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NOTE

Some Remarks on Application of Gas-Adsorption Chromatography Data for Investigations of the Adsorptive Properties of Adsorbents

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Abstract

The consequance of assuming Jovanović local adsorption model are discussed on the basis of integral equation for total retention volume for heterogeneous surfaces.

In our previous paper (*1*) we discussed the expression for the total retention volume and a method for determining the energy distribution function. It was shown that, assuming Jovanović (*2*) behavior for the adsorbed phase, the total retention volume may be expressed as a Laplace transform. In this note we discuss another solution of this problem.

Assuming Jovanović local behavior, the total adsorption isotherm on a heterogeneous surface $\Theta_t(p)$ may be written as follows (*3*):

$$1 - \Theta_t(p) = \int_0^\infty \exp\left[-\frac{p}{K}\exp\left(\frac{\varepsilon}{RT}\right)\right]\chi(\varepsilon)\, d\varepsilon \qquad (1)$$

where $\chi(\varepsilon)$ is the energy distribution and K is a constant. Using the sub-

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stitutions $x = \varepsilon/RT$; $p = \exp(-y)$ from Eq. (1), we obtain

$$\Psi(y) = \frac{1 - \Theta_t(p)}{RT} = \int_0^\infty \exp\left[-\frac{1}{K}\exp(x - y)\right]\chi(x)\, dx \qquad (2)$$

Multiplication by the intergrating factor e^{-sy} and intergration over $(-\infty, \infty)$ yields

$$\bar{\Psi}(s) = \Gamma(s)K^s \int_0^\infty \exp(-sx)\chi(x)\, dx \qquad (3)$$

where $\Gamma(s)$ denotes the gamma function and $\bar{\Psi}(s)$ is the bilateral Laplace transform of the $\Psi(y)$:

$$\bar{\Psi}(s) = \int_{-\infty}^{\infty} \exp(-sy)\Psi(y)\, dy \qquad (4)$$

The analytical solution of Laplace transform (3) may be found from the following rule

$$\chi(x) = \frac{1}{2\pi i}\int_{\beta - i\infty}^{\beta + i\infty} \exp(sx)\frac{\bar{\Psi}(s)}{\Gamma(s)K^s}\, ds \qquad (5)$$

where β is any point of real positive semiaxis. Expanding $1/\Gamma(s)$ into a series

$$\frac{1}{\Gamma(s)} = \sum_{j=1}^{\infty} \alpha_j s^j \qquad (6)$$

and substituting this expansion into Eq. (3), we obtain a general equation for analytical solution of Eq. (5) with respect to $\chi(\varepsilon)$.

$$\chi(\varepsilon) = \sum_{j=1}^{\infty} \alpha_j \frac{\partial^j}{\partial \varepsilon^j}\left\{-\Theta_t\left[\exp\left(\ln k - \frac{\varepsilon}{RT}\right)\right]\right\}(RT)^{j-1} \qquad (7)$$

The coefficients α_j's can be evaluated from the following system of successive equations

$$\begin{aligned} \alpha_1 &= 1 \qquad \alpha_{k+1} = \frac{1}{k+1}\sum_{r=0}^{k} (-1)^{r+1}\, \delta_{r+1}\alpha_{k-r+1} \\ \delta_1 &= \gamma \qquad \delta_{r>1} = \zeta(r) \end{aligned} \qquad (8)$$

where γ is Euler's number, and $\zeta(r)$ denotes the Weierstrass function. According to

$$V_N(p) = FRT\frac{\partial N_t(p)}{\partial p} \qquad (9)$$

where N_t is the total amount adsorbed, V_N is retention volume, F denotes the James-Martin compressibility factor, the expression for $\chi(\varepsilon)$ may be rewritten as

$$\chi(\varepsilon) = \sum_{j=1}^{\infty} \alpha_j \frac{\partial^{j-1}}{\partial \varepsilon^{j-1}} \left\{ V_N \left[\exp\left(\ln K - \frac{\varepsilon}{RT} \right) \right] \exp\left(-\frac{\varepsilon}{RT} \right) \right\} \frac{(RT)^{j-3}}{F} K \tag{10}$$

As it was shown, the total retention volume as a pressure function may be described by the following equation (*4*)

$$V_N(p) = \exp\left(\sum_{k=0}^{n} B_k p^k \right) \tag{11}$$

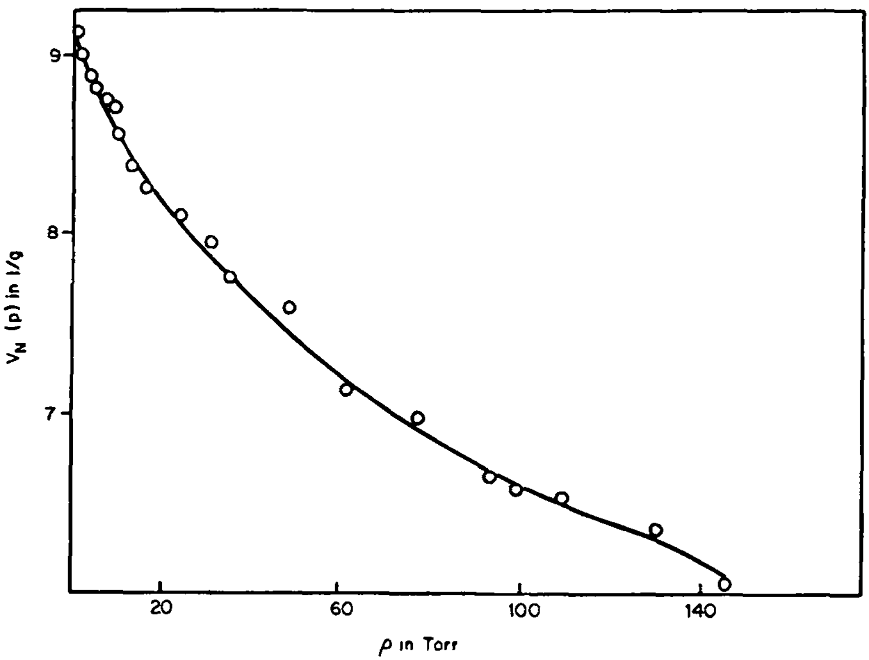

FIG. 1. The retention volume as a pressure function for hexane on silica gel modified with *n*-octanol at 376°K. The solid line denotes the $V_N(p)$ function calculated according to Eq. (11), and the circles denote the experimental data.

where B_k's are constants. Thus, from Eqs. (10) and (11), we have

$$\chi(\varepsilon) = \sum_{j=1}^{\infty} \alpha_j \frac{\partial^{j-1}}{\partial \varepsilon^{j-1}} \left\{ \exp\left[\sum_{k=0}^{n} B_k K^k \exp\left(-\frac{\varepsilon k}{RT} \right) \right] \exp\left(-\frac{\varepsilon}{RT} \right) \right\} \frac{(RT)^{j-3}}{F} K \tag{12}$$

The above result is in excellent agreement with our previous investigations (*4*).

In order to illustrate the use of the above-described procedure in evaluating the energy distribution function, we have carried out chromatographic measurements and numerical calculations for hexane on silica gel modified with *n*-octanole in an autoclave at 523 °K (the pressure of the *n*-octanole vapor was 25 atm, the time of modification was 6 hr). The surface area of the adsorbent determined by using the thermal desorption of nitrogen method was 151.9 m^2/g. The granule size was 0.15 to 0.20 mm.

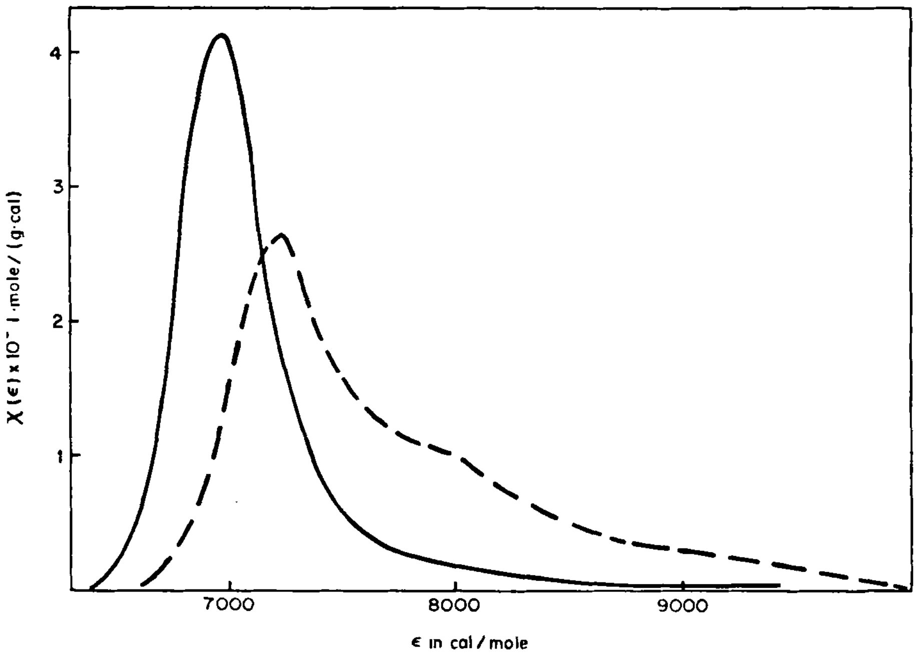

FIG. 2. The energy distribution functions for hexane on silica gel modified with *n*-octanol at 376.4 °K. The solid line denotes the $\chi(\varepsilon)$ calculated by summing up Eq. (12) to $j = 3$, and the dashed line is for a summing up to $j = 1$.

The hexane and silica gel were produced by POCh, Gliwice, Poland. Hydrogen was used as carrier gas, passed over 4A and 5A molecular sieves. The flow rate was 45 ml/min, the chromatographic column 2 m × 4 mm contained 16.79 g of the adosrbent. The temperature was 376.4°K. The apparatus used was Giede 18.3 (GDR). The results of our measurements are presented in Fig. 1.

In accordance with Eq. (11), the experimental data were approximated by polynomial $\ln V_N(p) = \sum_{k=0}^{n} B_k p^k$ using the method of least squares. The best polynomial was that of the third degree, the sum of square deviations was 1.2837×10^{-7}, and the mean standard error was
The constant K was used 312.1×10^4 Torr (*1*, *4*). The solid line in Fig. 2 denotes the energy distribution function calculated according to Eq. (12) by using $j = 3$, whereas the dashed line was evaluated from Eq. (12) for $j = 1$.

REFERENCES

1. A. Waksmundzki, S. Sokołowski, J. Rayss, Z. Suprynowicz, and M. Jaroniec, *Separ. Sci.*, *11* (1), 29 (1976).
2. D. S. Jovanović, *Colloid Poly. Sci.*, *235*, 1203 (1970).
3. S. Sokołowski, *Vuoto*, *8*, 45 (1975).
4. Z. Suprynowicz and M. Jaroniec, *J. Chromatogr.*, In Press.

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