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EFFECTS OF SURFACE HETEROGENEITY IN NON-LINEAR AND NON-EQUILIBRIUM GAS-ADSORPTION CHROMATOGRAPHY

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SUMMARY

It is shown that one can investigate quantitatively the effects of surface heterogeneity in non-linear and non-equilibrium gas-solid chromatography on the basis of elution theories developed for homogeneous surfaces. One such theory, that of Zhitomirskii *et al.*, was accepted for the purpose of this work and a new formulation for the kinetics of adsorption on heterogeneous surfaces was developed and applied. The effect of surface heterogeneity on elution curves is shown, and the possibility of determining quantitatively adsorption and desorption rate coefficients in adsorption systems with heterogeneous surfaces is demonstrated. A parameter that describes quantitatively the degree of surface heterogeneity has been determined.

INTRODUCTION

The theory of gas-solid chromatography (GSC) is an important but difficult subject. Many papers have been published after the pioneering work of Cremer¹, Huber², Keulemans³, Janák⁴ and Smolkova and Grubner⁵, but even the basic contributions in this field are too numerous to list here. Kiselev and Iashin⁶ and Snyder⁷ reviewed the literature up to the late 1960s and other fundamental results can be found in the reviews by Huber⁸ and Conder and Purnell⁹. In most papers linear adsorption isotherms were considered¹⁰⁻¹⁶, while the very interesting case of non-linear adsorption isotherms has been treated by Zhukhovizkii and co-workers^{17,18}, Zolotarev¹⁹, Buys and De Clerk²⁰⁻²², Acrivos²³, Blauton *et al.*²⁴ and Thomas²⁵.

Except for a few workers²⁶⁻²⁸, most have adopted the model of a homogeneous adsorbent surface but, apart from graphitized carbons, such ideal surfaces are rarely found in chromatographic practice. The first advanced attempts to describe quantitatively the effects of surface heterogeneity in GSC were those by Dougharty²⁹, who

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developed appropriate expressions for peak moments in GSC systems with heterogeneous surfaces. Because of the great mathematical complexity of his theory, even illustrative model calculations were not performed by the author. We decided to carry out an investigation of surface heterogeneity effects on the basis of the theoretical formulation of GSC by Zhitomirskii *et al.*³⁰.

THEORETICAL

Zhitomirskii *et al.*³⁰ succeeded in obtaining an exact analytical solution for the elution function in non-linear and non-equilibrium GSC. The starting point of their theory is the following well known set of partial differential equations:

$$\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} + u_g \frac{\partial c}{\partial z} = 0 \quad (1)$$

$$\frac{\partial a}{\partial t} = k_a (a_{\max} - a) c - k_d a \quad (2)$$

where c and a are the adsorbate concentrations in the free 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 column length and t is the time. In eqn. 2, a_{\max} is the adsorbate concentration on the surface at monolayer coverage.

The initial conditions for the elution function $c(t)$ were as follows:

$$z = 0, c(0, t) = \psi(t) \quad (3)$$

$$t = 0, a(z, 0) = 0, c(z, 0) = 0 \quad (4)$$

where $\psi(t)$ is the inlet function for which the authors accepted a rectangular inlet pulse:

$$\psi(t) = \begin{cases} c_0, & t \leq T \\ 0, & t > T \end{cases} \quad (5)$$

Then, the solutions for $c(t)$ and $a(t)$ are obtained exactly and are expressed by appropriate Bessel functions. When the chromatographic column is sufficiently long, asymptotic expressions can be used for the Bessel functions, and the elution function $c(t)$ takes the following simple form:

$$c(t) = \left(\frac{\sqrt{b_1}}{\sqrt{2\pi} t^{\frac{3}{2}} 2k_a} \right) \cdot \left\{ \frac{1}{\sqrt{2\pi} \sqrt{b_1} t^{\frac{3}{2}}} \left[1 - \frac{(k_d t/b_2)^{\frac{1}{2}}}{1 + (k_d t/b_2)^{\frac{1}{2}}} \right] + \right. \\ \left. + \exp(b_2 - b_3 - b_1 \sqrt{t} + k_d t) + \frac{1}{\sqrt{2\pi} (\sqrt{b_2} - \sqrt{k_d t})} \right\} \quad (6)$$

In this equation

$$b_1 = 2\sqrt{k_d} k_a \left(\frac{z}{u_g} \right) a_{\max} \quad (7)$$

$$b_2 = k_a \left(\frac{z}{u_g} \right) a_{\max} \quad (8)$$

and

$$b_3 = k_a \left(\frac{m}{F} \right) \quad (9)$$

where F is the volumetric velocity of the carrier gas and m is the amount of adsorbate introduced into the column. The theory also yields a simple relationship between the concentration at the peak maximum (c_{\max}) and the retention time (t_{\max}):

$$c_{\max} = \frac{-1}{2k_a t_{\max}} - \frac{k_a}{k_a} + \left[\left(\frac{z}{u_g} \right) \left(\frac{a_{\max}}{t_{\max}} \right) \left(\frac{k_a}{k_a} \right) \right]^{\frac{1}{2}} \quad (10)$$

Now, eqn. 2 assumes that the adsorption in the column follows a Langmuir model, leading to monolayer adsorption of fully localized molecules, without lateral interactions. The adsorbent surface is assumed to be homogeneous, *i.e.*, all adsorption sites have the same adsorption energy, ε . The Langmuir isotherm has the following explicit form:

$$\theta(p) = \frac{kp}{1 + kp} \quad (11)$$

where p is the pressure of adsorbate and

$$k = \frac{k_a}{k_d} = k_0 \exp \left(\frac{\varepsilon}{RT} \right) \quad (12)$$

For heterogeneous surfaces, adsorption sites are distributed among various adsorption energies belonging to some interval Ω . For the purpose of mathematical convenience, this interval is often assumed to be $(0, +\infty)$ or $(-\infty, +\infty)$. For the model of localized adsorption without lateral interactions between adsorbed molecules the differential distribution of adsorption energy, $\chi(\varepsilon)$, is usually accepted as the quantitative measure of surface heterogeneity. By means of $\theta(p, \varepsilon)$ and $\chi(\varepsilon)$, the equation for the overall adsorption isotherm $v(p)$ can be written as follows:

$$v(p) = v_0 \int \theta(p, \varepsilon) \chi(\varepsilon) d\varepsilon \quad (13)$$

where v_0 is the amount adsorbed at monolayer coverage. Various analytical expressions have been used to represent the function $\chi(\varepsilon)$ ³¹, gaussian distributions probably being most often considered. There are good reasons to assume such distributions as a correct representation of surface heterogeneity at sub-monolayer surface coverages³². For these reasons, and on the basis of some other mathematical considerations, we shall further represent $\chi(\varepsilon)$ by the following bell-shaped, gaussian-like distribution:

$$\chi(\varepsilon) = \frac{1}{\varrho} \frac{\exp \left(\frac{\varepsilon - \varepsilon_0}{\varrho} \right)}{\left[1 + \exp \left(\frac{\varepsilon - \varepsilon_0}{\varrho} \right) \right]^2} \quad (14)$$

which reduces to the Dirac delta function $\sigma(\varepsilon - \varepsilon_0)$ when the heterogeneity parameter ϱ tends to zero. Eqn. 14 has the important advantage that the integral in eqn. 13 can

then be expressed by appropriate derivatives of $\theta(p, \varepsilon)$ with respect to ε , taken at $\varepsilon = \varepsilon_0$. In general, we have³³

$$\begin{aligned} \Theta(p, \varepsilon_0) &= \int_{-\infty}^{+\infty} \theta(p, \varepsilon) \frac{1}{\varrho} \cdot \frac{\exp\left(\frac{\varepsilon - \varepsilon_0}{\varrho}\right)}{\left[1 + \exp\left(\frac{\varepsilon - \varepsilon_0}{\varrho}\right)\right]^2} d\varepsilon \\ &= [\theta(p, \varepsilon)]_{\varepsilon=\varepsilon_0} + \frac{\pi^2}{6} \cdot \varrho^2 \left[\frac{\partial^2 \theta}{\partial \varepsilon^2} \right]_{\varepsilon=\varepsilon_0} + \dots \end{aligned} \quad (15)$$

The non-physical part of the integral in eqn. 15 from $-\infty$ to 0 does not introduce a greater contribution, as both $\theta(\varepsilon)$ and $\chi(\varepsilon)$ are then rapidly decreasing functions³⁴.

In this way, the adsorption isotherm $v(p)$ for a heterogeneous surface can be expressed by a new isotherm equation for a hypothetical homogeneous surface with adsorption sites that have an adsorption energy of ε_0 . Let us consider the isotherm $\theta(p)$ in more detail. After performing appropriate differentiations, we obtain

$$\Theta(p, \varepsilon_0) = \left[\theta + \frac{\pi^2}{6} \left(\frac{\varrho}{RT} \right)^2 \theta (1 - \theta) (1 - 2\theta) \right]_{\varepsilon=\varepsilon_0} \quad (16)$$

or, in terms of pressure p :

$$\Theta(p, \varepsilon_0) = \frac{k'p}{1 + k'p} \left[1 + \frac{\pi^2}{6} \left(\frac{\varrho}{RT} \right)^2 \frac{1 - k'p}{(1 + k'p)^2} \right] \quad (17)$$

where

$$k' = k_0 \exp\left(\frac{\varepsilon_0}{RT}\right) \quad (18)$$

The behaviour of $\Theta(p)$ differs from that of $\theta(p)$. At the initial low pressures, $\Theta(p)$ has higher values than $\theta(p)$, but is smaller at higher relative pressures. Thus, the behaviour of $\Theta(p)$ is typical of adsorption systems with heterogeneous surfaces (e.g., ref. 35). It still remains to establish the highest reasonable value of ϱ for the degree of approximation adopted in eqn. 15. This is carried out by utilizing the condition that the derivative $\partial\Theta/\partial p$ should not be negative at any value of p . A simple analysis yields the following two values of p_1 and p_2 as the possible zero points of the derivative $\partial\Theta/\partial p$:

$$p_1 = \frac{2A - 1 - \sqrt{3A^2 - A}}{k'(1 + A)} \quad (19)$$

where $A = \left(\frac{\pi^2}{6}\right) \left(\frac{\varrho}{RT}\right)^2$ and

$$p_2 = \frac{2A - 1 + \sqrt{3A^2 - A}}{k'(1 + A)} \quad (20)$$

As the pressure must have real values, then

$$\left(\frac{\pi^2}{6}\right) \left(\frac{\varrho}{RT}\right)^2 \geq 2.0 \text{ or } \frac{\varrho}{RT} > 1.1 \quad (21)$$

is the necessary condition such that the zero points for $\partial\Theta/\partial p$ could exist.

In order to use $\Theta_{a_{\max}}$ as the isotherm "a" in the basic differential equations (eqns. 1 and 2), we would have had to know its equivalent kinetic derivation and then to solve the system of these differential equations for the new kinetic mechanism. Both of these problems are very difficult to solve, and we shall adopt here another strategy, as follows.

We shall replace the isotherm $\Theta(p, k')$ by some Langmuir isotherm $\theta(p, k)$ with some effectively changed parameter $k = mk'$, such that $\theta(p, mk')$ approximates best $\Theta(p, k')$ in the pressure range $(0, c_{\max})$. This best approximation is found from the condition

$$\frac{\partial}{\partial m} \int_0^{c_{\max}} \left\{ \frac{m k' p}{1 + m k' p} - \frac{k' p}{1 + k' p} \left[1 + \frac{\pi^2}{6} \left(\frac{p}{RT} \right)^2 \frac{1 - k' p}{(1 + k' p)^2} \right] \right\} dp = 0 \quad (22)$$

In other words, we shall use for "a" some Langmuir isotherm with the effectively changed parameter mk' . Of course,

$$m = m(p, k', c_{\max}) \quad (23)$$

When the velocity of the carrier gas is sufficiently low, *i.e.*, the elution process can be assumed to run at equilibrium, the function $c(t)$ will depend parametrically only upon the ratio $k = k_a/k_d$. Then, the effects of surface heterogeneity can be taken into account directly by replacing k' with mk' . If, however, equilibrium is not attained, then we have to decide the way in which the change in k' is affected by changes in k_a and k_d . This problem leads us to the kinetics of adsorption on heterogeneous surfaces.

Although over 30 years have passed since Roginskii^{36,37} considered this problem, his theoretical results are still of major importance. His theory, however, requires much additional information, such as the distribution of adsorption and desorption activation energy. Therefore, we shall adopt here some other means of investigating this problem. Let us consider to this purpose the equation³⁸

$$\frac{1}{v_0} \theta_1(p) = \frac{(k_r p)^r}{1 + (k_r p)^r}, \quad 0 < r \leq 1 \quad (24)$$

which has been found to describe well the adsorption on many heterogeneous surfaces^{39,40}. In the limit $r \rightarrow 1$, eqn. 24 becomes a Langmuir isotherm. Assuming, as in our theory, that the local adsorption on the energetically homogeneous areas of the surface is governed by the Langmuir equation, Sips⁴¹ evaluated the energy distribution function $\chi_1(\epsilon)$ corresponding to Bradley's equation²⁴. This function has the following form*:

* Eqn. 24 is only a useful empirical relationship. Its related energy distribution function (eqn. 25) was found from the appropriate inverse Stieltjes transform. Honig and Hill⁴² formulated the necessary mathematical conditions to be fulfilled by the overall adsorption isotherms, which are Stieltjes transforms of some function $\chi(\epsilon)$. These conditions are not fulfilled exactly by eqn. 24. Therefore, the function $\chi_1(\epsilon)$ from eqn. 25 is temperature dependent and does not tend to a delta function as r tends to unity.

$$\chi_1(\varepsilon) = \frac{1}{\pi RT} \frac{\sin(\pi r) \exp\left[\frac{r(\varepsilon_m - \varepsilon)}{RT}\right]}{1 + 2\cos(\pi r) \exp\left[\frac{r(\varepsilon_m - \varepsilon)}{RT}\right] + \exp\left[\frac{2r(\varepsilon_m - \varepsilon)}{RT}\right]} \quad (25)$$

where ε_m is the most probable energy of adsorption on a given heterogeneous surface. It can be seen that the distribution from eqn. 25 is very similar to the energy distribution from eqn. 14, accepted by us, if $\varepsilon_m = \varepsilon_0$. It can be further shown that

$$k_r = k_0 \exp\left(-\frac{\varepsilon_m}{RT}\right) \quad (26)$$

We can formally consider the following set of equations:

$$V_a = k_a p (1 - \theta_1)^{1/r} \quad (27)$$

$$V_d = k_d \theta_1^{1/r} \quad (28)$$

where V_a and V_d denote the adsorption and desorption rates, respectively, as the kinetic derivation of eqn. 24. From these equations, it follows that

$$k_r = \left[\frac{k_a}{k_d}\right]_{\varepsilon=\varepsilon_m} \quad (29)$$

In this way, we have defined the adsorption and desorption rate coefficients for a given heterogeneous surface, as being equal to their values for the areas of surface corresponding to the most probable energy of adsorption ε_m (or ε_0 if the adsorption energy distribution is described by eqn. 14).

The special behaviour of the rates of adsorption and desorption on heterogeneous surfaces is described by the functional relationships $V_a(\theta_1)$ and $V_d(\theta_1)$ given by eqns. 27 and 28. Let us re-write these equations in the form

$$V_a = k'_a p (1 - \theta_1) \quad (30)$$

$$V_d = k'_d \theta_1 \quad (31)$$

where

$$k'_a = (1 - \theta_1)^{1/r-1} \quad (32)$$

$$k'_d = \theta_1^{1/r-1} \quad (33)$$

In the kinetic picture of adsorption, our procedure of replacing eqn. 17 with eqn. 11, with the effectively changed parameter mk' , is equivalent to replacing eqns. 32 and 33 with the following:

$$k'_a = \overline{k_a} = \frac{k_a}{\theta_1} \int_0^{\theta_1} (1-x)^{1/r-1} dx = \frac{rk_a}{\theta_1} [1 - (1 - \theta_1)^{1/r}] \quad (34)$$

$$k'_d = \overline{k_d} = \frac{k_d}{\theta_1} \int_0^{\theta_1} x^{1/r-1} dx = \frac{rk_d}{\theta_1} \theta_1^{1/r} \quad (35)$$

Therefore, we can write

$$mk' = \frac{\bar{k}_a}{k_d} = \frac{k_a}{k_d} \left[\frac{1 - (1 - \theta_1)^{1/r}}{\theta^{1/r}} \right] \quad (36)$$

If the surface becomes homogeneous with adsorption energy $\varepsilon = \varepsilon_0 = \varepsilon_m$, then $\varrho \rightarrow 0$, $r \rightarrow 1$ and $m \rightarrow 1$. Then, $k' = k_r = k_a/k_d$. The effective constant mk' is calculated here by means of eqn. 22.

In non-equilibrium GSC processes, only in the limiting cases of very low and very high adsorbate concentrations in the column can the problem be solved quantitatively.

With very low concentrations in the column, which correspond to small relative coverages of the surface, the effective adsorption rate constant will still be k_a , while the effective desorption rate constant will be k_d/m . The opposite situation will occur at very high concentrations in the column (very high relative coverages of the surface) *i.e.*, the effective adsorption rate constant will be $k_a m$ while the effective desorption rate constant will be k_d . Of most interest is the region of low adsorbate concentrations in the column, as typical chromatographic processes are carried out by using small doses of adsorbate. For this reason, we performed some illustrative calculations of the effect of surface heterogeneity on the shape of the elution curve, $c(t)$, only in the region of low adsorbate concentrations in the free gas phase, and these calculations are considered in the next section.

Our conclusions concerning the effect of surface heterogeneity on the rates of adsorption and desorption may be important in catalysis studies, in which the rate of adsorption of substrates and the rate of desorption of products are very important factors governing the effectiveness of catalytic processes.

We should mention that eqns. 32 and 33 provide only basic information on the way in which heterogeneity of the surface affects the rates of adsorption and desorption at very low and very high concentrations of the adsorbate in the free gas phase, *i.e.*, the way in which the surface heterogeneity affects the adsorption and desorption rate constants, when estimated chromatographically by using various sample sizes of the adsorbate. Eqns. 32 and 33 are not valid in the limit $p \rightarrow 0$, as Bradley's equation (eqn. 24) does not then behave correctly as it does not reduce to Henry's law, which is the limit of all correct adsorption isotherms (see footnote, p. 5). However, eqn. 17 reduces correctly to Henry's law when $p \rightarrow 0$ and therefore the parameter m can also be interpreted in this limit.

RESULTS AND DISCUSSION

In our illustrative calculations, we employed parameters similar to those used by Zhitomirskii *et al.*³⁰. Thus, we assumed $k_a = 10^5$ ml/mg·min, $k_d = 400$ min⁻¹ and $a_{\max} = 10$ mg/ml. For $k' = k_a/k_d = 250$ ml/mg, we evaluated both $\theta(p, k')$ and $\Theta(p, k')$, assuming that $\varrho/RT = 1.0$. The results are shown in Fig. 1. The behaviour of $\Theta(p)$ in comparison with $\theta(p)$ is typical for heterogeneous surfaces.

Further, we evaluated m for various concentration ranges $[0, c_{\max}]$, taking $k' = 250$ and 100 ml/mg. The results are shown in Fig. 2. It can be seen that m has a tendency to stabilize at very small and very large values of c_{\max} . It can also be seen

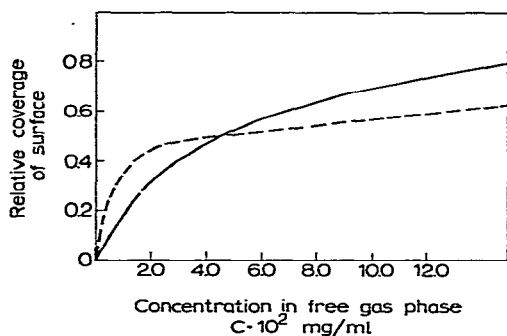


Fig. 1. Effect of surface heterogeneity on the shape of adsorption isotherms. The solid line corresponds to the Langmuir isotherm from eqn. 11 with $k = 250$ ml/mg and $q/RT = 0.0$. The broken line denotes the isotherm from eqn. 17 with $k' = 250$ ml/mg and $q/RT = 1.0$.

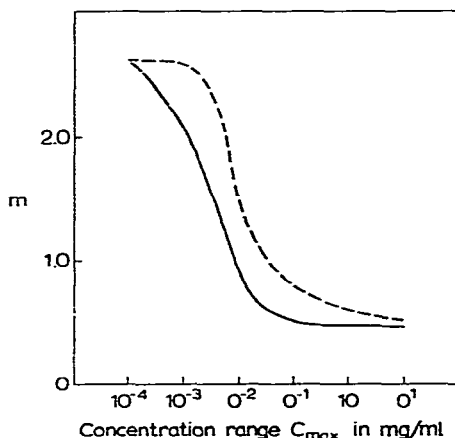


Fig. 2. Effect of the concentration range, c_{\max} , on the value of the best-fit parameter, m , to be used to approximate the isotherm in eqn. 17 by the isotherm in eqn. 11 in this concentration range. The solid line corresponds to adsorption systems with $k' = 250$ ml/mg and $q/RT = 1.0$ and the broken line is related to adsorption systems with $k' = 100$ ml/mg and $q/RT = 1.0$.

that the greater the adsorption constant k' , the greater is the effect of surface heterogeneity at low adsorbate concentrations and the smaller the effect at high adsorbate concentrations in the free gas phase. The adsorption energy ε has only a minor effect on the pre-exponential constant k_0 . Thus, the greater the most probable adsorption energy $\varepsilon_0 = \varepsilon_m$, the larger is the decrease in the rate of desorption at low adsorbate concentrations, and the smaller is the decrease in the adsorption rate at high adsorbate concentrations in the free gas phase.

Zhitomirskii *et al.*³⁰ proposed a method for estimating chromatographically the adsorption and desorption rate constants. The process must be carried out far from equilibrium, and the most convenient way is to use eqn. 10, relating c_{\max} to t_{\max} . The dependence of c_{\max} on t_{\max} can be measured experimentally by introducing different amounts of adsorbate into the column at a constant flow-rate, the experiments being repeated for different flow-rates. The dependence of $c_{\max} \cdot t_{\max}^{1/2}$ on $(z/u_g)^{1/2}$ which, according to eqn. 10, must be a straight line, can be constructed from inter-sections of the curves obtained with straight lines of equation $t_{\max} = \text{constant}$. From the tangent of this straight line one obtains $k_d \cdot a_{\max}/k_a$ and from the intercept on the ordinate one obtains $(k_a \cdot l \cdot t_{\max})^{-1} + k_d/k_a$. 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} .

Our considerations show that the above procedure should be applied very carefully. As we already have seen, surface heterogeneity affects both adsorption and desorption rates, although in different ways at different adsorbate concentrations. There may be some balancing of these effects in some concentration regions with the ratio k_a/k_d appearing as a pressure-independent value. This feature, however, is not a sufficient check of surface homogeneity, and the measured rate constants k_a and k_d may have apparent values that differ from their true values. It seems to us that the

following modification of this procedure is necessary in order to estimate reliable values of the adsorption and desorption rate constants:

(1) Firstly, this procedure should be applied in the region of low adsorbate concentrations in the free gas phase, where one should estimate the correct value of the adsorption rate constant, k_a . In other words, experiments should be carried out with very small doses of the adsorbate.

(2) Next, the method should be applied in the region of very high adsorbate concentrations in the column, to estimate reliably the desorption rate constant, k_d . This can be done by using large doses of the adsorbate.

(3) The investigations should be extended to lower and higher ranges of c_{\max} until the estimated k_a and k_d values become pressure-independent.

We shall now demonstrate the effect of surface heterogeneity on the shape of the elution function $c(t)$ with small doses of the adsorbate introduced into the column. Let us assume an adsorption system with a homogeneous surface on which $\varepsilon = \varepsilon_0$ and the other parameters are $k_a = 10^5$ ml/mg·min, $k_d = 400$ min⁻¹ and $a_{\max} = 10$ mg/ml. Let us assume further that the chromatographic process is running at $z/u_g = 0.01$ min and a very small dose of adsorbate is used, corresponding to $m/F = 10^{-5}$ mg/ml·min. The related elution peak is shown as the solid line in Fig. 3.

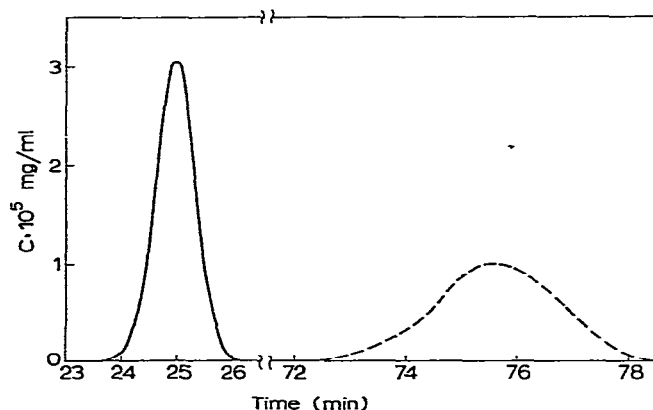


Fig. 3. Effect of surface heterogeneity on the shape of elution curves at low concentrations of adsorbate in the free gas phase (low doses of adsorbate corresponding to $m/F = 10^{-5}$ mg/ml·min). The adsorption system is characterized by the values $k_a = 10^5$ ml/mg·min, $k_d = 400$ min⁻¹, $a_{\max} = 10$ mg/ml and $z/u_g = 10^{-2}$ min. The solid line corresponds to the situation when $q/RT = 0.0$, i.e., to a homogeneous surface. The broken line corresponds to the situation when $q/RT = 1.0$. In the latter instance, the apparent value of k_d is, according to our theory, 133 ml/mg.

If we now assume a heterogeneous surface with the most probable adsorption energy equal to ε_0 and a distribution of adsorption energy characterized by $q/RT = 1.0$, at such small concentrations of adsorbate in the free gas phase the best-fit parameter m will be about 3.0. Consequently, the effective desorption rate constant k'_d/m will be about 133 min⁻¹, while the effective adsorption rate constant will still be 10^5 ml/mg·min. With $z/u_g = 10^{-2}$ min and $m/F = 10^{-5}$ mg/ml·min, the evaluated elution curve $c(t)$ has a shape corresponding to the broken line in Fig. 3. It can easily be seen that this latter peak is much flatter, appears at much higher retention times

and some loss of symmetry is observed in comparison with the peak corresponding to a homogeneous surface.

All of the features obtained here by mathematical means have been observed in practice. Our theory may make it possible to estimate quantitatively both the adsorption and desorption rate constants k'_a and k'_d and the heterogeneity parameter ϱ in the same set of experiments. If we assume that we have already estimated k_a and k_d according to the modified procedure recommended here, then we have also estimated the parameter $m(c_{max})$ for the initial region of concentrations in the free phase, usually called the Henry region. According to eqn. 22, in this pressure region we have

$$m k' p = k' p \left[1 + \frac{\pi^2}{6} \left(\frac{\varrho}{RT} \right)^2 \right] \quad (37)$$

Thus:

$$\varrho = \frac{RT}{\pi} [6(m - 1)]^{\frac{1}{2}} \quad (38)$$

However, at present we do not have appropriate experimental data at our disposal to illustrate this procedure. This aspect will be considered in future publications.

CONCLUSIONS

It is possible to investigate quantitatively the effects of surface heterogeneity in non-linear and non-equilibrium GSC by using a new formulation for the kinetics of adsorption on heterogeneous surfaces. In the absence of exceptional behaviour of the activation energies of adsorption and desorption on adsorption sites that have different adsorption energies, this new formulation of the kinetics of adsorption can be summarized as follows:

(1) at low adsorbate concentrations in the free gas phase, the surface heterogeneity decreases the rate of desorption, while the rate of adsorption remains unchanged;

(2) at high adsorbate concentrations, the surface heterogeneity decreases the rate of adsorption, but does not affect the rate of desorption;

(3) the adsorption and desorption rate constants are defined as being equal to their values for surface sites with the most probable energy of adsorption.

It is possible to estimate quantitatively these rate constants by using the procedure described here. Simultaneously, a parameter is estimated that describes quantitatively the degree of surface heterogeneity. As the degree of surface heterogeneity increases, the elution peaks corresponding to small sample sizes of adsorbate become increasingly flatter. They appear at increasingly longer elution times, and the peak symmetry is gradually lost.

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