Surface heterogeneity and surface area from linear inverse gas chromatography
Application to glass fibers

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Abstract

A new method of measuring surface heterogeneity of non-porous adsorbents by inverse gas chromatography (IGC) is developed. In contrast with the methods described in the literature which are based on nonlinear chromatography (thermodynamics of adsorption) this method is based on linear chromatography (kinetics of adsorption). The mass balance equation of linear chromatography with axial diffusion term and the Langmuir kinetic equation on an open (non-porous) heterogeneous surface are solved by the method of Laplace transforms. The expressions for four semi-invariants of an elution profile are obtained. These are linear combinations of the moments of the distribution of sites in residence time of adsorbed molecule with coefficients determined from elution profile of non-adsorbing gas. Four semi-invariants of elution profiles of benzene and methane on a column packed with E-glass fiber were determined experimentally at temperatures around 100 °C. The mean, the standard deviation of the normal distribution in adsorption energy as well as the sticking coefficient and pre-exponential factor of the Frenkel equation are determined for benzene on E-glass. A method of the specific surface determination from linear IGC is proposed.
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1. Introduction

The overwhelming majority of solid surfaces are heterogeneous which means that they are composed of sites (patches) with different properties. The latter may be, for example, the energy of interaction of an adsorbed molecule (part of the molecule) with the site which determines adsorption or adhesion prop-erties of a surface; in chromatography, the most important property of a site is the residence time of an adsorbed molecule which is the average time the site holds the molecule. Therefore one of the important problems of the surface science (theory of adsorption, adhesion, chromatography, etc.) is to determine the distribution of sites with respect to a relevant property. There exists extensive literature on the subject [1,2]. It is devoted mainly to the energy distribution of sites (EDS). In previous papers, we considered also the distribution of sites in adsorption entropy and the entropy/energy relation for different sites [3,4].

The distribution of sites in, e.g., adsorption energy

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is usually calculated from an equilibrium adsorption isotherm [1,2]. The most popular method is based on the assumption that the experimental isotherm of adsorption is just the sum of isotherms on all the sites (local isotherms) and that one knows the dependence of a local isotherm on the adsorption energy. Then one can find (by solving an integral equation) the EDS that brings the sum of local isotherms into coincidence with the experimental isotherm [1,2]. An equilibrium isotherm of adsorption can be measured by the inverse gas chromatography (IGC) from the plot of retention volume vs. the concentration of probe molecules (solute) in the carrier gas. The method is called the elution by characteristic point (ECP) [5]. Correspondingly one can determine the EDS from IGC [1,2,4,6]. Although IGC provides for considerable experimental advantages in determining EDS [4], it should be emphasized here that determination of EDS by the ECP method is basically the same as determination EDS from an equilibrium adsorption isotherm measured by the static adsorption techniques.

The purpose of this paper is to show that IGC makes it possible to study the surface heterogeneity by a method which is basically different from that mentioned above. This method uses not only the information on adsorption equilibrium but mainly the information on the kinetics of adsorption. This is because, generally, the response of a chromatographic column to an impulse injection (elution profile) depends not only on the equilibrium adsorption isotherm but on the kinetics of adsorption as well.

At low coverages, an isotherm of adsorption becomes almost linear. This region of the adsorption isotherm is called the Henry region and the slope of the isotherm to the, e.g., axis of gas concentration is called the Henry constant. The Henry constant on a heterogeneous surface is the sum of those on all the sites. Thus if one knows the distribution of sites in the Henry constant (which depends on EDS), one can calculate the Henry constant on a heterogeneous surface. But the converse is not true: One cannot, determine the EDS from only one experimental value of the Henry constant at a fixed temperature (an unknown function cannot be determined from only one experimental value). It is still possible to determine the EDS from the temperature dependence of the Henry constant [6]. However, the temperature dependence of the Henry constant is usually employed to determine the energy and the entropy of adsorption (see Ref. [4] and references therein). Thus the method [6] makes some implicit assumption on the dependence between the energy and the entropy of adsorption.

The chromatography in the Henry region is called linear chromatography. It is an exactly solvable model [7]. Moreover, there are several methods of solution. One method is called the stochastic theory of chromatography [7–10]. This theory considers chromatography as a molecular stochastic Poisson process. It gives the elution profile for a homogeneous surface composed of identical sites [8,9]. Generally speaking, a deviation of an experimental elution profile from the theoretical one can be considered as an indication to the surface heterogeneity. This is similar to the above mentioned evaluation of surface heterogeneity by the deviation of an experimental isotherm of adsorption from the theoretical (local) isotherm.

There are, however, considerable differences between the two methods (see, however, the end of Section 4). First, the theoretical elution profile mentioned above corresponds to linear chromatography model [7]. Thus the only equilibrium adsorption characteristic that determines the elution profile is the Henry constant. In fact, it determines only the position of the elution profile. The shape of the elution profile (e.g., its central moments) which is used for the surface heterogeneity analysis described below is determined by the kinetics of adsorption and the column effects (axial diffusion). (The latter are to be excluded by comparison of the elution profiles of adsorbing and non-adsorbing gases). Second, there is no simple relation between elution profiles corresponding to heterogeneous and homogeneous surfaces similar to the integral equation that connects the isotherm of adsorption on a heterogeneous surface with the local isotherm corresponding to an adsorption site. This complication is counterbalanced by the fact that the experimental isotherm in IGC is obtained by the approximate ECP method (which neglects kinetics of adsorption and axial diffusion) while linear chromatography is an exactly solvable model.

In the next section we consider the Langmuir model of a heterogeneous surface. This means that

the surface is considered as composed of sites that can adsorb only one molecule, the state of a site (occupied or vacant) being independent of the states of the neighboring sites. A computer simulation shows that this is an adequate model of an amorphous surface especially in the Henry region [11,12]. We describe this model by the mass balance equation with the Langmuir kinetics (the reaction-dispersive model [7]). (An attempt to consider the heterogeneous surface in the stochastic theory of adsorption mentioned above have not yet given tractable results for a general case considered here [9]). The model takes into account the kinetics of adsorption and axial diffusion but neglects the diffusion resistance of the transport from the carrier gas to the surface. Thus it cannot be applied to porous solids but we believe (see arguments in Section 4) that it is applicable to non-porous surfaces similar to those of glass fibers.

The main result is Eq. (16) which expresses the semi-invariants [first absolute moment of the elution curve m_1, its variance σ^2, skewness κ_3/σ^3 and kurtosis (excess) κ_4/σ^4] of the elution profile through the absolute moments of the distribution of sites in the residence time of a molecule $\langle \nu\tau^k \rangle$. The other parameters in Eq. (16) are to be determined from the elution profile of a non-adsorbing gas and the total number of sites on the surface. The residence time is connected to the adsorption energy by the Frenkel equation (Eq. (26)) which makes it possible to convert the distribution of sites in residence time into their distribution in energy (Section 2.3).

We consider here adsorption of benzene on E-glass. It is shown in Section 4 that from the IGC point of view this surface can be considered as homogeneous with respect to benzene at 100 °C but at 70 °C the same surface displays features of a heterogeneous surface. It is shown in Section 2.4 that for a homogeneous surface the temperature dependence of the first moment (similar to the net retention volume [5]) makes it possible to determine not only the energy of adsorption but also the product of the total number of sites by some important kinetic characteristics. The peculiarity of glass fibers is that their specific surface is directly measurable through their diameter and density. Thus we determined those kinetics characteristics designated as $\nu\tau_0$ in Eq.

(41). Now one can measure the specific surface of dispersed solids (not only glass fibers) made of E-glass directly by IGC. Analysis of surface heterogeneity (at lower temperatures) allowed us further to separate $\nu\tau_0$ into the pre-exponential factor of the Frenkel equation τ_0 and ν that determines the sticking coefficient for benzene on E-glass. Knowing all these constants we were able to determine the mean and the standard deviation of EDS for benzene on E-glass. As indicated in the Conclusion, we consider our results only as a first step in developing of IGC on heterogeneous surfaces starting from its linear end.

2. Theoretical

2.1. Moments of the response curve for a heterogeneous surface

The basis for our consideration is the following mass balance equation [7]:

$$\frac{\partial C}{\partial t} + \frac{1-\epsilon}{\epsilon} \cdot \frac{\partial q}{\partial t} + u \cdot \frac{\partial C}{\partial z} = D \cdot \frac{\partial^2 C}{\partial z^2} \qquad (1)$$

where $C(z,t)$ and $q(z,t)$ are the concentrations of the solute in the mobile and stationary phases, respectively; z is a coordinate along the column; t is time; ϵ is the fraction of the mobile phase volume in the column (porosity of the column packing); u is the average mobile phase velocity and D accounts for the fluctuation of u (eddy diffusion) and for the molecular diffusion of solute in the carrier gas [7]. Eq. (1) neglects the compressibility of the carrier gas (it is derived for liquid chromatography [7] and accordingly we call the probe molecules in the carrier gas *solute*). Its application to IGC is justified for those cases where the compressibility correction [5] is small (as is the case for IGC on glass fibers; see Section 3).

The initial conditions for Eq. (1) are:

$$C(z,0) = 0; \quad q(z,0) = 0 \qquad (2)$$

The boundary conditions correspond to a semi-infinite column [$C(\infty,t)$ is bounded] with an injector of volume V_{in} on the left end where N_{in} moles of solute are injected at $t = 0$:

$$V_{\text{in}} \cdot \frac{\mathrm{d}C(0,t)}{\mathrm{d}t} = -vC(0,t); \quad C(0,0) = \frac{N_{\text{in}}}{V_{\text{in}}} \tag{3}$$

Here v is the flow-rate of the carrier gas.

In the case of adsorption chromatography:

$$q = A\rho\Gamma \tag{4}$$

where A and ρ are specific surface and density of the packing material (e.g., glass, for glass fiber column packing), respectively; Γ is adsorption per unit area. We assume that the surface is heterogeneous and is composed of sites of n different kinds and adsorption on each site is described by the Langmuir model. This means that:

$$\Gamma = \sum_{i=1}^{n} \Gamma_i \tag{5}$$

and:

$$\frac{\mathrm{d}\Gamma_i}{\mathrm{d}t} = v_i C(\Gamma_i^0 - \Gamma_i) - \frac{\Gamma_i}{\tau_i}; \quad \Gamma_i(0) = 0 \tag{6}$$

Here Γ_i is the number of occupied sites of the i-kind per the unit of surface. The total number of these sites is Γ_i^0 and each site is characterized by the residence time of an adsorbed molecule τ_i. In Eq. (6), Γ_i and Γ_i^0 refer to some macroscopic patch of the surface at some column coordinate z. It is implied that Γ_i^0 does not depend on z and Γ_i depends on z only through C in Eq. (6). For adsorption from the ideal gas, $v_i C$ is the number of impacts of gas molecules at concentration C on the i-adsorption site per unit time where [4]:

$$v_i = \sqrt{\frac{RT}{2\pi M}} \sigma_i \alpha_i N_{\text{A}} \tag{7}$$

Here N_{A} is the Avogadro number; M is the molecular mass of a probe molecule; R and T are the gas constant and temperature, respectively; σ_i is the effective area of the site and α_i is the sticking coefficient. Define some standard value:

$$v = \sqrt{\frac{RT}{2\pi M}} \cdot a_{\text{m}} \alpha N_{\text{A}} \tag{8}$$

with a_{m} taken as the molecular area of a probe molecule and $0 < \alpha < 1$ (for a molecule of complex shape, only a small fraction of collision with an adsorption site lead to adsorption of the molecule).

The initial conditions for Eq. (6) and Eqs. (4) and (5) provide for the second condition in Eq. (2).

Consider the case when:

$$\Gamma_i \ll \Gamma_i^0 \tag{9}$$

Then Eq. (6) can be approximated by the following linear equation:

$$\frac{\mathrm{d}\Gamma_i}{\mathrm{d}t} = v_i C\Gamma_i^0 - \frac{\Gamma_i}{\tau_i}; \quad \Gamma_i(0) = 0 \tag{10}$$

and since Eq. (1) is also linear, the whole model is called *linear chromatography* [7].

Laplace transform Eqs. (5) and (10) to obtain:

$$\tilde{\Gamma} = \tilde{C} \sum_{i=1}^{n} \frac{v_i \tau_i \Gamma_i^0}{1 + p\tau_i} \tag{11}$$

where p is the Laplace transform parameter conjugated to t. Laplace transform Eqs. (1), (3) and (4) and make use of Eq. (11) to obtain:

$$f(p)\tilde{C} + u \cdot \frac{\mathrm{d}\tilde{C}}{\mathrm{d}z} - D \cdot \frac{\mathrm{d}^2\tilde{C}}{\mathrm{d}z^2} = 0;$$

$$\tilde{C}(0) = \frac{N_{\text{in}}}{pV_{\text{in}} + v} \tag{12}$$

where $\tilde{C}$ is considered to be a function of z, p being a parameter, and:

$$f(p) = p\left(1 + A\rho \cdot \frac{1 - \epsilon}{\epsilon} \sum_{i=1}^{n} \frac{v_i \tau_i \Gamma_i^0}{1 + p\tau_i}\right) \tag{13}$$

Since $\epsilon < 1$ and $Df(p) > 0$, the solution to Eq. (12) (bounded at the infinity) is:

$$\tilde{C}(z,p) = \frac{N_{\text{in}}}{V_{\text{in}}} \cdot \frac{\exp\left\{-z\left[-u + \sqrt{u^2 + 4Df(p)}\right]/2D\right\}}{p + v/V_{\text{in}}} \tag{14}$$

The function $\tilde{C}(p,z)$ at $z = L$ where L is the length of the column is the generating function of the moments of the response curve and $\ln \tilde{C}(p,L)$ is the generating function for semi-invariants (cumulants) [13]. The relations between semi-invariants and moments are:

$$\kappa_1 = m_1; \quad \kappa_2 = \mu_2 = \sigma^2; \quad \kappa_3 = \mu_3;$$

$$\kappa_4 = \mu_4 - 3\mu_2^2 \tag{15}$$

where m_1 is the absolute first moment and μ_i are the central moments. The semi-invariants of the response of the column to the injection described by Eq. (3) (elution profile) are:

$$m_1 = \frac{L}{u} \cdot (1 + B\langle \nu\tau \rangle) + \frac{V_{in}}{v}$$

$$\sigma^2 = \frac{2L}{u} \cdot B\langle \nu\tau^2 \rangle + \frac{2DL}{u^3} \cdot (1 + B\langle \nu\tau \rangle)^2 + \left(\frac{V_{in}}{v}\right)^2$$

$$\kappa_3 = \frac{6L}{u} \cdot B\langle \nu\tau^3 \rangle + \frac{12LD}{u^3} \cdot B\langle \nu\tau^2 \rangle(1 + B\langle \nu\tau \rangle)$$

$$+ \frac{12D^2L}{u^5} \cdot (1 + B\langle \nu\tau \rangle)^3 + 2 \cdot \left(\frac{V_{in}}{v}\right)^3$$

$$\kappa_4 = 24 \cdot \frac{L}{u} \cdot B\langle \nu\tau^4 \rangle + 48 \cdot \frac{LD}{u^3} \cdot B\langle \nu\tau^3 \rangle(1 + B\langle \nu\tau \rangle)$$

$$+ 24 \cdot \frac{LD}{u^3} \cdot B^2\langle \nu\tau^2 \rangle^2 + 144 \cdot \frac{LD^2}{u^5} \cdot B\langle \nu\tau^2 \rangle(1 + B\langle \nu\tau \rangle)^2$$

$$+ 120\frac{LD^3}{u^7} \cdot (1 + B\langle \nu\tau \rangle)^4 + 6 \cdot \left(\frac{V_{in}}{v}\right)^4 \qquad (16)$$

Here:

$$\langle \nu\tau^k \rangle = \sum_{i=1}^{n} \nu_i \tau_i^k \frac{\Gamma_i^0}{\Gamma^0} \qquad (17)$$

is the k-absolute moment of the distribution of adsorption sites with respect to retention times; Γ^0 is the total number of adsorption site per unit of surface and Γ_i^0/Γ^0 is the fraction of sites of the i-type. In Eq. (16):

$$B = A\rho \cdot \frac{1 - \epsilon}{\epsilon} \cdot \Gamma^0 \qquad (18)$$

and the semi-invariants of the elution profile of an inert solute ($\tau_i = 0$ in Eq. (17)) are:

$$m_1^0 = \frac{L}{u} + \frac{V_{in}}{v}; \quad \sigma_0^2 = \frac{2DL}{u^3} + \left(\frac{V_{in}}{v}\right)^2$$

$$\kappa_3^0 = \frac{12D^2L}{u^5} + 2 \cdot \left(\frac{V_{in}}{v}\right)^3;$$

$$\kappa_4^0 = \frac{120D^3L}{u^7} + 6 \cdot \left(\frac{V_{in}}{v}\right)^4 \qquad (19)$$

One can use the first three of these equation to determine L/u, D/u^2, and V_{in}/v from the values of m_1^0, σ_0^2, κ_3^0. (The value of κ_4^0 can be then evaluated for control). Substitution of these parameters into Eq.

(16) allows one to determine the moments of the site distribution in retention time $\langle \nu\tau^k \rangle$ ($k = 1, \ldots, 4$) from the experimental values of m_1, σ^2, κ_3, and κ_4 if one knows B.

The total number of adsorption sites in the column is:

$$N_{tot} = A\rho(1 - \epsilon)\Gamma^0 FL \qquad (20)$$

where F is the cross section area of the column tube. The flow-rate of the carrier gas is:

$$v = F\epsilon u \qquad (21)$$

Now divide Eq. (20) by Eq. (21) and use Eq. (18) to obtain:

$$N_{tot} = vB(L/u) \qquad (22)$$

Since v can be measured and L/u also can be evaluated from experiment, the value of B is directly connected to the total number of sites on the surface inside the column. In the BET method, the surface area is determined as the total number of sites multiplied by the molecular area a_m [14]. Since the diameter of glass fiber and the bulk density of glass can be measured as well as the total mass of glass fibers in the column, one can determine the total surface in the column. Dividing it by a_m one obtains N_{tot} and then can use Eq. (22) to determine B.

We have described how to determine from IGC the absolute moments $\langle \nu\tau^k \rangle$ which determine the distribution of sites in residence time of an adsorbed molecule. Now we describe how to use this moments to evaluate the distribution of sites in adsorption energy and how to evaluate from the Henry constant the specific surface of glass fibers (without measuring their diameters) or other non-porous adsorbents.

2.2. A standard state for the gas adsorption

At equilibrium ($d\Gamma_i/dt = 0$), Eq. (6) gives the Langmuir equation on a group of identical sites:

$$\Gamma_i = \Gamma_i^0 \cdot \frac{\nu_i\tau_i C}{1 + \nu_i\tau_i C} \qquad (23)$$

where $\nu_i\tau_i$ is the Henry constant for the i-site. To make the Henry constant dimensionless, we introduce a standard concentration C_0 and rewrite Eq. (23) as:

$$\theta_i = \frac{K_H^i C/C_0}{1 + K_H^i C/C_0} \qquad (24)$$

where $\theta_i = \Gamma_i/\Gamma_i^0$ and:

$$K_H^i = \nu_i \tau_i C_0 \qquad (25)$$

is the dimensionless Henry constant. Here ν_i is given by Eq. (7) and τ_i is the adsorption residence-time determined by the Frenkel equation [4,10]:

$$\tau_i = \tau_i^0 \exp(-\Delta U_i/RT) \qquad (26)$$

The meanings of τ_i^0 and ΔU_i are discussed below (see Eqs. (30) and (31)).

Another form of the Langmuir equation for a site (used in Ref. [4]) is:

$$\theta_i = \{1 + \exp[(\mu_i' - \mu)/RT]\}^{-1} \qquad (27)$$

Here μ is the chemical potential of adsorbate and μ' is the free energy of a molecule adsorbed on a site.

As in our previous paper [4], the standard state of adsorbate is determined as that when adsorbate is in equilibrium with the gas phase at concentration $C = 1/(\nu\tau_0)$. The value of ν is given by Eq. (8) so that this value of C contains two yet undetermined constants: α in Eq. (8) and τ_0 (in Ref. [4], $\alpha = 0.1$ and $\tau_0 = 10^{-12}$ s). Since in equilibrium the chemical potentials of adsorbate equals that of gas:

$$\mu = RT \ln(C\nu\tau_0) + \mu_0(T)$$
$$= RT \ln(C/C_0) + RT \ln(C_0\nu\tau_0) + h_0 - Ts_0 \qquad (28)$$

where $\mu_0(T)$, h_0 and s_0 are the chemical potential, the molar enthalpy, and the molar entropy of the ideal gas at $C = 1/\nu\tau_0$ (h_0 does not depend on C), respectively. (The gas is considered as ideal because Eq. (9) is valid only at small values of C).

In Eq. (27):

$$\mu_i' = -RT \ln Z_{ads}^i = U_{min}^i - RT \ln Z_{th}^i$$
$$= U_{min}^i + \epsilon_{th}^i - Ts_{th}^i \qquad (29)$$

where Z_{ads} is the partition function of an adsorbed molecule; U_{min} is the minimal energy of the molecule on a site; Z_{th} is the partition function for the energy spectrum referred to U_{min} (thermal partition function); ϵ_{th} and s_{th} are the thermal energy and entropy, respectively.

Substitution of Eqs. (28) and (29) in Eq. (27) gives Eq. (24) with:

$$K_H^i = \exp(\Delta S_i/R) \exp(-\Delta U_i/RT) \qquad (30)$$

where:

$$\Delta U_i = U_{min}^i + \epsilon_{th}^i - h_0;$$
$$\Delta S_i = s_{th}^i - s_0 + R \ln(\nu\tau_0 C_0)$$

Here ΔU_i and ΔS_i are the differences between the energy and the entropy of a mole of molecules adsorbed on i-sites and the same molecules in the ideal gas state at concentration C_0.

Comparison of Eqs. (25), (26) and Eq. (30) shows that:

$$C_0 \nu_i \tau_i^0 = \exp(\Delta S_i/R) \qquad (31)$$

2.3. Energy distribution from moments of residence time

It follows from Eqs. (31), (26) and (17) that:

$$\langle \nu\tau^k \rangle = \sum_{i=1}^n \nu_i^{1-k} C_0^{-k} \exp[k(\Delta\mu_i'/RT)](\Gamma_i^0/\Gamma^0) \qquad (32)$$

where:

$$\Delta\mu_i' = \Delta U_i - T\,\Delta S_i$$

is the the molar free energy of an adsorbed molecule Eq. (29) with respect to that of the ideal gas at the standard concentration $C = 1/\nu\tau_0$.

Assume now that the distribution of sites in $\Delta\mu'$ is continuous and normal:

$$f(\Delta\mu') = \frac{1}{\sqrt{2\pi\sigma_g^2}} \cdot \exp\left[-\frac{(\Delta\mu' - \mu_g)^2}{2\sigma_g^2}\right] \qquad (33)$$

Assume also that all the ν_i are equal to ν Eq. (8). Then Eq. (32) can be approximated as:

$$\langle \nu\tau^k \rangle = \frac{1}{C_0^k \nu^{k-1}} \int_{-\infty}^{\infty} d\Delta\mu' f(\Delta\mu') \exp\left(-\frac{k\,\Delta\mu'}{RT}\right) \qquad (34)$$

and gives:

$$\langle \nu \tau^k \rangle = \frac{1}{C_0^k \nu^{k-1}} \exp\left[-\frac{\mu_g k}{RT} + \frac{\sigma_g^2 k^2}{2(RT)^2} \right] \qquad (35)$$

This equation gives for $k = 1, 2$:

$$\left(\frac{\sigma_g}{RT} \right)^2 = \ln\left(\frac{\nu \langle \nu \tau^2 \rangle}{\langle \nu \tau \rangle^2} \right) \qquad (36)$$

$$\left(\frac{\mu_g}{RT} \right) = \frac{1}{2} \ln(\nu \langle \nu \tau^2 \rangle) - \ln(C_0 \langle \nu \tau \rangle^2) \qquad (37)$$

Finally, if one assumes that in Eq. (31) τ_i^0 is constant ($\tau_i^0 = \tau_0$) as well as $\nu_i = \nu$, then ΔS_i is also constant which can be multiplied by T and subtracted from $\Delta \mu'$ and μ_1 in Eq. (33). The result is the normal energy distribution of sites with variance given by Eq. (36) and mean energy:

$$U_0 = \mu_g + RT \ln(C_0 \nu \tau_0) \qquad (38)$$

2.4. The total number of sites

Finally we consider how to evaluate the total number of sites N_{tot}. From Eqs. (16), (19) and (22) it follows:

$$\upsilon(m_1 - m_1^0) = N_{tot} \langle \nu \tau \rangle \qquad (39)$$

Assume now that the surface is homogeneous. It will be shown in Section 4 that at sufficiently high temperatures a heterogeneous surface can be considered (from IGC point of view) as a homogeneous surface. Then one can use Eqs. (8) and (26) to evaluate $\langle \nu \tau \rangle$ and obtain:

$$\ln[\upsilon(m_1 - m_1^0)] = \ln(N_{tot} \nu \tau_0) - \Delta U / RT \qquad (40)$$

here we designated τ_i^0 as τ_0.

3. Experimental

3.1. Chemicals

Methane from the the methane cylinder kit (Restek, Bellefonte, PA, USA) was used as a non-adsorbed gas. Benzene of HPLC grade (Aldrich, Milwaukee, WI, USA) was used without purification.

The chromatographic column was a glass tube 23 cm×3.9 mm I.D. filled with 2.208 g continuous glass fiber. The glass fiber was drawn from E-glass marbles and pulled through the column. The diameter of the fiber measured by the Phillips XL 20 electron microscope was 9.2 ± 0.2 μm and the density of E-glass was 2.5 g/cm^3. This gives 0.174 m^2/g for the specific surface of the fiber and 0.384 m^2 for the total surface area of E-glass in the column.

3.2. Equipment and procedures

As in our previous work [4], we used a HP5890 series II (Hewlett-Packard, USA) gas chromatograph. In the present work, it was supplemented by the DP95 Digital RTD thermometer (OMEGA Engineering, Stamford, CT, USA) for more accurate temperature measurements. The resolution of the thermometer was ±0.001 °C and its accuracy was 0.05% of full scale (200 K in our case). According to the thermometer, the stability of temperature in the GC oven was no worse than 0.01 °C and the temperature difference of 10 °C could be measured with accuracy better than 1%.

In our experiments the pressure drop over the column varied from 25 to 35 kPa so that the pressure gradient correction factor [5] deviated from unity by about 10% and the flow-rate of the carrier gas (helium) varied from 10 to 20 ml/min.

A 2-l static dilution bottle with valve (Supelco, Bellefonte, PA, USA) and a gas-tight syringe were used for injection of very small amounts of benzene. With 10 μl of liquid benzene injected in the bottle, 1 μl of gas mixture taken from it contains about 0.05 nmol of benzene. This method provides accuracy of injected amount of about 20%. More accurate evaluation of injected amount gives the areas of peaks.

We used two methods for evaluation of the values of moments of experimental elution profiles. The first method was based on the direct numerical integration of experimental peaks. The second method consisted in approximation of an experimental peak by a curve-fitting function and consequent calculation of the moments of that function. The second method may be more accurate even for the lowest moment (area of the peak) and many curve-fitting functions were proposed to fit chromatographic peaks [15]. We used a linear combination of two

Fraser–Suzuki functions [16] as a fitting function and determined its eight parameters with the help of the Levenberg–Marquardt nonlinear least-squares method [13].

4. Results and discussion

Compare Figs. 1 and 2. These show responses of the the chromatographic column described in the previous section to the impulse injections of a very small amount of benzene. The solid line in Fig. 1 is an elution profile of the column that initially does not contain benzene molecules at its surface because the surface was preliminary treated for an hour at 150 °C in a flow of pure He. This elution profile is qualitatively similar to that of butanol on the E-glass surface (cf. Fig. 2 in Ref. [4]). In both cases the tail of an elution profile corresponds to adsorption on sites of different strengths. However, the quantitative difference between the elution profiles in Fig. 1 and that presented as the solid line in Fig. 2 of Ref. [4] is very big. First, the quantity of injected benzene in Fig. 1 is four orders of magnitude smaller than that in Fig. 2 of Ref. [4]. (The total surface in the column

Fig. 2. Benzene and methane on E-glass at 100 °C. Solid line: injection of 0.25 nmol of benzene after heat treatment of the column at 200 °C; dashed line: injection of the same amount as described in Fig. 1; dotted line—methane.

described in Ref. [4] was an order of magnitude larger than in the present case but even that taken into account the loading in the present case is still three orders of magnitude smaller than in [4]).

The injection of such a small amount of butanol in our column produces no detectable response. This is because the surface of E-glass is strongly heterogeneous with respect to butanol that is composed of sites with a rather wide range of energies of adsorption. A useful rule for adsorption on heterogeneous surfaces (condensation approximation [1,2]) is that a molecule always adsorb on the strongest vacant site. Thus the smaller is an injected amount, the stronger will be the sites that hold a molecule during its travel along the column. Since the residence time of a molecule on a site exponentially depends on the energy of adsorption Eq. (26), even a relatively narrow distribution of sites in energy can smear them over a rather wide interval of residence times (which, however, depends on temperature—see below). This makes the elution profile of a very small injected amount on a strongly heterogeneous surface very broad which together with its small area drastically decreases the signal below a detectable level.

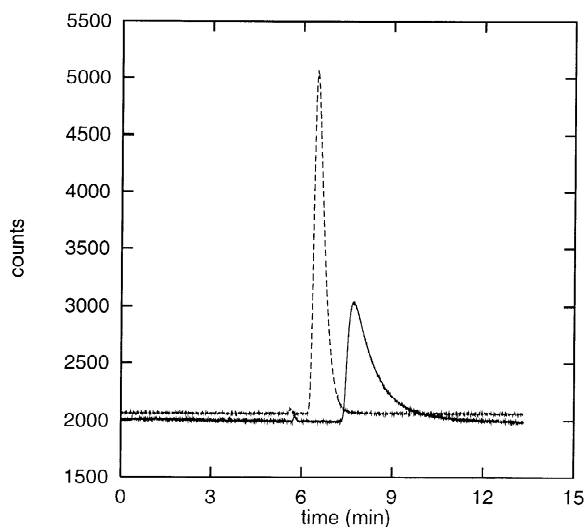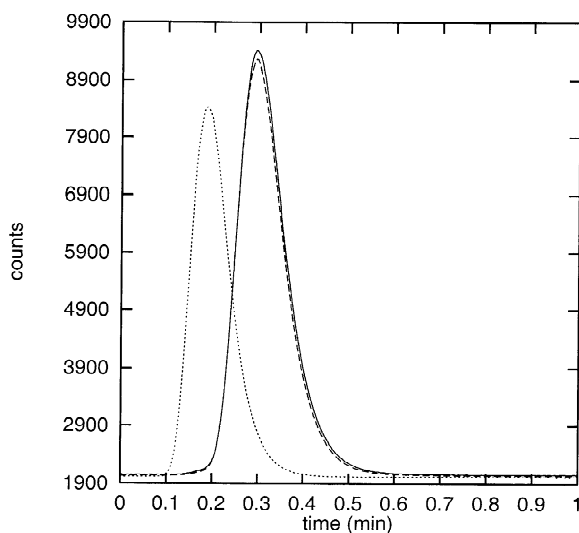The fact that the elution profile of a very small

Fig. 1. Benzene on E-glass at 50 °C. Solid line: injection of 0.25 nmol of benzene after heat treatment of the column at 150 °C; dashed line: injection of the same amount after the end of the previous elution profile (without preliminary heat treatment). The methane elution profile looks like that in Fig. 2.

injected amount of benzene is well detectable (in contrast with butanol) means that the heterogeneity of a E-glass surface is much smaller with respect to benzene than with respect to butanol. Nevertheless the surface of E-glass is still heterogeneous with respect to benzene at 50 °C. This follows (in addition to the asymmetric shape of the solid line) from comparison of the solid and broken lines in Fig. 1. The broken line was obtained by injection of the same amount of benzene in 30 min after the first injection (that produced the solid line). The difference of the two elution profiles in Fig. 1 can be explained as follows. The solid line in Fig. 1 shows the dependence on time of the amount of benzene molecules that were eluted by the flow of He from the column for the first 15 min. After that the amount of benzene molecules that comes out of the column is negligibly small. This, however, does not mean that there is no benzene molecule in the column. The strongest sites on the surface are still occupied by benzene molecules. Thus for the second portion of injected molecules these sites are not active; only weaker sites can now adsorb injected molecules. This is the reason why the second elution profile (broken curve) is shifted to the left with respect to the first one (solid curve in Fig. 1).

The situation is qualitatively different at higher temperature (Fig. 2). Here, as in Fig. 1, the solid curve is the elution profile on the column that was kept for an hour at 200 °C. The dashed curve is the second injection without preliminary heat treatment. Now these two elution profiles almost coincide. Besides, they have no tails typical for adsorption on heterogeneous surfaces. The small asymmetry of these peaks as well as that for methane is due to small efficiency (short length, small surface area of packing) of our column (see Ref. [7], p. 207). Now our column responds to the impulse injection of benzene as if the surface of E-glass is homogeneous. Of course, the increase of temperature from 50 to 100 °C can not make a heterogeneous surface homogeneous. The distribution of sites in energy (EDS) is the same in both cases but the distribution of sites in residence time is drastically different. This is because the residence time of a molecule on a site τ_i depends on temperature in such a way Eq. (26) that even relatively small increase of temperature can drastically decrease τ_i and correspondingly make the

variation of τ_i over different sites very small. From the point of view of linear chromatography, a surface with narrow distribution of sites in residence time can be considered as approximately homogeneous.

Thus we can use Eq. (40) to analyze the elution profile in Fig. 2. The left-hand-side of Eq. (40) is presented in Fig. 3 for three temperatures around 100°. The slope of the linear regression gives $\Delta U = 71.2$ kJ/mol with a rather high accuracy. The molecular area of benzene is 43 Å^2 [14]. Thus for the surface of 0.384 m^2 (see Section 3) $N_{\text{tot}} = 1.48$ μmol. Now from the intercept of the straight line in Fig. 3 and this value of N_{tot}, one obtains from Eq. (40):

$$\nu\tau_0 = 1.03 \cdot 10^{-10} \, \text{m}^3/\text{mol} \tag{41}$$

This value of $\nu\tau_0$ enables one to determine N_{tot} (and, in fact, the specific surface) of an E-glass fiber from the temperature dependence of the left-hand-side of Eq. (40) for benzene.

Now we apply Eqs. (16) and (19) for the analysis of an elution profile at the temperature which is intermediate between the temperatures of Figs. 1 and 2. The results are presented in Table 1. The first line
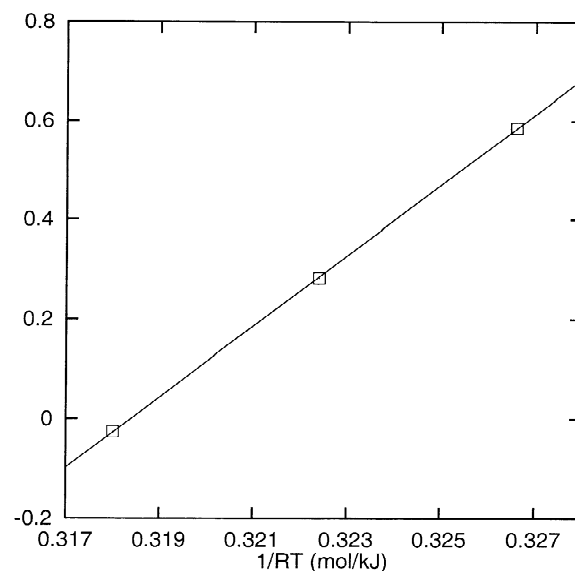

Fig. 3. The temperature dependence of $\ln[\nu(m_1 - m_1^0)/mL]$ (ordinate) on inverse temperature. Symbols are experimental points at 95.04, 100.09, and 105.11 °C. The regression line has the slope 71.2±0.5 kJ/mol and intercept −22.6±0.2 ln(mL).

Table 1
Semi-invariants Eq. (15) of the benzene and methane elution profiles on E-glass at 70 °C

No.	Molecule	m_1 (min)	σ_0^2 (min^2)	κ_3 (min^3)	κ_4 (min^4)
1	CH_4	0.1947	$1.902 \cdot 10^{-3}$	$8.230 \cdot 10^{-5}$	$7.11 \cdot 10^{-6}$
2	CH_4	0.1947	$1.902 \cdot 10^{-3}$	$8.230 \cdot 10^{-5}$	$6.52 \cdot 10^{-6}$
3	C_6H_6	0.8232	$2.248 \cdot 10^{-2}$	$4.52 \cdot 10^{-3}$	$1.56 \cdot 10^{-3}$
4	C_6H_6	0.8232	$2.248 \cdot 10^{-2}$	$1.89 \cdot 10^{-3}$	$1.65 \cdot 10^{-3}$

Experimental values are in lines 1 and 3 and calculated values are in lines 2 and 4. Line 4 corresponds to $\alpha = 0.0054$ and $a_m = 43$ Å^2 in Eq. (8).

of the table presents semi-invariants Eq. (15) of the methane profile that looks like that in Fig. 2. Substitution of their values in the right-hand sides of the first three Eq. (19) gives for $L = 23$ cm (length of the column) and $\upsilon = 13.2$ ml/min (flow-rate of He): $u = 2.37$ cm/s; $D = 0.88$ cm^2/s; $V_{in} = 0.42$ cm^3. The back substitution of these values in Eq. (19) gives the second line in Table 1. The first three semi-invariants in the first and the second lines naturally coincide which only testifies to the correctness of the solution of the first three equations from Eq. (19). The fourth semi-invariants in the first and the second lines of Table 1 are also close to each other which can be considered as an argument to the consistency of the method.

Now we use the above values of L, u, D, V_{in} and υ and experimental semi-invariants of benzene elution profile (the third line in Table 1) to determine from Eq. (16) the values of the absolute moments of the distribution of sites in the retention time $\langle \nu \tau^k \rangle$. First we use Eq. (22) and the value of N_{tot} as well as other values given above to determine $B = 0.690$ mol/m^3. Then we find $\langle \nu \tau \rangle$ and $\langle \nu \tau^2 \rangle$ and substitute them in Eqs. (36) and (37) to find the mean μ_g and the variance σ_g of the Gaussian distribution of sites in free energy. The values of ν in Eqs (36) and (37) is calculated by Eq. (8) with $\sigma = 43$ Å^2 (the molecular area of benzene [14]) and some tentative value of the sticking coefficient α, say $\alpha = 0.1$. We also define $C_0 = 1$ mol/m^3. The value of C_0 does not influence the final results. It was introduced just to make some intermediate variables, such as for example the left-hand-side of Eq. (31), dimensionless. Then we substitute the values of μ_g, σ_g and ν in Eq. (35) and calculate all the values of $\langle \nu \tau^k \rangle$ $k = 1, \ldots, 4$. These together with other parameters mentioned above can be substituted in Eq. (16) to calculate four semi-invariants. Of these, the first two coincide with the

experimental values of m_1 and σ^2 because the latter were used to determine $\langle \nu \tau \rangle$ and $\langle \nu \tau^2 \rangle$. The values of the other two calculated semi-invariants (κ_3 and κ_4) depend on the value of α in Eq. (8). We found the value of α (presented in Table 1) that makes the difference between experimental and calculated values of $\kappa_3 + \kappa_4$ minimal. The calculated values of semi-invariants are presented in in the fourth line of Table 1. The mean of the value of μ_g in Eq. (37) is 6.09 kJ/mol and we can use Eqs. (38) and (41) to determine $U_0 = -59.5$ kJ/mol. Besides, from Eq. (36), $\sigma_g = 7.92$ kJ/mol. These are parameters of the Gaussian EDS.

The value of $0 < \alpha < 1$ in Eq. (8) is the fraction of molecules hitting the surface (site) which are adsorbed. This fraction should be small: not only the velocity of a molecule approaching the surface should be sufficiently low but the orientation of that molecule should be in a narrow interval of solid angles to make adsorption possible. Thus the value of $\alpha = 0.0054$ we obtained seems reasonable. We substitute it in Eq. (8) and then in Eq. (41) to obtain $\tau_0 = 3.3 \cdot 10^{-14}$ s. This value of τ_0 is less than $\tau_0 = 10^{-12}$ s that was widely used in the literature (see Ref. [4] and references therein). The value of $\tau_0 = 10^{-12}$ s is the result of theoretical evaluation of the frequency of oscillation of a nitrogen molecule at the graphite basal plane. The attraction of a benzene molecule to the glass surface is clearly larger than that of a nitrogen molecule to graphite so that the smaller value of τ_0 for benzene seems reasonable. Finally we substitute the above value of τ_0 and U_0 in Eq. (26) to obtain $\tau = 38.2$ μs. This is the residence time of a benzene molecule on the majority of sites at 70 °C.

This value of τ should be compared to the time scale of molecular diffusion of benzene in helium. This time scale can be evaluated as d^2/D where d is

the diameter of fiber and D is the molecular diffusivity of benzene in helium at 70 °C. The latter is on the order of magnitude of the axial diffusivity given above (10^{-4} m^2/s) and the former is on the order of 10^{-5} m. Thus the time scale of molecular diffusion of benzene in helium is 1 µs which is less than the value of τ given above. This justifies our results in Section 2.1 where we neglected molecular diffusion of solute in the carrier gas in comparison to the kinetics of adsorption. It also explains why we cannot use the elution profiles at higher temperatures (for example those in Fig. 2) for the analysis of the surface heterogeneity: At higher temperature the values of τ will be too small on the time scale evaluated above.

There is also an experimental reason why one cannot use elution profiles obtained at lower temperatures (for example, those in Fig. 1). As seen from Eqs. (16), the semi-invariants of experimental elution profiles do not depend on injected amount. This is a characteristic feature of linear chromatography. Linear chromatography is valid when Eq. (9) holds true. This means that all the sites, even the strongest one, are almost empty. As explained above, this is not true for the first (solid line) elution profile in Fig. 1. To make linear chromatography conditions valid at 50 °C one has to decrease the injected amount even more but the sensitivity of our chromatograph does not allow one to do that.

The method of study of the surface heterogeneity described above is based on the fact that the kinetics of adsorption on different sites is different. This is its main distinction (emphasized in the Introduction) from the most popular method of the surface heterogeneity study which is based on the difference of the equilibrium isotherms on different sites. In the Langmuir model, the isotherm of adsorption on a site depends only on the local Henry constant K_H^i in Eq. (24). The latter depends on the residence time of an adsorbed molecule τ_i in Eq. (25) which, in turn, exponentially depends on the energy of adsorption ΔU_i in Eq. (26). Another factor which K_H^i depends upon is ν_i in Eq. (25). However, one can see from Eq. (7) that variation of ν_i on different sites is due to variation of the sticking coefficient α_i and the effective area of the site σ_i. We neglected the variation of ν_i on different sites in comparison to that of τ_i because the latter exponentially depends on the

variation of site's energies Eq. (26). Thus the only parameter in our model that determines the equilibrium adsorption on an i-site is τ_i. One can see from Eqs. (6) and (10) that τ_i determines also the kinetics of adsorption on a site. Thus in the Langmuir model, the adsorption equilibrium and the kinetics of adsorption are intrinsically connected: the stronger is the site, the longer it holds an adsorbed molecule, the larger is its local Henry constant (the steeper is the local isotherm), and the slower is the kinetics of adsorption on that site. Therefore, the method described in this paper and those using adsorption isotherms with the local Langmuir isotherm to determine the surface heterogeneity are, in fact, based on the same foundation: both of them use the variation of the residence time τ_i on different sites to determine the surface heterogeneity.

5. Conclusion

Thus, the method of studying surface heterogeneity described in this paper is based on the variation of kinetics of adsorption on different sites of a heterogeneous surface and works in the area of linear chromatography. This is in contrast with conventional method of studying surface heterogeneity by IGC which is based on nonlinear chromatography and uses ECP approximation (see Section 1) that totally neglects kinetics of adsorption and is based only on adsorption thermodynamics.

Linear chromatography is a rigorous model but condition of its applicability is very restrictive, especially for heterogeneous surfaces. In fact, it follows from this study that one can apply the method described in this paper only to open (non-porous) and weakly heterogeneous surfaces. In principle, this can always be achieved because the heterogeneity of a surface depends on a probe molecule.

Besides, the heterogeneity of a surface with respect to the residence time of a probe molecule (that is important for IGC) depends on temperature. It follows from the above results that the surface of E-glass can be considered as homogeneous with respect to adsorption of benzene at 100 °C and as heterogeneous with respect to the same probe molecule at 50 °C. This allowed us to determine some

important kinetic characteristic of adsorption of benzene on E-glass: sticking coefficient and residence time.

One can consider the method developed in this paper and that commonly used for the surface heterogeneity study (ECP described in Section 1) as the limiting cases of some more general model that is still to be developed. This model should either extend ECP to take into account kinetics of adsorption and column effects or extend the method described in this paper to account for nonlinearity of the adsorption isotherm. In this work, we have made only the first step in which we determined some basic relationships but had to make some sweeping approximations. These are first of all the Gaussian distribution of sites in energy and constancy of τ_0 (entropy of adsorption) for all the sites. We hope to remove those approximations in the course of our future work.

6. Nomenclature

A	Specific surface of column packing
a_m	Molecular area of probe molecule
C	Concentration of solute in mobile gas phase
C_0	Standard value of C
D	Effective diffusion coefficient of the solute in the mobile phase
F	Cross section area of column (tube)
h_0	Molar enthalpy of solute in ideal gas state at $C = 1/\nu\tau_0$
K_H^i	The Henry constant for i-sites
L	Length of column
M	Molecular mass of solute
m_1	First absolute moment of chromatographic peak
m_1^0	m_1 For non-adsorbing solute (methane)
N_{in}	Total amount of injected solute
N_A	The Avogadro number
N_{tot}	Total number of adsorption sites in column
q	Concentration of solute in immobile solid phase
R	Gas constant
s_0	Molar entropy of solute in ideal gas state at $C = 1/\nu\tau_0$

s_{th}^i	Mean thermal entropy of molecule adsorbed on site of i-kind
T	Absolute temperature
t	Time
U_{min}^i	Minimal energy of molecule adsorbed on site of i-kind
u	Average mobile phase velocity
V_{in}	Volume of injector
Z_{ads}^i	Partition function of molecule adsorbed on site of i-kind
z	Coordinate along column

Greeks

α_i	Accommodation coefficient for the i-site
Γ	Number of adsorbed molecules (adsorption) per unit area
Γ_i	Number of occupied sites of i-kind per unit area
Γ_i^0	Total number of sites of i-kind per unit area
Γ^0	Total number of adsorption sites per unit area
ϵ	Fraction of mobile phase volume in column (porosity)
ϵ_{th}^i	Mean thermal energy of molecule adsorbed on site of i-kind
κ_i	i-Semi-invariant of chromatographic peak
κ_i^0	κ_i For non-adsorbing solute
μ_i'	Free energy of molecule adsorbed on i-site
μ_i	i-Central moment of chromatographic peak
μ	Chemical potential of adsorbate
ν_i	$\nu_i C$ is the number of impacts of gas molecules at gas concentration C on i-adsorption site per unit time
ν	Some standard value of ν_i
ρ	Density of packing material
σ_i	Area of i-site
σ	Standard deviation of chromatographic peak
σ_0	σ For non-adsorbing solute (methane)
σ_g	Standard deviation of Gaussian distribution
τ_i	Mean time of adsorption (residence time) on i-site
τ	Some standard value of τ_i

τ_i^0	Pre-exponential constant in the Frenkel equation for i-site
τ_0	Standard value of τ_i^0
θ_i	Coverage of sites of i-kind
υ	Flow-rate of the carrier gas

Acknowledgements

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