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A. Waksmundzki[a]; S. Sokolowski[a]; J. Rayss[a]; Z. Suprynowicz[a]; M. Jaroniec[a]
[a] DEPARTMENT OF PHYSICAL CHEMISTRY, INSTITUTE OF CHEMISTRY, LUBLIN, NOWOTKI, POLAND

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Application of Gas-Adsorption Chromatography Data to Investigation of the Adsorptive Properties of Adsorbents

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A. WAKSMUNDZKI, S. SOKOLOWSKI, J. RAYSS,
Z. SUPRYNOWICZ, and M. JARONIEC

DEPARTMENT OF PHYSICAL CHEMISTRY
INSTITUTE OF CHEMISTRY UMCS
20031 LUBLIN, NOWOTKI 12, POLAND

Abstract

In this paper we discuss the expression for the total retention volume, treated as a pressure function, and the analytical methods for determination of the energy distribution function directly from gas-adsorption chromatagraphy data. It is shown that by assuming Jovanovich and Langmuir local behavior for the adsorbed phase, the total retention volume may be expressed as Laplace and generalized Stieltjes transforms, respectively. The utility of our theoretical considerations is demonstrated for the hexane–Polsorb C adsorption system.

INTRODUCTION

Among the most important applications of gas-adsorption chromatography are measurements of various physicochemical quantities and functions describing adsorptive properties. This problem is most important from both theoretical and practical points of view. The fundamental papers concerning this problem are the monographs of Janak (*1*), Keulemans (*2*), Giddings (*3*), Cremer (*4*), and Huber (*5*). The majority of authors have assumed that an adsorbent surface is energetically homogeneous. The effects of adsorbent heterogeneity have been discussed only in a qualitative way (*6–9*).

In our previous papers we have discussed an approximate method for evaluating the adsorbent heterogeneity from retention volume treated as a pressure function (*10–12*). In this paper we discuss analytical methods for the determination of the energy distribution function directly from gas-adsorption chromatography data.

THEORY

General Considerations

The starting point for the essential part of our theory is the well-known equation, first developed by Conder and Purnell (*13*), in the form valid for all concentrations:

$$V_N = j\frac{\partial N(\rho_0)}{\partial \rho_0} \tag{1}$$

where V_N is the absolute retention volume, j is the James-Martin compressibility factor, N is the amount of adsorbate in the surface phase, i.e., where the adsorption process takes place, and ρ_0 is adsorbate density in the free gas-phase. In the above equation the surface phase is treated as energetically homogeneous. In other words, $\varepsilon(\mathbf{r})$, where ε is the energy of adsorption and $\mathbf{r}$ is the position in the adsorption space, is a function of the perpendicular distance z from a solid surface only, i.e., $\varepsilon(\mathbf{r}) = \varepsilon(z)$.

In the case of an energetically heterogeneous stationary phase, the total chromatographic process can be treated as the sum of elementary processes taking place in small patches of the solid surface which are characterized by the value ε_i. Defining in this way n contributions to the total volume retention $V_{N,t}$, we obtain

$$V_{N,t} = j\sum_{i=1}^{n} \frac{\partial N_i(\rho_0, \varepsilon_i)}{\partial \rho_0} = j\sum_{i=1}^{n} \frac{\partial \Theta_l(\rho_0, \varepsilon_i)}{\partial \rho_0} N_{m,i} \tag{2}$$

In the above, $N_i(\rho_0, \varepsilon_i)$ is the amount of adsorbate on the surface patch, characterized by adsorption energy ε_i, $N_{m,i}$ denotes the capacity of the ith surface patch, and $\Theta_l(p, \varepsilon_i)$ is the local adsorption isotherm (*14, 15*). Summation (2) can be substituted by integration:

$$V_{N,t} = j\int_\Omega \frac{\partial \Theta_l(\rho_0, \varepsilon_i)}{\partial \rho_0} \chi(\varepsilon)\, d\varepsilon \tag{3}$$

where Ω is the range of possible variations ε, and $\chi(\varepsilon)$ is the energy distribution function satisfying the normalization condition

$$\int_\Omega \chi(\varepsilon)\, d\varepsilon = N_m \tag{4}$$

where N_m denotes the capacity of the surface phase. Assuming idealness of the volume phase, from Eq. (3) we obtain (*10–12*)

$$V_{N,t}(p) = jRT \int_{\Omega} \frac{\partial \Theta_l(p, \varepsilon)}{\partial p} \chi(\varepsilon)\, d\varepsilon \tag{5}$$

Let us analyze Eq. (5) more closely. Out of its functions, the only one accessible for experimental measurements is function $V_{N,t}(p)$. The analytical form of the function $\partial\Theta_l(p, \varepsilon)/\partial p$ can be determined by assuming a priori the adsorption model in the energetically homogeneous patch of the surface phase.

In this way we have a direct possibility of calculating the energy distribution function from Eq. (5). For this purpose the integral Eq. (5), which is a Fredholm integral equation of the first kind, should be solved. The case of linear chromatography, when

$$\frac{\partial \Theta_l(p, \varepsilon)}{\partial p} = \frac{1}{K} \exp\left(\frac{\varepsilon}{RT}\right) \tag{6}$$

where K is Henry's constant, has been discussed in detail (*10–12*). In this paper the problem of direct solution of the integral Eq. (5) will be presented for the case when the function $\partial\Theta_l(p, \varepsilon)/\partial p$ is the function p, i.e., the distribution coefficient is function ρ_0. We shall assume two models defining the functional relation $\partial\Theta_l/\partial p$: those of Jovanovich (*16*) and Langmuir. As will be shown below, in the first case we obtain a particularly simple form of Eq. (5), i.e., the form of a Laplace transform (*17*), whereas in the second case we obtain a generalized Stieltjes transform (*18*).

Jovanovich Local Model

The Jovanovich isotherm, originally introduced for kinetic considerations (*16*) and more recently on the basis of statistic mechanics (*19*), has the form

$$\Theta_l(p_1\varepsilon) = 1 - \exp\left\{-\frac{p}{K}\exp\left(\frac{\varepsilon}{RT}\right)\right\} \tag{7}$$

Assuming further that $\Omega = [\varepsilon_a, \infty]$ (*20*), we obtain from Eqs. (5) and (7)

$$V_{N_1,t}(p) = j\frac{RT}{K}\int_{\varepsilon_a}^{\infty} \exp\left(\frac{\varepsilon}{RT}\right)\exp\left\{-\frac{p}{K}\exp\left(\frac{\varepsilon}{RT}\right)\right\}\chi(\varepsilon)\, d\varepsilon \tag{8}$$

Applying the substitutions

$$t = \frac{p_s}{K}\left[\exp\left(\frac{\varepsilon}{RT}\right) - \exp\left(\frac{\varepsilon_a}{RT}\right)\right] \text{ and } x = \frac{p}{p_s} \tag{9}$$

we obtain

$$G(x) = \int_0^\infty \exp(-tx)F(t)\,dt \tag{10}$$

where

$$G(x) = \frac{V_{N,t}(x)p_s}{j(RT)^2}\exp\left[\frac{xp_s}{K}\exp\left(\frac{\varepsilon_a}{RT}\right)\right] \tag{11}$$

$$F(t) = \chi[\varepsilon(t)]$$

where p_s is the saturated vapor pressure. In this way the problem of determining the function $\chi(\varepsilon)$ has been reduced to the solution of a Laplace transform. This problem may be solved by using of Papoulis method (*21*) of expanding the function into a series of Laguerr functions

$$F(t) = \sum_{k=0}^{\infty} C_k\varphi_k(t) \tag{12}$$

where

$$\varphi_k(t) = \frac{d^k}{dt^k}\left[\frac{t^k}{k!}e^{-t}\right] \tag{13}$$

Approximating the experimental data $G(x)$ by the polynomial, we obtain

$$G(x) = \sum_{k=0}^{s} a_k x^k \tag{14}$$

There results in an instant relationship between the coefficients numerically determined from Eq. (14) and the coefficients C_k from Eq. (12):

$$C_k = \sum_{j=0}^{k}\binom{k}{j}a_{k-j} \tag{15}$$

Therefore, by replacing the infinite series by their finite partial sum in numerical calculations, we obtain

$$\chi[t(\varepsilon)] = \sum_{k=0}^{s} C_k\frac{d^k}{dt(\varepsilon)^k}\left[\frac{t(\varepsilon)^k}{k!}e^{-t(\varepsilon)}\right] \tag{16}$$

Langmuir Local Model

When we assume a Langmuir model of local adsorption, i.e.,

$$\Theta_l(p, \varepsilon) = \left[\frac{K}{p}\exp\left(-\frac{\varepsilon}{RT}\right) + 1\right]^{-1} \tag{17}$$

we obtained the following form of Eq. (5):

$$V_{N,t}(p) = j\frac{RT}{K}\int_{\varepsilon_a}^{\infty} \frac{\exp(\varepsilon/RT)}{[1 + \exp(\varepsilon/RT)(p/K)]^2}\chi(\varepsilon)\,d\varepsilon \tag{18}$$

Using the substitutions

$$\begin{aligned} \exp\left(\frac{\varepsilon}{RT}\right) &= u + \exp\left(\frac{\varepsilon_a}{RT}\right) \\ \frac{K}{p} &= y - \exp\left(\frac{\varepsilon_a}{RT}\right) \end{aligned} \tag{19}$$

we reduced Eq. (18) to the form of a generalized Stieltjes transform:

$$g(y) = \int_0^{\infty} \frac{f(u)}{(u + y)^2}\,du \tag{20}$$

where

$$f(u) = \chi[\varepsilon(u)] \tag{21}$$

$$g(y) = V_{N,t}[p(y)]\frac{k}{jRT}p^2(y) \tag{22}$$

The transform will be solved for the case where the function is given in the form of the series

$$g(y) = \sum_{i=1}^{n} A_i y^{2-[1/(i+k)]} \qquad k > 1 \tag{23}$$

The above approximation of the experimental function is equal to the approximation of the total adsorption isotherm with Freundlich's series of isotherms. As shown in our studies, such an approximation is very effective (*22*). Thus the following form of energy distribution function is obtained from the solution of the generalized Stieltjes transform (*23*):

$$\chi(\varepsilon) = \sum_{i=1}^{n} \frac{1}{\Gamma[1/(i + k)]\Gamma[(i + k + 1)/(i + k + 2)]} \times \left\{\exp\left(\frac{\varepsilon}{RT}\right) - \exp\left(\frac{\varepsilon_a}{RT}\right)\right\}^{-1/(i+k)} \tag{24}$$

where Γ is the so-called gamma function.

NUMERICAL CALCULATIONS PROCEDURE

The method for numerical calculation is analogous in both cases. In the case of the Jovanovich model, the experimental function $G(x)$ is approximated with polynomials by using the method of least squares. The coefficients a_k determined in this way serve for the numerical determination of the coefficients C_k from Eq. (15). In accordance with Eq. (16), knowledge of the coefficients C_k allows us to determine the form of the function.

In the case of the Langmuir model of local adsorption, we approximate the experimental data $g(y)$ with the Series (23), choosing numerically the values of the parameters $\{A_i\}$, n, k $(i = 1, 2, \ldots, n)$. The knowledge of the coefficients $\{A_i\}$, n, k allows us to determine the function $\chi(\varepsilon)$ from Eq. (24).

EXPERIMENTAL

In order to illustrate the use of gas-adsorption chromatography data in evaluating the energy distribution function, we have carried out chromatographic measurements and calculations for hexane on Polsorb C. The adsorbent-Polsorb C, produced by Permedia, Lublin, Poland, has a granule size of 0.1 to 0.2 mm. The properties of Polsorb C (as chromatographic packing) were discussed previously (*24*, *25*). The solute, hexane, was produced by Poly Science Corp. Hydrogen was used as the carrier gas, passed over 5A and 6A molecular sieves. The flow rate was 50 ml/min, and the chromatographic column, 1 m × 4 mm i.d., contained 21 g of adsorbent. The temperature was 348.2°K. The above condition were choosen to eliminate dynamics effects as far as possible. The apparatus was a Chromatoprep N-502. The results of our measurements are shown in Fig. 1.

DISCUSSION

By using these experimental data for $V_{N,t}(p)$, we have calculated the energy distribution function $\chi(\varepsilon)$. The Langmuir local isotherm was used for calculations. Numerical calculations were performed according to the general treatment described under "Numerical Calculations Procedure." The constant K was calculated according to the Hobson relation (*26*), and was equal to 3.04863×10^6 Torr, and $\varepsilon_a = 0$ (*14*). The line in Fig. 2 denotes the energy distribution function for hexane on Polsorb C. It appears from Fig. 1 that two kinds of adsorption sites exist. Such a conclusion is in excellent agreement with our previous studies of Polsorb C (*24*).

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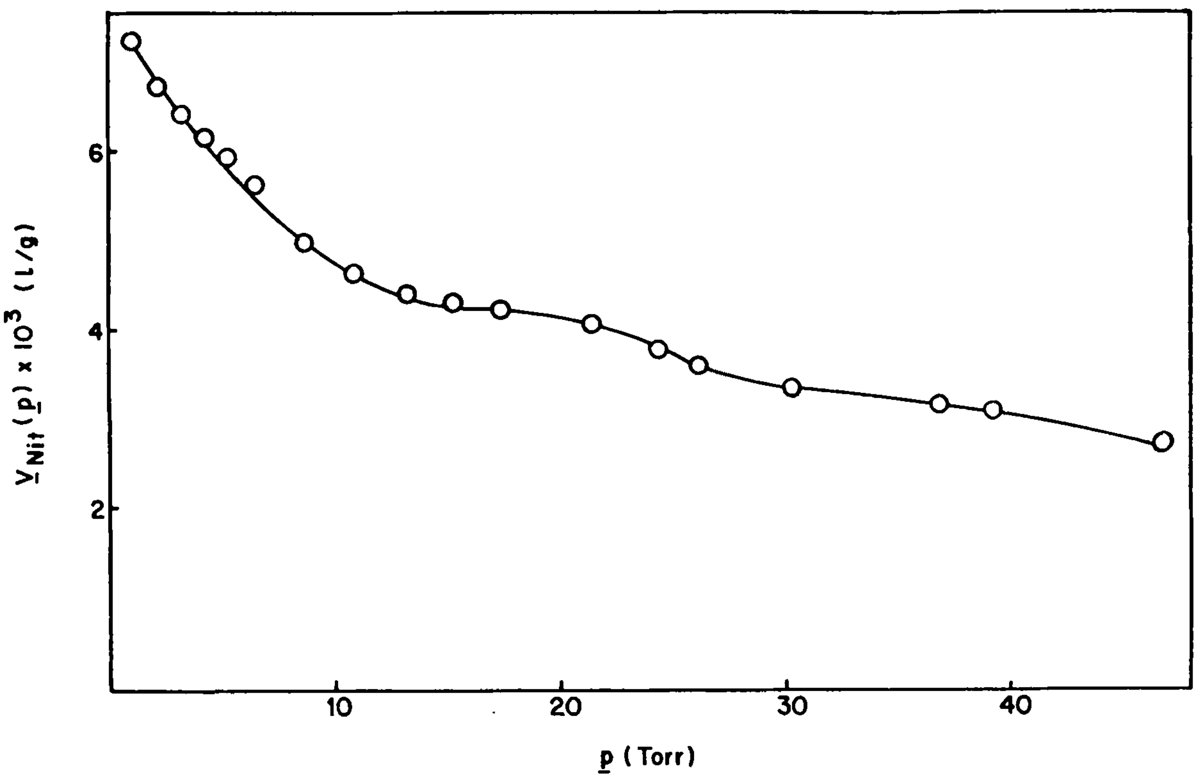

FIG. 1. Experimental values of the retention volume of hexane, corresponding to different pressures in the free gas phase.

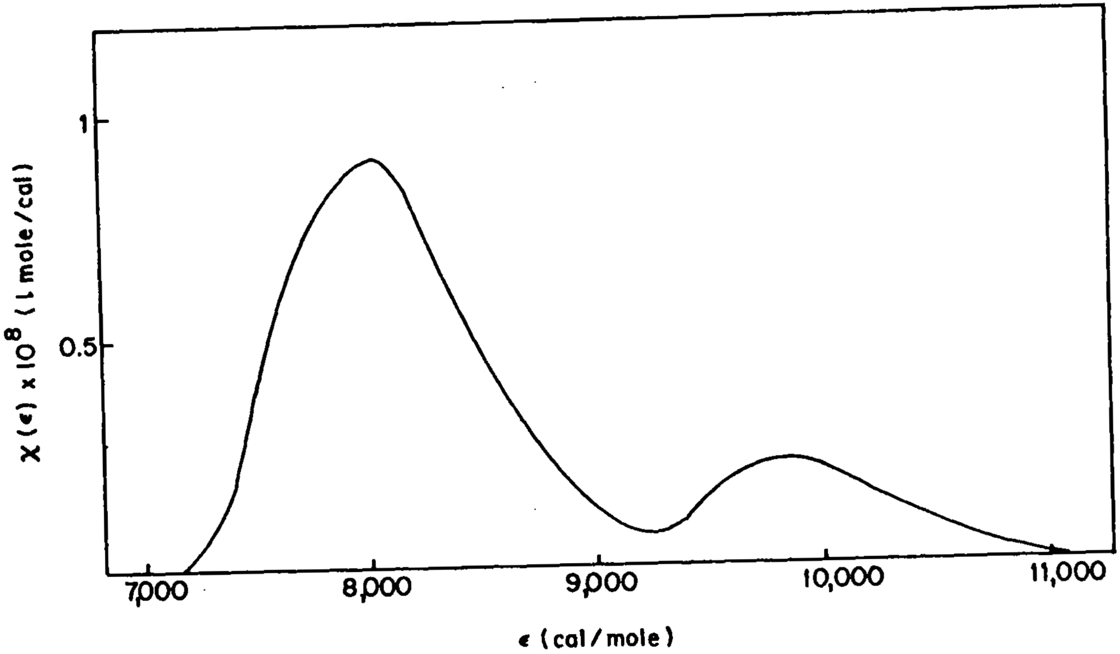

FIG. 2. The energy distribution function for hexane on Polsorb C.

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