

CALCULATION OF ADSORPTION ENERGIES
IN SLIT-LIKE AND WEDGE SHAPED MICROPORES

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Introduction

The analysis of the structure of microporous carbons has been undertaken using a wide range of techniques. The results of these studies suggest that microporous carbons consist of lamellae present singly or in stacks of two or three turbostratic layers¹. The lamellae are apparently curved forming larger micropores in the shape of a triangle and small ultra-micropores between adjacent curved lamella or stacks of lamellae. The average diameter of the lamellae is a function of the heat treatment temperature and presumably also the extent of carbon conversion.

The physisorption of gases, although experimentally tedious, probably remains the most versatile method of analysis, and the results of such studies, in large part, form the basis of our understanding of the pore structure of these materials. In our work, we have undertaken to measure² the isosteric heats of adsorption of different gases on microporous carbons with the objective of obtaining information on pore size. As is well known, the physisorption of molecules in small pores is enhanced over that of a single surface due to the added attractive force of the second surface. This effect, though, is appreciable only in pores smaller than about 10Å. Consequently, it is possible to use heat of adsorption data to determine the size of the ultramicropores. This approach has been previously used by Everett and Powl³, who considered adsorption in both slit-like and cylindrical pores, by Stoeckli⁴, and by Chihara et al.⁶ to determine pore widths in microporous carbons.

The problem with this approach, as pointed out by Wickens⁶, is that it is necessary to assume a monosize pore distribution in order to obtain a pore spacing from the isosteric heat. The intention of this study was to determine the adsorption energies for a range of probable pore configurations with the objective of determining a site energy distribution for physisorption. The basic model used in the calculations assumes that the pores are formed by finite sized lamellae having 1 to 3 turbostratic layer planes per surface. Calculations were done as a function of lamellae diameter, pore spacing, the position of the adsorbate molecule, the number of turbostratic layers, and the pore angle.

Model Development

Adsorption energies were calculated by numerically summing the Lennard-Jones potential for the interaction of an adsorbate molecule with each carbon atom in a microcrystallite. The calculations assume that the total adsorption energy can be obtained from the sum of the pair-wise interaction energies between the adsorbate molecule and the individual atoms in the solid. The adsorbate molecule and each atom in the solid are assumed to act as single force centers.

The positions of the carbon atoms in the basal plane were calculated, in polar coordinates, relative to the center of a hexagonal unit in the basal plane. The size of the lamella (the basal plane) is measured by the number of hexagon rings around a central hexagon. A maximum of eight hexagon rings was considered in these calculations. This corresponds to a maximum lamellae (area equivalent) diameter of 38 Å. Usually three basal planes were included in the calculation of the adsorption potential for a surface. The position of carbon atoms in the normal direction to the basal plane is not specified for crystallites in a microporous carbon since adjacent basal planes are turbostratically stacked. It was assumed in these calculations that carbon atoms in adjacent layers are stacked directly on top of each other. However, because of the large spacing between adjacent layers (3.4 Å) compared to the spacing between atoms in a basal plane (1.42 Å along a hexagon edge), the specific stacking arrangement has a negligible effect on the calculated adsorption energy.

Calculations were done for three positions of the adsorbate molecule: above the midpoint of a hexagon (position *s*); directly over a carbon atom (position *c*); and above a bond between 2 carbon atoms (position *cb*).

The Lennard-Jones potential model for the pair-wise interaction is:

$$u(r) = 4\epsilon_{gs}\{(\sigma_{gs}/r)^{12} - (\sigma_{gs}/r)^6\} \quad (1)$$

where *r* is the distance between the adsorbate molecule and a carbon atom in the solid; ϵ_{gs} is the depth of the potential energy minimum for the pair-wise interaction; and σ_{gs} is the distance at which the pair-wise interaction potential is zero. Values⁷ of 7.98×10^{-15} ergs and 3.45 Å were used for ϵ_{gs} and σ_{gs} in the calculations. Here σ_{gs} is the arithmetic mean of the spacing between basal planes and the distance parameter in the Lennard-Jones potential for the adsorbate molecule (Argon) in the gas phase.

Results

Figure 1 gives the interaction energy of an adsorbate molecule with a single carbon surface of three basal planes as a function of the basal plane size (given in terms of the number of hexagon rings around the central hexagon) and for the three positions of the adsorbate molecule above the surface. For lamella as large or larger than that formed by 4 rings (~20 Å in diameter), the adsorption energy is independent of lamella size. Below 20 Å, however, the adsorption potential decreases significantly with lamella size. The difference in adsorption energies between the *s* and *c* or *cb* positions is less than 4%, while between the *c* and *cb* positions there is only a very

small difference in adsorption energy. As a result, energy barriers to translational motion of the adsorbate molecule across the surface are small so that physisorbed molecules exist as a mobile film on a graphite surface. Also shown in figure 1 are the interaction energies obtained by integrating the Lennard-Jones potential over a single basal plane and by summing the contribution of individual planes in the direction normal to the basal plane. Steele⁷ has shown that the adsorption energy obtained by integration over a single layer plane is nearly the same as summation, provided that $\sigma_{gg}/\sigma_{ss} > 1.5$. (Here σ_{ss} is the spacing between atoms in the crystal surface.) However, because of the different atomic spacings in the normal and parallel directions to the basal plane in a graphite crystal, integration in the normal direction does not give an adsorption energy that agrees with summation unless the adsorbate molecule is 1.5 times larger than basal plane spacing. Agreement between the integration and summation calculation and the discrete summation is excellent for lamella larger than $\sim 11\text{\AA}$. Integration, however, does not yield information on the magnitude of energy barriers to translational motion of the adsorbate across the solid surface.

Increasing the number of layers from 1 to 2 layers increases the adsorption energy by less than 10%. Additional layers beyond 2 increase the adsorption energy by approximately 3%.

Figure 2 gives the adsorption energy as a function of pore spacing for a slit-like pore. There are two pore spacings, on each side of the maximum adsorption energy spacing, at which the adsorption energies are equal. These are referred to here as the tight and loose configurations. The maximum interaction energy is obtained at a pore spacing of 6.8\AA . For pores wider than 7.7\AA , the adsorption potential is a maximum in the pore at two positions, each located 3.4\AA from a surface. This is shown in Figure 3, where the adsorption energy is plotted as a function of position in an 8.6\AA pore. In pores smaller than 7.7\AA , the equilibrium position of the adsorbate molecule will be at the center of the pore.

The adsorption energy in a 6.4\AA pore, as a function of the radial position of the adsorbate (i.e. in a direction parallel to the surface) in the pore, is plotted in Figure 4. The calculations show an $\sim 10\%$ difference in the adsorption energies between the *s* and *c* or *cb* positions. Consequently, even in a tight pore configuration, physisorbed molecules are largely mobile. Furthermore, there is no preference for movement over the *c* or *cb* positions. At a slightly wider width of 6.8\AA , the difference in adsorption energies between the *s* and *c* or *cb* configurations is 4%, so that adsorbed molecules are almost fully mobile in pores of this size or larger.

Calculations were also done for wedge shaped pores at small angles and for an angle of almost 90° . Figure 5 shows the adsorption energies in a 10° pore for a molecule equidistant from each surface as a function of the lateral position of the molecule in the pore. If the pore angle is small, the maximum interaction energy occurs at the point where the surfaces are $\sim 6.8\text{\AA}$ apart (the actual vertical separation between the two surfaces at the maximum interaction energy is 6.9\AA). The maximum interaction energy is 2% less than in a parallel pore. The uneven variations in adsorption energy (near the maximum value) occur because the molecule position changes among the *s*, *c*, and *cb* configurations as it is moved into the wedge. The change in adsorption energy with lateral position will depend

on the angle between planes; however, there will always be a position where the interaction energy is at a maximum. This point, though, can reside in a fairly shallow energy well (if the pore angle is small) so that a molecule in a wedge shaped pore may retain a significant degree of lateral mobility. For large pore angles, the adsorbate molecule will not be as mobile; however, the adsorption energy will be less than for a small angle pore since the adsorbate will interact with the edge of at least one plane. If the pore angle is formed by the edges of both surfaces, the interaction energy is approximately 25% lower than for the small angle case.

Discussion

The calculations show that the adsorption energy in a micropore depends on a range of factors: the lamella size, the pore spacing and angle, and the number of turbostratic layer planes per surface. The adsorption energies calculated by summation show that physisorbed molecules retain their mobility even in tight pores and that there is a significant degree of lateral mobility in small angle wedge shaped pores. For most other cases, however, the discrete summation method has no particular advantage over the integration method used in previous studies^{3,4}.

The determination of an average adsorption energy for a molecule in a microporous carbon requires both an estimate of the site energy distribution and information on the fraction of sites of a given energy that are occupied. Presumably, slit-like pores will be uniformly distributed with respect to pore spacing, so that a site energy distribution could be obtained from the data in figure 2. Such a distribution will be skewed towards the maximum adsorption energy. Similarly, small angle wedge shaped pores will also skew the distribution towards the maximum adsorption energy. A site energy distribution calculated from the data in Figure 5 is shown in Figure 6. Large angle wedge shaped pores will only contribute sites with energies some 25% lower than the adsorption energy in small angle pores.

In order to determine the fraction of sites with the same energy that are occupied, the Volmer isotherm equation⁸ was evaluated at a number of different adsorption energies. (The pre-exponential factor for the equilibrium constant was obtained from the data of Floess et al.²). As shown by the isotherms in figure 7, adsorption in the Henry's Law regime (at 184 K) occurs predominantly on sites with energies above 3.6 kcal. (At lower temperatures, low energy sites will be occupied to a greater extent in the Henry's Law regime.) Nevertheless, since the site energy distribution is also skewed towards high energy sites, adsorption in the Henry's Law regime will occur predominantly in slit-like pores that are approximately 6.8Å wide and in small angle wedge shaped pores. The heat of adsorption in the Henry's Law regime will therefore be principally due to adsorption in these pores, and an average pore spacing calculated from heat of adsorption data will be a weighted average pore spacing for the pores that have the highest adsorption potential.

The calculations also showed that adsorbate molecules are mobile on a carbon surfaces and that they retain a high degree of lateral mobility even in a tight pore configuration. As a result, diffusion in a microporous carbon will depend on the rate of transport from one microporous slit to an adjacent one and not on the rate of

transport in a micropore itself. Therefore, if diffusion is modeled⁹ as a molecule jumping from energy well to energy well over a potential barrier, the potential barrier will be that for adsorption in a micropore and the distance between energy wells will be proportional to the average lamella diameter in a microporous carbon.

References

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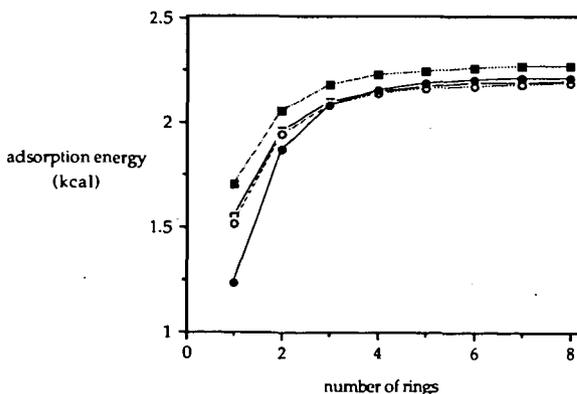


Figure 1. Adsorption energy as a function of lamella diameter: (■) s position; (○) c position; (□) cb position; (●) integral-sum calculation.

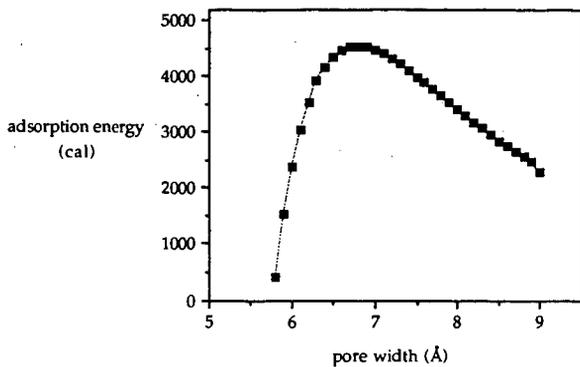


Figure 2. Adsorption energy as a function of pore width.

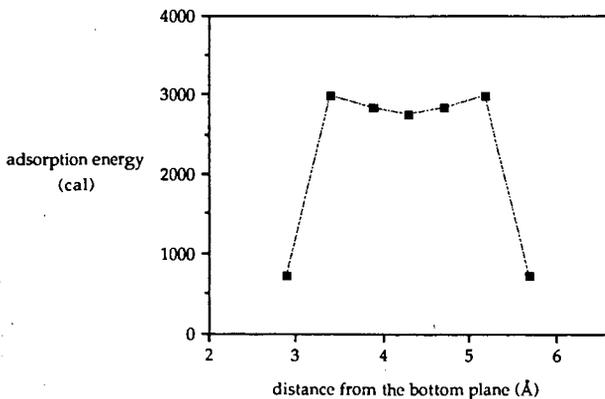


Figure 3. Adsorption energy as a function of adsorbate position in a 8.6 Å pore.

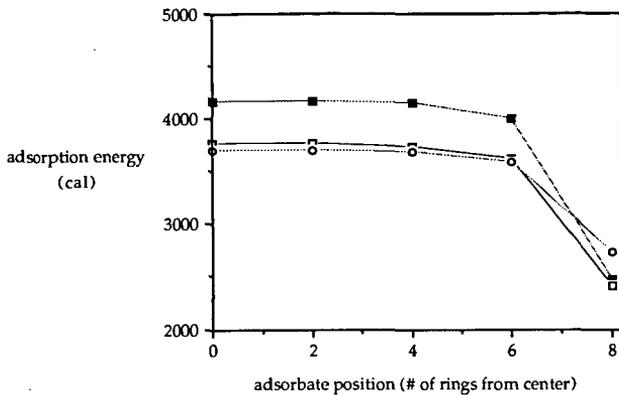


Figure 4. Adsorption energy as a function of the radial position of a molecule in a slit-like pore. Pore width: 6.4Å; (■) s position; (○) c position; (□) cb position.

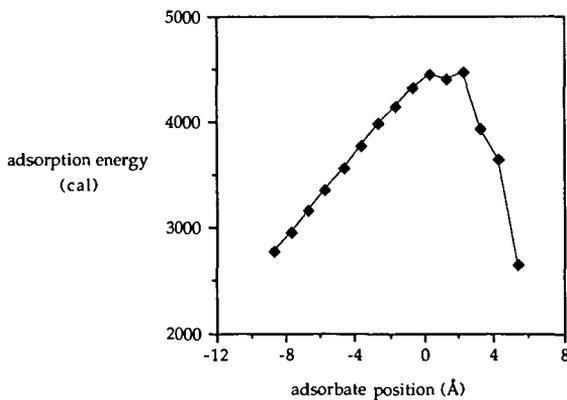


Figure 5. Adsorption energy as a function of position in a 10° pore. (0 = center of lamella; positive direction is into the angle; adsorbate equidistant from both planes.

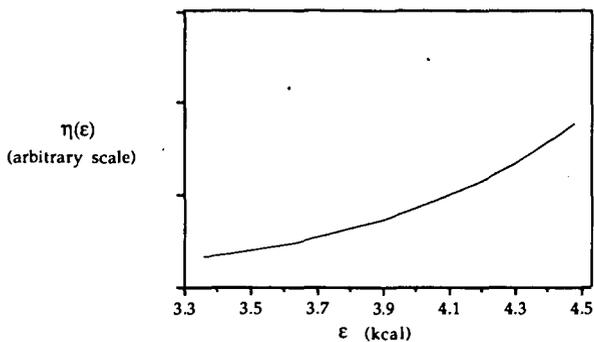


Figure 6. The density of the site energy distribution in a 10° wedge shaped pore.

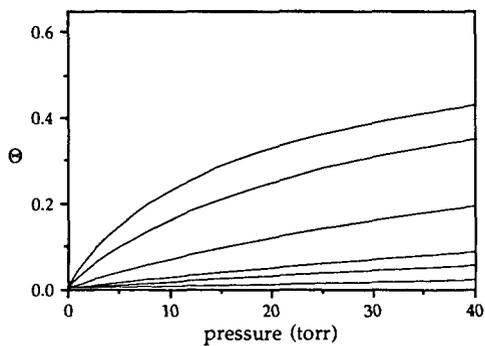


Figure 7. Volmer adsorption isotherms at 184 K for sites with adsorption energies of 4.4, 4.0, 3.6, 3.2, 3.0, and 2.6 kcal (curves from top to bottom).