

Henry's law behavior on multilayer adsorption considered layer location dependence of the bonding energy

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결합에너지의 층별 의존성이 고려된 다층흡착에서의 헨리법칙 거동

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Abstract A purpose of this paper is to derive an adsorption isotherm on multilayer in which the layer location dependence of the bonding energy is considered and to represent that an adsorption on multilayer satisfies Henry's experimental law by analyzing the derived adsorption isotherm in the limit of low pressure.

요 약 본 논문에서는 먼저 다층흡착에서 각 흡착층의 결합에너지가 서로 다른 경우의 흡착등온선을 유도한다. 그리고 유도된 흡착등온식이 저압영역에서 헨리의 실험법칙을 잘 만족시킴을 보인다.

1. Introduction

In recent years, many interests are concentrated on surface of which properties depend on the concentration of very small particles with order of nanometer scale. Surface

gives important effects on the physical properties of materials in that as the size of a material grows the number of particles dominate throughout whole bulk materials. Solid surface has some specific structures and physical properties such as surface recon-

struction and surface relaxation which are significantly different from those of the bulk. Moreover, it is in the solid surface interfaced with gaseous or liquid phase that energy, particles and electrons transfers occur incessantly [1,2].

Studies on surface include the subject such as elastic and inelastic scattering [3,4], adsorption, desorption [5,6], surface diffusion of particles on surfaces [7], and surface phase transition [8-11] etc. Our interest here is on the adsorption of particles.

Isotherm contains the various physical informations for adsorption itself as well as for the dynamic behaviors of particles on surface, and for the surface structures. Since Langmuir [12] has suggested an adsorption isotherm on monolayer to investigate the adsorption phenomena of hydrogen atoms on tungsten/filament surface, many isotherms have been reported by theory or experiment [8,13].

As an important property of adsorption on multilayer, in most cases, the amount of adsorbed particles is linearly proportional to the pressure of gases above the layers, at the sufficiently low pressure, which is known to be Henry's experimental law [14-16]. Previously, the author showed theoretically that an adsorption on multilayer obeys Henry's law [17]. In that theory, the bonding energy of a particle adsorbed in each layer is assumed to be constant irrespective of the location (height) of the layer. But in the adsorption on multilayer, in the great majority cases, the particles are more stably adsorbed on the layer near the solid than far

from the solid, that is, the bonding energy is dependent on the location of the layer. A purpose of this paper is as follows: we derive an adsorption isotherm on multilayer in which the layer location dependence of the bonding energy is considered and to represent that an adsorption on multilayer satisfies Henry's law by analyzing the derived adsorption isotherm in the limit of low pressure.

2. Model and theorem

We introduce a model. Many monolayers (n layers) are interspaced between a gas phase and a solid phase to form multilayers. A gas phase is assumed to comprise of the ideal gases of temperature T in equilibrium. Let us number the monolayers in sequence by 1, 2, 3, ..., n from the monolayer near the solid surface to the one far from the surface, and represent the number of particles adsorbed on the j th layer by X_j . The particles adsorbed on the j th layer form the $(j+1)$ th layer and serves as the active sites for the $(j+1)$ th layer. X_0 represents the number of sites for the first layer particles to be adsorbed. Since an active site can accommodate only one particle, the following inequalities hold

$$X_0 \geq X_1 \geq X_2 \geq \dots \geq X_n \geq 0. \quad (1)$$

We assume the bonding energies are different along the layer and let the bonding energy of a particle adsorbed in the j th layer be

$-E_j (< 0)$.

In the absence of the interactions between adjacent layers the canonical partition functions of each layer become independent each other. And more, if the interactions between adsorbed particles within a layer are excluded, the particles are expected to be distributed at random. In this case, the canonical partition function $Q(X_j, T)$ in the j th layer becomes

$$Q(X_j, T) = \frac{X_{j-1}!}{X_j!(X_{j-1}-X_j)!} \exp\left(\frac{E_j X_j}{kT}\right), \quad (2)$$

and the chemical potential becomes for j th layer by using the Stirling formula

$$\begin{aligned} \frac{u_j}{kT} &= -\frac{d}{dX_j} \ln Q(X_j, T) \\ &= \ln\left(\frac{X_j}{X_{j-1}-X_j}\right) - \frac{E_j}{kT}, \end{aligned} \quad (3)$$

where k is a Boltzmann constant.

Because the layers and gas phase are in equilibrium, the chemical potentials satisfy the following relations :

$$u_1 = u_2 = \dots = u_n, \quad (4)$$

and

$$u_n = u_g, \quad (5)$$

where u_g is the chemical potential of gas phase.

Substituting Eq. (3) into Eq. (4), we get

$$\frac{X_1}{X_0-X_1} \exp\left(-\frac{E_1}{kT}\right) = \frac{X_2}{X_1-X_2} \exp\left(-\frac{E_2}{kT}\right)$$

⋮

$$= \frac{X_n}{X_{n-1}-X_n} \exp\left(-\frac{E_n}{kT}\right), \quad (6)$$

and Eq. (5) gives

$$\ln \frac{X_n}{(X_{n-1}-X_n)} - \frac{E_n}{kT} = \ln f(T) + \ln P, \quad (7)$$

where P is the pressure of gas phase, and $f(T)$ is given by [18]

$$f(T) = \frac{1}{kT} \left(\frac{h^2}{2\pi m kT} \right)^{3/2} \quad (8)$$

Here h is the Planck constant, and m the mass of a gas particle (or an adsorbed particle). Let the pressure satisfying $X_n = X_{n-1}/2$ be P_0 and let b be a ratio of pressures with a reference pressure P_0 ,

$$\frac{P}{P_0} = b. \quad (9)$$

Then Eq. (7) reduces to

$$X_n = b(X_{n-1} - X_n), \quad (10)$$

and Eq. (6) is rearranged as the following sequence of equations

$$\begin{aligned} (X_0 - X_1) X_n S_n &= S_1 X_1 (X_{n-1} - X_n) \\ (X_1 - X_2) X_n S_n &= S_2 X_2 (X_{n-1} - X_n) \\ &\vdots \\ (X_{n-2} - X_{n-1}) X_n S_n &= S_{n-1} X_{n-1} (X_{n-1} - X_n), \end{aligned} \quad (11)$$

where S_j 's are Boltzmann factors

$$S_j = \exp\left(-\frac{E_j}{kT}\right), \quad (12)$$

and satisfy the following inequalities

$$0 \leq S_i \leq 1. \quad (13)$$

From Eq. (10) and Eq. (11), we get relations

$$X_j = (X_{j-1} - X_j) b W_j, \quad (14)$$

where W_j 's are the ratios of Boltzmann factors defined by

$$W_j = \frac{S_n}{S_j}, \quad (15)$$

satisfying

$$W_j (j \neq n) > 0, \text{ and } W_n = 1. \quad (16)$$

The total number of adsorbed particles N is obtained through Eq. (14) as

$$\begin{aligned} \frac{N}{X_0} &= (X_1 + X_2 + \dots + X_n) / X_0 \\ &= \frac{1}{X_0} \left(\frac{bW_1 X_0}{1+bW_1} + \frac{bW_2 X_1}{1+bW_2} + \dots + \frac{bW_n X_{n-1}}{1+bW_n} \right) \\ &= \sum_{j=1}^n \frac{b^j W_1 W_2 \dots W_j}{(1+bW_1)(1+bW_2) \times \dots \times (1+bW_j)} \end{aligned} \quad (17)$$

This equation contains implicitly the bonding energy $-E_j$, and reduces to a Langmuir adsorption isotherm for monolayer $n=1$:

$$\frac{N}{X_0} = \frac{bW_1}{1+bW_1} \quad (18)$$

Since we have omitted the interactions between adjacent layer or between adsorbed particles within a layer, Eq. (17) is useful

only for the limit of low particle density, that is, for the range of low pressure.

3. Result and concluding remarks

An adsorption isotherm on multilayer Eq. (17) becomes approximately for the limit of low pressure,

$$\frac{N}{X_0} = C_n b, \quad (19)$$

where

$$C_n = (W_1 X_0 + W_2 X_1 + \dots + W_n X_{n-1}) / X_0 \quad (20)$$

It is reasonable to use an inequality

$$E_1 > E_2 > \dots > E_n > 0 \quad (21)$$

or equivalently

$$W_1 > W_2 > \dots > W_n, \quad (22)$$

since the particles are more stably adsorbed on the layer near the solid. From Eq. (1) and Eq. (22), we know C_n is finite for arbitrary values of n . Thus Eq. (19) represents Henry's law such that the amount of adsorbed particles is linearly proportional to the pressure of gases at sufficiently low pressure.

When the bonding energies are all the same along the layers,

$$E_1 = E_2 = \dots = E_n, \quad (23)$$

which implies that $W_j=1$ for all j , our result Eq. (17) for the adsorption isotherm on multilayer becomes

$$\frac{N}{X_0} = \sum_{j=1}^n \left(\frac{b}{1+b} \right)^j = b \left[1 - \left(\frac{b}{1+b} \right)^n \right]. \quad (24)$$

This equation becomes

$$\frac{N}{X_0} \sim b \quad (25)$$

for low pressure, which is identical to the result of the previous report.

In summary, we introduced a multilayer model such that the molecules are allowed to adsorb just on the particles already adsorbed or on the substrate sites and such that the bonding energies are different along the layers. And we derived an adsorption isotherm for the multilayer model. By analyzing the derived adsorption isotherm, we showed theoretically that an adsorption on multilayer obeys Henry's experimental law.

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