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## THEORETICAL APPROACH TO GAS-SOLID CHROMATOGRAPHY APPLIED TO THE SLOW ATTAINMENT OF ADSORPTION EQUILIBRIUM AND TO THE LANGMUIR ISOTHERM

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### SUMMARY

Gas-solid chromatography with the slow attainment of adsorption equilibrium, described by the Langmuir isotherm, has been treated theoretically. An analytical solution was obtained for the relevant set of non-linear equations. A relationship was derived for the concentration at the peak maximum,  $c_{\max.}$ , as a function of the retention time,  $t_{\max.}$ :

$$c_{\max.} = \frac{2}{2k_a t_{\max.}} + \sqrt{\frac{z}{u_g} \left[ \frac{k_a a_{\max.}}{k_d} - \frac{1}{\sqrt{t_{\max.}}} - \frac{k_d}{k_a} \right]}$$

where  $k_a$  and  $k_d$  are the rate constants of adsorption and desorption, respectively,  $z$  is the column length,  $u_g$  is the linear carrier gas velocity and  $a_{\max.}$  is the amount of compound adsorbed for complete coverage of the surface. This equation was used for the calculation of  $k_a/k_d$  and  $a_{\max.}$  from experimental data on the adsorption of toluene by silica-alumina catalysts. The absolute values of  $k_a$  and  $k_d$  were calculated from the condition of closeness between experimental and calculated curves making use of the obtained analytical solution. The rate constants for the adsorption and desorption of toluene and the value of  $a_{\max.}$  were also found.

### INTRODUCTION

The mathematical treatment of gas-solid chromatography is very important but is not a simple task. In most papers, this problem has been connected with a linear adsorption isotherm. A reasonable analytical solution for a set of equations has been obtained and expressions for the chromatographic peak moments have been derived<sup>1-7</sup>. Considerable difficulties arose in the treatment of non-linear adsorption isotherms, owing to the absence of general methods for solving non-linear equations that contain partial derivatives describing processes with non-linear isotherms, and therefore only asymptotic and approximate solutions have been given. An asymptotic solution of the frontal chromatography problem for a non-linear adsorption isotherm was obtained by Zhukhovizkii and co-workers<sup>8,9</sup>. The adsorption isotherm has been

approximated by a polynomial solution, and in this case approximate expressions for the moments were found<sup>10-12</sup>. A case of weak non-linear isotherms was treated by Zolatorev<sup>13</sup>, and the problem of gas-solid chromatography has been treated by numerical methods taking into consideration the adsorption and diffusion kinetics and the chemical reactions involved<sup>14-16</sup>.

We have succeeded in obtaining an exact analytical solution of the elution gas chromatography problem for a Langmuir isotherm in the case of slow attainment of adsorption equilibrium for an arbitrary inlet function. The solution to a similar problem for frontal chromatography was described by Thomas<sup>17</sup>. As a result, a simple equation was obtained that permits the adsorption and desorption rate constants and the maximum amount of a compound that can be adsorbed per unit area of the surface to be calculated from experimental data.

#### THEORETICAL

Let us consider the following set of equations:

$$\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} + u_g \cdot \frac{\partial c}{\partial z} = 0; \quad \frac{\partial a}{\partial t} = k_a (a_{\max.} - a) c - k_d a \quad (1)$$

with the conditions

$$\begin{aligned} z = 0 \quad c(0,t) &= \psi(t) \\ t = 0 \quad a(z,0) = 0; \quad c(z,0) &= 0 \end{aligned} \quad (2)$$

where  $c$  and  $a$  are the adsorbate concentrations in the gas phase and on the surface, respectively,  $k_a$  and  $k_d$  are the adsorption and desorption rate constants, respectively,  $u_g$  is the linear velocity of the carrier gas,  $z$  is the coordinate of the column length,  $t$  is time,  $\psi(t)$  is the inlet function and  $a_{\max.}$  is the adsorbate concentration on the surface for monolayer coverage.

By substituting

$$x = z/u_g; \quad y = t - z/u_g \quad (3)$$

the system will become

$$\frac{\partial a}{\partial y} = - \frac{\partial c}{\partial x}; \quad \frac{\partial a}{\partial y} = k_a a_{\max.} c - k_d ca - k_d a \quad (4)$$

It follows from eqn. 4 that there exists a function  $q(a,c)$  such that

$$c = \frac{\partial q}{\partial y}; \quad a = - \frac{\partial q}{\partial x}$$

This function satisfies the equation

$$\frac{\partial^2 q}{\partial x \partial y} + A \frac{\partial q}{\partial x} + B \frac{\partial q}{\partial y} + C \frac{\partial q}{\partial x} \frac{\partial q}{\partial y} = 0 \quad (5)$$

where  $A = k_d$ ,  $B = k_a a_{\max.}$  and  $C = k_d$ .

After substituting

$$Cq = \ln f(x,y) - Bx - Ay \quad (6)$$

eqn. 5 becomes linear:

$$\frac{\partial^2 f}{\partial x \partial y} - ABf = 0 \quad (7)$$

The functions  $c(x,y)$  and  $a(x,y)$  are related to  $f(x,y)$  as follows:

$$c = \frac{1}{C} \left( \frac{\partial \ln f}{\partial y} - A \right) \quad (8)$$

$$a = -\frac{1}{C} \left( \frac{\partial \ln f}{\partial x} - B \right) \quad (9)$$

The initial and boundary conditions for eqn. 7 can be obtained from eqns. 8, 9 and 2:

$$\begin{aligned} y = 0 & \quad f(x,0) = e^{Bx} \\ x = 0 & \quad f(0,y) = \psi_0(y) = \exp \int_0^y [A + C\psi(y)] dy \end{aligned} \quad (10)$$

As the potential function  $\psi$  is determined by the accuracy of the constant,  $f(x,y)$  can be obtained to the accuracy of the constant multiplier (eqn. 6). Therefore, we can assume that  $f(0,0) = 1$ .

Applying a Laplace transform to eqn. 7:

$$p \frac{\partial \tilde{f}}{\partial x}(x,p) - \frac{\partial f}{\partial x}(x,0) - AB\tilde{f} = 0 \quad (11)$$

where  $p$  is the parameter of the Laplace operator and  $\tilde{f}$  is the Laplace transform of  $f(x,y)$ .

It follows from eqn. 6 that  $\frac{\partial f}{\partial x}(x,0) = Be^{Bx}$  for  $y = 0$  and from eqn. 10 that  $\tilde{f}(0,p) = \tilde{\psi}_0(p)$  for  $x = 0$ .

The solution of eqn. 7 is

$$\tilde{f}(p,y) = \left[ \tilde{\psi}_0(p)p - \psi_0(0) + (\psi_0(0) - 1) - \frac{A}{p-A} \right] \frac{e^{\frac{AB}{p}y}}{p} + \frac{e^{By}}{p-A} \quad (12)$$

After conversion of the Laplace transformation, we obtain

$$\begin{aligned} f(x,y) = & \int_0^y \frac{\partial \psi_0(\xi)}{\partial \xi} I_0(2\sqrt{ABx}(y-\xi)) d\xi + (\psi_0(0) - 1) I_0(2\sqrt{ABxy}) - \\ & A \int_0^x e^{A\xi} I_0(2\sqrt{AB}(y-\xi)x) d\xi + e^{Ax+Bx} \end{aligned} \quad (13)$$

The solution of eqns. 1 and 2 can be obtained by simple calculation using expressions 8 and 9. In the case of a rectangular inlet pulse:

$$\psi(t) = \begin{cases} C_0 & t \leq T \\ 0 & t > T \end{cases}$$

the expression for the chromatographic curve when  $t > T$  is

$$c = \frac{A}{C} \frac{(\gamma - 1) I_0(2\sqrt{ABx}r) + \alpha A \int_0^T e^{\alpha\xi} [I_1(2\sqrt{ABx}(r - \xi))] \sqrt{\frac{Bx}{(r - \xi)A}}}{f(x,r)} - \frac{I_0(2\sqrt{ABx}(r - \xi)) d\xi - \gamma A^2 \int_0^T e^{-\lambda\xi} \left[ \sqrt{\frac{Bx}{A(r - \xi)}} I_1(2\sqrt{ABx}(r - \xi)) \right]}{Cf(x,r)} - \frac{I_0(2\sqrt{ABx}(r - \xi)) d\xi}{Cf(x,r)} \quad (14)$$

where  $\alpha = Cc_0 + A$ ,  $\gamma = \exp(Cc_0T)$  and  $I_1(z)$  and  $I_0(z)$  are Bessel functions of an imaginary argument.

The following solution was obtained for a narrow rectangular pulse:

$$c = \frac{A(\gamma - 1) \sqrt{\frac{r}{u}} I_1(2\sqrt{uv})}{C(\gamma - 1) \left[ I_0(2\sqrt{uv}) + e^u \int_0^u e^{-t} I_0(2\sqrt{vt}) dt \right] - e^{u+v}} \quad (15)$$

$$a = \frac{B(\gamma - 1) I_0(2\sqrt{uv})}{C(\gamma - 1) \left[ I_0(2\sqrt{uv}) + e^u \int_0^u e^{-t} I_0(2\sqrt{vt}) dt \right] - e^{u+v}} \quad (16)$$

where  $v = Bx$  and  $u = Ay$ .

A simple correlation between the concentrations in the gas phase and on the adsorbent surface follows from eqns. 15 and 16:

$$\frac{a}{c} = \frac{k_a a_{\max.}}{k_d} \sqrt{\frac{k_d y}{k_a a_{\max.} x}} \frac{I_0(2\sqrt{k_d k_a a_{\max.} xy})}{I_1(2\sqrt{k_d k_a a_{\max.} xy})} \quad (17)$$

Asymptotic expansions<sup>18,19</sup> can be used for high values of Bessel function arguments:

$$I_0(z) \simeq I_1(z) \simeq \sqrt{\frac{1}{2\pi z}} \cdot e^z \quad (18)$$

$$\begin{aligned} \lambda(u,r) &= e^u \int_0^u I_0(2\sqrt{vt}) e^{-t} dt = \\ &= \frac{1}{2} [1 - \operatorname{erf}(\sqrt{v} - \sqrt{u})] e^{u+v} - \frac{(u/v)^{\frac{1}{2}}}{(u/v)^{\frac{1}{2}} - 1} \cdot I_0(2\sqrt{vr}) \end{aligned} \quad (19)$$

where

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$$

From eqn. 15 and taking eqn. 18 into consideration, one can obtain the relationship between the concentration at the peak maximum,  $c_{\max}$ , and the retention time,  $t_{\max}$ :

$$c_{\max} = \frac{1}{2k_d t_{\max}} \left[ \frac{z}{u_g} \right] \frac{k_d a_{\max}}{k_a} \frac{1}{\sqrt{t_{\max}}} \frac{k_d}{k_a} \quad (20)$$

It will be shown later that this relationship can be used for the treatment of experimental data.

The equation for the concentration in the gas phase (eqn. 15) can be simplified by using the asymptotic expansions in eqns. 18 and 19:

$$c = \frac{\sqrt{b_1} \sqrt{2\pi} t^{0.25} \cdot 2k_d}{\sqrt{b_1} \sqrt{2\pi} t^{0.25} \left[ 1 - \frac{(k_d t/b_2)^{0.25}}{1 + (k_d t/b_2)^{0.25}} \right] + \exp(b_2 - b_3 - b_1 \sqrt{t} - k_d t)} \cdot P \quad (21)$$

where

$$P = 0.5 [1 - \operatorname{erf}(\sqrt{b_2 - k_d t})] \exp(b_2 - k_d t - b_1 \sqrt{t})$$

For high values of  $\sqrt{b_2 - k_d t}$ , the expression for  $P$  can be simplified by using the asymptotic expansion for  $\operatorname{erf}(z)$ :

$$P = \frac{1}{(\sqrt{b_2 - k_d t}) \sqrt{2\pi}} \quad (22)$$

where

$$b_1 = 2 \sqrt{k_d k_a} z / u_g \cdot a_{\max}$$

$$b_2 = k_a \frac{z}{u_g} a_{\max}$$

$$b_3 = k_a c_0 T = k_a m/F$$

where  $F$  is the volumetric velocity of the carrier gas and  $m$  is the amount of adsorbate introduced in the column.

It was of interest to investigate the chromatographic peak shape as a function of the experimental parameters and constants.

## EXPERIMENTAL AND RESULTS

The use of eqn. 21 would require a high accuracy of calculation, which would make calculations difficult, and a programme was therefore worked out and the chromatographic peaks were calculated by a computer.

Fig. 1 shows typical calculated curves for different values of the dimensionless parameter  $m/F$ . Solid curves correspond to high rate constants of adsorption and de-

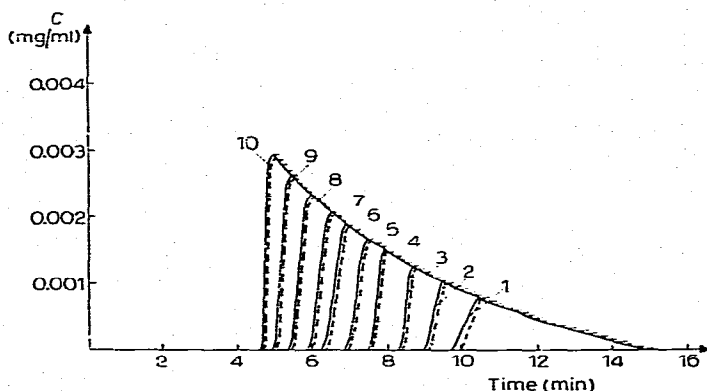


Fig. 1. Calculated peaks for various values of the parameter  $m$ . The numbers on the curves from 1 to 10 correspond to the following values of  $m/F$ : 0.002, 0.003, 0.004, ..., 0.01 mg/ml·min. The broken lines correspond to rate constants  $k_a = 10^5$  ml/mg·min and  $k_d = 400$ /min. The solid lines correspond to  $k_a = 2.5 \times 10^4$  ml/mg·min and  $k_d = 100$ /min; in both cases  $a_{\max} = 10$  mg/ml and  $z/u = 0.01$  min. The hatched curve was calculated by De Vault's equation for the Langmuir isotherm.

sorption ( $k_a = 2.5 \cdot 10^4$  ml/mg·min;  $k_d = 10^2$ /min). The peaks have vertical fronts and the envelope of the peak tops coincides with that calculated using the De Vault equation for the Langmuir adsorption isotherm (see ref. 20):

$$c = \left( a_{\max} \cdot \frac{s k_a}{k_d} \cdot l / (v - 1) \right) / \frac{k_a}{k_d} \quad (23)$$

where  $l$  is the length of the column,  $v$  is the volume of the carrier gas passed through the column and  $s$  is the cross-section of the column. It follows that at sufficiently high values of  $k_a$  and  $k_d$ , the non-equilibrium model is consistent with the equations for ideal non-linear chromatography.

The broken lines in Fig. 1 correspond to rate constants of adsorption and desorption of  $k_a = 10^5$  ml/mg·min and  $k_d = 400$ /min. It can be seen from Fig. 1 that close to equilibrium the peak shapes that correspond to the same Henry coefficient but to different  $k_a$  and  $k_d$  values virtually coincide. The results for an essentially non-equilibrium range are different. Fig. 2 shows computed curves for rate constants 100 times lower than those corresponding to the solid curves in Fig. 1; at the same ratio of constants, the fronts are seen to be diffuse, particularly for very small doses.

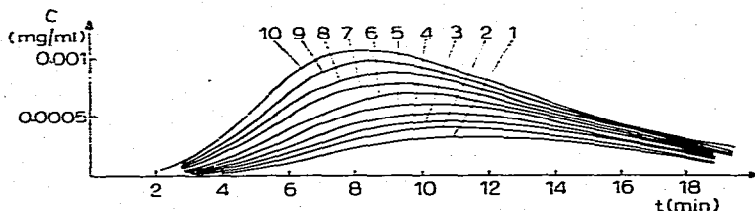


Fig. 2. Calculated peaks for  $k_a = 2.5 \cdot 10^2$  ml/mg·min and  $k_d = 1$ /min; the other parameters are the same as for the curves in Fig. 1.

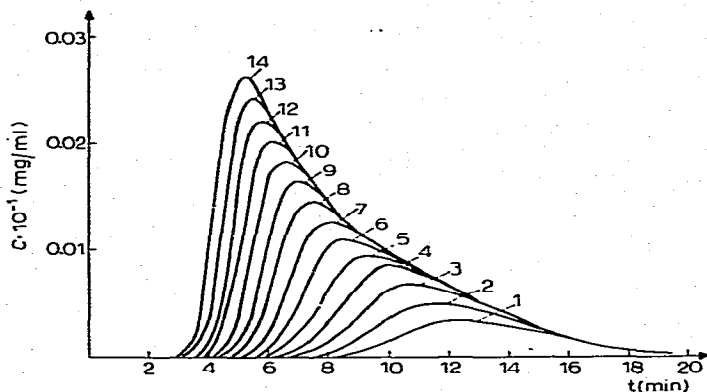


Fig. 3. Calculated peaks for  $k_a = 10^3$  ml/mg·min and  $k_d = 4$ /min: the other parameters are the same as for the curves in Fig. 1.

For the non-equilibrium case, the chromatographic peak shapes depend not only on the ratio of  $k_a$  to  $k_d$  but also on their absolute values.

Curves for  $k_a = 10^3$  and  $k_d = 4$  are shown in Fig. 3. A four-fold change of  $k_a$  and  $k_d$  results in a considerable change in shapes of the curves.

Fig. 4 shows calculated curves for  $k_a = 1000$  ml/mg·min and  $k_d = 1$ /min. It can be seen from a comparison of Fig. 4 with Figs. 2 and 3 that when a lower Henry coefficient is taken for decreasing  $k_d$  values, the peak fronts will be more diffuse than in the case of increasing  $k_d$  values. The theoretical results obtained can be used to calculate adsorption and desorption rate constants and also  $\alpha_{\max.}$  from experimental

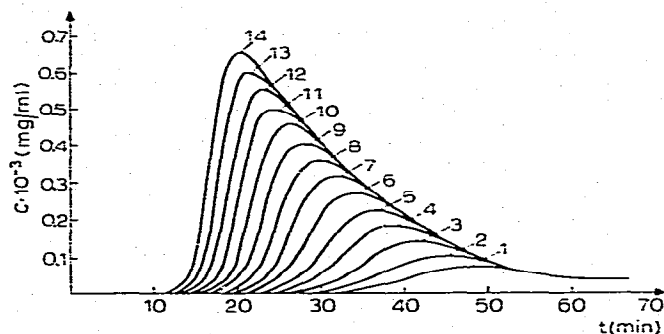


Fig. 4. Calculated peaks for  $k_a = 1000$  ml/mg·min and  $k_d = 1$ /min: the other parameters are the same as for the curves in Fig. 1.

data. It is advisable to use the dependence of concentration at the peak maximum,  $c_{\max.}$ , on the retention time,  $t_{\max.}$  (eqn. 20). This dependence of  $c_{\max.}$  on  $t_{\max.}$  can be measured experimentally by introducing different amounts of the substance into the column at a constant flow-rate; such experiments must be repeated for different flow-rates. The dependence of  $c_{\max.} \sqrt{t_{\max.}}$  on  $\sqrt{z}/u_0$ , which, according to eqn. 20, must be a straight line, can be constructed from intersections of the curves obtained

with straight lines of equation  $t_{\max.} = \text{constant}$ ; from the tangent of this straight line we obtain  $\sqrt{k_d a_{\max.}/k_a}$ , and from the intercept on the ordinate we obtain  $1/k_a \cdot l \cdot t_{\max.} + k_d/k_a$ . Each of the constants  $k_a$ ,  $k_d$  and  $a_{\max.}$  can be obtained from two such straight lines for two values of  $t_{\max.}$ . A shortcoming of this method is that small errors that arise when constructing experimental lines can lead to highly erroneous values of  $k_a$  and  $k_d$ , and therefore great accuracy is required in such experiments.

On the other hand, it was found that the first term in eqn. 20 can often be neglected. It is sufficient to carry out the experiments at only one flow-rate and different amounts of adsorbate in order to determine the constants. The dependence of  $C_{\max.}$  on  $1/\sqrt{t_{\max.}}$  must be linear. The tangent of this straight line gives  $\sqrt{z/u} \cdot \sqrt{k_d a_{\max.}/k_a}$  and the intercept on the ordinate gives  $k_d/k_a$ .

Experiments with very small amounts of adsorbate, corresponding to a linear isotherm, can be used in order to obtain absolute values of  $k_a$  and  $k_d$ . In this case,  $k_a \cdot a_{\max.}$  and  $k_d$  can be found by the moments method<sup>21</sup>, after measuring the half-width and the retention time of the peak. All three constants can be calculated using the ratio  $k_d/k_a$  obtained for the non-linear range. When the isotherm is not linear, even at very low concentrations, the moments method is not applicable and a correlation between the computed and experimental peaks is needed in order to calculate the absolute values of the constants.

As the correlation

$$c_{\max.} = \left[ \frac{z}{u} \right] \sqrt{\frac{k_d a_{\max.}}{k_a}} \frac{1}{\sqrt{t_{\max.}}} - \frac{k_d}{k_a}$$

is approximate, before proceeding to experimental verification of the method, we tested it on computed model peaks. The dependence of  $c_{\max.}$  on  $1/\sqrt{t_{\max.}}$ , shown in Fig. 5, was constructed from the peaks calculated for different flow-rates. In accordance with eqn. 24, a straight line was obtained for each of the three fixed velocities, all three lines converging at the same point. The values of  $k_d/k_a$  and  $a_{\max.}$  calculated from tangents of straight lines and intercepts on the ordinate were 53 and 12.2 mg/cm<sup>3</sup>, respectively. The Henry coefficients and  $a_{\max.}$  values showed satisfactory agreement

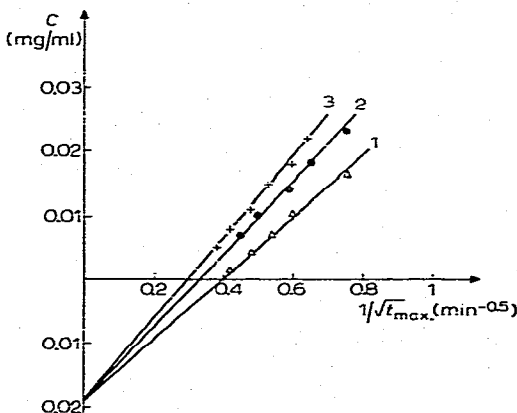


Fig. 5. Treatment of calculated curves using eqn. 24:  $k_d/k_a = 57$  ml/mg and  $a_{\max.} = 13$  mg/ml. Curves 1, 2 and 3 correspond to flow-rates  $F_1 = 80$  ml/min,  $F_2 = 57$  ml/min and  $F_3 = 48$  ml/min, respectively.



with those used in calculations. It can be concluded that the assumptions made in deriving eqn. 24, namely the validity of utilizing the asymptotic expansion for Bessel functions and neglecting the first term in eqn. 20, do not introduce large errors in the rate constants within the range important in practical applications.

The results of the above theoretical treatment were applied to the experimental data on the adsorption of toluene on silica-alumina catalysts. The experiments consisted in measuring the elution curves for toluene using a column filled with the catalyst. All experiments were conducted in a stream of hydrogen. As eqn. 24 is correct for a high Bessel function argument,  $2\sqrt{k_a k_d z/u_g} a_{\max.}$ , the weight of adsorbent in the column was chosen such that the value of  $z/u_g$  was sufficiently long. Increasing  $z/u_g$  by using flow-rates below 20 ml/min was not advantageous because of the diffusion effect that was disregarded in our model. The weight of the catalyst used was 2 g and the volumetric flow-rate of the carrier gas was varied from 40 to 100 ml/min. A katharometer was used as the detector. The catalyst was pre-heated in a flow of hydrogen at 500° for 6 h. As with a fresh sample, the peak shape changed from pulse to pulse. The catalyst was pre-treated with large amounts of toluene, after which the peak shape became reproducible.

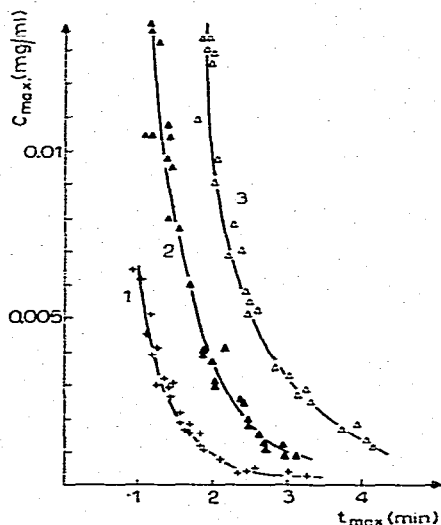


Fig. 6. Experimental dependences of the maximum peak concentration,  $c_{\max.}$ , on the retention time,  $t_{\max.}$ , of toluene using a silica-alumina catalyst at 350°. Curves 1, 2 and 3 correspond to flow-rates of 109, 75 and 53 ml/min, respectively.

Fig. 6 shows the dependence of  $a_{\max.}$  on  $t_{\max.}$  obtained at 350° for different flow-rates (53, 75 and 109 ml/min) and for different amounts of toluene introduced into the column. Fig. 7 shows the dependence of  $c_{\max.}$  on  $1/\sqrt{t_{\max.}}$  derived from the curves in Fig. 6. It can be seen that the experimental points for all three flow velocities fall satisfactorily on straight lines. The constants were calculated from the tangents of these straight lines and the intercepts on the ordinates using the equations

$$\frac{k_d}{k_a} = A$$

and

$$a_{\max.} = \frac{(\operatorname{tg} \varphi)^2 u_d}{A z}$$

where  $\varphi$  is the angle of slope of the line in Fig. 9 and  $A$  is the intercept on the ordinate cut by the straight line. The constants found are given in Table I.

Absolute values of the rate constants  $k_a$  and  $k_d$  were selected by a computer from the condition of closeness of the experimental and calculated curves. The precise values of  $a_{\max.}$  had also to be obtained.

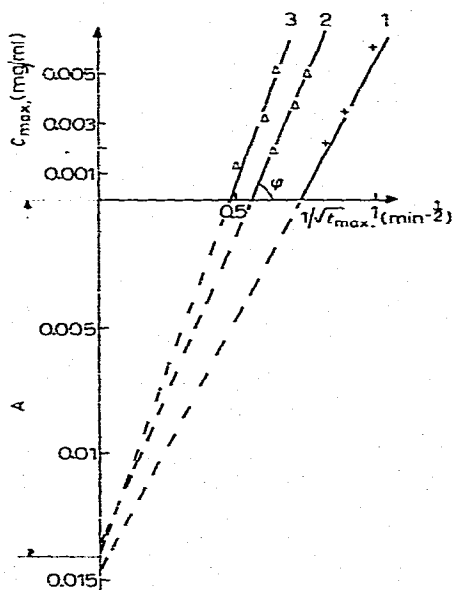


Fig. 7. Treatment of the experimental curves shown in Fig. 6 using eqn. 24. Curves 1, 2 and 3 correspond to flow-rates of 109, 75 and 53 ml/min, respectively.

In selecting the values of the rate constants, the following considerations applied. The shape of a peak tail is determined essentially by the value of  $k_a a_{\max.}/k_d$ , and the steepness of the front is determined by the absolute values of  $k_a$  and  $k_d$ . These considerations are illustrated in Fig. 8. It is seen from curves 1 and 2 that small changes in  $a_{\max.}$  considerably displace the position of the peak tail. Comparison of curves 2 and 3 shows that the peak front sharpens with increase in  $k_a$  and  $k_d$ , whereas

TABLE I

VALUES OF CONSTANTS CALCULATED FROM FIG. 9 FOR THREE DIFFERENT FLOW-RATES

$F$ (ml/min)	$A$ (mg/ml)	$\operatorname{tg} \varphi$	$k_a/k_d$ (ml/mg)	$a_{\max.}$ (mg/ml)
53	0.014	0.03	71.5	3.2
75	0.134	0.024	74.5	3.2
109	0.0147	0.21	68	3.1
Mean	0.014	—	71.5	3.2

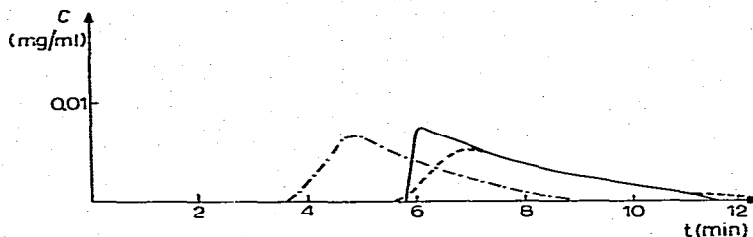


Fig. 8. Dependence of chromatographic peak shapes on adsorption constants: (1) (---)  $k_a = 570$  ml/mg·min;  $k_d = 10$ /min;  $a_{max.} = 10$  mg/ml; (2) (—)  $k_a = 570$  ml/mg·min;  $k_d = 10$ /min;  $a_{max.} = 13$  mg/ml; (3) (-·-·-)  $k_a = 5700$  ml/mg·min;  $k_d = 100$ /min;  $a_{max.} = 13$  mg/ml.

the shape of the peak tail remains virtually unaltered. Therefore, we varied  $a_{max.}$  starting from the approximate values obtained above, until a satisfactory description of the peak tail was obtained. Then, by changing the absolute values of  $k_a$  and  $k_d$ , we succeeded in satisfactorily describing the peak fronts. The accuracy of the determination of  $k_a$  and  $k_d$  depends on the closeness of the system to equilibrium. For the essentially non-equilibrium region (see Figs. 2 and 3) the shape of the peak front is very sensitive to the absolute values of  $k_a$  and  $k_d$ . Therefore, a precise determination of the constants is possible. When approaching equilibrium, the dependence of the peak front on  $k_a$  and  $k_d$  becomes weaker and the accuracy of the determination decreases accordingly.

In Fig. 9, the experimental curve obtained at  $T = 350^\circ$  and  $F = 75$  ml/min is compared with the calculated curve corresponding to  $k_a = 3475$  ml/mg,  $k_d = 50$ /min and  $a_{max.} = 4$  mg/ml. The experimental and calculated curves can be seen to coincide reasonably well. It should be noted that exact coincidence of the experimental and calculated curves was not obtained for all experimental conditions, deviations being observed at low flow-rates of the carrier gas. This can be explained by the effect of diffusion.

The results presented in this paper show that the analytical solution of the problem of non-equilibrium elution chromatography for the Langmuir isotherm can be applied to the description of experimental peak shapes and to the calculation of adsorption constants.

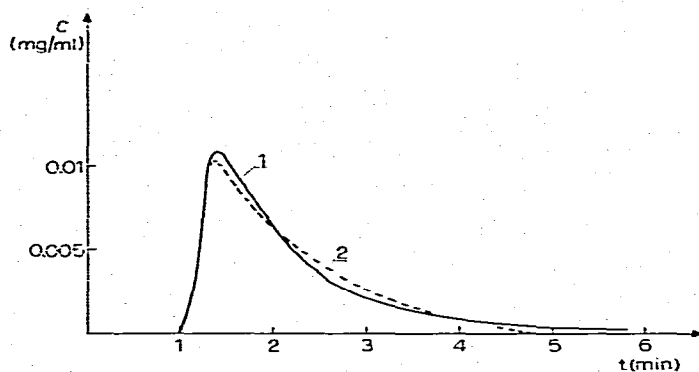


Fig. 9. Comparison of calculated curve (1) with the experimental curve (2) for  $k_a = 3475$  ml/mg·min,  $k_d = 50$ /min and  $a_{max.} = 4$  mg/ml.

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