (16) for various volumes of coating liquid applied on to Chromosorb P and trimethylchlorsilane modified Chromosorb P (particle size 0.15–0.25 mm and 0.25–0.50 mm). The distribution function for pore radii with respect to pore volume and the mean pore radii were taken from ref. 11. The structural constant β was calculated from the previously derived relation[7]. The internal pore volume was determined using eqn. (4) where S^+ has been determined by experiment. We have calculated the mean square deviation for the volume of internal pores calculated in the above manner, measured by experiment, and quoted in ref. 11, as ± 6.35 %. The magnitude of the interstitial space V_M was calculated as four tenths of the total volume of column reduced to 1 g column packing. The calculated intraparticle obstructive coefficients are listed in Table I.

TABLE I

CORRELATION OF CALCULATED AND MEASURED OBSTRUCTIVE COEFFICIENTS

Support	Particle size (mm)	% squalane	V_L (ml·g⁻¹)	ρ	$r(V_L) \cdot 10^4$ (cm)	γ_v by eqn. 16	$\gamma_{v\ exp.}$	$\gamma_v/\gamma_{v\ ex}$
Chromosorb P	0.25–0.50	0	0	1.000	0	0.528	0.533	0.991
		1	0.0125	0.520	0.10	0.294	0.303	0.970
		5	0.0625	0.405	0.18	0.205	0.221	0.928
		10	0.125	0.314	0.26	0.152	0.155	0.981
		20	0.250	0.168	0.33	0.105	0.096	1.094
Chromosorb P + TMCHS	0.25–0.50	0	0	1.000	0	0.483	0.484	0.998
		1	0.0125	0.785	0.09	0.380	0.397	0.957
		5	0.0625	0.570	0.16	0.276	0.273	1.011
		10	0.125	0.373	0.25	0.181	0.196	0.924
		20	0.250	0.280	0.32	0.134	0.116	1.155
Chromosorb P + TMCHS	0.15–0.25	0	0	1.000	0	0.510	0.495	1.030
		1	0.0125	0.785	0.09	0.401	0.417	0.962
		5	0.625	0.570	0.16	0.292	0.305	0.957
		10	0.125	0.373	0.25	0.191	0.185	1.035
		20	0.250	0.280	0.32	0.143	0.140	1.021

TABLE II

EXPERIMENTAL AND CALCULATED CONSTANTS K (EQN. 17)

Support	Particle size (mm)	$K_{exp.}$	K by eqn. 17	K_{exp}/K
Chromosorb P	0.25–0.50	0.543	0.528	1.028
Chromosorb P + TMCHS	0.25–0.50	0.466	0.483	0.965
Chromosorb P + TMCHS	0.15–0.25	0.517	0.511	1.012

A change of the obstructive coefficient with respect to the volume of coating liquid will be manifested mainly by a change in the intraparticle obstructive coefficient. The dependence of γ on the relative area ρ is a straight line with a slope (Fig. 3A)

$$K = V_\varepsilon/(V_\varepsilon + V_M) \tag{17}$$

We compared the slope of the straight line relationship of γ/ρ obtained experimentally with the slope calculated from eqn. (17) (Table II). In the expression for the obstructive coefficient γ, the interstitial obstructive coefficient γ_M is represented by the intercept on the axis of ordinates. Since it is not only the intraparticle obstructive coefficient (viz. 16) but mainly the interparticle obstructive coefficient which is dependent[2] on the interstitial space V_M, a change in the interstitial space brings about a change in the slope K as well as in the intercept on the axis of ordinates, γ_M.
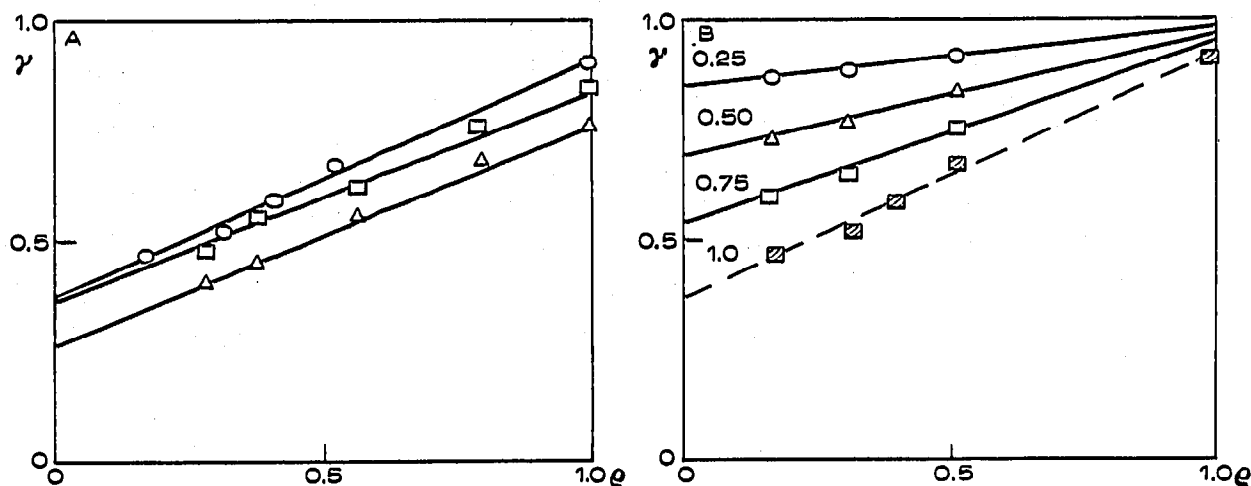

Fig. 3. (A) The dependence of the obstructive coefficient, γ, on the relative area, ρ, for: (O) Chromosorb P (0.25–0.50 mm); (□) Chromosorb P + TMCHS (0.25–0.50 mm); (△) Chromosorb P +TMCHS (0.15–0.25 mm). (B) The dependence of the obstructive coefficient, γ, on the relative area, ρ, for various times of diffusion in the porous material (Chromosorb P).

We have verified by experiment the influence of the interstitial space on the constant K_{exp} (eqn. 17). We placed in the column half of the previous amount of packing so that one half of the column remained empty. Thus, different densities of column packing were replaced by different times of diffusion of the gas in the porous and empty column spaces. We have in this way replaced columns varying in their interstitial spaces by a single column on which the obstructive coefficients were measured. (Fig. 3B).

From the slopes obtained by experiment (Fig. 3B) we have calculated k by eqn. (14). We also have determined k from the relation

$$k = \frac{1}{V_\varepsilon + \left(\dfrac{t_e}{t} V_{Me} + \dfrac{t_f}{t} V_{Mf}\right)} \qquad (18)$$

where t is the total time of diffusion of the substance in the column, t_e is the time of diffusion of the solute in the empty column space, t_f is the time of diffusion of the solute in the packed part of column, V_{Me} is the dead-volume of the empty column and V_{Mf} is the interstitial space between the particles of the packed column part. Correlation of k values calculated by eqns. (14) and (18) is shown in Table III.

TABLE III

EXPERIMENTAL AND CALCULATED CONSTANTS k FOR CHROMOSORB P (EQN. 18)

t_f/t	V_M $(ml \cdot g^{-1})$	$k_{exp.}$ by eqn. 14	k by eqn. 18	$k_{exp.}/k$
1.00	1.033	0.467	0.457	1.022
0.75	1.894	0.350	0.327	1.070
0.50	3.617	0.225	0.210	1.071
0.25	8.783	0.108	0.101	1.069

The effect of surface silanization on the structure of internal support pores is obvious from the plot of relative support area against the volume of coating liquid (Fig. 4) and from the dependence of the obstructive coefficient on the volume of coating liquid for Chromosorb P and Chromosorb P modified with trimethylchlorosilane (Fig. 5).

The specific area of material modified with trimethylchlorosilane (3.97 m² g⁻¹) and the intraparticle obstructive coefficient of the latter (0.484) are smaller than the specific area (5.78 m² g⁻¹) and the intraparticle obstructive coefficient (0.533) of the
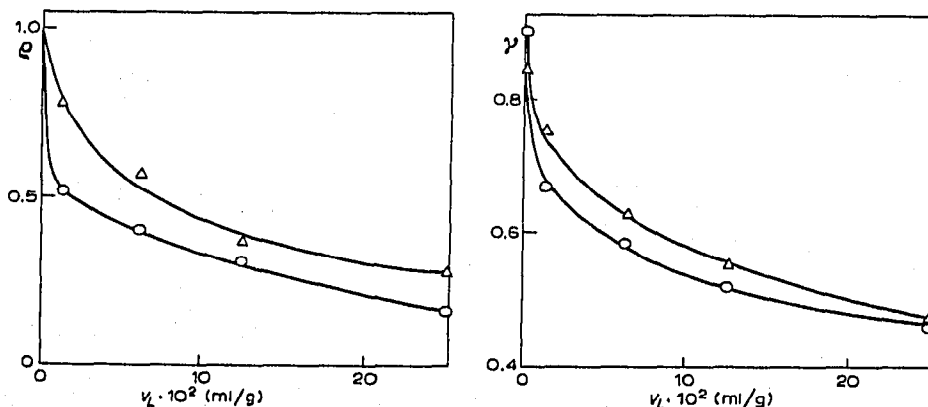

Fig. 4. The dependence of relative area, ρ, on the applied volume of liquid, V_L, for: (O) Chromosorb P; (△) Chromosorb P + TMCS.

Fig. 5. The dependence of the obstructive coefficient, γ, on the applied volume of liquid, V_L, for: (O) Chromosorb P; (△) Chromosorb P + TMCS.

uncoated unmodified support. This agrees with the assumption as to a lesser penetrability of the modified supports in contrast to the unmodified ones. On application of the first portions of the liquid, the intraparticle obstructive coefficient for an unmodified support decreases at a greater rate than does that for a modified support. The difference between the intraparticle obstructive coefficients of a modified and an unmodified support increases to a particular volume of liquid applied (approximately 0.01 ml g^{-1}) (Fig. 6). The course of the plot agrees with the assumption that initial additions of liquid do not close the smallest pores in the modified support surface and the structure which had been less penetrable is becoming more penetrable than that of unmodified supports. With successive applications of liquid the difference becomes less and the obstructive coefficients for modified and unmodified surfaces approach each other.
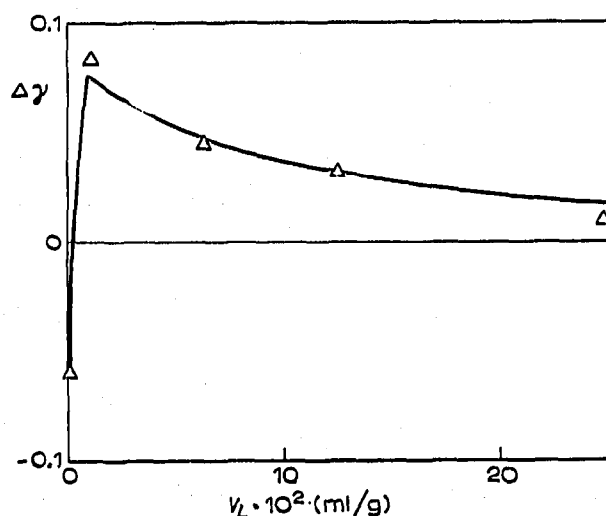

Fig. 6. The plot of the differences in the obstructive coefficients *versus* the volume of coating liquid.

The intraparticle obstructive coefficient represents about 50 % or more of the total obstructive coefficient. Thus filling up the intraparticle pore space with a stationarly liquid also pronouncedly influences the value of the total obstructive coefficient.

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