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A Study of the Mechanism of Micropore Filling. I. Molecular Sieve Effects*

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The adsorptive properties of two microporous carbons and a microporous silica have been investigated and compared using argon and benzene. The micropore volumes determined using the Theory for Volume filling of Micropores (TVFM) agreed to within 4% of the total micropore volumes determined from the α_s method of pore analysis. Adsorption data of argon at 77 °K and benzene at 298 °K on the microporous carbons were interpreted in terms of the Dubinin-Astakhov and Dubinin-Radushkevich equations, and Weibull and Gaussian distributions of the adsorption free energy with pore volume, respectively. The Weibull distribution was found to apply better than the Gaussian distribution, although variations from linear D-A plots occurred. The adsorption data on the silica sample were best interpreted as a two-term D-R equation. Plots of the distribution of adsorption energy with pore volume of the silica sample for each term of the D-R equation and their effective contribution to the cumulative distribution curve gave conclusive evidence of the ordering of the adsorption process within micropores of varying dimensions.

INTRODUCTION

Micropores have been defined by IUPAC¹ as being voids or cavities in solids having a width less than 2 nm. From an interpretation of the TVFM applied to certain microporous solids, Dubinin² proposed that micropores should be classified into two categories: micropores of width $x < 0.6-0.7$ nm and supermicropores of width $0.6-0.7 \text{ nm} < x < 1.5-1.6$ nm. Micropores are commensurate with the molecules adsorbed. Physical adsorption in micropores is characterized by volume filling of the adsorption space because of the adsorption field force. The adsorption field in micropores is substantially increased due to the superposition of the adsorption potentials of the opposite walls^{3,4}. Experimental evidence of an increased net differential heat of adsorption has been given by Diano⁵ and Zettlemoyer et al.⁶. Supermicropores represent an intermediate porosity between micropores and mesopores; they possess some properties of both micropores and mesopores simultaneously.

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Adsorption in very narrow pores has long been associated with the interpretation of the Type I isotherm. If the solid has an appreciable external surface area, then the adsorption isotherm will be a composite of Type I behavior from the micropores and Type II behavior from the external surface. The composite isotherm will be Type II and will manifest itself in an increased value of the BET constant c as compared with that for a non-porous solid. An analysis of a composite Type II isotherm (or a Type IV isotherm if mesopores are also present) can be made using the comparison-plot method of deBoer (t -plots)⁷ or Sing (α_s -plot)⁸. The α_s -plot is favored by us over the t -plot for the determination of porosity because it is independent of the BET calculation of the standard surface monolayer capacity. The α_s method is a comparison of the adsorption mechanism on a test surface with that on a standard surface. The criterion for the choice of a standard is in question⁹. Some favor c values closely alike; we agree with Sing¹⁰ in that the choice of standard must be based on a non-porous surface, which has similar physisorption properties to those of the external surface of the sample being examined. If the physisorption properties of the test surface are identical to that of the standard, then the α_s -plot is a straight line passing through the origin. Deviation downward from linearity in the low relative pressure region ($p/p_0 < 0.4$) usually implies the presence of micropores; deviation upwards from linearity in the relative pressure region ($p/p_0 < 0.4$) implies the presence of mesopores, i. e., capillary condensation.

Dubinina and Radushkevich¹¹, in extending the Polanyi adsorption potential treatment¹², proposed an equation for the estimation of the micropore volume from the low pressure parts of the adsorption isotherm. The so-called Dubinin-Radushkevich (D-R) equation is based on a Gaussian distribution of the micropore size distribution. The limitations of this treatment have been recognized¹³⁻¹⁵ and the treatment has been extended¹³, assuming a random, or Weibull¹⁶ distribution of micropore size. Nevertheless, the theory must still be regarded as a curve-fitting procedure in an attempt to determine the characteristic free energy of adsorption of an adsorbent/adsorbate system and to determine an adsorbent total micropore volume.

The purpose of this paper is to demonstrate further the properties of some microporous solids and to compare the micropore volume determined using both the α_s -method and the TVFM. Furthermore, it is to test the flexibility of the TVFM to describe the adsorption isotherm of microporous solids derived from different sources.

EXPERIMENTAL

The microporous solids examined were two polymer-based carbons (Ambersorb XE 347 from Rohm & Haas, PA, and Carbosieve-S from Supelco, PA) and a microporous silica (Silica G-200-0 from Unilever, U.K.). Ambersorb XE 347 (referred to as AX7) is derived from the heat treatment of a macroreticular sulphonated styrene/divinylbenzene copolymer. A detailed analysis of its chemical structure and physical properties has been given elsewhere¹⁷. Carbosieve-S (referred to as C-S), the supplier states, is derived from the heat treatment of a Saran-type copolymer (i. e. poly(vinylidene chloride)/poly(vinyl chloride)).

The argon used for volumetric adsorption was Union Carbide »zero-gas« grade; transfer from cylinder to apparatus precautions included passing the gas through hot copper turnings (673 K) and slow passage through an activated molecular sieve zeolite maintained at 77 K. The benzene used was Mallinckrodt AR grade, thiophene free, and dried using an activated molecular sieve zeolite.

The specific surface areas of these materials were determined volumetrically at 77 K using argon.

The benzene adsorption isotherms were measured on a greaseless rig at 298 ± 0.05 K using an all-quartz spring arrangement (Worden Quartz Co.) with a sensitivity of $1 \mu\text{g g}^{-1}$. The equilibrium vapor pressure for both systems was measured with a 1000 torr capacitive differential manometer (Datametrics Inc.) which has a sensitivity of 2×10^{-3} torr. Sample activation conditions, in all cases, were 298 K at 5×10^{-6} torr for 16 hr.

A well characterized, non-porous and monodispersed polystyrene¹⁸ was used as the standard for an α_s -analysis of the AX7 and the C-S argon adsorption isotherms. Because the mother polymer for AX7 contained polystyrene, it was expected that the adsorption process on polystyrene would simulate that on the external surface of both AX7 and C-S. The water adsorption isotherm on the silica¹⁹ has a B-point equivalent to 2.2 molecules nm^{-2} (a monolayer would have 9.4 molecules nm^{-2}). Thus, Cab-O-Sil (from Cabot, Mass.) was used as the standard surface for the α_s -treatment of argon adsorbed by silica.

RESULTS

The argon and benzene adsorption isotherms plotted in the format: volume uptake vs. relative pressure, all displayed an enhanced adsorption in the low pressure regions ($p/p_0 < 0.1$), typical of micropore filling. The adsorption isotherm of both adsorbates by AX7 had Type II character, implying an appreciable external surface area. The sharpness of the knee for argon adsorbed by both AX7 and C-S was indicative of a narrow micropore size distribution. A very rounded knee for both argon and benzene adsorbed by silica was indicative of a wide micropore size distribution.

An α_s -analysis was made of the argon adsorption isotherms of AX7, C-S and silica to determine the contribution of the micropore equivalent and external equivalent surface area to the total equivalent specific surface area. The results of this analysis and a comparison of the areas with those determined using a B-point analysis are identified in Table I. In all cases, the B-point

TABLE I
Comparison of B-points and α_s -equivalent Specific Surface Areas

	B-point Analysis		α_s -Analysis			
	B pt, cc (STP) g^{-1}	ΣB_i $\text{m}^2 \text{g}^{-1}$	$V_{\mu\text{p}}$ ml g^{-1}	$\Sigma_{\mu\text{p}}$ $\text{m}^2 \text{g}^{-1}$	Σ_{ext} $\text{m}^2 \text{g}^{-1}$	Σ_{TOT} $\text{m}^2 \text{g}^{-1}$
AX7	168	759	0.197	694	64	758
C-S	341	1540	0.434	1533	14	1547
Silica	227	1024	0.281	990	16	1006

and α_s -total equivalent specific surface areas agree within 2% of the B-point equivalent area. This close agreement of areas implies a good choice of standard for both the carbons (polystyrene) and silica (Cab-O-Sil). The argument for choice of standard concerning the matching of the adsorption process on the standard to that on the external surface of the test sample has been fulfilled.

The argon and benzene adsorption isotherms on the three adsorbates are shown in Figures 1 and 2, respectively. To elucidate the shape of the isotherms at low pressures, they have been plotted as volume uptake (ml g^{-1}) vs. \ln (pressure). The adsorption of gases and vapors by microporous solids such

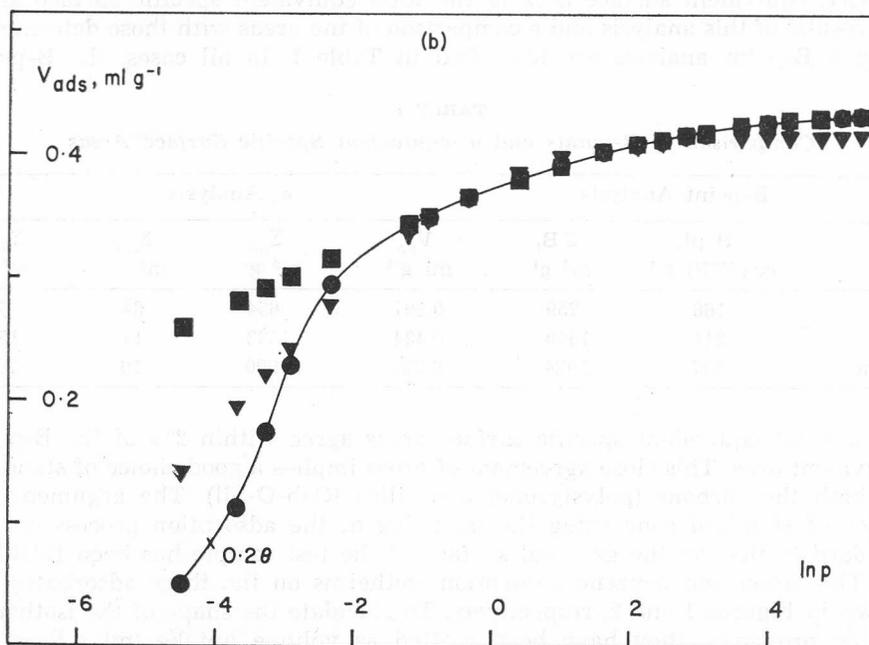
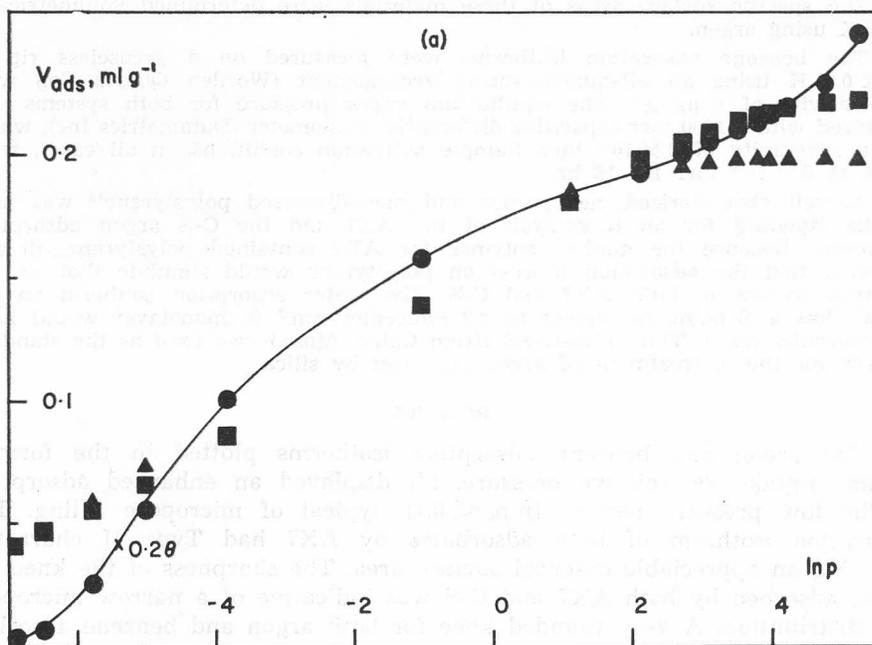


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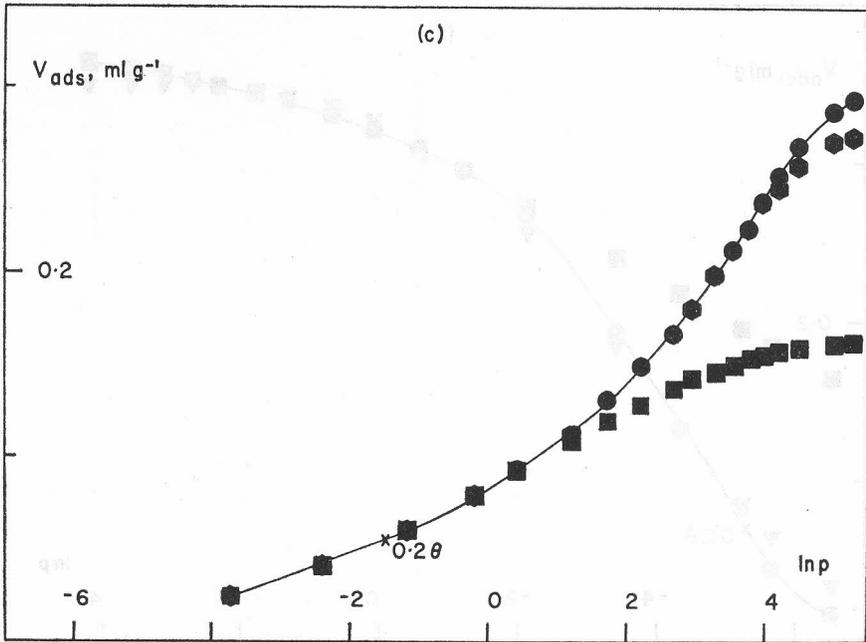


Figure 1. Adsorption isotherms of argon at 77 K on:

- a) AX7, ●, measured; ▲, $n = 3$; ■, $n = 2$.
 b) C-S, ●, measured; ▼, $n = 4$; ■, $n = 2$.
 c) Silica, ●, measured; ●, $n = 2 + 2$; ■, $n = 2$.

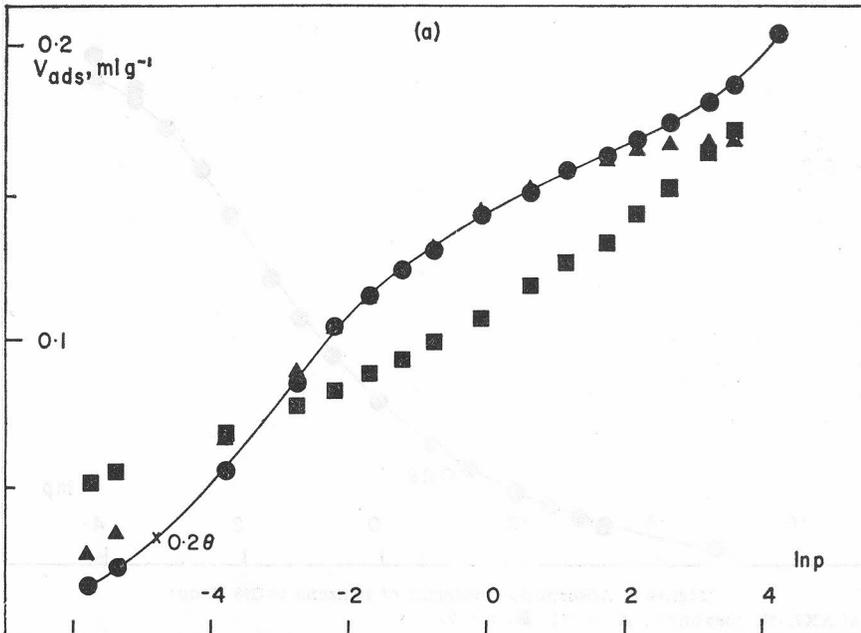


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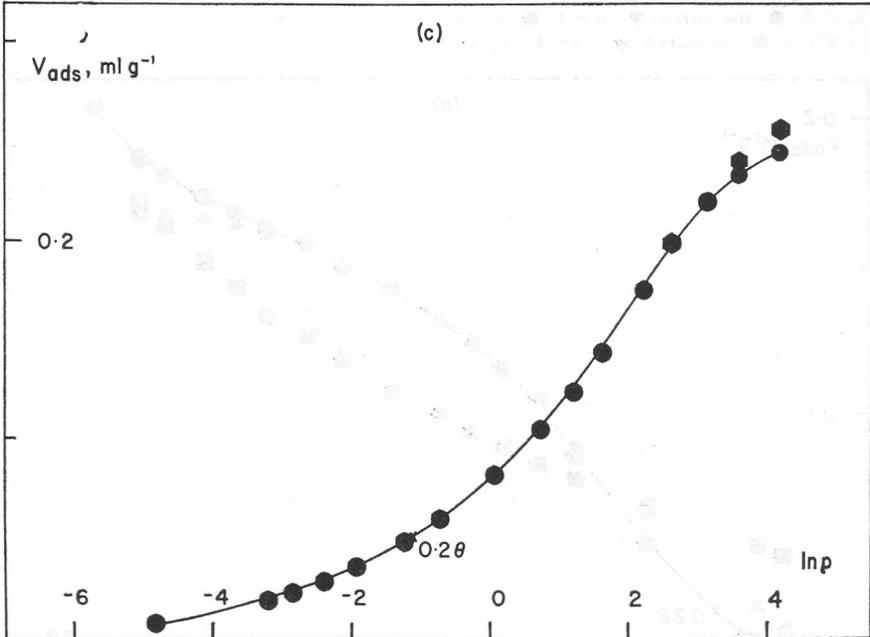
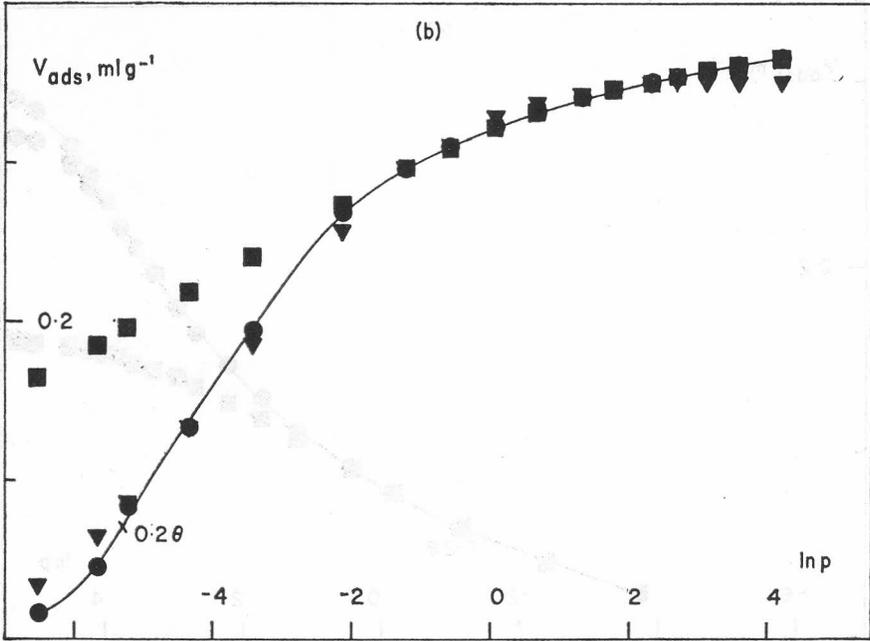


Figure 2. Adsorption isotherms of benzene at 298 K on:

- a) AX7, ●, measured; ▲, $n = 3$; ■, $n = 2$.
 b) C-S, ●, measured; ▼, $n = 4$; ■, $n = 2$.
 c) Silica, ●, measured; ●, $n = 2 + 2$.

as carbons and zeolites is described by the generalized equation of Dubinin and Astakhov¹³:

$$\omega = \omega_0 \exp [-(A/\beta E_0)^n] \quad (1)$$

where ω is the volume of adsorbate condensed in the micropore at temperature T and relative pressure, p/p_0 ; ω_0 is the total micropore volume or limiting volume of adsorption; $A = RT \ln p_0/p$ is the differential molar work of adsorption (a measure of the differential Gibb's free energy of adsorption) and n , β and E are parameters whose values are dictated by the adsorbent/adsorbate system; n is an indication of the degree of heterogeneity (or narrowness) of the micropore size distribution. For molecular sieve carbons, such as those used in this investigation, $2 < n < 3$ corresponds to a relatively homogeneous pore size distribution. For molecular sieve zeolites, adsorbents having a very narrow micropore size distribution, $3 < n < 6$. β is a shifting factor, or an »affinity coefficient« and depends on the adsorbate only. By convention² $\beta = 1$ for benzene. Dubinin has shown that:

$$\beta = P/P_0 \approx V/V_0 \quad (2)$$

where P is the parachor of the adsorbate and P_0 is the parachor of benzene; V is the adsorbate molar volume, V_0 is the molar volume of benzene. From the molar volume ratio for argon, $\beta = 0.32$. Dubinin has also shown²:

$$\beta = E/E_0 \quad (3)$$

where E_0 is the characteristic free energy of adsorption of benzene by a given adsorbent. The adsorption of a different adsorbate can be used to determine a value of E .

A value of n is determined from the experimentally derived data and adjusted to the nearest integer value. The purpose of adjustment is so that the micropore volume filling by one adsorbate can be compared with the micropore filling by another adsorbate. The calculated values of ω_0 , n , β and E for the adsorption of argon and benzene by AX7, C-S and silica are identified in Table II. The adsorption isotherms of both argon and benzene

TABLE II
Micropore Limiting Adsorption Volume, ω_0 , and the Dubinin-Astakhov Equation Parameters, n , β and E

	Argon			Benzene		
	n	ω_0 ml g ⁻¹	E kJ mole ⁻¹	ω_0 ml g ⁻¹	E_0 kJ mole ⁻¹	β
AX7	3	0.199	6.705	0.168	21.182	0.32
	2	0.223	6.048	0.193	20.023	0.32
C-S	4	0.418	6.174	0.350	22.228	0.28
	2	0.435	8.776	0.364	30.734	0.28
Silica		ω_{01}	E_1	ω_{02}	E_2	
Argon	2	0.162	4.167	0.111	1.498	
Benzene	2	0.158	13.162	0.100	6.280	
β			0.32		0.24	

on AX7 resulted in $n = 3$; for C-S, $n = 4$; for silica, $n = 2 + 2$, i. e. a wide or a bimodal micropore size distribution. Two linear regions were observed in the linear form of the D-A equation for argon and benzene on silica plotted as $\ln \omega$ vs. A^2 . The carbons have molecular sieve properties^{6,19} and, according to Dubinin's classification for such systems, $n \approx 2$. Thus, the necessary calculations have been made to determine ω_0 and E for $n = 2$. A summary of these results is also included in Table II. Using the constants in Table II, the isotherms for both argon and benzene on the carbonaceous adsorbents have been generated and compared with the measured isotherms, Figure 1 and 2, respectively. For the argon/silica system, $n = 2$ gave a very poor fit to the measured isotherm, see Figure 1c; no further calculations were made involving $n = 2$ for the silica systems.

Equation 1 can be rewritten to give an indication of the micropore fractional filling, Θ :

$$\frac{\omega}{\omega_0} = \Theta = \exp [-(A/\beta E_0)^n] \quad (1a)$$

Differentiation of Eq. 1a with respect to A gives the probability density distribution of fractional filling of the total micropore volume, i. e. an indication of the probability of the fractional filling of the micropores as a function of relative pressure:

$$-\frac{d\Theta}{dA} = \frac{n A^{n-1}}{(\beta E_0)^n} \exp [-(A/\beta E_0)^n] \quad (4)$$

This expression is an approximate energy distribution similar to that derived by Cerofolini²⁰ and by Stoeckli et al.²¹. It can be used to investigate the relation which exists between the parameters of the D-A equation (Eq. 1) and the distribution of micropore widths.

The adsorption distribution curves for both argon and benzene on the three adsorbents are summarized in Figure 3 and 4, respectively. For the carbonaceous adsorbents, the distribution curves have been determined for the calculated n values and for $n = 2$.

Dubinin has summarized the separate influence of n and E on the shape of the distribution curve². As n increases from 2 to 6 for a constant value of E , the distribution narrows with the maximum approaching the characteristic free energy of adsorption. Also, as the value of E increases (from say 1 to 20 kJ mole⁻¹) for a constant value of n , the distribution curve widens. These same features are evident in the theoretically derived curves from the parameters for n and E shown in Table II. In each case, the values of ω_0 and E used herein were those determined from the linear portion of the linear form of the D-A equation plotted as $\ln \omega$ vs. A^n . Also, $\beta = 1$ for every isotherm and probability density curve.

The probability density distribution of adsorption for both argon (Figure 3c) and benzene (Figure 4c) on silica have been plotted to show the contribution of the micropore filling and the super-micropore filling to the cumulative distribution filling, i. e.:

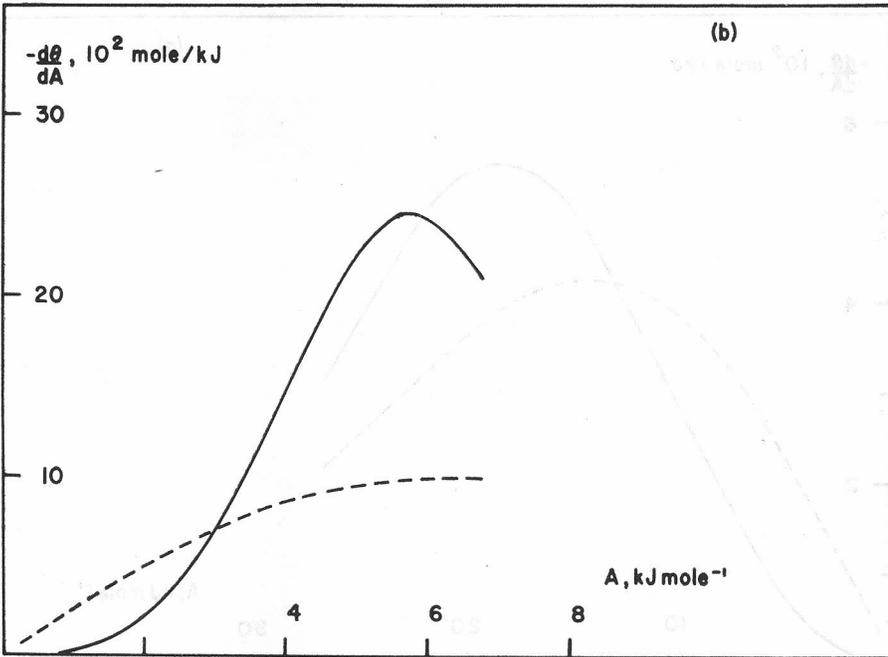
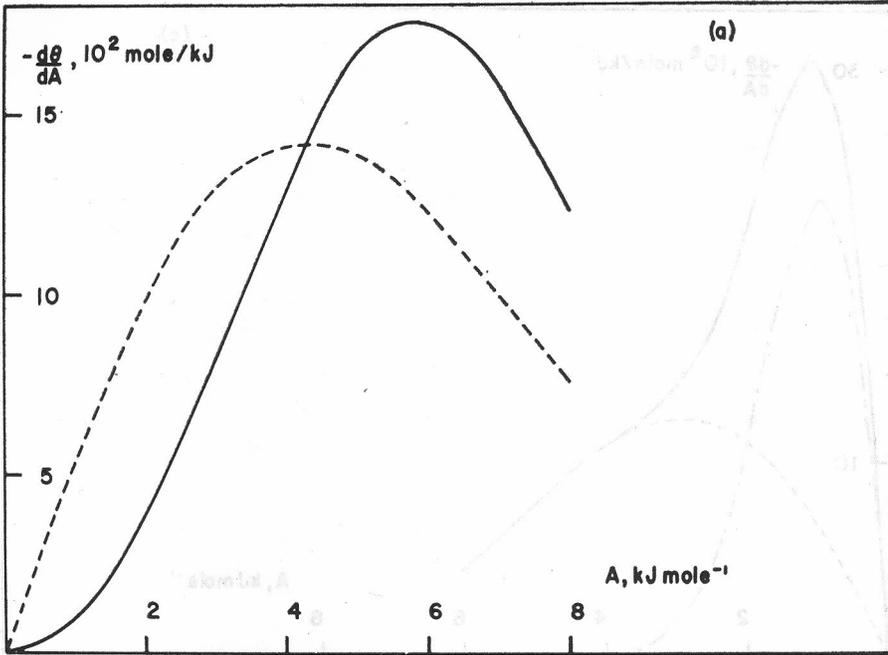


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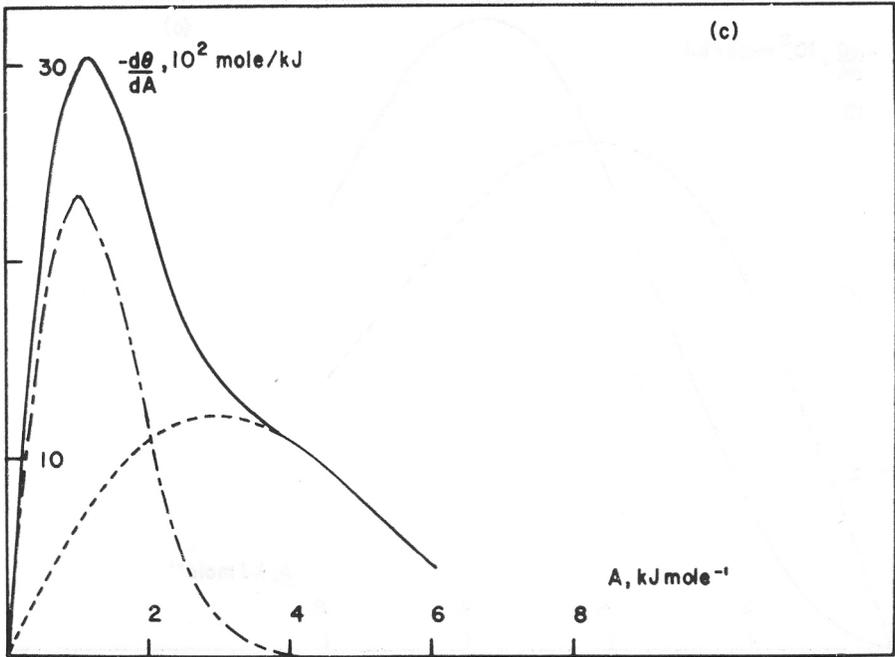


Figure 3. Distribution of differential molar work of adsorption of argon with pore volumes:
 a) AX7, —, $n = 3$; ---, $n = 2$.
 b) C-S, —, $n = 4$; ---, $n = 2$.
 c) Silica, —, cumulative; ---, micropores; ···, super-micropores.

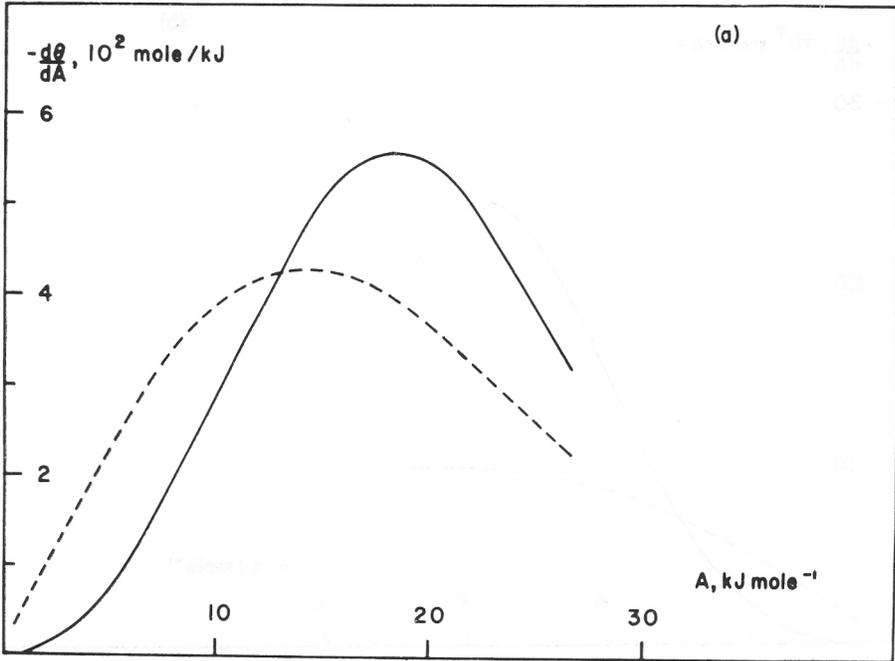


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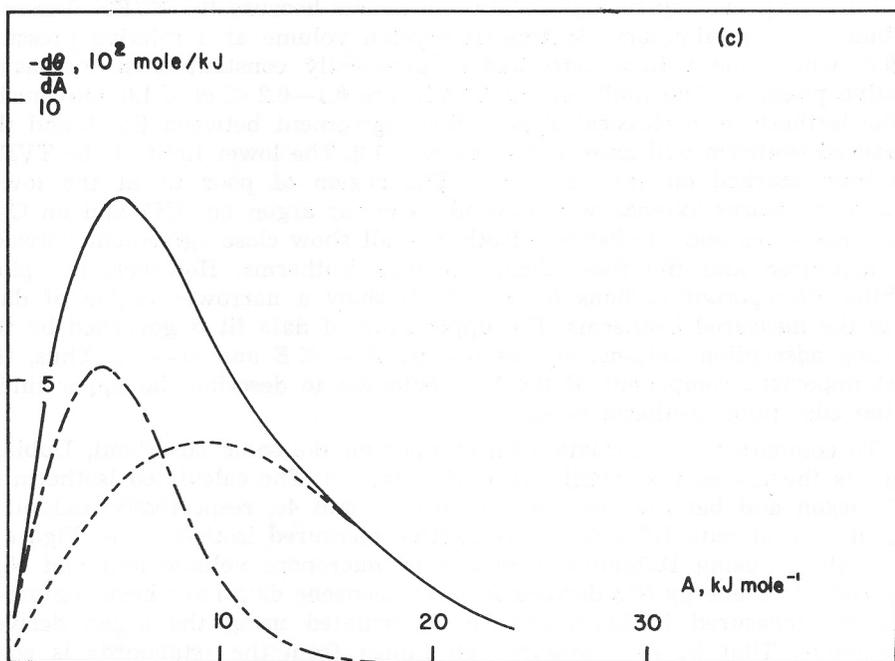
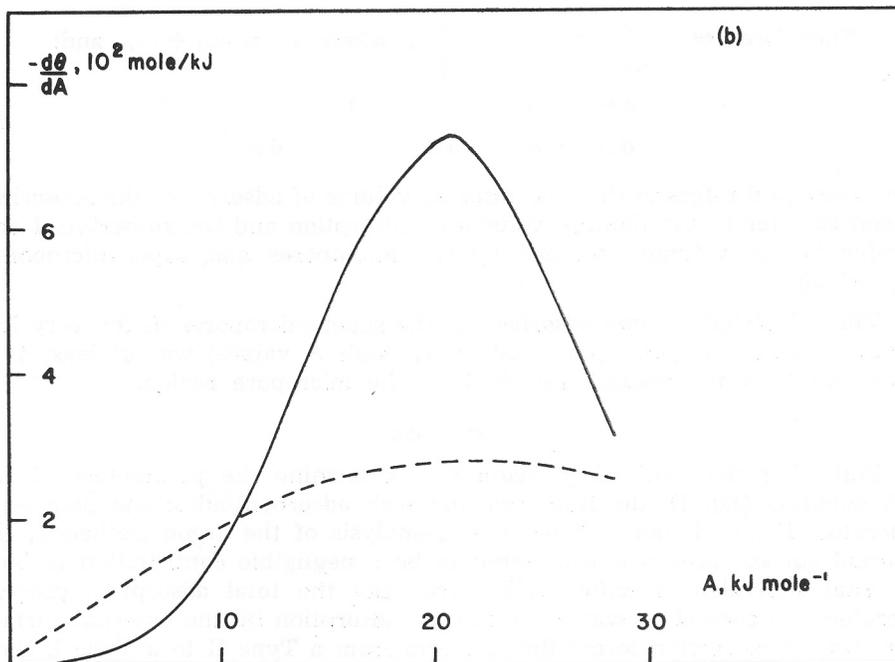


Figure 4. Distribution of differential molar work of adsorption of benzene with pore volumes:

a) AX7, —, $n = 3$; ----, $n = 2$.

b) C-S, —, $n = 4$; ----, $n = 2$.

c) Silica, —, cumulative; ----, micropores; - · - ·, super-micropores.

$$\text{Therefore, } \Theta = \frac{\omega}{\omega_0} = \frac{\omega_1}{\omega_0} + \frac{\omega_2}{\omega_0}, \text{ where } \omega_0 = \omega_{01} + \omega_{02} \text{ and:}$$

$$- \frac{d\Theta}{dA} = \frac{1}{\omega_0} \cdot \frac{d\omega_1}{dA} + \frac{1}{\omega_0} \cdot \frac{d\omega_2}{dA}. \quad (6)$$

The subscript 0 refers to the total limiting volume of adsorption, the subscripts 01 and 02 refer to the limiting volume of adsorption and the subscripts 1 and 2 refer to the volume adsorbed by the micropores and super-micropores, respectively.

The calculated volume adsorbed by the super-micropores in the very low relative pressure regions, $p/p_0 < 10^{-3}$ (i. e., high A values) was at least 1000 times less than the volume adsorbed by the micropore region.

DISCUSSION

Following the outlined procedure² to determine the parameters of the D-A equation (Eq. 1), the isotherms for each adsorbent/adsorbate pair were generated, Figure 1 and 2. From the α_s -analysis of the argon isotherms, the external surface area was considered to be a negligible contribution to both the total equivalent specific surface area and the total adsorption process. Therefore, no correction was made for the adsorption by the external surface area; such a correction forces the isotherm from a Type II to a Type I. Both C-S and silica contain such a small external surface area that a good fit of Eq. 1 was expected up to high relative pressures because the TVFM demands a choice of a preliminary limiting adsorption volume at a relative pressure > 0.3 , where the volume adsorbed is practically constant with increasing relative pressure. The limits of the TVFM are $0.1-0.2 < \Theta < 1.0$. Obviously, if the isotherm is a classical Type I then agreement between Eq. 1 and the measured isotherm will extend close to $\Theta = 1.0$. The lower limit of the TVFM has been marked on each isotherm. The region of poor fit at the lower relative pressures extends well beyond 0.2Θ for argon on AX7 and on C-S. The argon/silica and the benzene isotherms all show close agreement between the measured and the theoretically derived isotherms. However, the plots for the microporous carbons for $n = 2$ all show a narrower region of data fit to the measured isotherms. The upper limit of data fit is governed by the limiting adsorption volume, ω_0 . As $p \rightarrow p_0$, $A \rightarrow \ll E$ and $\omega \rightarrow \omega_0$. Thus, the most important component of the D-A equation to describe the upper limits of the adsorption isotherm is ω_0 .

To compare one adsorbate with another on the same adsorbent, Dubinin suggests the use of the »similarity coefficient«, β . The calculated isotherm of both argon and benzene on silica (Figure 3c and 4c, respectively) exhibit a high degree of data fit with the respective measured isotherms. In Figure 5 the isotherm using Dubinin's technique of micropore volume (ω_0) and characteristic free energy (E_0) derived from the benzene data have been compared with the measured isotherm and that calculated using the argon derived parameters. That is, the isotherm determined from the »standard« is compared with the isotherm determined from the measured data. The comparative fit is very poor; the benzene micropore volume should have decreased a greater percentage of the argon micropore volume ($> 2.5\%$), while the benzene

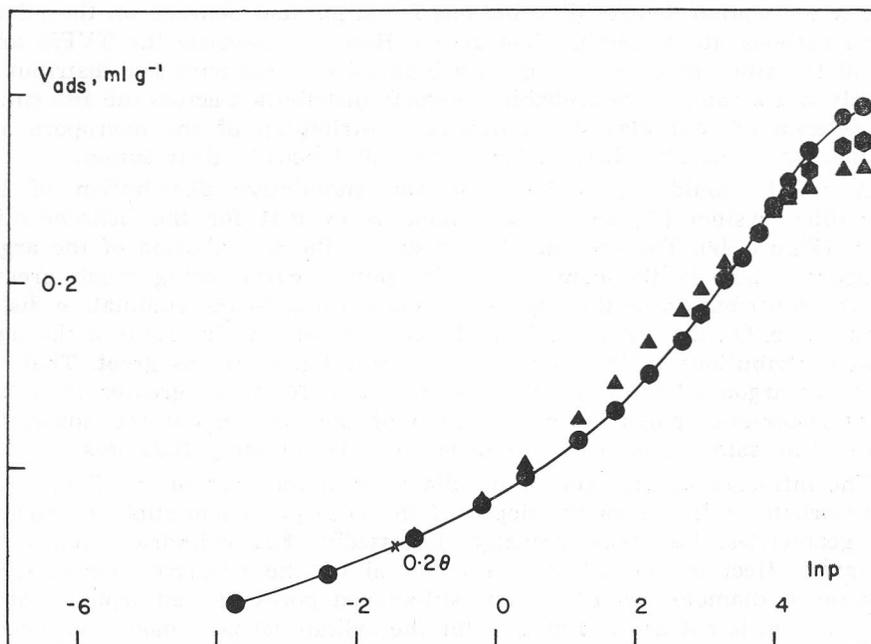


Figure 5. Argon adsorption isotherm on silica; ●, measured; ◆, $n = 2 + 2$ (TVFM argon derived); ■, $n = 2 + 2$ (TVFM benzene derived).

super-micropore volume should not have been influenced at all by a molecular sieve effect between argon and benzene. The total micropore volume of silica determined from benzene adsorption is in a much closer agreement to the argon volume ($\approx 5\%$ of the argon volume) than the corresponding volumes of the microporous carbons ($\approx 15\%$ of the argon volume). Thus, for a good comparison of one theoretically generated isotherm with another, not only must β be the correct value but also the total micropore volume, ω_0 , must be comparable. The total micropore volumes determined by applying the TVFM to the argon isotherms are in excellent agreement with the total micropore volumes from the α_s -analyses. The only drawback of the α_s -plot method of isotherm/pore volume analysis is that the presence of both micropores and super-micropores cannot be differentiated.

By definition, an adsorption isotherm indicates the density of distribution of adsorption sites. The first derivative of the D-A equation also gives an indication of the probability density distribution of adsorption. Dubinin and Astakhov adopted a Weibull or random distribution of adsorption sites during the formulation of the »Dubinin-Astakhov Equation«. The first derivative of the adsorption volume with respect to the differential molar work of adsorption (which is a function of the relative pressure) also gives an indication of the process of adsorption of an adsorbent that is assumed to have a random distribution of adsorption sites. When $n = 2$ the D-A equation reduces to the Dubinin-Radushkevich equation and the adsorption site distribution reduces to a Gaussian form.

The adsorption density distributions for argon and benzene on the microporous carbons are somewhat featureless. However, because the TVFM analysis of the silica isotherms suggests a bimodal or wide pore size distribution not only was a cumulative probability density distribution across the adsorption size determined, but also the individual contribution of the micropore and supermicropore density distribution to the total density distribution.

A small shoulder is evident on the cumulative distribution of the argon/silica system (Figure 3c) but none is evident for the benzene/silica system (Figure 4c). The shoulder is a result of the contribution of the argon micropore filling to the cumulative distribution curve being much greater than the contribution of the super-micropore filling to the cumulative distribution curve. On the other hand, in the case of benzene the ratio of the individual contributions to the cumulative distribution is not as great. That the volume of argon adsorbed by the micropores is 10^5 times greater than that by the super-micropores is an indication of the ordering of the adsorption process. The same ratio for benzene is an order of magnitude less.

The influence of the ratio of the diameter of the pore to the diameter of the adsorbate molecule on the depth of the adsorption potential, for various pore geometries, has been recently discussed^{3,4}. For cylindrical pores the maximum effect of the adsorption potential on the adsorbate exists when the ratio of diameters is 1.1 : 1. For slit-shaped pores, the adsorption potential minimum is not as deep at that for the cylindrical pore model but occurs close to the width ratio 1.3 : 1.

Approximately the same total pore volume is filled for benzene as for argon (approximately 5% less than the argon volume). These findings imply that most of the pores are probably slit-shaped. Since this slight difference in pore volume constitutes a molecular sieve effect, a semi-quantitative analysis of the pore structure can be proposed. The argon molecule is approximately 0.29 nm in diameter and will first fill those pores that are between 0.30 nm (for slits) and 0.32 nm (for cylinders). The benzene molecule, however, is approximately 0.35 nm ($\times 0.5 \times 0.5$) and will first fill those pores that are approximately 0.36 nm (a slit geometry assumed). Thus, the difference in pore volumes is contained in micropores of width $0.30 < x < 0.36$ nm.

Assuming a low relative pressure, 1×10^{-6} , for each adsorbate, the number of molecules adsorbed by the micropores and super-micropores can be calculated. The results are summarized in Table III. The ratios of the two molecules clearly indicate a molecular sieve effect, as implied by the calculations of Everett and Powl⁴. The high ratio of argon to benzene in the micropores compared to the same ratio for the super-micropores clearly indicates the preference of adsorption sites for each molecule.

TABLE III

Number of Molecules Adsorbed at a Relative Pressure of 10^{-6}

	Micropores	Super-micropores
Argon	37.6×10^{18}	1.7×10^6
Benzene	1.3×10^{18}	97.7×10^6
Argon: Benzene	30 : 1	1 : 56

It is considered that a detailed analysis of the micropore structure of microporous solids and the adsorption process of these solids can be made by an investigation of the low relative pressure part of the isotherm when the pores are being filled with adsorbate. Although a strict adherence to the D-A or Dubinin-Radushkevich equations may not apply over the whole of the adsorption field, these very same equations can be used to determine the form of the adsorption free energy distribution and elucidate the mechanism of micropore filling by different adsorbates. Dubinin has extended the TVFM to encompass the enthalpy and entropy of adsorption in a micropore². These equations are presently being tested by means of measuring the heats of immersion of the three materials in various liquids and by multi-temperature isotherm measurements.

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SAŽETAK

Istraživanja mehanizma zapunjanja mikropora. I. Efekti molekulskih sita

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Proučavana su adsorpcijska svojstva dva tipa mikroporoznog ugljika i jednog tipa mikroporoznog SiO₂. Kao adsorbati upotrijebljeni su argon i benzen. Volumeni

mikropora određeni primjenom dviju teorija slažu se do oko 4%. Za opis raspodjele slobodnih energija adsorpcije u ovisnosti o volumenu pora primijenjene su Weibullova i Gaussova funkcija. Rezultati pokazuju da Weibullova raspodjelna funkcija bolje opisuje eksperimentalne podatke, iako pokazuje odstupanja od linearne funkcije opisane jednačbom Dubinjina i Astahova. Adsorpcijski podaci za SiO_2 najbolje se opisuju dvočlanom jednačbom Dubinjina i Raduškeviča. Analiza rezultata pokazuje da adsorbati zapunjavu pore redom, počevši od dimenzija najbližih promjeru njihovih molekula.