

Application of a new numerical method for characterizing heterogeneous solids by using gas–solid chromatographic data

M. Heuchel^{*}, M. Jaroniec and R. K. Gilpin^{*}

Department of Chemistry, Kent State University, Kent, OH 44242 (USA)

(Received June 17th, 1992)

ABSTRACT

A new numerical method for calculating the adsorption energy distribution function from retention volume data obtained by gas–solid adsorption chromatography is introduced. The method, which considers the ill-posed character of the problem, is applicable to all physico-chemical models that describe the local adsorption on one kind of sites. Using Langmuir and Jovanovic local isotherms the distribution functions are determined for *n*-hexane and 1-hexene on a glass and for cyclohexane and cyclohexene on two silica gels with different pore sizes.

INTRODUCTION

In recent years the problem of finding the distribution of adsorption energies for heterogeneous adsorbents has been considered in detail (see refs. 1 and 2 and references cited therein). The application of gas chromatography (GC) has received a great deal of attention because the technique is an effective method of obtaining information about the interaction of gases with solid surfaces and can be used to collect both temperature- and pressure-dependent data [3]. Although both types of data have been used for evaluating energetic heterogeneity of adsorbents [1,4], pressure-dependent GC measurements appear especially appropriate for calculating the energy distributions of different solids [3,5].

There are two possible ways of using GC for calculating the distribution of adsorption energies.

One of these involves the initial calculation of the adsorption isotherm from retention measurements and then using an analytical or numerical algorithm for evaluating the energy distribution function from the isotherm. Recently, Guiochon and co-workers [6–8] have employed this approach to obtain the energy distributions for different alumina samples. Also, Roles and Guiochon [9–11] have reexamined the procedure of calculating adsorption isotherms and have discussed the precision and accuracy of this procedure. The above approach also has been used by Jagiello and co-workers [12–14] for studying energetic heterogeneity of modified silicas.

The other way of using GC measurements for calculating the energy distribution functions is based on theoretical equations, which relate directly retention volume measurement to the energy distribution. This later approach has a long history. In 1974 Rudzinski *et al.* [15] showed that the energy distribution function could be expressed as a series, which contained derivatives of the retention volume with respect to equilibrium pressure. According to this formulation, a crude approximation of the energy distribution is expressed by the retention volume,

Correspondence to: R. K. Gilpin, Department of Chemistry, Kent State University, Kent, OH 44242, USA.

^{*} Permanent address: Department of Chemistry, Leipzig University, O-7010 Leipzig, Germany.

whereas a better approximation of this distribution is obtained from the first derivative of the retention volume with respect to pressure. Rudzinski *et al.* [15] and later Boudreau and Cooper [16] used the latter more refined approach for calculating the energy distribution function of different solids. In 1976 Suprynowicz *et al.* [17] proposed an integral equation for expressing the overall retention volume in terms of the energy distribution function, which characterizes energetic heterogeneity of solid surfaces. These authors [17] and others [18] used this integral representation to propose simple analytical equations for calculating the energy distribution functions of different modified silicas. These works are discussed in recent monographs by Paryjczak [3] and Jaroniec and Madey [1]. Recently, this integral equation was solved analytically for a γ -type distribution in order to model the pressure dependence [5] and temperature dependence [4] of retention volume on energetically heterogeneous surfaces.

The integral representation of the overall retention volume on energetically heterogeneous surfaces gives a direct relationship between GC measurements and the energy distribution function. Therefore, numerical inversion of this integral with respect to the energy distribution function seems to be a promising approach for evaluating the energetic heterogeneity of different solids on the basis of GC measurements, which has not been discussed in the literature.

The aim of the current work has been to develop a numerical method for inverting the integral equation of the retention volume with respect to the energy distribution. In addition, problems associated with the calculation of the above distribution from GC data (*e.g.*, ill-posed nature of this numerical problem) have been considered. A regularization method [19] has been used for inverting the retention integral equation.

THEORY

One of the fundamental measurable quantity in chromatography is the net specific retention volume, V_N , which is defined as follows:

$$V_N = (V_R - V_M)/w \quad (1)$$

In the above V_R is the corrected retention volume, V_M is the void volume, and w is the adsorbent's mass.

For a heterogeneous surface consisting of L different types of adsorption sites ($l = 1, 2, \dots, L$) the total specific retention volume, $V_{N,i}$, can be represented as a sum

$$V_{N,i} = \sum_{l=1}^L V_{N,i,l} \quad (2)$$

where $V_{N,i,l}$ denotes the specific net retention volume of the l th type of adsorption sites. If n_l^0 is the total number of adsorption sites of the l th type, then a new retention volume $V_{N,i,l}^*$ can be introduced, and the total net specific retention volume rewritten in the following form

$$V_{N,i} = \sum_{l=1}^L n_l^0 V_{N,i,l}^* = n^0 \sum_{l=1}^L f_l V_{N,i,l}^* \quad (3)$$

where

$$V_{N,i,l}^* = V_{N,i,l}/n_l^0 \quad (4)$$

and

$$f_l = n_l^0/n^0, \quad n^0 = \sum_{l=1}^L n_l^0 \quad (5)$$

In the above n^0 denotes the total number of all adsorption sites and f_l is the fraction of adsorption sites of the l th type. If the total number of types of adsorption sites is large (*i.e.*, $L \rightarrow \infty$) then the summation in eqn. 3 can be replaced by an integration

$$V_{N,i}(p) = n^0 \int_{\varepsilon_m}^{\infty} V_{N,i}^*(p, \varepsilon) F(\varepsilon) d\varepsilon \quad (6)$$

where p is the equilibrium pressure, ε is the adsorption energy, ε_m is the minimum adsorption energy, and $F(\varepsilon)$ is the distribution function of ε normalized to unity:

$$\int_{\varepsilon_m}^{\infty} F(\varepsilon) d\varepsilon = 1 \quad (7)$$

In order to solve the integral eqn. 6 with respect to the energy distribution function $F(\varepsilon)$ it is necessary to assume a model for the local retention, $V_{N,i,l}^*$. Since adsorption determines retention in gas–solid chromatography, an expression for $V_{N,i,l}^*$ can be obtained by using the relationship between retention volume and the amount adsorbed, n_i . For an ideal gas the relationship between the total net specific retention volume, $V_{N,i}$, and n_i is given by:

$$V_{N,i}(p) = jRT(\partial n_i/\partial p)_T \quad (8)$$

In the above T is the absolute temperature, R is the universal gas constant and j is the compressibility correction factor [20]. Eqn. 8 is valid for an adsorbate which fulfils the ideal gas law. Since chromatographic measurements are usually carried out for very small amounts of the adsorbate at relatively high temperatures, the mobile phase can be considered as an ideal phase.

For a heterogeneous surface, the total amount adsorbed n_i , is a simple sum of the amounts adsorbed on the l th type of adsorption sites, n_l . If θ_l denotes the relative coverage of adsorption sites of the l th type, then the specific retention volume, $V_{N,i}^*$, defined by eqn. 3 is related to θ_l as follows:

$$V_{N,i}^*(p) = V_{N,i} n_i^0 = jRT(\partial\theta_l/\partial p)_T \text{ where } \theta_l = n_l/n_i^0 \quad (9)$$

Substitution of eqn. 9 into eqn. 6 gives the relationship between the total net specific retention volume, $V_{N,i}$, and the relative surface coverage $\theta(p, \varepsilon)$:

$$V_{N,i}(p) = jRTn_i^0 \int_{\varepsilon_m}^{\infty} [\partial\theta(p, \varepsilon)/\partial p]_T F(\varepsilon) d\varepsilon \quad (10)$$

According to eqn. 10 in order to determine $F(\varepsilon)$ it is necessary to know the isotherm $\theta = \theta(p, \varepsilon)_T$, which describes the adsorption of gas molecules on sites with adsorption energy ε . Since the GC sample's concentration is very small, the local adsorption $\theta(p, \varepsilon)$ can be modelled as a monolayer adsorption without lateral interactions. In the current paper, two well known models have been considered: the Langmuir and Jovanovic models.

The Langmuir model describes the case when adsorbed molecules form a localized monolayer without lateral interactions. For this model thermodynamics gives the following expression for the relative surface coverage θ

$$\theta(p, \varepsilon) = \frac{Kp}{1 + Kp} \quad (11)$$

where K is so-called Langmuir constant given by

$$K = K^0(T) \exp(\varepsilon/RT) \quad (12)$$

In the above $K^0(T)$ is the pre-exponential factor, which is the ratio of the partition function of an isolated molecule in the gas and adsorbed phases and thus, it reflects changes in the rotational, vibrational and translational degrees of freedom during the adsorption of an isolated molecule.

Detailed expressions for K^0 are given in a monograph by Clark [21]. In the current calculations a low-temperature approximation for K^0 was used, which according to Ross and Olivier [22] leads to the following equation:

$$K^0 = kT \left(\frac{2\pi m_a kT}{h^2} \right)^{3/2} \quad (13)$$

where m_a is the molecule mass, k is the Boltzmann constant and h is the Planck's constant.

The second local isotherm, proposed by Jovanovic [23], has the following form:

$$\Theta(p, \varepsilon) = 1 - \exp(-Kp) \quad (14)$$

where K is again the Langmuir constant given by eqn. 12. It has been shown elsewhere [1] that at moderate pressure eqn. 14 reduces to the Langmuir eqn. 11. Eqn. 14 has been used in earlier work to describe the local retention, $V_{N,i}^*$ [5].

NUMERICAL PROCEDURE FOR DETERMINING THE ENERGY DISTRIBUTION FUNCTION FROM RETENTION DATA

General considerations

From a mathematical point of view, eqn. 10 is a linear Fredholm integral equation of the first kind, which can be written in a more general form as follows:

$$g(y) = \int_a^b K(x, y) f(x) dx \quad (15)$$

The integral kernel $K(x, y)$ corresponds to the first derivative of the local adsorption isotherm with respect to the pressure $[\partial\theta(p, \varepsilon)/\partial p]_T$ where $\theta(p, \varepsilon)$ represents the physico-chemical model of adsorption on sites with the adsorption energy ε . The function $g(y)$ in eqn. 15 is a known function representing the experimentally measured retention volumes $V_{N,i}(p)$.

Expressions like eqn. 15 also have been derived for the adsorption of gases on energetically heterogeneous surfaces [2,24,25] and in microporous heterogeneous solids [1], overall thermodesorption rates [26], gas–solid virial coefficients [27], and liquid–solid adsorption excess quantities [28]. In the last 15 years numerous attempts have been made to calculate $f(x) \equiv F(\varepsilon)$ from experimental data, especially in the field of gas adsorption where the earliest

method, known as the “condensation approximation” (CA-method), was introduced by Roginskij in 1944 [29]. Distribution functions determined by this method are often used in other iterative procedures as a first approximation [1]. Some authors have assumed a-priori the shape of $F(\varepsilon)$, e.g., Gaussian or γ -distribution [1,5], and used these functions to integrate eqn. 10 analytically for local isotherms like the Jovanovic equation. The resulting expressions for the overall retention volume contain free parameters, which can be determined by a numerical least square fit using the experimental $V_{N,t}(p)$ data.

In spite of their elegance, every analytical representation has two main disadvantages: (i) the correct shape of the distribution function is unknown, and (ii) a variety of different analytical distribution functions often can be used to describe experimental data, which usually are measured in a limited region with a insufficient accuracy.

The second case is known as the so-called numerical ill-posedness of the integral eqn. 15, which arises from small changes in $V_{N,t}(p)$, caused by experimental errors, that can influence significantly $F(\varepsilon)$. Likewise, errors generated in numerical calculations or errors arising from the quadrature of the integral eqn. 10 can lead to a similar situation. Thus, the ill-posedness of eqn. 15 is mainly a mathematical numerical problem. Additionally, since the integral kernel contains a theoretical adsorption isotherm, which has only a hypothetical character, the assumed local adsorption model may not accurately represent the experimental observations.

Recommendations for handling numerical unstable problems have been made by Tichonov and Arsenin [30,31], who introduced the regularization method. Subsequently, this method was first applied to gas adsorption by House [32] and Merz [33]. A short summary of the developments in regularization methods can be found elsewhere [19]. In the field of gas–solid adsorption chromatography only Roles and Guiochon [6] have mentioned the ill-posed nature of the determination of $F(\varepsilon)$, but their approach assumes the shape of the distribution function and is not a numerical regularization method, which seems to be a better approach to deal with ill-posed problems.

In the current work eqn. 10 will be solved by a regularization method based on the singular value decomposition developed by Von Szombathely [34],

which already has been used successfully to calculate gas adsorption isotherms on energetically heterogeneous surfaces [19].

REGULARIZATION METHOD

Each regularization requires discretization of the integral equation by a quadrature. The integral equation has to be transformed to a system of linear equations

$$\mathbf{g}(y) = \int_a^b K(x,y)f(x)dx \Leftrightarrow \mathbf{g} = \mathbf{A}\mathbf{f} \quad (16)$$

where $\mathbf{g} = (g_i)_{1 \dots m}$ is a vector of m experimental data points, $g_i = g(y_i)$. The vector $\mathbf{f} = (f_i)_{1 \dots n}$ represents the unknown function, $f(x)$, with n interpolation nodes in the integration range $[a,b]$. The (m,n) matrix \mathbf{A} contains the product of the kernel-values, $K(x_j, y_i)$, and the corresponding quadrature weights. Such a linear system of equations is commonly solved by minimizing the residual, i.e., the sum of least squares:

$$\text{Min} (\|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2) \quad (17)$$

The idea of regularization is to replace an ill-posed problem by a well-behaved one which smoothes the resulting function and changes the original condition given by eqn. 17 only insignificantly. This can be done by addition of a second minimizing term to eqn. 17 which stabilizes the numerical solution:

$$\text{Min} (\|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2 + \gamma \|\mathbf{W}(\mathbf{f})\|^2) \quad (18)$$

The regularization parameter γ is a measure for the weighting of both terms in eqn. 18. The second term in eqn. 18 is defined as the norm of the function f

$$\|\mathbf{W}(\mathbf{f})\|^2 \approx \int_a^b \mathbf{f}^2(t)dt \quad (19)$$

where t is the integration variable.

It was shown [19] that this choice additionally minimizes the residual and suppresses oscillations in the numerical solution. In principle the regularization method still can be improved through inclusion of additional restrictions on the solution, e.g., restriction of the solution to non-negative values (NNLS) [19].

The regularization parameter γ is usually chosen on the basis of a lot of numerical experience. A

detailed description of strategies for finding the optimal γ -value in the case of gas adsorption is given in [19]. Usually, to start a high regularization parameter, e.g., $\gamma = 1$, is assumed, which results in a strongly smoothed distribution function with a residual $\| \mathbf{A} \mathbf{f} - \mathbf{g} \|^2$ generally higher than the one calculated from experimental errors. Subsequently γ is reduced until experimental accuracy is reached.

In the current work calculations were carried out using the program INTEG developed by Von Szombathely [19]. This regularization program uses singular value decomposition (SVD) of matrix \mathbf{A} , which represents the discretized operator \mathbf{A} in eqn. 16. The above algebraic technique leads to minimization of numerical errors, fast optimization of the result by choosing different regularization parameters, and allows very often a judgment about the validity of the physico-chemical model of adsorption leading to the operator in eqn. 16.

EXPERIMENTAL

n-Hexane and 1-hexene on a porous glass at 374.2 K

The details of the GC measurements have been given previously [17]. A controlled porosity glass (i.e., 7% Na₂O, 23% B₂O₃ and 70% SiO₂) was prepared from sodium borosilicate glass, and had a BET specific surface area of 50.5 m² g⁻¹ and a particle size distribution between 0.2–0.3 mm. Porosimetric analysis for a similar porous glass [35] gave no indications of the presence of micropores in these types of adsorbents and allowed determination of the pore radius associated with the maximum of the pore size distribution equal to 13.5 nm.

Adsorbates, *n*-hexane and 1-hexene, were of GC purity. The GC measurements were carried out on a Chromatron (GCHF 18.3) gas chromatograph with a thermal conductivity detector. The experimental dependence of the specific retention volume, $V_{N,i}$ on the adsorbate pressure p for *n*-hexane and 1-hexene were measured by the peak maxima elution method [3]. These measurement conditions were chosen in order to minimize dynamic effects.

Cyclohexane and cyclohexene on wide- and narrow-pore silica gel at 400 K

These experimental data are published in ref. 36. The wide-pore silica gel (the particle fraction of 0.20–0.39 mm) and the narrow-pore silica gel (the

particle fraction of 0.15–0.20 mm) had BET specific surface areas as measured by nitrogen adsorption of 35 m² g⁻¹ and 180 m² g⁻¹, respectively. Analysis of the pore-size distribution leads to the average pore radii of 2 nm for the narrow-pore silica gel and 14 nm for the wide-pore silica. The bulk density measured with helium were 2.1 g cm⁻³ for the wide-pore silica and 2.5 g cm⁻³ for the narrow-pore silica gel. The solutes cyclohexane and cyclohexene were purified by using a 5 Å molecular sieve. The measurements of the $V_{N,i}(p)$ data were carried out with the chromatograph described above.

RESULTS AND DISCUSSION

The adsorption energy distribution functions were calculated using all of the data points shown in Fig. 1. Summarized in Table I are the number of data points, the lowest (p_{\min}) and highest (p_{\max}) pressures and the standard deviation of the fit between actual data and calculated data using the energy distribution obtained by solving eqn. 10 with INTEG and by assuming the Jovanovic equation for the local adsorption.

The numerical determination of $F(\epsilon)$ with INTEG has the general advantage that there is no limitation concerning the chosen local isotherm and thus, very complicated (non-analytical) local isotherms can in principle be used. As mentioned earlier, in GC the sample concentrations are small and the retention can be represented by equations associated with simple adsorption models as those proposed by Langmuir and Jovanovic. To illustrate how the particular model influences $F(\epsilon)$, Fig. 2 shows the distribution functions of the adsorption energy $F(\epsilon)$ for *n*-hexane on the porous glass calculated by assuming the Langmuir model (eqn. 11) and the Jovanovic model (eqn. 14). For the same regularization parameter $\gamma = 0.1$ the general shape and the location of the peak maxima are in close agreement for both models. However, since the Jovanovic local isotherm seems to have better smoothing properties, as can be seen in the energy range about 25 kJ/mol, this model was chosen to carry out all additional calculations. Further, the choice of the Jovanovic equation to represent the local isotherm is consistent with approaches often used in the theory of GC [5].

The distribution function $F(\epsilon)$ also is influenced by the pre-exponential factor K^0 . The determination

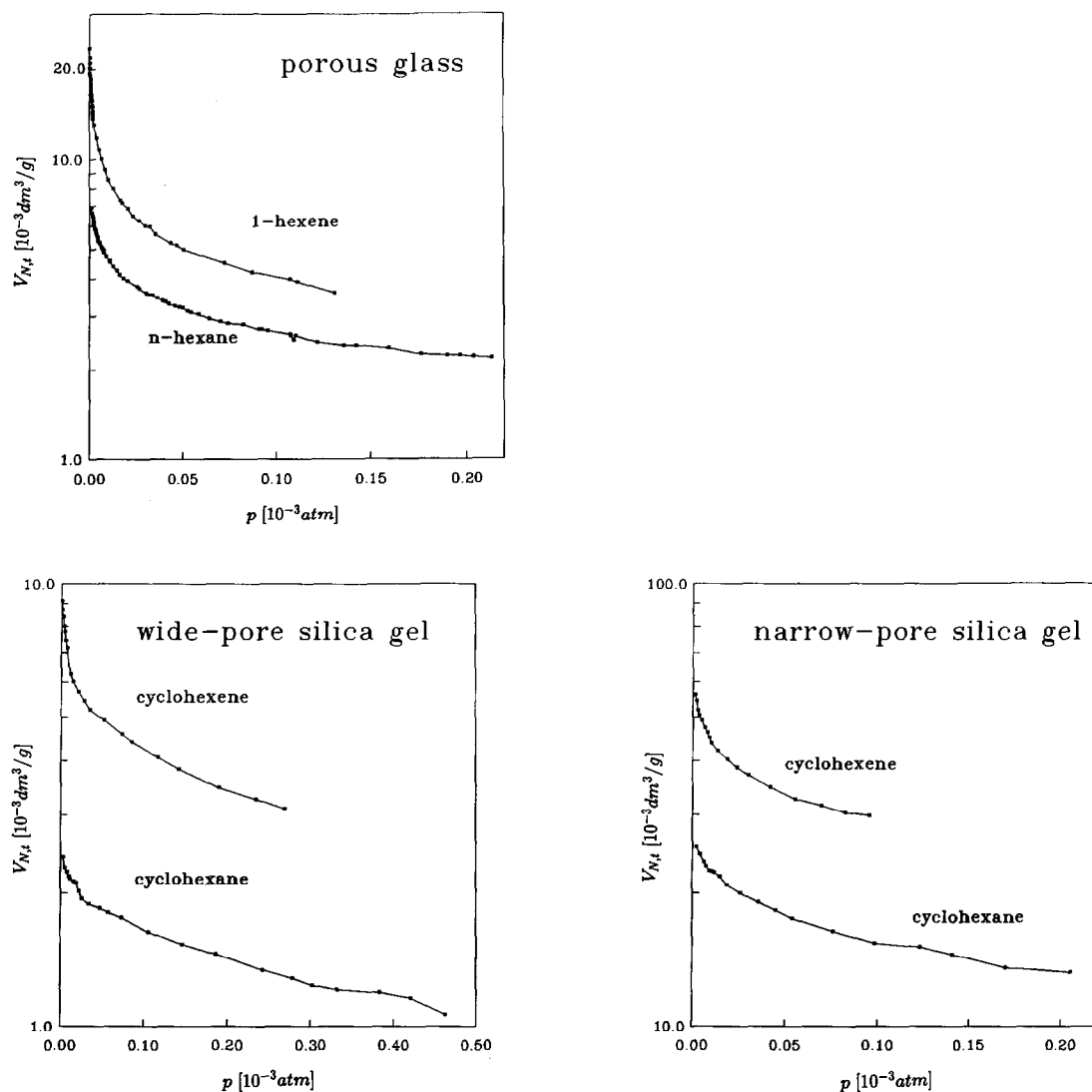


Fig. 1. $\ln V_{N,t}$ vs. p representation for the experimental systems studied.

of K^0 has received considerable attention in the literature [1,2,21]. The calculation of K^0 on the basis of pure statistical thermodynamics requires the approximation of the partition functions for molecules in the mobile and stationary phases. Especially for organic vapors typically used in GC experiments, the theoretical calculation of the partition function is often complicated. Simpler methods for determining K^0 refer only to simple gases and low temperatures. An alternative way of calculating K^0

values is from measurements of solute retention at different temperatures [35].

The influence of the pre-exponential factor K^0 on the distribution function $F(\epsilon)$ calculated from chromatographic data using INTEG is shown in Fig. 3. The solid line represents the distribution function for *n*-hexane on porous glass using K^0 calculated according to eqn. 13. The dotted and dashed lines show $F(\epsilon)$ calculated for values of K^0 differing by one order of magnitude from that obtained by

TABLE I
INFORMATION ABOUT EXPERIMENTAL SYSTEMS

Experimental system	T (K)	p_{\min} (atm · 10 ³)	p_{\max} (atm · 10 ³)	Number of points used	Standard deviation (eqn. 10)
<i>n</i> -Hexane/glass	374	0.92	213.3	67	±0.02
1-Hexene/glass	374	0.14	131.3	45	±0.14
Cyclohexane/wide-pore silica	400	2.77	462.3	23	±0.02
Cyclohexane/narrow-pore silica	400	1.82	205.3	19	±0.10
Cyclohexene/wide-pore silica	400	0.91	268.2	20	±0.04
Cyclohexene/narrow-pore silica	400	0.91	95.3	18	±0.20

means of eqn. 13. All functions are very similar in shape but they are shifted 2 kJ/mol on the energy axis. The same tendency also was observed by calculating $F(\epsilon)$ from adsorption isotherms for different values of K^0 . Since obviously the pre-exponential factor did not change the shape of $F(\epsilon)$, eqn. 13 was used to evaluate K^0 .

The energy distributions for both *n*-hexane and 1-hexene on porous glass show only one peak. It follows from Fig. 4 that the specific interaction of 1-hexene with the surface of the adsorbent is greater than *n*-hexane. The maximum of the adsorption

energy distribution is approximately 32 kJ/mol for 1-hexene which is nearly 10 kJ/mol higher than the maximum of $F(\epsilon)$ for *n*-hexane. Jaroniec *et al.* [5] derived an analytical equation for $V_{N,i}$ assuming the Jovanovic local isotherm and a γ -type distribution for $F(\epsilon)$. The authors applied this equation to the same experimental data and obtained exponential type distribution functions with peak maxima at 23 kJ/mol and 33 kJ/mol, respectively, for *n*-hexane and 1-hexene. These values and the difference in the adsorption energies are in very good agreement with current pure “numerical” results using the regular-

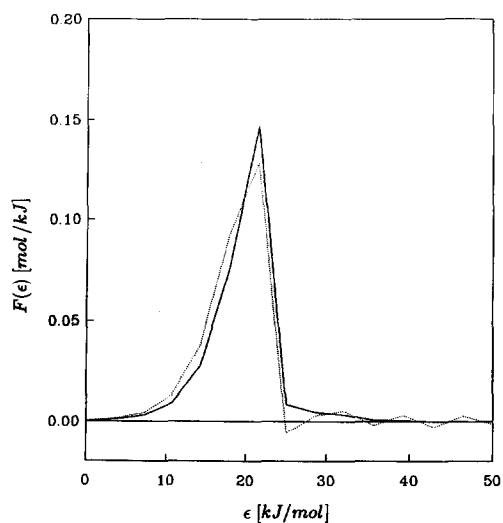


Fig. 2. Comparison of the distribution functions of the adsorption energy $F(\epsilon)$ for *n*-hexane on porous glass calculated with INTEG using the Jovanovic (solid line) and Langmuir (dotted line) local isotherm models.

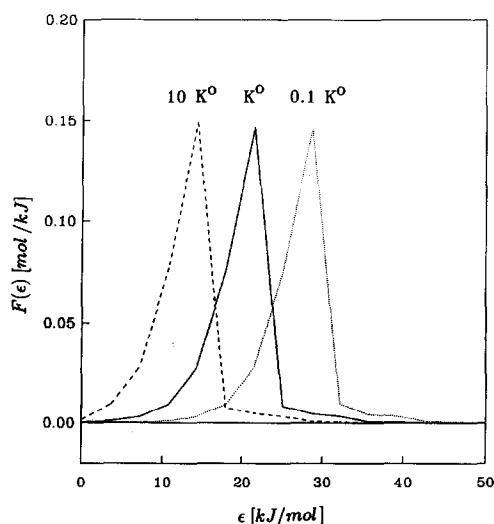


Fig. 3. Dependence of the numerically calculated distribution function on the value of the pre-exponential factor K^0 in the Jovanovic local isotherm for *n*-hexane on porous glass.

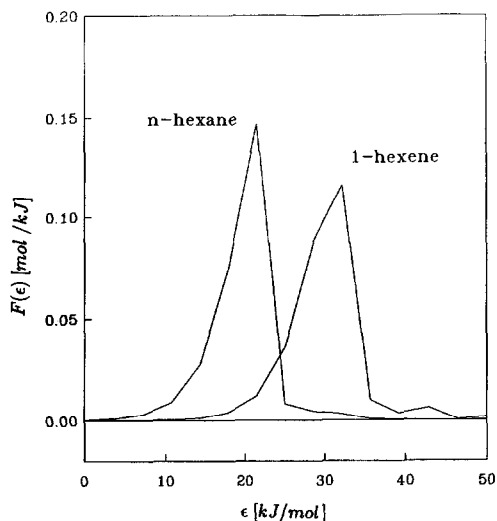


Fig. 4. Distribution functions of the adsorption energy $F(\epsilon)$ for *n*-hexane and 1-hexene on controlled porous glass. The calculations were carried out with INTEG using the Jovanovic local isotherm model and a constant regularization parameter $\gamma = 0.01$.

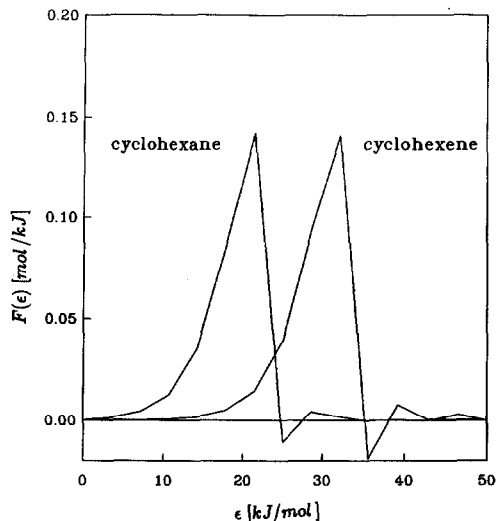


Fig. 6. Distribution functions of the adsorption energy $F(\epsilon)$ for cyclohexane and cyclohexene on narrow-pore silica gel calculated with INTEG (for details see Fig. 4).

ization method. However, the present method gives a better representation of the lower-energy part of the $F(\epsilon)$ -function, which was not predicted by the analytical method.

Figs. 5 and 6 show the calculated distribution functions for cyclohexane and cyclohexene on wide-

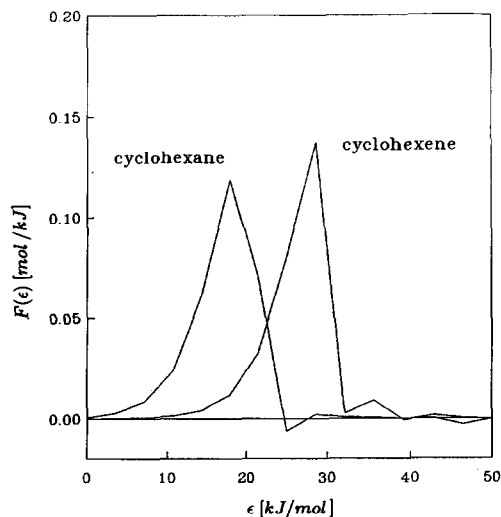


Fig. 5. Distribution functions of the adsorption energy $F(\epsilon)$ for cyclohexane and cyclohexene on wide-pore silica gel calculated with INTEG (for details see Fig. 4).

and narrow-pore silica gels. For both adsorbents cyclohexene was more strongly adsorbed than cyclohexane. For cyclohexane and cyclohexene on wide-pore silica gel the adsorption energies associated with the maxima in the distribution $F(\epsilon)$ were 18 and 28 kJ/mol, respectively. However, for the narrow-pore adsorbent these values were slightly higher, 21 and 32 kJ/mol. These results are consistent with greater interactions (*i.e.*, about 10–11 kJ/mol in the adsorption energy) which arises from the double bond in cyclohexene. Similarly, this trend is in good agreement with the double bond contribution of 1-hexene in comparison to *n*-hexane on porous glass. Further the current result indicates the observed π -electrons effects are similar between the silica gels and the porous glass.

The influence of the pore-size on the adsorption behavior can be seen by a comparison of the distribution functions for cyclohexane on the wide- and narrow-pore silicas shown in Fig. 7. For the narrow-pore silica gel the distribution function $F(\epsilon)$ is slightly sharper and the maximum of the distribution is shifted approximately 3 kJ/mol to higher values of ϵ (4 kJ/mol for cyclohexane). The 3–4 kJ/mol increase in ϵ can be attributed to either the presence of fine pores in the narrow-pore silica gel, or a difference in surface composition. Although

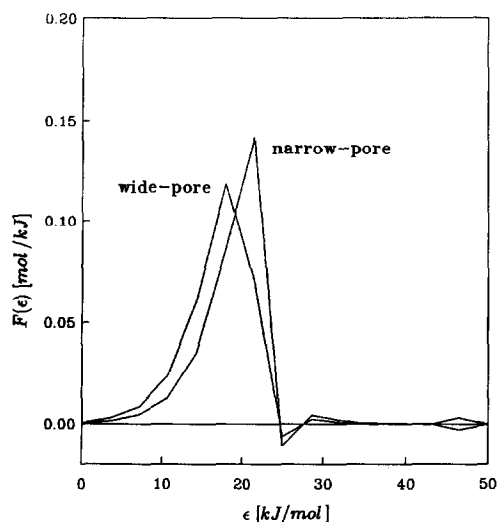


Fig. 7. Comparison of the distribution functions $F(\epsilon)$ for cyclohexane on wide- and narrow-pore silica gel (for details see Fig. 4).

neither of these can be ruled out, it seems more possible that pore structure may play a larger role.

CONCLUSIONS

The numerical regularization method INTEG is a useful procedure for determining the distribution function of the adsorption energy from gas chromatographic measurements. A comparison of the shapes of $F(\epsilon)$ curves calculated for different systems provides information about the interaction of solute molecules with solid surfaces. Studies of relative changes in the $F(\epsilon)$ functions should be useful for analyzing surface treatments of adsorbents and chromatographic packings, e.g., activation and chemical modification of adsorbents and stationary phases for GC.

ACKNOWLEDGEMENT

This work was supported by US Army Research Office Grant DAAL03-90-G-0061.

REFERENCES

- M. Jaroniec and R. Madey, *Physical Adsorption on Heterogeneous Solids*, Elsevier, Amsterdam, 1988.
- W. Rudzinski and D. H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, New York, 1991.
- T. Paryjczak, *Gas Chromatography in Adsorption and Catalysis*, Ellis Horwood, Chichester, 1986.
- R. K. Gilpin, M. Jaroniec and M. B. Martin-Hopkins, *J. Chromatogr.*, 513 (1990) 1.
- M. Jaroniec, X. Lu and R. Madey, *J. Phys. Chem.*, 94 (1990) 5917.
- J. Roles and G. Guiochon, *J. Phys. Chem.*, 95 (1991) 4098.
- J. Roles, K. McNerney and G. Guiochon, *Anal. Chem.*, 64 (1992) 25.
- J. Roles and G. Guiochon, *Anal. Chem.*, 64 (1992) 32.
- J. Roles and G. Guiochon, *J. Chromatogr.*, 591 (1992) 233.
- J. Roles and G. Guiochon, *J. Chromatogr.*, 591 (1992) 245.
- J. Roles and G. Guiochon, *J. Chromatogr.*, 591 (1992) 267.
- J. Jagiello, G. Ligner and E. Papirer, *J. Colloid Interface Sci.*, 137 (1990) 128.
- E. Papirer, S. Li, H. Balard and J. Jagiello, *Carbon*, 8 (1991) 1135.
- I. Tjiburg, J. Jagiello, A. Vidal and E. Papirer, *Langmuir*, 7 (1991) 2243.
- W. Rudzinski, A. Waksmundzki, R. Lebeda and Z. Suprynowicz, *J. Chromatogr.*, 92 (1974) 25.
- S. P. Boudreau and W. T. Cooper, *Anal. Chem.*, 59 (1987) 353.
- Z. Suprynowicz, M. Jaroniec and J. Gawdzik, *Chromatographia*, 9 (1976) 161.
- R. Lebeda and S. Sokolowski, *J. Colloid Interface Sci.*, 61 (1977) 365.
- M. von Szombathely, P. Bräuer and M. Jaroniec, *J. Comp. Chem.*, 13 (1992) 17.
- J. R. Conder and J. H. Prunell, *Trans. Faraday Soc.*, 64 (1968) 3100.
- A. Clark, *The Theory of Adsorption and Catalysis*, Academic Press, New York, 1970.
- S. Ross and J. P. Olivier, *On Physical Adsorption*, Interscience, New York, 1964.
- D. S. Jovanovic, *Kolloid Z. Polym.*, 235 (1969) 1203.
- A. W. Adamson, *Physical Chemistry of Surfaces*, Wiley, New York, 1990.
- A. W. Adamson and I. Ling, *Adv. Chem. Ser.*, 33 (1961) 51.
- J. A. Britten, B. J. Travis and L. F. Brown, *AIChE Symp. Ser.*, 79 (1983) 7.
- A. Waksmundzki, S. Sokolowski and W. Rudzinski, *Z. Phys. Chem.*, 257 (1976) 833.
- A. Drabrowski, M. Jaroniec and J. Oscik, *Surface Colloid Sci.*, 14 (1987) 83.
- S. S. Roginskij, *Dokl. Akad. Nauk SSSR*, 61 (1944) 194.
- A. N. Tichonow, *Dokl. Akad. Nauk SSSR*, 39 (1943) 195.
- A. N. Tichonow and V. Ja. Arsenin, *Methody resenija nekorrektnych zadacz*, Nauka, Moskov, 1979.
- W. A. House, *J. Colloid Interface Sci.*, 67 (1978) 166.
- P. H. Merz, *J. Comput. Phys.*, 38 (1980) 64.
- M. von Szombathely, *Ph. D. Thesis*, Leipzig University, Leipzig, 1988.
- J. Gawdzik, Z. Suprynowicz and M. Jaroniec, *J. Chromatogr.*, 121 (1976) 185.
- A. Waksmundzki, W. Rudzinski, Z. Suprynowicz, R. Lebeda and M. Lason, *J. Chromatogr.*, 92 (1974) 9.