

# Inferences on the Mechanism of Adsorption in Supermicropores from Potential Calculations for Noble Gas Adsorption

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It is well established that adsorption in the micropores of carbons occurs by a volume-filling mechanism.<sup>1</sup> Upon extensive activation (> ~ 50% burn-off), porous carbons develop a very open micropore structure consisting of supermicropores ( $0.6 < r < 1.6$  nm). The mechanism of adsorption within these pores has been the subject of some speculation yet little is understood.

Everett and Powl<sup>2</sup> have shown that supermicropores are distinct from micropores in that (i) the interaction potential within the supermicropores consists of two symmetrical minima close to the pore walls, and (ii) the depth of the potential minima is the same as that on a plane surface. The latter finding suggests that the first step in adsorption is monolayer formation on the pore wall which should occur at the same  $P/P_0$  as on a plane surface. Gregg and Sing<sup>3</sup> suggest that at  $P/P_0 \sim 0.1-0.2$ , a monolayer forms on the pore walls which significantly enhances the adsorption affinity in the pore core (the volume of the pore remaining after the adsorbed layer(s) are formed on the pore wall) and, thus, complete pore filling occurs. They refer to this phenomenon as the cooperative mechanism. In this study, we have tried to infer the adsorption mechanism for Ne, Ar, Kr, and Xe within supermicropores by examining the adsorption potential within the pore core.

Two basic assumptions are made in performing the potential calculations: (i) the pore walls are composed of carbon basal planes, and (ii) the adsorbed layers on the pore walls form a close-packed layer. The interaction potential at various positions in the pore,  $\epsilon_{tot}$ , is calculated by summing the interaction of the adsorbate with each wall,  $\epsilon_c$ , and each adsorbed layer,  $\epsilon_a$ .

The adsorbate-carbon interaction for each pore wall is described by eqn. (1)<sup>4</sup>

$$\epsilon_c(z) = \epsilon_c^* \sum_{j=0}^{\infty} \left[ \frac{2}{3} \left( \frac{\sigma_{gs}}{z+jd} \right)^{10} - \frac{5}{3} \left( \frac{\sigma_{gs}}{z+jd} \right)^4 \right] \quad (1)$$

where  $z$  is the distance from the carbon surface,  $\epsilon_c^*$  is the potential minimum for interaction with a single carbon plane,  $\sigma_{gs}$  is the value of  $z$  where  $\epsilon_c = 0$ . We define  $z$  as the half-width of the supermicropore. The values of  $\epsilon_c^*$  and  $\sigma_{gs}$  used here were

determined by Steele<sup>4</sup> and are shown in Table 1. Note that the summation over all  $j$  assumes the walls to be infinitely thick. The first term in the series solution of eqn. (1) is equivalent to assuming the pores are composed of a single layer plane (slp) of carbon atoms. Calculations assuming infinitely thick and slp pore wall conditions have been performed.

The adsorbate-adsorbed layer interaction for each wall can be described by

$$\epsilon_a(z_a) = \epsilon_a^* \left[ \frac{2}{3} \left( \frac{\sigma}{z_a} \right)^{10} - \frac{5}{3} \left( \frac{\sigma}{z_a} \right)^4 \right] \quad (2)$$

where  $z_a$  is the distance from the adsorbed layer(s),  $\sigma$  is the kinetic diameter of the adsorbate, and  $\epsilon_a^*$  is given by:<sup>2</sup>

$$\epsilon_c^* = (6/5) \pi n \epsilon_{12}^* \sigma^2 \quad (3)$$

where  $\epsilon_{12}^*$  is the potential minimum for the interaction of two adsorbate atoms,  $n$  is the surface density of atoms in the adsorbed layer, and  $\sigma$  is as described previously. The values used in the potential calculations are shown in Table 1.

The calculations were performed by varying the pore half-width and calculating the potential at various positions within the pore core assuming either one or two layers existed on the pore walls.

## Results and Discussion

The calculations showed, as expected, that for narrow pore-widths, the interaction potential was repulsive. As the pores are widened the potential energy becomes zero at the pore centerline and repulsive at all other positions within the pore core. Under these conditions, these pores do not volume-fill at any adsorption pressure. As the pores are widened further, an attractive potential is produced; the potential minimum occurs at the pore centerline.

If the cooperative mechanism described by Gregg and Sing was operative we would expect that the ratio of  $\epsilon_{tot}/\epsilon_{min}$  would be greater than 1 for some value of  $z$  within the pore core. This would

Table 1. Parameters for Interaction Potential Equations.

Adsorbate	Eqn. (1)		Eqn. (2) and (3)		
	$\epsilon_c^*/k, K^{(c)}$	$\sigma_{gs}, nm^{(c)}$	$\epsilon_{12}/k, K^{(d)}$	$\sigma, nm^{(d)}$	$n, nm^2$
Ne	348	0.294	32.8	0.282	0.072 <sup>(a)</sup>
Ar	959	0.338	93.3	0.3542	0.138 <sup>b</sup>
Kr	1255	0.342	178.9	0.3655	0.195 <sup>b</sup>
Xe	1608	0.378	231.0	0.4047	0.25 <sup>b</sup>

(a) Calculated from liquid density of 27 K, ref. (5); (b) ref. (3); (c) ref (4); (d) ref (5).

indicate that the adsorption affinity ( $\epsilon_{tot}$ ) in the core is larger than for the adsorption of the first layer ( $\epsilon_{min}$ ) resulting in pore filling. The maximum values of this ratio at the pore center-line for the various adsorbates and the corresponding half-widths are shown in Tables 2 and 3.

Table 2. Interaction Potential Minima for Adsorption in Supermicropores - Infinitely Thick Pore Walls.

Adsorbate	# of Adsorbed Layers	$\epsilon_{tot}/\epsilon_{min}$	Pore Half-Width $z, nm$
Ne	1	0.96	0.57
	2	0.85	0.86
Ar	1	0.80	0.69
	2	0.70	1.04
Kr	1	0.85	0.70
	2	0.76	1.07
Xe	1	0.81	0.78
	2	0.71	1.19

Table 3. Interaction Potential Minima for Adsorption in Supermicropores - slp Pore Walls.

Adsorbate	# of Adsorbed Layers	$\epsilon_{tot}/\epsilon_{min}$	Pore Half-Width $z, nm$
Ne	1	1	0.572
	2	0.91	0.86
Ar	1	0.85	0.69
	2	0.77	1.04
Kr	1	0.91	0.70
	2	0.85	1.07
Xe	1	0.89	0.78
	2	0.82	1.19

The results show that for most adsorbates the adsorption affinity in the core is less than for adsorption of the first layer, i.e., the pore core will fill only at higher  $P/P_0$ . The one exception is Ne adsorbing in a pore having a monolayer on the pore wall; the pores are composed of a slp of carbon atoms. The existence of two adsorbed layers on the pore wall reduces the adsorption affinity in the pore core.

#### Conclusion

Adsorption in supermicropores occurs by adsorption of a monolayer on the pore wall followed by adsorption in the pore core at higher relative pressure.

#### References

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