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GAS CHROMATOGRAPHY WITH A VAPOUR MOBILE PHASE AT THE FINITE CONCENTRATION OF SORBATE

I. THE SORPTION EFFECT

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SUMMARY

The characteristic features of the sorption effect in chromatography with a vapour mobile phase are examined. A peak having a pronounced leading edge is usually formed under these conditions.

INTRODUCTION

The use of water vapour as the mobile phase¹ in gas chromatography expands the possible range of applications, leading in a number of cases to more symmetrical peaks and better separations. Additional advantages arise in preparative chromatography, where sophisticated devices to circulate the carrier gas can be avoided, and, sometimes, the recovery of separated fractions is simplified.

Few studies have been made of the peculiarities of band diffusion at high sorbent concentrations in chromatography with a vapour mobile phase (VPC). The present work examines the sorption effect; the temperature effects associated with sorption-desorption of a component in VPC will be described later.

THEORETICAL

Asymmetry of a peak at high sample concentrations is usually explained by the non-linearity of the sorption isotherm. Recently²⁻⁵ it has been shown that a high concentration of the eluted substance can itself result in peak asymmetry as a consequence of the flow-rate variation along the column: in the section of the sorbent occupied by the eluted substance the flow is made up of the carrier gas and the substance itself, and the flow-rate here is higher and varies with concentration. This effect, called the "sorption effect", results in asymmetric peaks with tailing. A more complicated situation occurs in VPC. In this case, high sample concentrations disturb the previously established sorption equilibrium with respect to the vapour eluent, which is then desorbed from the packing.

Let us first consider the physical picture of the band movement in conventional elution chromatography and in chromatography with a vapour mobile phase. We shall proceed from the assumption that sorption equilibrium is established instan-

taneously and the boundaries of the band are sharp. The theory is valid at constant mass flow-rate of the eluent.

Let the band of the eluted substance, under the conditions of elution chromatography, occupy the sorbent section whose boundaries are delineated in Fig. 1 by solid lines. Sorption equilibrium is established between the gaseous and the stationary phases inside the band. The part of the band located in the gaseous phase will be displaced over a small distance, dx , by the flow of the carrier gas and will then occupy the position shown in Fig. 1 by dashed lines. The sorption equilibrium at the edges of the band will have been disturbed too: the portion of the sorbent at the left margin of the band will come into contact with the pure carrier gas, and here the sorbate will be displaced by the carrier gas flow into the band; the portion of the sorbent at the right margin of the band, previously free of the sorbate, will now be in contact with the carrier gas containing the substance which will be adsorbed and removed from the carrier gas flow.

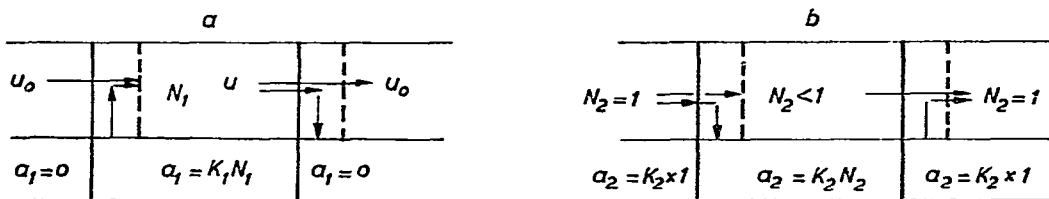


Fig. 1. Mechanism of band displacement with nitrogen (a) and water vapour (b) as the carrier gas.

As a result the flow of the substance suddenly increases very sharply at the left boundary of the band and then decreases again at the right boundary to its initial value. This effect will be more pronounced for readily adsorbed components. At high sample concentrations the increase in the flow-rate inside the band will be greater. Therefore, a chromatographic peak can be visualized as resulting from a large number of bands with sharp boundaries, with the highest flow-rate corresponding to the maximum of the peak; tailing of the peak is thus observed.

In chromatography with vapour eluents the situation is more complicated since, in this case, not only the substance but also the eluent itself undergoes sorption-desorption. Outside the chromatographic band the sorbent is in equilibrium with the pure water vapour, the mole fraction of which in the gaseous phase is $N_2 = 1$. Since the gaseous phase inside the band contains a certain amount of the sorbate, $N_2 < 1$, and the quantity of water in the sorbent is also smaller than outside the band. When the part of the band located in the gaseous phase is displaced over a small distance, dx , and occupies the position designated in Fig. 1b by the dashed line, a section of the sorbent with a decreased water content will appear at the left boundary of the band. An additional quantity of the eluent will then be sorbed here, and, therefore, a smaller amount of it will enter the band: the eluent flow inside the band will become lower than to the left of it. At the right boundary of the band the portion of the sorbent previously in equilibrium with pure water will come into contact with the gaseous phase containing a smaller amount of it. The eluent will be desorbed from this portion of the sorbent, and its flow to the right of the band will become greater than inside it

and equal to the flow to the left of the band. The flow-rate of the vapour eluent inside the band is thus smaller than outside it. The higher is the sorbate concentration the stronger is this effect. Therefore, inside the band with the usual Gaussian concentration profile the eluent flow is minimal in the region of the maximum sorbate concentration. Such a variation of the eluent flow inside the band must result in a chromatographic peak with a prominent leading edge.

For substances which are not adsorbed the above effect of the eluent flow-rate variation will be the only one, whereas in the case of adsorbed substances the overall effect will be a combination of those of the eluent flow-rate variation and the sorbate flow-rate variation. Depending on the extents of adsorption of the substance and the eluent, the flow-rate inside the band can become either higher or lower than outside it. If the substance is more strongly adsorbed than the eluent, the amount of desorbed substance at the left boundary of the band will exceed that of the adsorbed eluent, and the overall flow inside the band will be greater than outside it, causing tailing of the peak. The opposite occurs if the substance is less strongly adsorbed than the eluent.

Let us now examine quantitatively the dependence of the rate of displacement of the sorbate on its concentration. This problem, at high sorbate concentrations and taking account of eluent sorption, has been considered in terms of the "theory of chromatography without a carrier gas"^{6,7}.

Proceeding from the set of equations

$$\frac{\partial a_i}{\partial x} + \frac{\partial (uN_i)}{\partial x} = \frac{\partial a_i}{\partial t}$$

where N_i is the mole fraction in the gaseous phase, a_i is the packing concentration in mol/cm³, u is the flow-rate, x is the longitudinal coordinate, t is the time and indices $i = 1, 2$ refer to the substance and the eluent, general relationships were obtained^{6,7} for the flow-rate, u , and the rate of the band, v , which can be written as*

$$u = u_0 e^F \quad (1)$$

where

$$F = \int_0^1 \frac{\partial N_1}{r - N_1}; \quad r = \frac{\partial a_1 / \partial N_1}{\partial a_1 / \partial N_1 - \partial a_2 / \partial N_2} \quad (2)$$

$$v = \frac{\partial (uN_1) / \partial N_1}{\partial a_1 / \partial N_1} \quad (3)$$

Eqns. 1-3 are easily solved if the sorption isotherm is linear, when $\partial a_i / \partial N_i = \epsilon + \mu K_i$, where ϵ , μ are the fractions of packing volume occupied by the gas and the stationary phase and K_i is the distribution coefficient. In this case r is constant and:

$$F = \ln r / (r - N_1) \quad (4)$$

$$u = u_0 r / (r - N_1) \quad (5)$$

* A brief derivation of eqns. 1-3 was given in ref. 5.

$$v = \frac{u_0}{\partial a_1 / \partial N_1} \left(\frac{r}{r - N_1} \right)^2 \quad (6)$$

The quantity before the parentheses in eqn. 6 is equal to the rate of substance displacement at $N_1 \rightarrow 0$, and that in the parentheses is the correction for the sorption effect. It is seen that the rate of substance displacement depends on N_1 , which results in the peak asymmetry. Let us examine two limiting cases.

(1) The substance is not sorbed but the (vapour) eluent is sorbed. Then $\partial a_1 / \partial N_1 = \varepsilon$, $\partial a_2 / \partial N_2 = \varepsilon + \mu K_2$, $r = -\varepsilon / \mu K_2$ and:

$$v = u_0 \varepsilon / (\varepsilon + \mu K_2 N_1)^2 \quad (7)$$

From this expression it is seen that, with increasing N_1 , v decreases, *i.e.*, when un-sorbed substance is introduced into the vapour eluent flow, a peak with leading must be formed. At $N_1 \rightarrow 0$, $v = u_0 / \varepsilon$

(2) The substance is sorbed, but the eluent is not sorbed (conventional elution chromatography). Then $\partial a_1 / \partial N_1 = \varepsilon + \mu K_1$, $\partial a_2 / \partial N_2 = \varepsilon$, $r = \varepsilon / \mu K_1 + 1$ and

$$u = u_0 \Gamma_1 / (\Gamma_1 - \mu K_1 N_1) \quad (8)$$

$$v = u_0 \Gamma_1 / (\Gamma_1 - N_1)^2 \quad (9)$$

where:

$$\Gamma_1 = \varepsilon + \mu K_1$$

In this case, with increasing N_1 , v increases, *i.e.*, a peak with a pronounced tailing edge is formed. At $N_1 \rightarrow 0$ we get the usual expression:

$$v = u_0 / \Gamma_1$$

If both the substance and the eluent are sorbed:

$$v = u_0 \Gamma / [\Gamma_1 + (\Gamma_2 - \Gamma_1) N_1]^2 \quad (10)$$

In this case, the nature of the peak asymmetry depends on the relative strengths of the eluent and substance adsorptions. If the substance is sorbed more strongly than the eluent ($\Gamma_1 > \Gamma_2$), the sorption effect facilitates the formation of a peak with tailing. At $\Gamma_1 < \Gamma_2$ the opposite peak asymmetry occurs.

Isotherm non-linearity, superimposed on the sorption effect, produces a radical effect on peak asymmetry. In the case of conventional elution chromatography, $r = \varepsilon / \mu K_1 + 1$. In most cases of strongly adsorbed substances, $\varepsilon \ll \mu K_1$, which is also true when the isotherm is not linear. In packed layers, $\varepsilon \approx 0.5$, $\mu \approx 0.1$ and for instance for $K_1 > 50$, $\varepsilon / (\varepsilon + \mu K_1) < 0.1$. Then $r \approx 1$ and:

$$v = \frac{u_0}{\partial a_1 / \partial N_1} \left(\frac{1}{1 - N_1} \right)^2 \quad (11)$$

This means that in conventional elution chromatography the nature of the peak distortion, associated with the sorption effect, depends only little, if at all, on the shape of the sorption isotherm. If the latter is approximated by the polynomial

$$c_l = K_1 N_1 + b_1 N_1^2 \quad (12)$$

then:

$$v = \frac{u_0}{\varepsilon + \mu (K_1 + 2b_1 N_1)} \left(\frac{1}{1 - N_1} \right)^2 \quad (13)$$

When the isotherm is convex to the ordinate axis, $b_1 < 0$, and the isotherm effect enhances the sorption effect; when $b_1 > 0$ the two effects are partially compensated. By multiplying the terms in the denominator and combining those with the same power of N_1 , it is, however, easy to show that complete compensation, *i.e.*, the equality of all the coefficients in N_1 , is impossible. If K_1 is small, in eqn. 13 $1 + \varepsilon/\mu(K_1 + 2b_1 N_1)$ must be used instead of 1.

When the unadsorbed substance is introduced into a flow of vapour eluent the sorption isotherm of which is approximated by eqn. 12, we obtain:

$$r = -\varepsilon/\mu(K_2 + 2b_2 - 2b_2 N_1) \quad (14)$$

After substituting this expression into eqn. 2 we get:

$$F = \int_1^0 \frac{\mu (K_2 + 2b_2 - 2b_2 N_1)}{\varepsilon + \mu (K_2 + 2b_2 - 2b_2 N_1) N_1} dN_1^2 \quad (15)$$

which, after rearrangement and integration, yields

$$F = \ln \frac{\varepsilon}{\varepsilon + \mu (K_2 + 2b_2 - 2b_2 N_1) N_1} + \int_1^0 \frac{2\mu b_2 N_1}{\varepsilon + \mu (K_2 + 2b_2 - 2b_2 N_1) N_1} dN_1 \quad (16)$$

If we restrict ourselves to the case of only slightly curved isotherms, when $b_2 \ll K_2$, the second integral will become merely a correction to the whole expression for F , and it can be simplified*. Specifically, for strongly adsorbed components, ε can be disregarded. After integrating we get:

$$F = \ln \frac{\varepsilon}{\varepsilon + \mu (K_2 + 2b_2 - 2b_2 N_1) N_1} + \ln \frac{K_2 + 2b_2 - 2b_2 N_1}{K_2 + 2b_2} \quad (17)$$

Substitution of this expression into eqn. 1 then yields:

$$u = u_0 \frac{\varepsilon (K_2 + 2b_2 - 2b_2 N_1)}{[\varepsilon + \mu N_1 (K_2 + 2b_2 - 2b_2 N_1)] (K_2 + 2b_2)} \quad (18)$$

* In gas-liquid chromatography the partition isotherm is usually almost linear and the assumption $b_2 < k_2$ is valid.

Taking $N_1 \ll 1$ and disregarding the $2b_2N_1$ term, we get:

$$u = u_0\varepsilon/[\varepsilon + \mu N_1(K_2 + 2b_2)] \quad (19)$$

The corresponding expression for v will have the form

$$v = u_0\varepsilon/[\varepsilon + \mu N_1(K_2 + 2b_2)]^2 \quad (20)$$

which becomes eqn. 7 as $b_2 \rightarrow 0$. When $b_2 < 0$ (convex isotherm) the sorption effect is weakened, and when $b_2 > 0$ (concave isotherm) it is correspondingly increased compared with the sorption effect at a linear isotherm.

Finally, let us examine the case where the adsorptions of the eluent and the substance are of comparable strengths. In this case

$$r = \frac{\varepsilon + \mu(K_1 + 2b_1N_1)}{\mu(K_1 - K_2) + 2\mu[N_1(b_1 + b_2) - b_2]} \quad (21)$$

and, correspondingly:

$$F = \int_0^N \frac{\mu(K_1 - K_2) + 2\mu[N_1(b_1 + b_2) - b_2]}{\varepsilon + \mu K_1 + \mu N_1[2(b_1 + b_2)(1 - N_1) - (K_1 - K_2)]} dN_1 \quad (22)$$

Restricting ourselves to the case of relatively small N_1 values and disregarding the $N_1(b_1 + b_2)$ terms, after integration we get:

$$F = \frac{(K_1 - K_2) - 2b_2}{(K_1 - K_2) - 2(b_1 + b_2)} \ln \frac{\Gamma_1}{\Gamma_1 + N_1(\Gamma_2 - \Gamma_1) + 2\mu(b_1 + b_2)} \quad (23)$$

For a small isotherm curvature, when b_2 is a minor correction to the K_1 value, the factor before the logarithm can be taken as approximately equal to 1. We then obtain

$$u = \frac{u_0\Gamma_1}{\Gamma_1 + N_1[(\Gamma_2 - \Gamma_1) + 2\mu(b_1 + b_2)]} \quad (24)$$

and:

$$v = \frac{u_0\Gamma_1^2}{(\Gamma_1 + 2\mu b_1 N_1) \{ \Gamma_1 + N_1[(\Gamma_2 - \Gamma_1) + 2\mu(b_1 + b_2)] \}^2} \quad (25)$$

The expression in parentheses in the denominator represents the direct effect of the sorption isotherm on the rate of band displacement, whereas the expression in braces characterizes the influence of the sorption effect. At $b_1, b_2 < 0$ the leading edge of the peak decreases due to the sorption effect (at $\Gamma_1 < \Gamma_2$), and at $b_1, b_2 > 0$ it increases.

RESULTS AND DISCUSSION

The influence of the sorption effect on the form of chromatographic bands may be confirmed by the observation of asymmetric peaks for unadsorbed substances in VPC. Experiments were conducted on previously described apparatus⁶, using 20% polyethylene glycol adipate (PEGA) on polychrome as sorbent.

Fig. 2 shows the output curves for methane in nitrogen and in water vapour at different sample volumes. At small volumes (25–30 μl) the methane peak has the same form in water vapour and in nitrogen and is characterized by slight tailing. An increase in volume to $\geq 100 \mu\text{l}$ results in opposite form of peak asymmetry in the water vapour flow, whereas in nitrogen only an increase of the methane concentration in the band and a slight expansion of the band are observed.

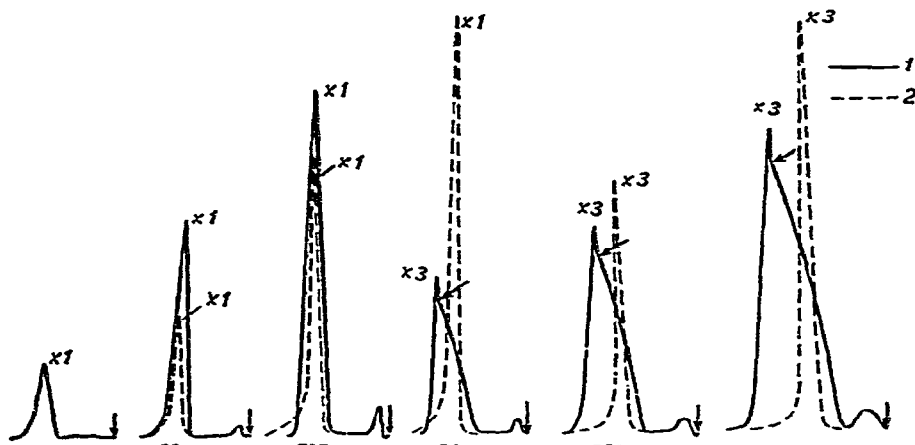


Fig. 2. The peaks of methane in a flow of water vapour (—) or nitrogen (---). Column: 1 m \times 4 mm. Temperature: 150°C. Sorbent: 20% PEGA on polychrome.

The same behaviour is observed when the peak is recorded with a katharometer or a flame-ionization detector. Similar results have been obtained on other sorbents with high capacities for water, e.g., on 1,2,3-tris(β -cyanatoxypropane). Hydrophobic phases of the E-301 type and an increase in column temperature result in a reduction or complete disappearance of the above effect.

Similar peak asymmetry is also observed for sorbed substances on stationary phases and adsorbents having high capacities for water such as PEGA, polyethylene glycol and silochrome. The formation of asymmetric peaks with prominent leading edges is more pronounced for the lower members of the homologous series of paraffins, alcohols and aromatic hydrocarbons. When nitrogen is used as the carrier gas, peaks with tailing are generally formed.

The change in the nature of peak asymmetry from tailing to leading when nitrogen carrier gas is replaced by water vapour has been noted previously^{9,10}, and explained in terms of the change in the shape of the sorption isotherm. However, it is also necessary to take account of the sorption effect. The asymmetry of methane peaks can only be explained in terms of the latter effect. In a number of cases the changes in peak asymmetry can be accounted for by the joint influence of the sorption effect and the shape of the isotherm.

Fig. 3 shows the relationship between the asymmetry coefficient of nonane and undecane peaks and the unit loading obtained on a column of 16.7% PEGA on polychrome at 120°C. The asymmetry coefficient was calculated from

$$A = 2(a_1 - a_2)/(a_1 + a_2)$$

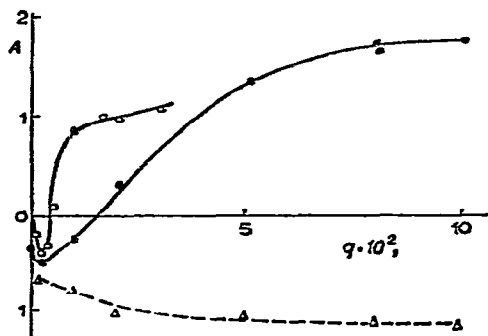


Fig. 3. Relationship between asymmetry coefficient and specific loading* in a flow of nitrogen (---) or water vapour (—). \circ = Nonane; Δ , \bullet = undecane. Sorbent: 16.7% PEGA on polychrome. Temperature: 120°C.

where a_1 and a_2 are the half-widths of the peaks at the leading and tailing edges. For peaks with a prominent leading edge, $A < 0$; for those with tailing $A > 0$ and for symmetric peaks $A = 0$. It can be seen that, with increasing specific loading*, A undergoes complex changes: initially symmetric peaks gradually acquire tailing, but then the nature of the asymmetry changes and peaks with pronounced leading edges are formed. It is impossible to explain such changes only in terms of the influence of the sorption isotherm, unless one assumes that the isotherms have a sigmoidal shape, which is not usually observed in the case of dissolution. All the experimental results are, however, simply explained by assuming that at least two factors affect the asymmetry: thus at moderate loadings the influence of the isotherm predominates, and at higher loadings that of the sorption effect predominates. It is a characteristic of the weakly sorbed nonane that the change to peaks with pronounced leading edges takes place at small loadings, in agreement with the above reasoning.

The present results thus confirm the significant role of the sorption effect in the formation of chromatographic bands at high sorbate concentrations.

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* The specific loading is the sample size (cm^3) divided by the cross-sectional area (cm^2) of the column.