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238. The Gas-Solid Interface Calculations of Adsorption Potentials in Slot-Like Pores of Molecular Dimensions

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(20. VI. 74)

Summary. Two theoretical models are presented for the calculation of adsorption potentials in slot-like pores of molecular dimensions, with respect to the adsorption by a single flat surface. The cases of continuous and layer-like solids are considered, with interatomic pair-potentials of the 6:12 type, and for pore widths ranging from two to four times the equilibrium distance of adsorption. Both models give good results for the adsorption of simple molecules by microporous carbons and graphitized carbon blacks.

1. Introduction. – A theoretical model for the adsorption of single molecules in cylindrical pores of molecular dimensions has recently been presented by *Gurfein et al.* [1].

Based on an intermolecular pair-potential of the *Lennard-Jones* type of eq. (1), the model gives the ratio of the adsorption potentials in the pore and on a flat surface, as a function of the radius of the capillary and the diameter of the molecule. We wish to present similar models for the case of slot-like pores, and to compare them with experimental results for the adsorption of simple molecules on graphitized and activated carbons [2]. The models are all improvements on earlier calculations of *Steele & Halsey* [3], who used hard-sphere potentials for the adsorption in cylindrical and parallel-walled pores.

2. The models. – Let us assume an intermolecular pair-potential of the *Lennard-Jones* type [4] [5],

$$\varphi(\mathrm{r}) = -\mathrm{C}/\mathrm{r}^6 + \mathrm{B}/\mathrm{r}^{12} \tag{1}$$

where C and B are constants for the attractive and repulsive parts of the potential, and r represents the distance between the particles (atoms or molecules).

The potential is often expressed in the equivalent form

$$\varphi(\mathrm{r}) = \varepsilon[(\mathrm{r}_0/\mathrm{r})^{12} - 2(\mathrm{r}_0/\mathrm{r})^6], \tag{2}$$

where ε represents the minimum of $\varphi(r)$, at the intermolecular distance r_0. In the case of potentials between different particles, A and B, the parameters of eq. (2) can be expressed in terms of the parameters of pure A and B by the so-called *combining rules*

$$\varepsilon_{AB} = (\varepsilon_{AA} \cdot \varepsilon_{BB})^{\frac{1}{2}} \quad \text{and} \quad r_{0AB} = (r_{0AA} + r_{0BB})/2. \tag{3}$$

(a) *The model for continuous solids.* The potential energy of a molecule at a distance Z from a semi-infinite and flat solid with a uniform density of ϱ atoms per unit volume is given by [5]

$$\Phi_1(Z) = -(\varrho\pi/3)\,(C/2Z^3 - B/15Z^9), \tag{4}$$

where C and B are (empirical) constants.

The minimum of the potential, at the distance $Z = Z_0$, is given by the condition

$$(\partial\Phi_1(Z)/\partial Z)_{Z=Z_0} = 0. \tag{5}$$

This leads to

$$B = (5/2)CZ_0^6, \tag{6}$$

which can be used to eliminate B from eq. (4). The minimum of the adsorption potential is then

$$\Phi_1(Z_0) = -\varrho\pi C/9Z_0^3. \tag{7}$$

In the case of slit-shaped pores of width L, between two semi-infinite and flat solids, we may write for the adsorption potential

$$\Phi_2(Z) = -(\varrho\pi/3)\,[(C/2)\,(1/Z^3 + 1/(L - Z)^3) - (B/15)\,(1/Z^9 + 1/(L - Z)^9)]. \tag{8}$$

The minimum of eq. (8) will occur at a new distance, Z_0', from the reference plane $Z = 0$, and it will depend on L. Let us introduce the variables ξ and χ, defined by

$$\xi = Z_0'/Z \quad \text{and} \quad \chi = L/Z_0. \tag{9}$$

With eq. (6) and (9), the minimum of potential (8) becomes

$$\begin{aligned}\Phi_2(\xi Z_0) &= -(\varrho\pi/3)\,[(C/2)\,(1/\xi^3 Z_0^3 + 1/(\chi - \xi)^3 Z_0^3) - (CZ_0^6/6)\,(1/\xi^9 Z_0^9 + 1/(\chi - \xi)^9 Z_0^9)]\\ &= -(\varrho\pi C/6Z_0^3)\,[1/\xi^3 + 1/(\chi - \xi)^3 - 1/3\,\xi^9 - 1/3\,(\chi - \xi)^9],\end{aligned} \tag{10}$$

where constant B has been eliminated using a similar procedure as in eq. (6) for the flat surface.

The ratio of the minima of the adsorption potentials in the slot-like pore and on the single flat surface is

$$\Phi_2(\xi Z_0)/\Phi_1(Z_0) = (9/6)\,[1/\xi^3 + 1/(\chi - \xi)^3 - 1/3\,\xi^9 - 1/3\,(\chi - \xi)^9]. \tag{11}$$

This expression does not contain the quantities ϱ, C and B.

The extremum of eq. (10) can be found numerically, by computer, and for different values of χ.

Fig. 1 shows the value of Z_0'/Z as a function of χ, starting at $\chi = 2$. (For this value, the width $L = 2Z_0$, and the adsorption potential has twice the value for a single surface.) As the width increases, the molecule is first drawn away from the reference surface, up to $L = 2.32Z_0$, where $\xi = 1.16$. Beyond this value, there are two symmetrical minima for the potential, and the equilibrium distance Z_0' from either wall of the pore reduces gradually to Z_0. This feature is also observed in the model of *Gurfein*.

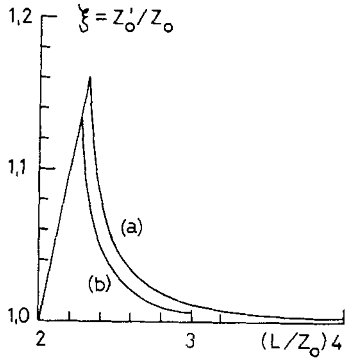

Fig. 1. *The variation of* Z_0'/Z_0 *with* L/Z_0 *(Models a and b)*

Fig. 2 shows the variation of ratio (11) with χ. The decrease is somewhat faster than in the simple hard-sphere model of *Steele & Halsey*, and for $L/Z_0 = 4$ the ratio is virtually equal to unity.

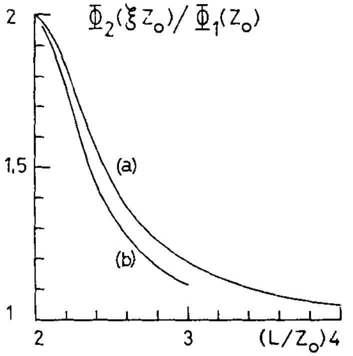

Fig. 2. *The ratio of the minima of the adsorption potentials in a parallel-walled pore and on a flat surface, as a function of* L/Z_0 *(Models a and b)*

(b) *The model of layer-like solids.* In order to improve the model for adsorption on graphitic surfaces, *Crowell & Steele* [6] considered the case of solids made up of layers with a uniform density of σ atoms per unit surface, and an interplanar spacing of d. It is shown that an intermolecular potential of type (1)–(2) leads to an adsorption potential on the flat solid, of the form

$$\Phi_I(Z) = -(\sigma\pi C/12d^4)\,[\psi^{(3)}(x) - 1.2\,(r_0/d)^6\,x^{-10}], \qquad (12)$$

where $x = Z/d$ and $\psi^{(3)}(x)$ is the tabulated [7] pentagamma function. In the derivation of eq. (12), it is also assumed that the repulsion terms can be neglected for all but the surface plane. For simple molecules like Ar, Kr, Xe and CH_4, adsorbed on graphitic surfaces, the minimum of potential (12) is given with a good approximation by

$$\Phi_1(Z_0) = -(\sigma\pi C/3Z_0^4). \tag{13}$$

This is an alternative expression, to be compared with eq. (7) [4] [5]. Following the same approach as in case (a), above, we find that the adsorption potential in a slot-like pore is given by

$$\begin{aligned}\Phi_2(\xi Z_0) = -(\sigma\pi C/12Z_0^4)\,[&\psi^{(3)}(\xi) + \psi^{(3)}(\chi-\xi)\\ &- 2.4976\cdot(1/\xi^{10} + 1/(\chi-\xi)^{10})]\end{aligned} \tag{14}$$

ξ has again the value which minimizes (14) for a given value of χ, and as for eq. (13), it is assumed that Z_0/d is close to unity. The ratio of the minima (14) and (13) is

$$\begin{aligned}\Phi_2(\xi Z_0)/\Phi_1(Z_0) = (3/12)\,[&\psi^{(3)}(\xi) + \psi^{(3)}(\chi-\xi)\\ &- 2.4976\cdot(1/\xi^{10} + 1/(\chi-\xi)^{10})].\end{aligned} \tag{15}$$

Fig. 1 and 2 (curves b) show the variation of ξ and ratio (15) with χ. The present model is very similar to model (a), but it shows a faster decrease in the influence of the second wall. The adsorbed molecule is first drawn away, up to $L/Z_0 = 2.28$, where $\xi = 1.14$, and then two symmetrical minima appear.

3. Discussion. – In the case of simple molecules adsorbed by typical microporous carbons and by graphitized carbon blacks, it was found that the ratio $\Phi_2(Z_0')/\Phi_1(Z_0)$ was close to 1.6 [2]. For *Gurfein*'s model, this leads to $D/d = 2$, where D and d represent the diameters of the cylindrical pore and of the adsorbed molecule. The values of d obtained from *Lennard-Jones* potentials vary from 3.4 to 4 Å for molecules like N_2, Ar, Kr, CH_4 and Xe [8]. This leads to a pore radius of 4 Å at most, as found for the simpler model of *Steele & Halsey* [2] [3].

For the present models of slot-like pores, it is found that

$$L = 2.4\ Z_0 \quad \text{and} \quad \xi = 1.08 \text{ (model a)}$$
$$L = 2.3\ Z_0 \quad \text{and} \quad \xi = 1.08 \text{ (model b)}.$$

The important physical quantity is Z_0, the equilibrium distance from a single surface, in either model. For model (a), it is related mathematically to r_0 of potential (2) by [4]

$$Z_0 = 0.765\ r_0. \tag{16}$$

Using the experimental values of r_0 (3.40 Å for carbon [3] [5]) and combining rule (3), it is found that Z_0 varies from 2.9 to 3.2 for the molecules quoted above [9]. Therefore, the pore-width L is about 7–8 Å.

In the case of model (b), Z_0 is given by [6]

$$Z_0 = 0.885\ r_0, \tag{17}$$

and it is near 3.4 Å, the value of the interplanar spacing for graphite. This leads to a pore width L close to 8 Å.

X-ray investigations [10] and adsorption experiments with molecules of various sizes and shapes [11] lead to values of 5–8 Å for the effective radius of homogeneous active carbons. (This quantity is either equal to the radius of cylindrical pores, or to the width of slot-like pores.) As before, in the case of the simple model of *Steele & Halsey*, the comparison of the more elaborate models shows that slot-like pores give better results. This suggests again, but on the basis of theoretical models, that the smaller set of micropores can be regarded as fissures between graphitic layers, as suggested earlier by *Wolff* [12]. Such fissures could arise from the stacking of the microcrystallites of the active carbon.

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239. Configuration of Pilocarpus Alkaloids

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(9. X. 74)

Summary. The validity of stereoformula **1**, **2** and **3** for (+)-pilosine and related alkaloids is discussed.

In a recent publication [1], *Tedeschi et al.* question the correctness of stereoformulae **1**, **2** and **3** as reported by us in 1972 [2] [3] for (+)-pilosine, (+)-isopilosine, and (–)-epiisopilosine respectively. On the basis of circular dichroism data the authors propose structures which are epimeric at C(6).

As to the relative configurations, our deductions [2] are based on an X-ray analysis of (+)-isopilosine the result of which cannot be doubted [3]. The absolute configurations ensue from the transformation of (+)-isopilosine (**2**) into (+)-pilocarpine (**5**) *via* (+)-pilosinine (**4**). The absolute configuration of **5** has been determined independently by two groups [4] [5].

Discussing the CD. spectra of the alkaloids, *Tedeschi et al.* [1] suppose that for aromatic amino acids 'the sign at the low-wavelength phenyl transition (^1L_a) around