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Study of Effect of Lateral Intermolecular Interaction on Multilayer Physical Adsorption of Gas

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The effect of lateral intermolecular interactions among the adsorbate molecules has been incorporated into the theory of multilayer physical adsorption developed previously by the present authors within the frame of Bragg-Williams approximation and the resulting adsorption isotherm has been used to interpret the adsorption data of tetramethylsilane vapor on clean iron film which we failed to account for in our previous works. The result has shown that up to the point where the relative pressure is about 0.7 considerable improvement is obtained but beyond this point there still remains large difference between theoretical and experimental isotherm. Such difference is supposed to arise from the neglect of effect of vertical interaction between the adsorbate molecules and the adsorbent surface.

1. Introduction

In two previous papers^{1,2}, we have developed a modified version of the BET theory of multilayer physical adsorption³ by assuming that a second or higher layer molecule is most likely to be adsorbed above the center of a square or triangular array of molecules, rather than on the top of molecules themselves as assumed in the BET theory, in the next lower layer and thereby have successfully derived a generalized form of the adsorption isotherm which can describe the Type I, II, and III adsorption over wide range of temperature and pressure. The derived adsorption isotherms have successfully been tested for various adsorbate-adsorbent systems and the authors have been sufficiently convinced that they are on the right track of pursuing a realistic model of multilayer physical adsorption.

Unfortunately, in our previous treatments, however, the effects of lateral interactions among the adsorbate molecules and vertical interactions between the adsorbate and adsorbent molecules have not explicitly been taken into account, but only partly included in the average molecular partition functions, q_1 and q . Due to this the adsorption of tetramethylsilane vapor on clean iron film, in which the effects of such intermolecular interactions are expected to be substantial, have been found to greatly deviate from theoretical picture predicted by the derived isotherm.

It is not clear at this stage which of two type of intermolecular interactions stated above is more influential in the adsorption of TMS on the iron surface, and we feel that they must be investigated one after the other. Thus the objective of this paper lies in the elucidation of the effects of lateral interactions among the adsorbate molecules within the frame of Bragg-Williams approximation.⁴ The effects of vertical interactions between the adsorbent and adsorbate molecules will be studied later and published in a subsequent paper.

2. Theory

In accordance with our previous papers we write the adsorption isotherm as follows:

$$\omega = x + \frac{x^n y}{1 - y^n} \quad (1)$$

where ω is the average number of adsorbate molecules per site on the adsorbent surface, x is the degree of occupation for the first layer, and y is that for the second and higher layer. Note that we have assumed the degree of occupation is the same for all but the first layer.

In order to evaluate x and y in terms of thermodynamic quantities we need to know the canonical partition function for the entire adsorbed phase as in the previous case. In the Bragg-Williams approximation the partition function for the

i -th layer, Q_i , may be explicitly written as⁴

$$Q_i(M_i, N_i, T) = \frac{M_i!}{(M_i - N_i)! N_i!} q_i^{N_i} \exp\left(-\frac{N_i^2}{M_i} \frac{cw}{2kT}\right) \quad (2)$$

where M_i is the number of sites available to the i -th layer molecules, N_i the number of molecules in the i -th layer, q_i the average molecular partition function for an i -th layer molecule in the absence of lateral intermolecular interactions, c and w respectively represent the number of nearest neighbor sites around an adsorbate molecule in a two-dimensional layer and the lateral interaction energy between a nearest neighboring pair of molecules. k and T are, as usual, the Boltzmann constant and the absolute temperature of the system, respectively. Then the canonical partition function for the entire adsorbed phase, Q , is approximately written as

$$Q = \prod_{i=1}^{\infty} Q_i(M_i, N_i, T) \quad (3)$$

As in the case of BET model, we will assume

$$q_1 \neq q_2 = q_3 = \dots = q \quad (4)$$

In order to facilitate the derivation of equilibrium conditions from which x and y can be determined we introduce the functions φ and ψ , as in our previous works, defined by

$$\varphi = -A/MkT \quad (5)$$

and

$$\psi = -\mu_A/kT \quad (6)$$

where A and μ_A denote, respectively, the Helmholtz free energy and the chemical potential for the adsorbed phase and M is the number of adsorption sites provided by the adsorbent surface.

Using the definitions of x and y [see Eq.(5) in reference 1], φ may be rewritten as

$$\begin{aligned} \varphi &= \frac{1}{M} \ln Q \\ &= -(1-x) \ln(1-x) - x \ln x + x \ln q_1 - \beta x^2 \\ &+ \frac{w-x}{y} \left[-(1-y) \ln(1-y) - y \ln y + y \ln q - \beta y^2 \right], \quad (7) \end{aligned}$$

where $\beta = cw/2kT$.

At equilibrium $(\partial\varphi/\partial x)_{\omega}$ must be set equal to zero, since the free energy A is minimized. Thus, we can obtain from Eq. (7)

$$\begin{aligned} \left(\frac{\partial\varphi}{\partial x}\right)_{\omega} &= \ln(1-x) - \ln x + \ln(q_1/q) - 2\beta x \\ &- \ln(1-y) + \ln y + \frac{ny^{n-1} - nx^{n-1}}{1 + (n-1)y^n} \ln(1-y) \end{aligned}$$

$$\begin{aligned} &+ \beta \left\{ 2y - \frac{ny^{n-1} - nx^{n-1}}{1 + (n-1)y^n} y^2 \right\} \\ &= 0. \quad (8) \end{aligned}$$

Furthermore, at equilibrium $(\partial\varphi/\partial\omega)_x = -\mu_A/kT$ [see Eqs. (16) and (17) in reference 1], which gives us

$$\begin{aligned} -(\mu_A/kT)_{\text{eq.}} &= (\partial\varphi/\partial\omega)_x \\ &= (\partial\varphi/\partial y)_x / (\partial\omega/\partial y)_x \\ &= -\ln y + \left\{ 1 - \frac{ny^{n-1}}{1 + (n-1)y^n} \right\} \ln(1-y) \\ &= \ln q - \beta \left\{ 2y - \frac{ny^{n-1}}{1 + (n-1)y^n} y^2 \right\} \quad (9) \end{aligned}$$

Since at equilibrium the chemical potential of the adsorbed phase, μ_A is equal to that of the vapor phase in equilibrium with it, we may write

$$\mu_A/kT = \mu_g^{\circ}/kT - \ln \xi \quad (10)$$

where μ_g° is the standard chemical potential of the vapor phase (being assumed to be ideal) and ξ is the relative pressure, p/p_0 . In other words μ_g° is the chemical potential of the saturated equilibrium vapor.

Equating Eq.(8) with Eq.(9), we have

$$\begin{aligned} -\ln y + \left\{ 1 - \frac{ny^{n-1}}{1 + (n-1)y^n} \right\} \ln(1-y) + \ln q \\ - \beta \left\{ 2y - \frac{ny^{n-1}}{1 + (n-1)y^n} y^2 \right\} = -\frac{\mu_g^{\circ}}{kT} - \ln \xi \quad (11) \end{aligned}$$

For convenience, let

$$A \equiv \frac{ny^{n-1}}{1 + (n-1)y^n}, \quad (12)$$

$$T \equiv \beta(2y - Ay^2), \quad (13)$$

and

$$a \equiv q e^{\mu_g^{\circ}/kT} \quad (14)$$

Then, Eq.(11) can simply be rewritten as

$$y = \frac{a\xi}{a\xi + (1-y)^A e^T} \quad (15)$$

Substitution of Eq.(8) into Eq.(11) can also yield the following relation:

$$\ln(1-x) - \ln x + \ln(q_1/q) - \frac{nx^{n-1}}{1 + (n-1)y^n} \ln(1-y)$$

$$\begin{aligned}
 & + \ln q - \beta \left[2x - \frac{nx^{n-1}}{1 + (n-1)y^n} y^2 \right] \\
 & = - \frac{\mu_g^0}{kT} - \ln \xi. \quad (16)
 \end{aligned}$$

Again, we let

$$B \equiv \frac{nx^{n-1}}{1 + (n-1)y^n} \quad (17)$$

and

$$S \equiv \beta(2x - By^2). \quad (18)$$

Then, Eq.(16) can be simplified to

$$x = \frac{a\xi}{a\xi + \frac{q}{q_1} (1-y)^B e^S} \quad (19)$$

Returning to the original notations, we finally obtain the following two relations from which x and y can be determined:

$$\begin{aligned}
 y = & \frac{a\xi}{ny^{n-1} \exp \left[\frac{cw}{2kT} \left(2y - \frac{ny^{n-1}}{1 + (n-1)y^n} y^2 \right) \right]} \\
 & a\xi + (1-y) \frac{ny^{n-1}}{1 + (n-1)y^n} \quad (20)
 \end{aligned}$$

and

$$\begin{aligned}
 x = & \frac{a\xi}{a\xi + \frac{q}{q_1} (1-y) \frac{nx^{n-1}}{1 + (n-1)y^n} \exp \frac{cw}{2kT} \left[\left(2x - \frac{nx^{n-1}}{1 + (n-1)y^n} y^2 \right) \right]} \\
 & \quad (21)
 \end{aligned}$$

Eqs.(20) and (21) reduce to our previous results in the absence of lateral interactions, that is, when $cw=0$. [see Eqs.(6) and (8) in reference 2]. To find theoretical isotherms we first calculate y from Eq.(20) by iterative method on digital computer for a given set of values of n , ξ , cw , and a . Thus obtained y value is then substituted into Eq.(21) and again the iterative method is used to calculate x for a given set of values of ξ , q/q_1 , n , cw , and a . [Eq.(20) has also a trivial solution, $y=1$ but this must be discarded.] Substitution of the values of x and y obtained by solving Eq.(20) and Eq.(21) into the adsorption isotherm given by Eq.(1) can then yield the values of ω for a given set of values of ξ , q/q_1 , n , cw , and a .

In Figure 1 through Figure 3 we have shown the calculated theoretical isotherms for various sets of q/q_1 and a assuming $n=3$ and $cw/2kT=-0.1$. Also, expected theoretical isotherms in the absence of lateral interactions ($cw=0$) have been shown by dashed curves under the same set of conditions. From these we see that the presence of lateral interactions among the adsorbate molecules increases the amount of ad-

sorption compared to the case of no lateral interactions. This conforms to our expectation since the presence of attractive

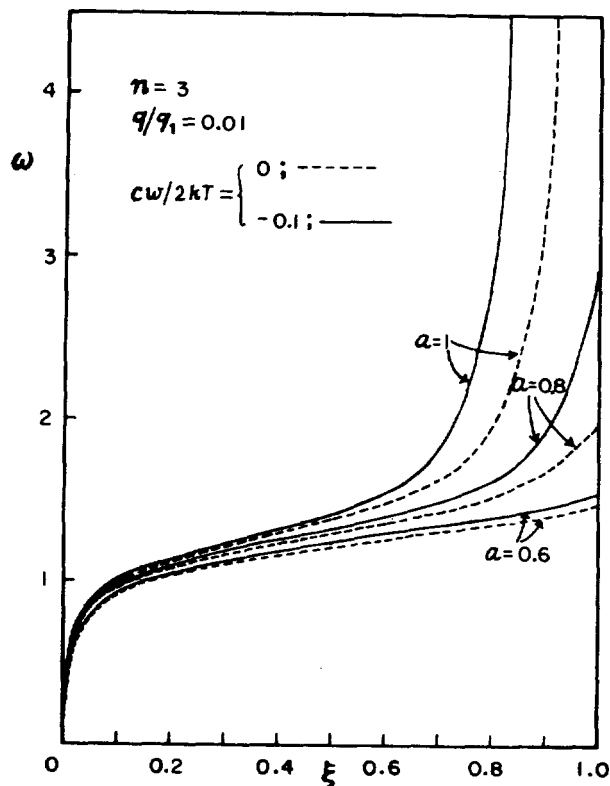


Figure 1. Theoretical adsorption isotherms for which $n=3$ and $q/q_1=0.01$

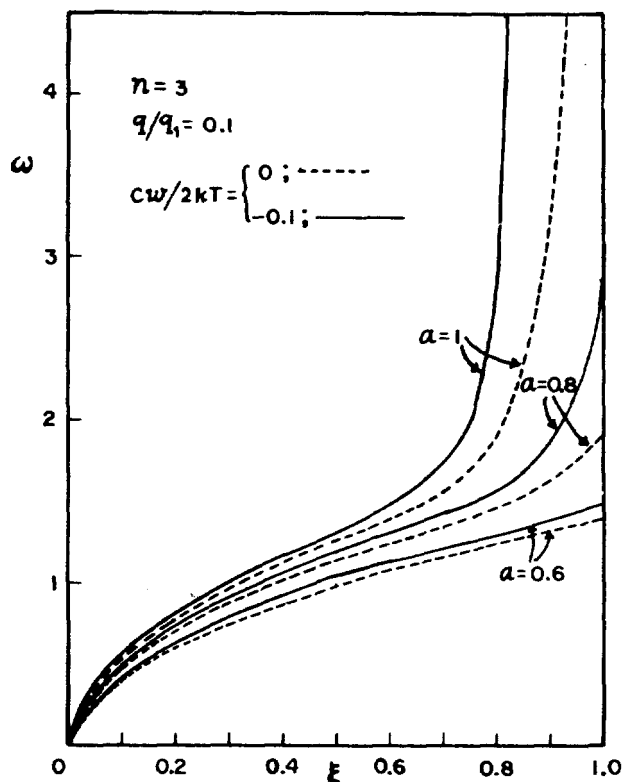


Figure 2. Theoretical adsorption isotherms for which $n=3$ and $q/q_1=0.1$

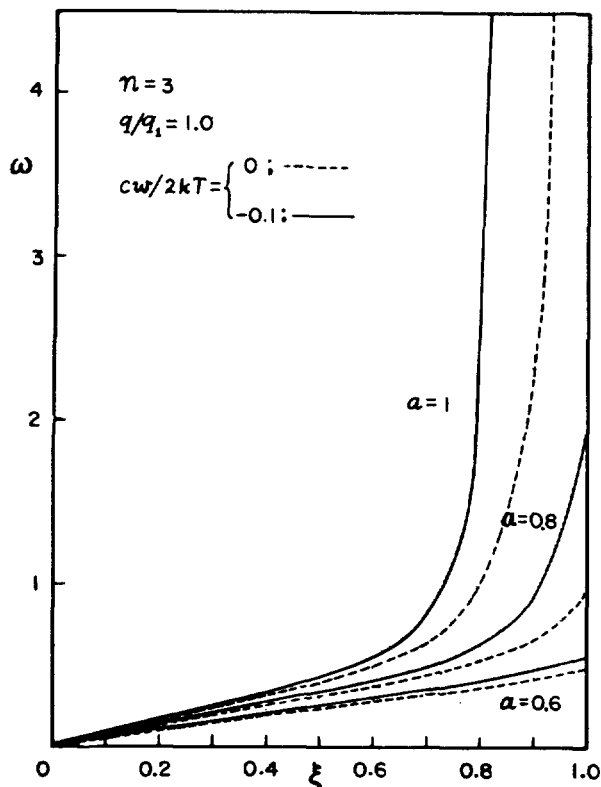


Figure 3. Theoretical adsorption isotherms for which $n=3$ and $q/q_1 = 1.0$

lateral interactions among the adsorbate molecules in one layer increases the possibility of clustering of molecules in the same layer, thereby increasing the possibility of formation of more available adsorption sites for the next upper layer.

3. Result and Discussion

The theoretical isotherm derived in the last section has been applied to interpret the adsorption data of TMS vapor on clean iron surface⁵ and the result has been demonstrated in Figure 4. The best agreement between theoretical isotherm and experimental one has been obtained when $n=3$, $q/q_1=0.01$, $a=0.8$, AND $cw/2kT=-0.3$. Also, the best overall agreement acquired without considering the effect of lateral interactions has been represented by a dashed curve in the same figure. From this we see that the inclusion of effect of lateral interactions into our calculations will yield the considerable improvement over the case in which such effect is ignored up to $\xi \approx 0.7$. Above this point, however, the agreement between theoretical and experimental curve rapidly deteriorates. It is in this region, we conjecture, that the vertical interaction between the adsorbate molecules and the adsorbent surface plays an important role. Such result can be anticipated because in the absence of strong vertical interaction some molecules will start the formation of third layer even before the second layer is completed and the lateral interaction will pull these molecules together to provide the adsorption sites available for the

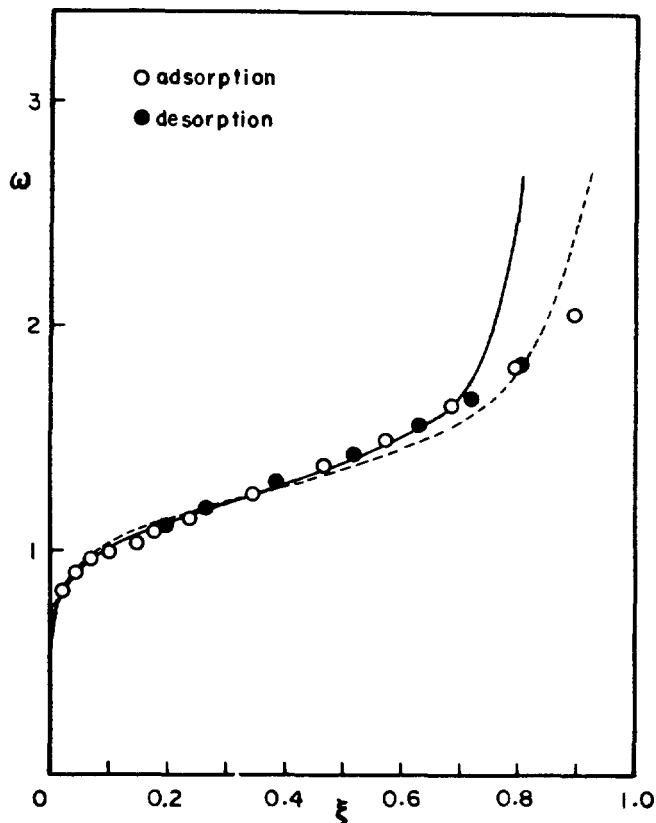


Figure 4. Comparison between theoretical and experimental isotherms of adsorption of TMS vapor on clean iron film. Solid curve has been obtained by setting $n=3$, $q/q_1=0.01$, $a = 0.8$, and $cw/2kT = -0.3$ while dashed curve corresponds to the case of $n = 3$, $q/q_1 = 0.006$, $a = 0.95$, and $cw/2kT = 0$. Experimental temperature is 23.3 °C.

fourth-layer molecules and so on. This seems to be the reason why the theoretical curve shown in Figure 4 diverges rapidly above the point $\xi \approx 0.7$. The presence of strong vertical interactions will cause the molecules in the higher layer to be pulled down to the lower layer and force the latter layer to be more completed than otherwise, thus reducing the amount of adsorption. In fact we have already made some preliminary calculations including such vertical interactions and the results looked quite promising. We intend to publish the more complete investigation of such effects in a subsequent paper.

In summary it may be concluded that for large molecules such as tetramethylsilane the effect of lateral intermolecular interactions among the adsorbate molecules plays an important role in their adsorption on a solid adsorbent surface in the low to medium pressure region.

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Photocycloaddition of 5,7-Dimethoxycoumarin to 5-Fluorouracil

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C_4 -Photocycloaddition of 5,7-dimethoxycoumarin(DMC) to 5-fluorouracil(5-FU) was studied in frozen aqueous solution. The major photoproduct was diagnosed and isolated by TLC and column chromatography. The structure of isolated photoproduct was identified as a C_4 -cycloaddition product of DMC and 5-FU by the characteristics of its UV, IR, NMR, mass spectra, elemental analysis, and photosplitting.

Introduction

Psoralens, naturally occurring coumarin derivatives in plants of the families *Umbelliferae* and *Rutaceae*, are known to photoreact with pyrimidine bases in DNA with near UV light. These biological effects have been attributed to this photoreaction.^{1,2}

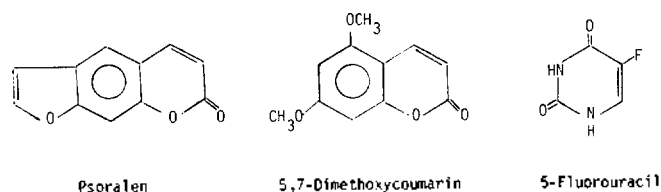
5,7-Dimethoxycoumarin(DMC) which has only one photochemical functional group (without the furan ring) in the molecule also intercalate with DNA and photobinds covalently to DNA bases causing the same biological effects as furocoumarins, unlike most other coumarins.³⁻⁵ Since DMC is as reactive as psoralens and since fewer photoproducts are formed due to the lack of bifunctionality compared to furocoumarins, the photoreaction of DMC with pyrimidine bases has been studied as a model reaction for the molecular basis of skin-photosensitization. The photoadducts of DMC to thymine⁶ and thymidine⁷ were isolated by chromatography and characterized.

The incorporation of 5-fluorouracil(5-FU) into the RNA of tobacco mosaic virus sensitizes both the intact virus^{8,9} to UV light. The sensitivity is proportional to the incorporation of 5-FU in place of uracil. The photosensitization by acetone or N-methylglutidone yields a C_4 -cycloaddimer from 5-FU in aqueous solution.¹⁰

5-FU has been shown to be the most reactive among the pyrimidine bases tested for photoreactivity with coummaryl compounds¹¹ and highly active with DMC.⁶

To see the base specificity of psoralens and DMC in the photoaddition of the compounds to DNA and as a model for

the photosensitization of psoralens, the photoaddition reaction of DMC to 5-FU is studied.



Experimental

Materials. DMC and 5-FU obtained from Aldrich chemicals gave only one spot on the silicagel thin layer chromatogram. Kieselgel G (Typ 60) and Kieselgel GF 254 were used for silicagel thin layer chromatography (TLC). Kieselgel 60 (Merck, 230 mesh) was used for column chromatography. Other common solvents were from Wako Chemical Company and used without further purification.

Spectroscopic Measurements. UV spectra were measured on a Cary 17 spectrophotometer and IR spectra were recorded in potassium bromide pellets on a Perkin-Elmer Model 267 grating spectrophotometer. NMR spectra were measured on a Varian T-60A spectrometer against tetramethylsilane internal standard in perdeuterated pyridine solvent. Mass spectra were determined with Hewlett Packard 5985 A GC/MS system. Fluorescence spectra were recorded on an Aminco-Bowman spectrofluorometer with Aminco-XY-recorder. Elemental analysis were carried out at ADD with a C.H.N. analyzer.

Irradiation Apparatus. Irradiations were carried out in a Rayonet Photochemical Reactor (The Southern New England