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Mieczyslaw Jaroniec[a][b]; Richard Madey[a]; Xiaochun Lu[a]
[a] DEPARTMENT OF PHYSICS, KENT STATE UNIVERSITY KENT, OHIO [b] Institute of Chemistry, M. Curie-Sklodowska University, Lublin, Poland

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Application of Gas–Solid Adsorption Chromatography for Characterizing Adsorbent Heterogeneity

MIECZYSLAW JARONIEC,* RICHARD MADEY,
and XIAOCHUN LU
DEPARTMENT OF PHYSICS
KENT STATE UNIVERSITY
KENT, OHIO 44242

Abstract

A new equation for the total net retention volume is used to describe pressure-dependent retention measurements for cyclohexane and cyclohexene on wide-pore and narrow-pore silicas. This equation gives a good representation of the above experimental data. Parameters of this equation permit evaluation of the distribution functions that characterize the energetic heterogeneity of solid adsorbents.

INTRODUCTION

Gas–solid adsorption chromatography (GSC) is an attractive method for studying physicochemical properties of adsorbents and catalysts (*1*) including characterization of their adsorbent heterogeneity (*2*). For heterogeneous adsorbents, Suprynowicz et al. (*3*) showed that the pressure-dependent net retention volume may be represented by an integral equation which contains an energy distribution function that characterizes adsorbent heterogeneity. Although Waksmundzki et al. (*4*), Gawdzik et al. (*5*), and Leboda and Sokolowski (*6*) showed that GSC is useful for studying adsorbent heterogeneity, the lack of an analytical equation for the total net retention volume on a heterogeneous solid makes difficult a wider application of GSC measurements for evaluating this heterogeneity. The theory of GSC for heterogeneous solids formulated by Jaroniec et al. (*7*) permits the derivation of a simple equation for the total net retention volume, which is useful for analyzing pressure-dependent retention mea-

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*Permanent address: Institute of Chemistry, M. Curie-Sklodowska University, 20031 Lublin, Poland.

surements. In this paper the above-mentioned equation will be used to represent pressure-dependent retention volumes for cyclohexane and cyclohexene on wide-pore and narrow-pore silica gels in order to show its utility for characterizing gas–solid systems with emphasis on the evaluation of adsorbent heterogeneity.

THEORY

In accordance with the theoretical studies by Suprynowicz et al. (*3*) and Jaroniec et al. (*7*), the total net retention volume $V_{N,t}$ in GSC on a heterogeneous solid is represented by the following integral equation:

$$V_{N,t}(p) = \int_{\epsilon_m}^{\infty} V_N^*(p,\epsilon)F_0(\epsilon)d\epsilon \qquad (1)$$

where

$$V_N^* = jRT(\partial\theta/\partial p)_T \qquad (2)$$

and

$$\int_{\epsilon_m}^{\infty} F_0(\epsilon)d\epsilon = n_t^0 \int_{\epsilon_m}^{\infty} F(\epsilon)d\epsilon = n_t^0 \qquad (3)$$

Here p is the adsorbate pressure, ϵ is the adsorption energy, ϵ_m is the minimum adsorption energy, V_N^* is the retention volume associated with the relative surface coverage θ, n_t^0 is the monolayer capacity of a heterogeneous solid surface, j is the correction factor (*4, 8*), $F(\epsilon)$ is the distribution function of the adsorption energy ϵ, T is the absolute temperature, and R is the universal gas constant.

Equation (2) represents the local retention on adsorption sites with the adsorption energy ϵ. To derive an equation for V_N^*, any adsorption isotherm equation that represents adsorption on an energetically-homogeneous surface may be used. Suprynowicz et al. (*3*) showed that the Jovanovic-type equation for the adsorption isotherm generates a simple equation for V_N^*:

$$V_N^* = jRTK \exp(-Kp) \qquad (4)$$

where

$$K = K_0(T) \exp(\epsilon/RT) \qquad (5)$$

Here K is Henry's constant for an energetically-homogeneous surface, and K_0 is the pre-exponential factor of this constant. Because Eq. (4) is a function of K, it is convenient to express the total net retention volume $V_{N,t}$ in terms of the distribution function of K. For a heterogeneous surface, the different adsorption energies generate different values of K (cf., Eq. 5); consequently, the distribution function $G(K)$ may be used to characterize the adsorbent heterogeneity (*2*). Combination of the integral Eq. (1) with Eq. (4) gives

$$V_{N,t} = jRTn_t^0 \int_{K_m}^{\infty} K \exp(-Kp)G(K)dK \tag{6}$$

where

$$G(K) = (RT/K)F[\epsilon(K)] \tag{7}$$

and

$$K_m = K_0 \exp(\epsilon_m/RT) \tag{8}$$

In a previous paper Jaroniec et al. (*7*) showed that the gamma-type distribution function is useful for characterizing adsorbent heterogeneity. This distribution function, presented in terms of the average value $\overline{K}'$ and the dispersion σ_K, has the following form:

$$G(K) = [(\overline{K}'/\sigma_K^2)^{(\overline{K}'/\sigma_K)^2}/\Gamma(\overline{K}'/\sigma_K)^2](K - K_m)^{(\overline{K}'/\sigma_K)^2-1} \times \exp[-(\overline{K}'/\sigma_K^2)(K - K_m)] \tag{9}$$

Here Γ denotes the gamma function. The average value $\overline{K}$ associated with the distribution function $G(K)$ (viz., Eq. 9) is given by

$$\overline{K} = K_m + \overline{K}' \tag{10}$$

The values $\overline{K}$ and σ_K characterize the distribution function $G(K)$.

Calculation of the integral that appears in Eq. (6) for the distribution function $G(K)$ defined in Eq. (9) gives the following equation for the total net retention volume $V_{N,t}$:

$$V_{N,t} = (V_{N,t}^0/\overline{K}) \exp(-K_m p)(1 + p\sigma_K^2/\overline{K}')^{-(\overline{K}'/\sigma_K)^2} \times [K_m + \overline{K}'(1 + p\sigma_K^2/\overline{K}')^{-1}] \tag{11}$$

where

$$V^0_{N,t} = \lim_{p\to 0} V_{N,t} = jRTn^0_t\bar{K} \tag{12}$$

Equation (12) results directly from Eq. (6) when $p \to 0$. The slope of the retention curve $V_{N,t}(p)$ at $p \to 0$ is expressed by

$$\left.\frac{\partial V_{N,t}}{\partial p}\right|_{p=0} = -V^0_{N,t}\left(\bar{K} + \frac{\sigma_K^2}{\bar{K}}\right) \tag{13}$$

Equations (12) and (13) characterize the behavior of the retention curve $V_{N,t}(p)$ in the region of low pressures.

RESULTS AND DISCUSSION

In this paper, Eq. (11) will be used to describe the pressure-dependent retention volume $V_{N,t}$ for cyclohexane and cyclohexene on two different samples of silica gel at 399.5 K. One sample of silica gel (wide-pore silica) possesses pores with an average pore radius equal to about 14 nm and a specific surface area equal to about 35 m^2/g; the other sample of silica (narrow-pore silica) possesses pores with an average pore radius equal to 2 nm and a specific surface area equal to 180 m^2/g. The above-mentioned experimental measurements were described in detail by Waksmundski et al. (*4*). To verify Eq. (11), we take these retention volumes in the same

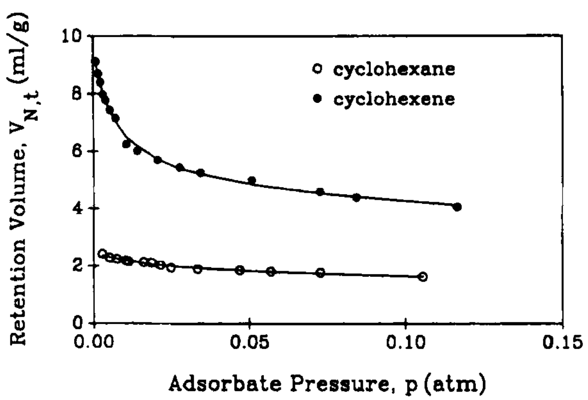

FIG. 1. Comparison of the experimental net retention volumes (circles) with the theoretical lines calculated according to Eq. (11) for cyclohexane and cyclohexene on the wide-pore silica at 399.5 K.

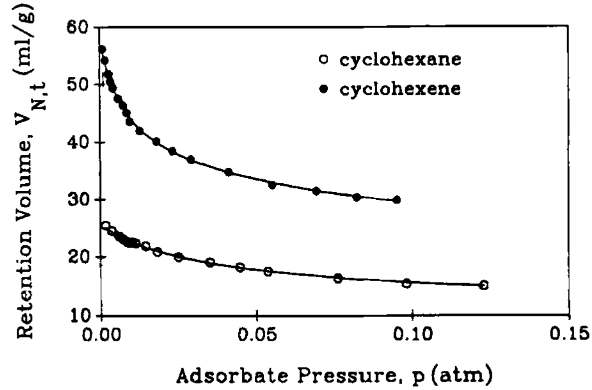

FIG. 2. Comparison of the experimental net retention volumes (circles) with the theoretical lines calculated according to Eq. (11) for cyclohexane and cyclohexene on the narrow-pore silica at 399.5 K.

pressure region for all chromatographic systems studied; the experimental points taken for analysis were measured at adsorbate pressures up to about 0.1 atm. Figures 1 and 2 present the experimental retention volumes $V_{N,t}$ plotted as circles against the adsorbate pressure p for all systems studied in comparison to the theoretical curves calculated according to Eq. (11). It follows from these figures that Eq. (11) gives an excellent representation of the total net retention volume for all systems studied. Table 1 contains the parameters $V_{N,t}^0$, K_m, $\overline{K}'$, and σ_K; this table also contains the average value $\overline{K} = K_m + \overline{K}'$. Because $V_{N,t}^0$ may be evaluated by extrapolation of the retention volume for an adsorbate pressure equal to zero, Eq. (11) possesses only three unknown parameters (K_m, $\overline{K}'$, σ_K) which were determined by the least-squares approximation method.

TABLE 1
Retention Parameters for Cyclohexane and Cyclohexene on Wide-Pore and Narrow-Pore Silicas at 399.5 K Calculated According to Eq. (11)

	Wide-pore silica		Narrow-pore silica	
Parameter	Cyclohexane	Cyclohexene	Cyclohexane	Cyclohexene
$V_{N,t}^0$ (ml/g)	2.46 ± 0.01	9.56 ± 0.01	25.7 ± 0.1	58.3 ± 0.1
K_m (atm^{-1})	1.20 ± 0.02	1.37 ± 0.02	0.98 ± 0.02	1.64 ± 0.02
$\overline{K}'$ (atm^{-1})	0.46 ± 0.02	1.43 ± 0.02	0.65 ± 0.02	1.22 ± 0.02
σ_K (atm^{-1})	4.9 ± 0.2	13.8 ± 0.2	4.9 ± 0.2	11.8 ± 0.2
$\overline{K}$ (atm^{-1})	1.66 ± 0.04	2.80 ± 0.04	1.63 ± 0.04	2.86 ± 0.04

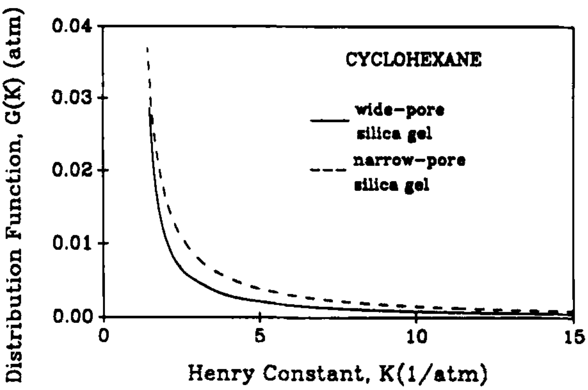

FIG. 3. Distribution function $G(K)$ calculated according to Eq. (9) for cyclohexane on the wide-pore and narrow-pore silicas.

Figures 3 and 4 show the distribution functions $G(K)$ calculated according to Eq. (9) for all chromatographic systems studied; however, Figs. 5 and 6 present the adsorption energy distribution functions (viz. Eq. 7) associated with the functions $G(K)$ shown in Figs. 3 and 4.

It follows from Figs. 4 and 5 that the distribution functions $G(K)$ calculated for wide-pore and narrow-pore silicas decrease exponentially. The narrow-pore silica shows almost the same energetic heterogeneity as the wide-pore silica because the dispersion values for the same adsorbate on

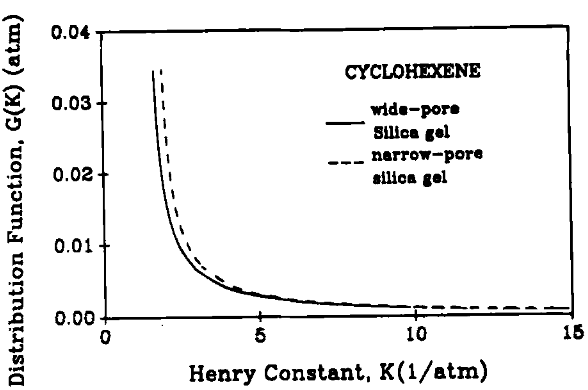

FIG. 4. Distribution function $G(K)$ calculated according to Eq. (9) for cyclohexene on the wide-pore and narrow-pore silicas.

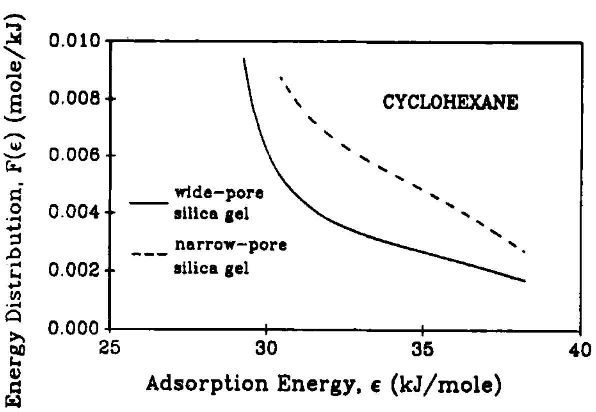

FIG. 5. Energy distribution function $F(\epsilon)$ for cyclohexane on the wide-pore and narrow-pore silicas.

both silicas are similar (cf. Table 1). Comparison of the dispersion values for cyclohexane and cyclohexene shows that cyclohexene is a better detector of the energetic heterogeneity of the silica surface than cyclohexane; the values of $\overline{K}$ and σ_K for cyclohexene on both silicas are significantly greater than those for cyclohexane (cf. Table 1). Because the interaction of cyclohexene with the silica surface is stronger than cyclohexane, this adsorbate is better for studying the energetic heterogeneity of the silica surface.

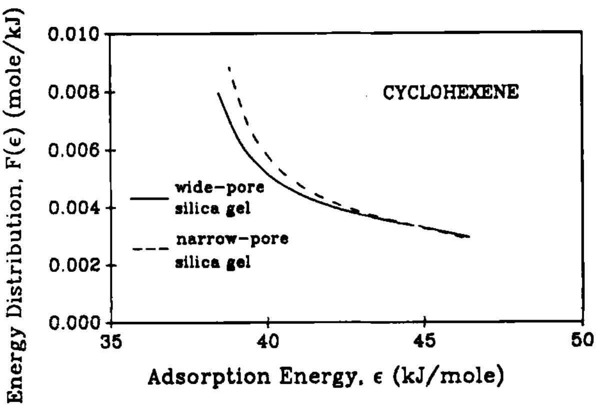

FIG. 6. Energy distribution function $F(\epsilon)$ for cyclohexene on the wide-pore and narrow-pore silicas.

CONCLUSION

It is shown that Eq. (11) associated with the gamma distribution function of Henry's constant describes well the pressure-dependent total net retention volume measured for hydrocarbons on wide-pore and narrow-pore silicas. Parameters of this equation permit calculation of the energy distribution functions that characterize the energetic heterogeneity of the silicas studied.

SYMBOLS

$F(\epsilon)$	normalized energy distribution function
$F_0(\epsilon)$	nonnormalized energy distribution function
$G(K)$	distribution function of Henry's constant
j	compressibility correction factor
K	Henry's constant for a homogeneous solid
$\overline{K}$	average value of Henry's constant
$\overline{K}'$	parameter of gamma distribution defined by Eq. (10)
K_m	minimum value of Henry's constant
K_0	pre-exponential factor in Henry's constant
n_t^0	monolayer capacity
p	adsorbate pressure
R	universal gas constant
T	absolute temperature
$V_{N,t}$	total net retention volume
$V_{N,t}^0$	extrapolated net retention volume at $p = 0$
V_N^*	retention volume for a homogeneous solid defined by Eq. (2)

Greek Letters

ϵ	adsorption energy
ϵ_m	minimum adsorption energy
σ_K	dispersion of Henry's constant
θ	relative surface coverage

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