ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

98-358

E17-98-358

V.N.Samoilov*, V.K.Fedyanin

CONSIDERATION OF INTERACTION IN ADSORBATE FOR POLYMOLECULAR PHYSICAL ADSORPTION

Submitted to «Journal of Physical Chemistry»

---

*Scientific Centre for Applied Research

1998

Eighty years ago (1916) Langmuir proposed a model of adsorption whose results are yet used effectively for interpreting the data on sorption. Langmuir postulated that

a) the adsorption heat of a molecule adsorbed by an active center is constant and

b) the adsorption can occur only on a free active center.

So, the "Langmuir adsorption" is a multilayer adsorption. However, experiments on adsorption, both on chemisorption [1] and physical adsorption, offer evidence of it being a monolayer adsorption. Though isotherms of adsorption are frequently of the Langmuir nature (chemisorption, physical adsorption on zeolites [2], polymolecular adsorption on a large class of compounds [3]), they are used for describing real open systems "adsorbate–adsorbent". The Langmuir model was corrected when assumptions a) and b) were neglected. It has long been shown that the dependence of the heat of adsorption on the covering Θ can be caused either by adsorption centers being non-equivalent (inhomogeneity of a surface) or by interaction in an adsorbate if we have a carefully prepared surface: annealing, high vacuum, cleaning by total bombardment. For real surfaces, both the types of dependences are to be taken into account. In this connection we mention studies by Temkin [1] on chemisorption in which consistent account was taken of the inhomogeneity of a catalyst surface. Brunaner, Emmett and Teller in their studies on polymolecular physical adsorption [4] retained the Langmuir assumptions. The Langmuir model assumes that when the monolayer is filled and a two-dimensional layer of adatoms arises with a maximally dense packing, its structure is dictated by the crystallographic structure of a face of the backing (d = 2, z = 3, 4, 6, d is the dimension and z is the number of nearest neighbors) and the adsorption is completed. If filling of 1cm^2 by a monomolecular layer requires σ_0 particles and the number of really adsorbed particles equals σ, the surface can accept $(\sigma - \sigma_0)$ particles. Consequently, $n\sigma/\sigma_0$ particles of n particles colliding with the surface return to the gas phase. $1 = \sigma/\sigma_0$ active centers can be adsorbed.

Since, according to kinetic theory, per 1 cm^2 n particles kept during the time τ [3] are falling, then

$$\sigma = n\tau, \tag{1}$$

and

$$\sigma = n(1 - \frac{\sigma}{\sigma_0})\tau; \qquad \sigma = \frac{\sigma_0 n\tau}{1 + \sigma_0 n\tau}. \tag{2}$$

It is more convenient to deal with the covering Θ:

$$\Theta = \frac{\sigma}{\sigma_0} = \frac{n\tau/\sigma_0}{1 + h\tau/\sigma_0} = \frac{K_n\rho}{1 + K_n p}, \tag{3}$$

where

$$K_n = \frac{N_\tau}{\sqrt{2\pi MRT}} = \frac{N\tau_0 \exp(Q/RT)}{\sqrt{2\pi MR'P\cdot\sigma_0}}$$

is the coefficient of adsorption in the kinetic approach; Q_0 is the heat of adsorption (see below). When $K_n\rho << 1$, we arrive at the Henry isotherm $\Theta = K_n\rho$. Adatoms in the Langmuir approach are fixed at regularly placed centers of a two-dimensional lattice. A dynamic equilibrium is set in and there is no motion on the surface. Though the surface mobility is important and the heat of adsorption changes the covering, formula (3) describes a large class of experiments (experimentally, other types of isotherms are obtained, as well) [5, 7] and considers the modification of the Langmuir isotherm owing to the interaction in an adsorbate.

The course of studies (1968-1997) was based on the quantum-statistical model of sorption that assumed the structure of active centers being regular for an open system "adsorbate-adsorbent" with interaction of Z nearest neighbors. The model Hamiltonian of a system of that type is given by the formula

$$\hat{H} = -\nu\sum\hat{n}_f - \frac{1}{2}\varepsilon\sum\hat{n}_f\hat{n}_g, \qquad n_f = 0,\ 1, \tag{4}$$

where $(f,\ g)$ are coordinates of active centers; ε is the interaction of adatoms; $\nu = \kappa T_{\ln}(ap)^{1/n}$; n is the dissociation coefficient: $A_n \to n[A]$. The whole thermodynamics is defined by $<\hat{n}_f> = \Theta$ and the $<\hat{n}_f\hat{n}_g>$ averaging runs over $\hat{H}$ (4); and $<\hat{A}> = S_p^n A\exp^{-\beta\ddot{H}}/S_p e^{-\beta\hat{H}}$. For physical adsorption to be considered below, $n=1$; ρ_ε is the equilibrium pressure in an adsorbate; $a = j_a(\beta)_0/j_0(\beta)\kappa T$ is the adsorption coefficient; $j_a(\beta)$ is the statistical sum of adatoms; $j_o(\beta)$ is the statistical sum of molecules in the gas phase. This approach can also be applied to adsorption from a solution [2, 5]. If a solute is adsorbed, the chemical potential of an adsorbent μ_a should be equated to $\mu_0 = \omega_1(p,T) + \kappa T\ln x_s$. In adsorption of a solvent $\mu_0 = \mu_0^0(p,T) + \kappa T\ln x_0$, $x_0 + x_s = 1$, $x_i(l = 0, S)$ is concentration of a solvent and a solute.

Here we will consider adsorption from the gas phase. In this approach, ε is set to be a constant independent of the covering* and can be determined from the total drop of isosteric heat of adsorption $q(\Theta)$ by the formula [1]

$$Z\varepsilon N_\Delta = q(\Theta\to 1) - q(\Theta\to 0). \tag{5}$$

(We made use of the Clausius-Clapeyron formula.) For the values we mentioned above formula (5) gives: $\varepsilon \geq 0$ describes physical adsorption and $\varepsilon < 0$ describes the chemisorption. (Sometimes physical sorption is characterized by a weak repulsion, which occurs for a considerable overlapping of wave functions of neighboring adatoms [6d].)

A detailed analysis was given for behavior of experimentally measured characteristics of chemisorption and physical adsorption (isotherms, heat, rates of adsorption and desorption, etc.). Besides quantum-statistical characteristics of molecules in the gas phase, experimental data on drops of heats of adsorption, the contribution of an electron system to equilibrium characteristics, the characteristics of an activated complex of sorption, and the influence of the electron system on its energy were used for the complete description.

For physical sorption, the contribution of the electron system is negligible and experimental observables are the drops of heats of adsorption at a complete covering determining interaction and renormalizing τ. (As for polymolecular adsorption, see below.)

In particular, for a monolayer covering, the formula

$$\Theta = \frac{ap\exp\beta\ z\varepsilon\ \Theta}{1 + ap\exp\beta\ z\varepsilon\ \Theta}, \qquad a = l_n\frac{ja(\beta)}{j_q(\beta)KT} \tag{6}$$

was obtained in the self-consistent-field approximation [6a,b]. When $\varepsilon = 0$, (6) transforms into the Langmuir isotherm (3); the structure $n\tau/\sigma_0$ coincides with the expression derived by statistical methods [9] with the change $Q \to \Delta Q$; in ref. [9] detailed expressions can be found for $j_n(\beta)$ and $j_0(\beta)$.

So, the interaction being included into an adsorbate changes the exponential factor in τ as follows:

$$\tau \to \hat{\tau} = \tau_0\exp\left(\frac{\beta\ z\varepsilon\ \Theta}{RT}\right) = \tau_0\exp(\beta\ \Delta Q\cdot\Theta)/RT. \tag{7}$$

We made here use of (5) and $N_A\cdot\kappa T = RT$. So, into τ given by (7) ($\Theta = 1$ describes fast adsorption) we should substitute the total drop of adsorption heat rather than the heat of adsorption and energy adsorption used in ref. [3]. It is interesting that the inclusion of interaction at low energies $\varepsilon \to Z\varepsilon N_A = \Delta Q$ results in the equation for Θ

$$\Theta = \kappa_n p\exp(\beta\ z\varepsilon\ \Theta) \tag{8}$$

that is different from the Henry equation. In what follows we replace the factor obtained in our model, *ap*, by $K_u p$, which slightly changes the factor of exponential but simplifies computer calculations and does not require additional statistical-mechanical calculations of $j_a(\beta), j_0(\beta)$. For chemisorption, our isotherms of a large

---

*This fact was established through analyzing ε at different concentrations of solvents.

class of adsorbent systems with $\Delta Q \cong 30-100$ kcal/mole gave the Langmuir-type isotherms on the whole interval of Θ: $0 \le \Theta \le 1$, i.e. we obtained the function Θ convex over the axis k with the saturation as $\beta z \varepsilon \Theta \to \infty$ and as $ap \to \infty$, $\Theta \to 1$.

Physical adsorption with $\varepsilon > 0$ at small $ap \exp \beta z \varepsilon \Theta$ is characterized by a linear behavior with a specific loop of attraction (condensation) [2,3].

Physically, this modification is quite clear: since as a rule for physical adsorption $\varepsilon \ge 0$ (but sometimes the case $\varepsilon \ge 0$ may happen), adatoms should overcome not only the forces of coupling with a substrate but also the forces of attraction for $\varepsilon > 0$ (when $\varepsilon < 0$, repulsion promotes desorption and we arrive at "classical" Langmuir isotherm) [2]. The feasibility of polymolecular adsorption was mentioned by Langmuir. He and some other authors attempted to obtain adsorbtion isotherm in this case, as well. Most successful turn out Brunauer, Emmett and Teller (1983) [4]. The BET isotherm is presently widely used in interpreting experimental data of the processes with polymolecular adsorption; some of them were mentioned earlier. In this paper we neglected the effects of interaction in an adsorbate and assumed that the energy of adsorption of the first monolayer and subsequent ones is constant. Later, we will take account of the interaction between adatoms within the mathematical BET scheme.

We note that the BET isotherm will be given by the same expression but with the renormalized parameters k, q. We will use the mathematical BET scheme proposed in [3] in order to derive a formula for the BET isotherm. Consider adsorption of "uniform" molecules of almost the same size whose interaction is described by the van der Waals potential with similar parameters.

Let us denote by Θ_2 the part of surface covered by a layer of molecules over which two molecules have been adsorbed thus forming a two-molecule layer (the corresponding substrate is the first monolayer and the covered part of the surface); and by Θ_i, the part of surface covered by a layer i molecular thick.

The total number of molecules adsorbed per 1 cm^2 is given by the formula:

$$\sigma = \sigma_0 \sum_{i=1}^{\infty} i\Theta_i, \tag{9}$$

where σ_0 is the number of molecules per 1 cm^2 in the filled monolayer. In equilibrium, all Θ_i are constant, and thus the uncovered part of the surface Θ_0 is constant:

$$\Theta_0 = 1 - \sum_{i=1} \infty\ \Theta_i. \tag{10}$$

Following the paper by Brunaner and Emmett [4], we carry out summation in (10) up to infinity. Later we discuss the case when the number of layers r_s is limited. A situation like that occurs in capillaries, which is especially important for adsorption on zeolites. The number of molecules got onto the uncovered surface Θ_0 and adsorbed on $(n\Theta_0)$ in dynamic equilibrium should be equal to the number of desorbed molecules $\nu\sigma_0\Theta_1$:

$$n\Theta_0 = \tilde{\nu}\sigma_0\Theta_1, \qquad \tilde{\nu}^{-1} = \tilde{r} = r_0 \exp\left(\frac{\Delta Q}{RT}\right). \tag{11}$$

In what follows we omit the tilda sign. Analogously, the first monolayer is formed of molecules of the uncovered surface $(n\Theta_0)$, molecules of the second layer corresponding to the surface part $\Theta_2 - \nu_1\sigma_0\Theta_2$, $\nu^{-1} = \tau_1 = (\tau_0 \exp(\Delta Q_1 / RT))$, and molecules desorbed from it $\nu\sigma_0\Theta_1$. Consequently,

$$n\Theta_0 + \nu_1\sigma_0\Theta_2 = \nu\sigma_0\Theta_2 + n\Theta_1; \qquad n\Theta_1 = \nu_1\sigma_0\Theta_2. \tag{12}$$

Continuing this reasoning we have for an i-th layer

$$n\Theta_{i-1} = \nu_{i-1}\sigma_0\theta_i, \qquad \nu_{i-1}^{-1} = \exp\left(\frac{\Delta Q_1}{RT}\right). \tag{13}$$

The uniformity of molecules validates the assumption

$$\tau_1 = \tau_2 = \ldots = \tau_i. \tag{14}$$

Introducing, like in [3], the parameter $x = n\tau_1/\sigma_0 = n/\sigma_0\tau_0^1(\exp(\Delta Q_1/RT))$ and summing up in (11) (it is explained in detail in [3]), we obtain the following expression for the total number of adsorbed particles in polymolecular adsorption:

$$\sigma = \frac{k\sigma_0 x}{(1-x)(1-x+kx)}, \qquad k\tau_1 = \frac{\tau}{\tau_2} = \frac{\tau_0}{\tau_0^1}(\exp\left(\frac{\Delta Q - \Delta Q_1}{RT}\right)). \tag{15}$$

Since $x = n\tau_1/\sigma_0$ is dimensionless and $n \approx p$, it is possible to write $x = \gamma \cdot p$; $g = \tau_1^0 = \sigma_0 = \gamma_1 = \gamma 1/\tau_1 \exp-(\Delta Q_1/RT)$; q is of the dimension of pressure, and the quantities (15) are defined by the following formulae:

$$x = \frac{p}{q}, \qquad \gamma = \frac{N}{\sqrt{2\pi RMT}}. \tag{16}$$

When the pressure p is reached at which

$$p = q = \frac{\tau_0}{\gamma}\exp\left(-\frac{\Delta Q_1}{RT}\right) = \sigma_0\sqrt{\frac{2\pi RM}{N^2}}\exp\left(\frac{\Delta Q_1}{RT}\right), \tag{17}$$

then $x = 1$; n_q are values n corresponding to the pressure $p = q$ such that $n_q\tau_1 = \sigma_0$.

A divergence in (15) arises at $p \to q$ because when summing we assumed that an infinite number of layers is adsorbed (at which pressures q this occurs and what is the real situation here, will briefly be discussed in what follows). On real surfaces, especially, when there are pores, the number of layers is limited. The evolution of formula (15) at $q = p_0$, where p_0 is the pressure of saturated vapors of an adsorbed substance with which q was identified in the original paper [7, 8], $p/p_0 << 1$; $q \neq p_0$, $q >> p_0$, will be discussed in a subsequent note.

Inserting $x = p/q$ into (15), we have

$$\sigma = \sigma_0\frac{kp}{(q-p)[1+(k-1p/q)]} = \sigma_0\frac{k(p/q)}{(1-p/q)[1+(k-1)p/q]}. \tag{18}$$

Here, like in the BET isotherm, there are three parameters:

$$\sigma_0; \quad k = \frac{\tau}{\tau_1} = \frac{\tau_0}{\tau_1^0}\exp\left(\frac{\Delta Q - \Delta Q_1}{RT}\right); \quad q = \frac{\sigma_0}{N} : \sqrt{2\pi RMT}\exp\left(-\frac{\Delta Q_1}{RT}\right). \tag{19}$$

Naturally, we can introduce a "common" covering

$$\Theta = \frac{\sigma}{\sigma_0} = \frac{kx}{(1-x)(1-x+kx)} = \frac{k(p/q)}{(1-p/q)[1+(k-1)p/q]}, \tag{20}$$

which is in molecular adsorption larger than unity. If the number of layers is restricted to the level r, we can introduce a multilayer covering in polymolecular adsorption:

$$\Theta_p = \frac{\Theta}{r} = \frac{\sigma}{\sigma_0}, \quad 0 \le \Theta_p \le 1. \tag{21}$$

If k, q are renormalized by the interaction in an adsorbate, then σ_0 can be estimated from sizes of molecules and the "area" of adsorption centers in a "fixed" adsorption. This is more or less feasible for chemisorption (repulsion) for covering $\Theta < 1$. However, with increasing temperature, say, in measuring on an isostere, at half coverings $\Theta = 1/2$ (diffraction of hydrogen slow electrons on tungsten $H_2 \to 2[H]_W$) at $T \cong 537^\circ$C, there occurs the transition "order-disorder" and the adsorption layer becomes mobile [10]. It is still more complicated to make that estimation for physical adsorption; as a rule σ cannot be estimated from adsorption data even for sufficiently "smooth" surfaces and shears. Thoroughly polished surfaces possess ledges of about 0.1 μ(10^{-4} mm). To determine a specific surface, when pores, especially narrow pores ($d \le 10A$), are present, is a complicated problem [5]. Since we measure the volume of an adsorbed substance and the number of adsorbed molecules $\sigma \cdot S$ (S is the specific surface [3, 5]), then, introducing the notation $V_r = \sigma \cdot S$ and $V_m = \sigma_0 \cdot S$, which is the volume of an adsorbed gas when the whole surface of an adsorbent is covered by a monolayer, we obtain instead of (18) the following formula:

$$V = \frac{kv_m\, p/q}{(1-p/q)[1+(k-1)p/q]}. \tag{22}$$

Now we will not discuss (22) at different ratios of p and q when it is necessary to employ also realistic values of $\Delta Q = N_A\varepsilon\,\Theta_1$, $\Delta Q_1 = zN_A\varepsilon_1\Theta_2$, or alternatively, confinement times τ, τ_1, rather, we will consider the case when (22) results in the Langmuir isotherm.

When $x = p/q = (n/\sigma_0^1)\tau_0^1\exp(\Delta_1/RT) << 1$, formula (22) transforms into the equation

$$\Theta = \frac{kx}{1+kx} = \frac{\gamma}{\sigma_0}\tau p\frac{1}{1+(\gamma/\sigma_0)\tau p} = \frac{K_u p\exp\beta\, Z\varepsilon\,\Theta}{1+K_u\exp\beta\, Z\varepsilon\,\Theta}, \tag{6'}$$

which coincides with (6). We took advantage of the equality $kx = \tau/\sigma_0\,\tau p$ ((15)-(17)). At $\varepsilon = 0$, formula (17) gives the classical Langmuir isotherm (3). If we identify q with the pressure of saturated vapor p_0, which is often assumed for the BET isotherm [3,5], the Langmuir isotherm describes an open adsorbate-adsorbent system of polymolecular adsorption at small p/p_0.

It is somewhat unexpected that formula (18) transforms into the Langmuir isotherm for $q >> p$, as well. Having the above relation between τ and τ_1 at hand, we will discuss that saturated vapor of a hypothetical polymolecular layer that would be generated at sufficiently high pressures. Till q is reached, the pressure p_0 is set and either in an adsorbate or in a near-adsorption layer, condensation takes place. The adsorption layer is limited and condensation does not provoke adsorption.

Indeed, when $q >> p$, we obtain

$$\frac{kpq}{(q-p)(q-p+kp)} \to \frac{kpq}{q(q+kp)} = \frac{(k/q)p}{(1+k(p/q))} = \frac{(\gamma\;\tilde{\tau}/\gamma_0)p}{1+(\gamma\;\tilde{\tau}/\gamma_0)p}, \tag{6''}$$

which coincides with (6), (6').

For illustration, we cite the value of q, when the surface limits the volume of a near-surface gas that is condensed in its neighborhood. Since $\sigma_{0/y} \cong 10^{-6}$, then

$q \geq 10^4\,\text{atm} \cdot \exp \Delta Q_1 / RT$ and (6) holds valid. If interaction is neglected, $q >> p_0$ changes into the equality $(\tau\ )_0 >> \tau_1$: the heat of evaporation of a liquid should be large as compared to the time of molecules on the surface of the first (monomolecular) layer. As a result, up to high p/p_0 there occurs monomolecular adsorption, whereas polymolecular adsorption is absent. The role of interaction in this case will be discussed elsewhere.

So, when $q > p_0$, the number of adsorbed layers (*r*) which are formed at $p = p_0$ is limited. It is also limited for the case of adsorption in capillaries, which is highly important for zeolites [2]. Brunaner, Emmett and Teller, having considered adsorption in a capillary space limited by flat-parallel walls, derived the following formula:

$$V = \frac{V_m kx[1-(rH)x^r + rx^{r+1}]}{(1-x)[1+(k-1)x-kx^{r+1}]}. \tag{23}$$

Here the number of adsorbed layers on every wall equals *r*; all the quantities, V_m, k, x, were introduced in the above consideration. At $r = 1$, we naturally odtain the Langmuir isotherm:

$$V = \frac{V_m kx}{1+kx}. \tag{24}$$

The data by Kemball [11] for adsorption of acetone on mercury lead to the conclusion on its polymolecular nature and this is described by an isotherm like that drawn in Fig.1.

The isotherm of adsorption of acetone on mercury [11]. At $p/p_0 = 1$ the fourth polymolecular layer appears. Note that many isotherms of adsorption of hydrocarbons on zeolites behave in a similar manner [2] with the only difference that the Langmuir part, the convexity towards the axis σ, extends up to $p/p_0 = 1$ (dotted line).

Note also that if we pass from σ and σ_0 to V and V_m, formula (5) is modified as follows:

$$Z\varepsilon\ N_A = q(v - v_m) - q * v \to 0. \tag{5'}$$

We made use of the simplest approximation of self-consistent field and exact system of equations for correlation functions obtained for the Hamiltonian (4) in [12, 6e, f]. Approximations including correlation effects were proposed in [12]; they can also be employed in problems of polymolecular adsorption, which will be carried out in a subsequent study.

References

[1] B.Trepnel. Chemisorption, I.L., Moscow, 1970, p.327.

[2] D.Brek. "Zeolitic molecular sieves", Mir, Moscow, 1970, p.781.

[3] Ya.De.Bur. "Dynamic character of adsorption", Moscow, I.L., 1962, p.290, edited by V.M.Gryaznov.

[4] S.Brunaner, E.Emmett, E.J.Teller. E.J.Am. Chem. Soe. 60, 309 (1938).

[5] S.Greg and K.Sing. "Adsorption. Specific surface, porosity", Mir, Moscow, 1984 (2nd edition).

[6] V.K.Fedyanin:
a) "State equations of particles adsorbed on the surface of a liquid or a gas with interaction between them taken into account", LSU, Proceedings of the 1st All-union symposium on surface phenomena in liquids and liquid solutions, 1972, pp.27-41.
b) "Consideration of interaction between molecules in problems of adsorption and absorption", J. Phys. Chem., 44, 1970, pp.495-503.
c) "Dissociation into adatoms, effects of interelectron interaction", J. Phys. Chem., 45, 1971, pp.2867-2875.
d) "Consideration of interaction between molecules in problems of adsorption and absorption. Adsorption of oxygen on transition metals and gold", J. Phys. Chem., 46, 1972, pp.119-127.
e) "On effective interaction between adatoms", J. Phys. Chem., 48, 1974, pp.1287-1295.
f) "Method of correlation functions in the Ising model", TSU, 1971, p.92.
g) "Application of Green functions to the study of the Ising model" in the book "Statistical Physics and Quantum Field Theory" edited by N.N. Bogoliubov, Nauka, Moscow, 1973.
h) "Equilibrium characteristics in a condensed state with the interaction of nearest neighbors", Atomizdat, Particles and Nucleus, v.5, №4, 1978, pp.658-689.
i) "Self-consistent solutions in the Ising model. Correlation Effects", JINR Preprint 97-30, Dubna, 1997.

[7] W.Guggengeim, Mixture, Clarendon Press, 1967, p.310.

[8] V.K.Fedyanin. "To the problem of the heat of adsorption with the interaction between molecules", Kinetics and catalysis, B1, 1969, pp.1391-1392; II, 12, 1971, pp.1353-1355.

[9] S.Kruyer. Proc. Kon. Ned. Ak. Wet B58, p.73, 1955.

[10] A.E.Mozol'kov and V.K.Fedyanin. "Diffraction of slow electrons by a surface", Energoizdat, Moscow, 1982, p.293.

[11] C.Kemball.Proc.Roy.Soc. ALGO, 1947, p.117.

[12] S.V.Tyablikov and V.K.Fedyanin. "Method of correlation function in the Ising model", FMM, 23, 1967, pp.193-199.

Received by Publishing Department
on December 21, 1998.