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HETEROGENEOUS MOBILE ADSORPTION: A PIECEWISE-LINEAR APPROACH

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Abstract

A model of randomly heterogeneous adsorbent surface, where each adsorption site has at least on neighboring site with a barrier E_{migr} low enough to allow unhindered lateral mobility between the sites, is introduced. A two-parameter piecewise-linear local isotherm is proposed to describe homogeneous adsorption. Parameters of local isotherm are assumed to vary from site to site as chance values distributed according to the Gamma probability density function. The overall isotherm in its normalized form is described by two independent parameters. Within the unifying frame of this model the Langmuir, Jovanovic, Toth and Volmer isotherms are interpreted as representing particular cases of surface heterogeneity.

Introduction

It is widely accepted that any real adsorbent surface should be considered heterogeneous (1,2). An irregular heterogeneous surface can be depicted either as an array of idealized homogeneous surface fragments, where identical adsorption sites are grouped together (the homotattic model), or as an array of identical adsorption sites randomly dispersed over the surface (3). The homotattic model fits well the physical reality of regular surfaces, such as different faces of a crystal. In applying it to non-crystalline surfaces one becomes involved in complicated assumptions concerning the nature and size of a homogeneous patch. Theoretical implications of such topography seem to be quite unrealistic and artificial. Moreover, quoting M. Jaroniec and R. Madey (4), "the surface model with a random distribution of adsorption sites seems to be acceptable for the majority of heterogeneous adsorbents". This assumption invariably leads to the following conclusion (3): "When sites with equivalent properties are distributed over the surface at random, the adsorption is always localized,...the equilibrium of adsorption on sites with identical properties will be obviously described by the Langmuir isotherm",

$$\theta = \frac{Kc}{1 + Kc} \quad , \qquad [1]$$

where θ (≤ 1) is the surface coverage, c is the adsorbate concentration, and K is the Langmuir constant.

In terms of the Langmuir-type local isotherm the complete description of surface heterogeneity is given by a topography of the Langmuir constant (K). If such topographic map may be replaced by a continuous distribution function denoting the frequency of sites with the Langmuir constant value between K and $K + dK$, the overall isotherm could be obtained by averaging.

$$\theta = \int \frac{Kc}{1 + Kc} f(K)dK \quad , \qquad [2]$$

where $f(K)$ is the distribution function.

Several popular empirical isotherms describing heterogeneous adsorption have been given some theoretical justification (2,4,5) by averaging Langmuir local isotherms. One of the richest among such semi-empirical isotherms is the generalized Langmuir (GL) equation, proposed by Marchewski and Jaroniec (6,7):

$$\theta = \left[\frac{(K'c)^n}{1 + (K'c)^n} \right]^{m/n}, \qquad [3]$$

where K' is the equilibrium constant averaged for a heterogeneous surface, and n and m are empirical heterogeneity parameters of the isotherm. It is assumed that $0 < n, m \leq 1$. The equation [3], though not derived from general physical considerations, has an advantage of generality, since many other frequently used empirical correlations, such as the Freundlich, generalized Freundlich, Langmuir-Freundlich, Toth and Radke-Prausnitz isotherms, may be derived from it (5).

It is worth noting, that the derivative $d\theta/dc$ as a function of the parameter m (at the limit $\theta = 0$) accepts in [3] only three values: $d\theta/dc = K'$ at $m = 1$; $d\theta/dc = \infty$ at $m < 1$; and $d\theta/dc = 0$ at $m > 1$. Thus, at all values but $m = 1$, it predicts unrealistic deviations from Henry's law. One may conclude, therefore, that the generalized Langmuir isotherm presents only two correlations relevant to a model of the strict monolayer heterogeneity, which is the subject of this work: the Langmuir ($m = 1$, $n = 1$) and Toth ($m = 1$, $n < 1$) isotherms. It will be shown below, that both and a wealth of other correlations, may be obtained on the basis of a local isotherm different from the Langmuir.

"Trail" Model of Heterogeneous Surfaces

It has been argued in the Introduction, that the adsorption is always localized, when sites with equivalent properties are distributed over the surface at random. Experimental evidence suggests, however, that molecules of adsorbed material do retain lateral mobility at most experimental conditions. Hill (8,9) evaluated the transition range in temperature between localized and mobile adsorption for small molecules as 25-100°K. Modern measurement techniques, such as NMR, neutron scattering and Mossbauer spectroscopy, essentially confirmed this prediction (for review see ref. 10, pp. 279-282). A realistic local isotherm has to reflect the lateral mobility of adsorbate molecules. The homotattic model of heterogeneous adsorption, indeed, allows molecules absorbed at a homogeneous patch to behave as a two-dimensional gas (3,8,10). This model has been, however, rejected for most non-crystalline surfaces.

The discrepancy between the experimentally proven mobility of the adsorbate on the majority of surfaces, and the generally accepted random heterogeneity of these surfaces can be resolved. Let us consider a randomly heterogeneous surface, where each site within sufficiently large cluster has at least one neighboring site with a barrier E_{migr} low enough to allow unhindered migration of the adsorbed molecule between these sites. Thus, two-dimensional patches of the homotattic model are reduced to "one-dimensional trails", allowing lateral mobility of adsorbed molecules. At moderate temperatures such postulate of "one-dimensional mobility" would not be overly discriminative.

Ideal Homogeneous Adsorbtion: Piecewise-Linear Approach

Since lateral mobility of adsorbate molecules is now incorporated in the concept of randomly heterogeneous surface, let us consider forms of local isotherm other than Langmuir. For a perfect gas in equilibrium with an ideal homogeneous surface, the Henry isotherm would describe the adsorption equilibrium (3) for both localized and non-localized adsorption models:

$$n = K_H C \qquad [4]$$

Here, n is the amount adsorbed, and K_H is Henry's constant.

It is quite clear that this simple formula [4] provides only a part of some realistic relation. From the definition of monolayer adsorption it follows, that the amount adsorbed (n) cannot exceed the value of maximal monolayer capacity (N). Thus, we shall expect n in [4] to be expressed by a positive function linearly increasing from the origin and eventually saturating.

In the localized adsorption model the maximal monolayer capacity is determined by the number of rigidly defined binding sites. This concept, however, rarely fits experimental results. Thus, frequently encountered variations of one-two orders of magnitude in N within relatively narrow temperature range are inconsistent with localized adsorption. Halsey (11) termed this phenomenon an "extreme violation of the Langmuir postulate that the number of sites is constant". Volmer's mobile hypothesis, where one would expect N to be roughly proportional to $1/T$ (°K^{-1}), also falls far off the mark.

Often saturation is encountered considerably below the monolayer. This is demonstrated by a discrepancy frequently observed between the cross-section of adsorbed molecule (α) and the specific surface area per molecule at saturation (σ), as shown here (Table 1) for the adsorption of organic homologues onto activated carbon from dilute aqueous solutions. Adsorpion isotherms obtained by G.Belfort et al. (12) fit the Langmuir hyperbola. Note that for 2-propanone $\theta_{max} = \alpha/\sigma$ is as low as 0.02. This value is considerably below the predictions both of the Langmuir and the Volmer isotherms. The "well-known but seldom used (13)" Volmer isotherm (14) developed for the adsorption of ideal gases in mobile homogeneous monolayers is of the same form as the Langmuir, though it predicts saturation at one half of the value derived from statistical mechanics of the Langmuir adsorption (13,15).

The extremely low saturation levels indicate that the saturation may occur not only before the molecules are immobilized due to the complete lack of free space on the surface but even before the expected onset of lateral interactions.

We propose to consider a possibility that the saturation phenomenon at these low surface coverages is related to surface reconstruction. It can be interpreted as an extremely cooperative phase transition of a complex system: surface-adsorbate, where adsorbate molecules interact only through the surface. Let us quote from G.F. Cerofolini (16): "the influence of the adsorbate upon the adsorbent is a well-known fact extensively considered in the past. This influence can be so great as to produce surface reconstruction."

Since lateral interaction are postulated to be negligible even near the maximal surface coverage, the idealized local isotherm deviates from Henry's law only when it reaches saturation. The surface phase undergoing phase transition acts as Blackman (17) limiting factor, abruptly changing the law of adsorption, and strictly imposing the upper adsorption limit. As a result, instead of a smooth convex curve, such as the Langmuir hyperbola, we suppose the idealized homogeneous local isotherm to be piecewise-linear (18), i.e. expressed by a simple broken two-part positive function, that starts from the origin with the slope K_H, linearly increases until $c = N/K_H$, and then remains constant with the value $n = N$ (Fig. 1). This function may be written as:

$$n = \min \{K_H c, N\} \qquad [5]$$

The function [5] may be regarded as an approximation of a phenomenologically expected smooth convex curve. We insist, however, to treat it as a strict mechanistic relation for this idealized case of strict homogeneity.

Heterogeneity: Main Assumptions of the Model

If the surface consists of homogeneous "trails", each described by a local piecewise-linear isotherm [5], the overall isotherm can be calculated by averaging local isotherms.

In the contrast to the Langmuir model of heterogeneous surface, two types of heterogeneity may be distinguished:

(a) Homogeneous "trails" may vary in adsorption energy (or critical escape velocity of an absorbed molecule), which is expressed in K_H (*energetic heterogeneity*).

(b) They may differ, as well, in fragment surface saturation properties, which are expressed in the maximal monolayer capacity, N (*geometrical heterogeneity*), which does not exist in the Langmuir hypothesis. Using the analogy with phase transition, each fragment may be characterized by its critical transition concentration (pressure), $c_{cr} = N/K_H$.

When both types of heterogeneity coexist, the model describes a *surface heterogeneity*.

Assuming K_H and N chance variables, all necessary properties of the adsorbent surface may be described by their joint probability density function $f(K_H, N)$. The problem is then reduced to the definition of mathematical expectancy of [5] with a weight $f(.,.)$. The overall isotherm will then be described by the average Henry's constant, K', and by the average maximum monolayer capacity, N'.

For the sake of simplicity, we assume that the adsorption energy of any chance "trail" is not related to its adsorption capacity. Thus, parameters K_H and N are independent random variables, and their joint probability density function can be expressed as a product of individual probability density functions of both variables:

$$f(K_M, N) = f_1(K_M)f_2(N) \qquad [6]$$

Now, the process of averaging can be separated into two parts:

$$n = \int_0^\infty f_1(N) \int^\infty f_2(K) \min\{Kc, N\}\, dK\, dN \qquad [7]$$

where the index in K_M has been dropped for the purpose of convenience. The process of integration can now be carried out in two steps: first with the respect to K (the inner integral), and then with the respect to N (the outer integral), as written in [7]. The order of integration may, of course, be reversed.

Heterogeneity: Derivation of the Model and its Properties

In our model the energetic and the geometric heterogeneity are assumed to be independent co-distributed properties of a heterogeneous surface. Both parameters of the local isotherm (K and N) are essentially positive. For description of their distribution, the Gamma probability density function, the most general standard function for positive variables, is usually adopted (4,19-22). As applied to our model, it shall be expressed for N and K in the following form (Fig. 2):

$$f_1(N) = \frac{\mu^\sigma}{\Gamma(\sigma)} N^{\sigma-1} \exp(-\mu N) \qquad [8]$$

$$f_2(K) = \frac{\beta^\alpha}{\Gamma(\alpha)} K^{\alpha-1} \exp(-\beta K) \qquad [9]$$

where $\Gamma(.)$ is the Gamma function.

Values α, β, μ, and σ introduced above as the parameters of probability density function determine the shape of the overall isotherm and obtain a physical meaning: the ratio α/β is the initial slope of the isotherm, and σ/μ is its plateau level.

Let us start with evaluation of the inner integral in [7], i.e. one with respect to K, at arbitrary finite and positive α and β:

$$n = \frac{c}{\beta\Gamma(\alpha)} \gamma\left[\alpha+1, \frac{\beta N}{c}\right] + \frac{N}{\Gamma(\alpha)} \Gamma\left[\alpha, \frac{\beta N}{c}\right] \qquad [10]$$

Here, $\gamma(.,.)$ is the incomplete Gamma function, and $\Gamma(.,.)$ the complementary incomplete Gamma functions (see Appendix).

In modern computer software both $\gamma(.,.)$ and $\Gamma(.,.)$, as well as the elementary functions, are standard inserted functions. Still, the equality [10] is rather involved and generally inconvenient for practical purposes. Assuming, however, that parameter α is an integer ($\alpha \geq 1$), one obtains (see Appendix) :

$$n = \frac{\alpha c}{\beta}\left[1 - e^{-\beta N/c} \sum_{i=0}^{\alpha} \left(1 - \frac{i}{\alpha}\right) \frac{(\beta N/c)^{i}}{i!}\right] \qquad [11]$$

In simple particular cases, when $\alpha = 1$, $= 2$, $= 3$, it follows from [11] that

$$n = (c/\beta)[1 - \exp(-\beta N/c)] \qquad [12]$$

$$n = (2c/\beta)[1 - \exp(-\beta N/c)] - N \exp(-\beta N/c) \qquad [13]$$

$$n = (3c/\beta)[1 - \exp(-\beta N/c)] - (N/2) \exp(-\beta N/c)[\beta N/c + 4] \qquad [14]$$

Overall isotherms [10]-[14], plotted as functions of adsorbate concentration c, give smooth convex curves starting from the origin with initial slope α/β (i.e. K') and eventually saturating at the plateau, N. These isotherms describe *energetic heterogeneity* (finite parameters α and β) combined with the surface homogeneity (infinite parameters σ and μ) at a fixed ratio $\sigma/\mu = N$).

Substituting form [11] in the outer integral in [7] and evaluating the outer integral with respect to N, one obtains (see Appendix):

$$\frac{\alpha c}{\beta}\left[1 - \sum_{i=0}^{\alpha} \left(1 - \frac{i}{\alpha}\right) \binom{\sigma+i-1}{i} \frac{\mu^{\sigma}(\beta/c)^{i}}{(\mu + \beta/c)^{i+\sigma}}\right] \qquad [15]$$

where $\binom{\sigma+i-1}{i} = \frac{(\sigma+i-1)!}{(\sigma-1)!\,i!}$ is the binomial coefficient.

Similarly to the above, in the simple cases, for $\alpha = 1$, $= 2$, and $= 3$, it follows from [15]:

$$n = \frac{c}{\beta}\left[1 - \frac{\mu^{\sigma}}{(\mu + \beta/c)^{\sigma}}\right] \qquad [16]$$

$$n = \frac{2c}{\beta}\left[1 - \frac{\mu^{\sigma}}{(\mu + \beta/c)^{\sigma}}\right] - \frac{\sigma\,\mu^{\sigma}}{(\mu + \beta/c)^{\sigma+1}} \qquad [17]$$

$$n = \frac{3c}{\beta}\left[1 - \frac{\mu^{\sigma}}{(\mu + \beta/c)^{\sigma}}\right] - \frac{2\,\sigma\,\mu^{\sigma}}{(\mu + \beta/c)^{\sigma+1}} - \frac{\mu^{\sigma}\beta\,(\sigma + 1)\,\sigma}{2c\,(\mu + \beta/c)^{\sigma+2}} \qquad [18]$$

The overall isotherms [15]-[18], as functions of adsorbate concentration c, give smooth convex curves, starting from the origin with the initial slope $\alpha/\beta = K'$ and saturating at the plateau $\sigma/\mu = N'$ (i.e. average maximum monolayer capacity) (Fig. 3). This set of isotherms describes the phenomenon of complex surface heterogeneity: the energetic heterogeneity (finite and integer parameter α and finite β) is combined with the geometrical heterogeneity (finite parameters σ and μ).

The overall isotherm reduces to Langmuir isotherm in the simplest particular case of the formalism elaborated above. Setting $\sigma = 1$ in [16], one readily finds:

$$n = \frac{c}{\beta + \mu c} \qquad [19]$$

which is analogous to the Langmuir isotherm [1].

Thus, within the assumptions of mobile heterogeneous adsorption, the Langmuir isotherm becomes a particular case of heterogeneity (mathematically, the simplest one). In suggesting that the Langmuir isotherm is not necessarily a proof of surface heterogeneity, we are guilty of no larger transgression, than G.Halsey (11) who has concluded, as early as 1948, : "Paradoxically enough, the obeying of the Langmuir isotherm is frequently a positive indication that the surface is non-uniform...".

The set of analytical expressions for overall isotherms obtained above by evaluating the integral [7] is restricted to a certain degree by the necessity to assume one of the four parameters introduced, namely α, to be an integer. At arbitrary α, one should recourse to numerical computation of functions $\Gamma(.)$, $\gamma(.,.)$ and $\Gamma(.,.)$ in [10] for the models of energetic heterogeneity, or to numerical calculation of the outer integral in [7] with [10] substituted into it for the complex heterogeneity. However, the set of analytical solutions can be expanded by reversing the integration order in [7].

$$n = \int_0^{\infty} f_2(K) \int_0^{\infty} f_1(N) \min\{Kc,\ N\}\, dN\, dK\ ; \qquad [20]$$

According to the main property of the δ-functioin (19), integral [20] tends to its inner integral at $f_2(K)$ tending to $\delta(K-\alpha/\beta)$ (α and $\beta \rightarrow \infty$).

At arbitrary, finite and positive σ and μ, and fixed K, computation of inner integral in [20] yields:

$$n = \frac{1}{\mu\Gamma(\sigma)}\,\gamma(\sigma+1,\ \mu Kc) \ + \ \frac{Kc}{\Gamma(\alpha)}\,\Gamma(\sigma,\ \mu Kc) \qquad [21]$$

Formula [21] represents an entire family of isotherms describing the *geometrical heterogeneity* (finite parameters σ and μ) combined with the energetic homogeneity (parameters α and $\beta \rightarrow +\infty$ at a fixed ratio α/β = K).

Let σ be an integer ($\sigma \geq 1$), while μ remains arbitrary positive. One obtains from [21]:

$$n = \frac{\sigma}{\mu}\left[1 - e^{-\mu Kc} \sum_{i=0}^{\sigma} \left(1 - \frac{i}{\sigma}\right) \frac{(\mu Kc)^i}{i!}\right] \qquad [22]$$

At simple particular cases when σ = 1, = 2, = 3, it follows from [22]:

$$n = (1/\mu)\ (1- \exp(-\mu Kc)) \qquad [23]$$

$$n = (2/\mu)\ (1 - \exp(-\mu Kc)) - Kc \exp(-\mu Kc) \qquad [24]$$

$$n = (3/\mu)\ (1- \exp(-\mu Kc)) - (Kc/2) \exp(-\mu Kc)\ (\mu Kc + 4) \qquad [25]$$

Overall isotherms [21]-[25], as functions of c, are smooth convex curves starting from the origin with the initial slope K, and eventually saturating at the plateau $n = \sigma/\mu = N'$.

Expression [23] is the well known Jovanovic (21-23) isotherm, for monolayer adsorption. This isotherm has been shown to fit numerous experimental data(23). It has been used as a local isotherm in description of heterogeneous adsorption (24). Again, as with the Langmuir isotherm, in our model it describes the mathematically simplest case of the geometrical heterogeneity.

Substituting [22] into new outside integral in [20] one obtains:

$$n = \frac{\sigma}{\mu}\left[1 - \sum_{i=0}^{\sigma} \left(1 - \frac{i}{\sigma}\right) \binom{\alpha+i-1}{i} \frac{\beta^{\alpha}(\mu c)^i}{(\beta + \mu c)^{\alpha+i}}\right] \qquad [26]$$

At $\sigma = 1$, $= 2$, and $= 3$, the form [26] becomes:

$$n = \frac{1}{\mu}\left[1 - \frac{\beta^{\alpha}}{(\beta + \mu c)^{\alpha}}\right] \qquad [27]$$

$$n = \frac{2}{\mu}\left[1 - \frac{\beta^{\alpha}}{(\beta + \mu c)^{\alpha}}\right] - \frac{c\alpha\, \beta^{\alpha}}{(\beta + \mu c)^{\alpha+1}} \qquad [28]$$

$$n = \frac{3}{\mu}\left[1 - \frac{\beta^{\alpha}}{(\beta + \mu c)^{\alpha}}\right] - \frac{2c\alpha\, \beta^{\alpha}}{(\beta + \mu c)^{\alpha+1}} - \frac{\mu c^{2}\beta^{\alpha}\, \sigma(\sigma + 1)}{2(\beta + \mu c)^{\alpha+2}} \qquad [29]$$

Overall isotherms [26]-[29], plotted as functions of adsorbate concentration c, are smooth convex curves starting from the origin with the initial slope $K' = \alpha/\beta$ and saturating at $N' = \sigma/\mu$ (Fig. 4). They depict a case of the surface heterogeneity, while the energetic heterogeneity (finite α and β) is combined with the geometrical heterogeneity (finite σ and μ), for an integer σ.

As expected, form [27] at $\alpha = 1$ is identical to form [16] at $\sigma = 1$, and reduces to Langmuir isotherm [1]. Form [27] at $\alpha = 2$ is identical to form [17] at $\sigma = 2$, etc. Generally, it can be shown by induction that formula [26] calculated at $\alpha = m$ is equivalent to formula [15] at $\sigma = m$, where m is an integer.

It is worth noting, that at the same concentration of adsorbate, any deviation from homogeneity lowers the surface coverage. This deviation increases with increasing heterogeneity. Mathematically, it follows from a well known iso-perimetrical problem of variational calculus. This statement can be proved by minimization of integral [7] using the Lagrangian factor. It is clear from Fig.3 that the isotherm depicting the energetic heterogeneity (INF) lies above all the isotherms depicting the complex heterogeneity. The INF isotherms are their limiting case (μ and $\sigma \longrightarrow \infty$). Similarly, the isotherm for the surface heterogeneity (INF in Fig. 4) is limiting for the complex heterogeneity (α and $\beta \longrightarrow \infty$). The piecewise-linear isotherm, the ultimate case of homogeneity, lies above any other isotherm (Fig. 1).

Discussion and Conclusions

The theory of heterogeneous monolayer adsorption is elaborated here starting from assumptions, that are no more, and probably less involved, than the assumptions leading to the formulation of Langmuir isotherm. The ideal homogeneous local isotherm is expressed in a mathematically simple form, convenient for building of complex models.

The local isotherm assumes the saturation to occur on an elementary homogeneous "trail" as a phase transition involving both adsorbent and adsorbate molecules. In contrast to the model developed by McAlpin and Pierotti (25), our postulated phase transition does not imply gradual localization of adsorbed molecules. The lateral mobility of adsorbed molecules is retained throughout the isotherm, hence no deviations from Henry's law are permitted until the idealized homogeneous surface saturates. This dictates the unusual form of the piecewise-linear isotherm, which plots as a two-part convex line (Fig. 1).

Highly cooperative or sharp transitions, of which PWL isotherm [5] (Fig. 1) is an example, are not uncommon in adsorption processes. Such are e.g. phase transitions of a two-dimensional gas to a two-dimensional liquid observed below critical temperatures. The phase transition, where the Henry isotherm intersects the transformed surface phase, is postulated to occur not only before the molecules become immobilized due to complete lack of free space (as in condensation hypothesis), but even before the onset of lateral interactions, and when the collision effect may be neglected.

It is important here to stress the continuously heterogeneous nature of mobile adsorption, which is usually neglected. In the localized adsorption model one can imagine adsorbate molecules occupying rigidly defined equivalent binding sites, while structural imperfections play a relatively minor role. In mobile adsorption the molecules of adsorbate form rather nonspecific (non-localized !) association with the surface. This lack of specificity may result from a multitude of low-energy interactions between an adsorbate molecule and a complex topography of the surface with its areas of varying curvature, composition and imperfection. Such a surface is heterogeneous by definition and can be realistically described mathematically as a collection of idealized elementary "trails" or one-dimensional patches of *continuously distributed* properties. Any adsorbent surface is considered heterogeneous *a priori. Thus, one should never expect to encounter a piecewise-linear isotherm experimentally, but rather as a local isotherm.*

The ability of the PWL model to mimic various experimental isotherms indicates the feasibility of the model. It has been shown here, that within assumptions of our model the Langmuir and the Jovanovic isotherms are obtained analytically as particular forms of surface heterogeneity. It should not come as a surprise, that the same forms may describe different adsorption phenomena. Fitting of experimental data to one of these isotherms does not constitute an exclusive evidence of homogeneity or heterogeneity of the surface in question. The fitting should be supported by the consistency of physical interpretation of the model parameters. Examples of such inconsistency in traditional interpretations are not lacking. Thus, maximal surface coverages observed by F.J. Wilkins and reported by G. Halsey (11) strongly deviate from the values predicted by Langmuir or Volmer equations on the basis of thermodynamic calculations. It is worth stressing that, as pointed out by G. Halsey, continuous variation of the maximal surface coverage with the temperature "presupposes continuously nonuniform surface". Our model, and, possibly, our model alone, would justify F.J. Wilkins's good fit to the Langmuir equation despite the obvious surface nonuniformity.

Numerous other popular isotherms can be viewed, as approximations of PWL model. The Volmer, Fowler and Hill - de Boer isotherms can be easily simulated by our model, as shown in Fig. 5.

$$Kp = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta}\right) \quad \text{(Complete Volmer)} \qquad [30]$$

$$Kp = \frac{\theta}{1-\theta} \exp\left(-K_{F}\theta\right) \quad \text{(Fowler)} \qquad [31]$$

$$Kp = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - K_{HDB}\theta\right) \quad \text{(Hill - de Boer)} \qquad [32]$$

S-shaped isotherms predicted by the forms [31] and [32] at $K_{F} > 1$ and $K_{HDB} > 2$ respectively, are incompatible with our formalism. Below these values of these parameters, however, the simulation is possible. The S-shaped form of the isotherms [31] and [32] is usually interpreted as a phase transition, resulting from limitation of adsorbate molecule mobility on the surface phase restrained by their neighbors. It has been already stated above, that our model is valid only below the critical concentrations predicted for such phase transitions.

In its normalized form ($K' = 1$, $N' = 1$) the PWL model presented here has two parameters (α and σ) describing heterogeneity, as has the generalized Langmuir isotherm (1). It has already been mentioned in the Introduction, that beside the simple Langmuir isotherm, the only other isotherm resulting from GL and obeying Henry's law is the Toth isotherm [33].

$$\theta = \frac{Kc}{[1 + (Kc)^n]^{1/n}} \qquad [33]$$

Within the limitations of GL model ($n \le 1$), it plots in ($\theta - \theta/c$) - coordinates as symmetrical curves lying below the main diagonal. Fig. 6 demonstrates four such curves plotted according to the normalized Toth isotherm, at K=1. Very similar symmetrical curves were simulated by our model (Fig. 6, panel B) at $\alpha/\beta = \sigma/\mu = 1$. This simulation required numerical integration. Note, that in their normalized form both models are one-parameter. Thus, for any practical purposes the Toth isotherm may be regarded and used as one of possible approximations of integral [7]. We have found empirically, that the parameter n in the Toth isotherm is $n \approx \alpha^2 = \beta^2 = \sigma^2 = \mu^2$, when normalized forms are compared.

As an approximation, the Toth isotherm is by no means unique. Other approximations can be easily obtained. For instance, a simple analytical approximation can be constructed by the means of our model. Combining forms [16] and [27] one obtains:

$$2n = \frac{c}{\beta}\left[1 - \frac{\mu^{\sigma}}{(\mu + \beta/c)^{\sigma}}\right] + \frac{1}{\mu}\left[1 - \frac{\beta^{\alpha}}{(\beta + \mu c)^{\alpha}}\right] \qquad [34]$$

Approximation [34] further extends our theory into the analytical domain.

One of the interesting features of the PWL model is its *unifying character*. Numerous experimental adsorption isotherms, previously derived on the basis of strikingly different assumptions to the physical nature of adsorption, are now interpreted in terms of surface heterogeneity. The unifying character of the model confirms the concept of essential heterogeneity of most adsorbents.

The flexibility of the PWL model ensures, that it would certainly fit a large number of experimental isotherms. Such fitting, however, is only a prerequisite for the correctness of any theory. It has been pointed out in the fundamental work of Feller (20), that "...a mathematical formula is never accepted as a proper expression of a natural law merely on account of its expressing rather roughly some isolated phenomena ...The crucial test for the theory ... would consist in a systematic study of the parameters involved when the external conditions are changed." Such systematic study requires further development of thermodynamics and phenomenology of our hypothesis, which is outside the scope of this paper. We believe, that the theory presented here "provides a competing mathematical form, ... which has the great merit of expressing ... phenomena on a *theoretically acceptable* basis" (20).

Our model provides the mathematical basis and the physical conception for an adsorption theory, which fulfills following realistic criteria: the surface is essentially heterogeneous, the adsorption is mobile, the surface and the adsorbate represent a composite phase, which undergoes a phase transition analogous to the surface reconstruction. The surface coverage at saturation is determined by the properties of the surface and of the adsorbate.

Our essentially heterogeneous model should be added to the list of interpretations considered by an experimentalist while interpreting his data, since an ideal homogeneous surfaces hardly ever exist, while heterogeneity is the rule.

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Appendix: Computation of integral [7]

After separating variables in [7], the inner integral, i.e. one with respect to K, can be rewritten as follows:

$$n = I_1 + I_2 =$$

$$\int_0^\infty f_2(K) \min\,[Kc, N]\, dK = c\int_0^{N/c} K\, f_2(K)\, dK + N\int_{N/c}^\infty f_2(K) dK \qquad [A1]$$

where $f_2(K)$ is the Gamma probability density function taken from [9]. Inserting $f_2(K)$ into [A1] one obtains:

$$I_1 = \frac{c\,\beta^\alpha}{\Gamma(\alpha)}\int_0^{N/c} K^\alpha\, e^{-\beta K}\, dK \qquad [A2]$$

$$I_2 = \frac{N\,\beta^\alpha}{\Gamma(\alpha)}\int_{N/c}^\infty K^{\alpha-1}\, e^{-\beta K}\, dK \qquad [A3]$$

Introducing an auxiliary variable $t = \beta k$ results in formula [10] where the following standard notations are used:

$$\int_0^A t^{\alpha-1}\, e^{-t}\, dt = \gamma(\alpha,A) \qquad [A4]$$

(the incomplete Gamma function), and

$$\int_A^\infty t^{\alpha-1}\, e^{-t}\, dt = \Gamma(\alpha,A) \qquad [A5]$$

(the complementary incomplete Gamma function).

Setting α into [A2] and [A3] to be integer, the integrals I_1 and I_2 can be evaluated through integration by parts:

$$I_1 = \frac{\alpha c}{\beta}\left[1 - e^{-\beta N/c}\sum_{i=0}^{\alpha}\frac{(\beta N/c)^i}{i!}\right] \qquad [A6]$$

$$I_2 = N\,e^{-\beta N/c}\sum_{i=0}^{\alpha-1}\frac{(\beta N/c)^i}{i!} - \frac{c\alpha}{\beta}\,e^{-\beta N/c}\sum_{i=0}^{\alpha}(i/\alpha)\frac{(\beta N/c)^i}{i!} \qquad [A7]$$

The sum of [A6] and [A7] gives formula [11].

Now, substituting [11] into [7], one comes to the following sum:

$$n = \frac{\alpha c}{\beta}\left[1 - \sum_{i=0}^{\alpha}\left(1 - \frac{i}{\alpha}\right)\frac{(\beta/c)i}{i!}\,I_{3i}\right] \qquad [A8]$$

where

$$I_{3i} = \frac{\mu\sigma}{\Gamma(\sigma)}\int_0^\infty N^{\sigma+i-1}\,e^{-(\mu+\beta/c)N}\,dN \qquad [A9]$$

According to the definition of the Gamma probability density function,

$$\frac{(\mu+\beta/c)^{\sigma+i}}{\Gamma(\sigma+i)}\int_0^\infty N^{\sigma+i-1}\,e^{-(\mu+\beta/c)N}\,dN = 1 \qquad [A10]$$

Now integral [A9] can be readily evaluated:

$$I_{3i} = \frac{\mu\sigma\,(\sigma+i)\ldots\sigma}{(\mu+\beta/c)^{\sigma+i}} \qquad [A11]$$

where the well-known recurrent equality $\Gamma(\sigma+i) = (\sigma+i)\ldots\sigma\Gamma(\sigma)$ was used.

Substituting [A11] into [A8] and noting that the ratio $(\sigma+i)\ldots\sigma/i!$ is the binomial coefficient, one obtains formula [15].

Evaluation of the integral [20] and derivation of formulae [21]-[26] can be done quite similarly.

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Table 1. Adsorption of alcohols and ketones on activated carbon.

Solute	Langmuir Constants K	Langmuir Constants N	Molecular Surface Area σ	Molecular Surface Area α
	mM^{-1}	mmol/g	nm^2	nm^2
1-Butanol	20.2	0.17	10.09	0.63
1-Pentanol	19.5	0.43	3.99	0.71
1-Hexanol	79.3	0.78	2.20	0.75
1-Heptanol	107.6	1.03	1.67	0.86
2-Propanone	3.2	0.13	13.20	0.31
2-Butanone	11.4	0.28	6.12	0.37
2-Pentanone	62.4	0.37	4.64	0.44
2-Hexanone	77.3	0.49	3.50	0.51
2-Heptanone	203.9	0.60	2.86	0.58
2-Octanone	87.1	1.66	1.03	0.58
2-Nonanone	68.9	2.13	0.81	0.72

The data presented in the able are taken from the publication by G.Belfort et al. (12). Values of cross-section of the adsorbed molecules (α) are given as in the original. Our estimates of σ in an optimally packed monolayer are 0.2-0.3 nm^2 for all the compounds.

Figure Legends

Figure 1. Piecewise-linear (PWL) and two other isotherms (Langmuir and Volmer) postulated to depict homogeneous monolayer adsorption.

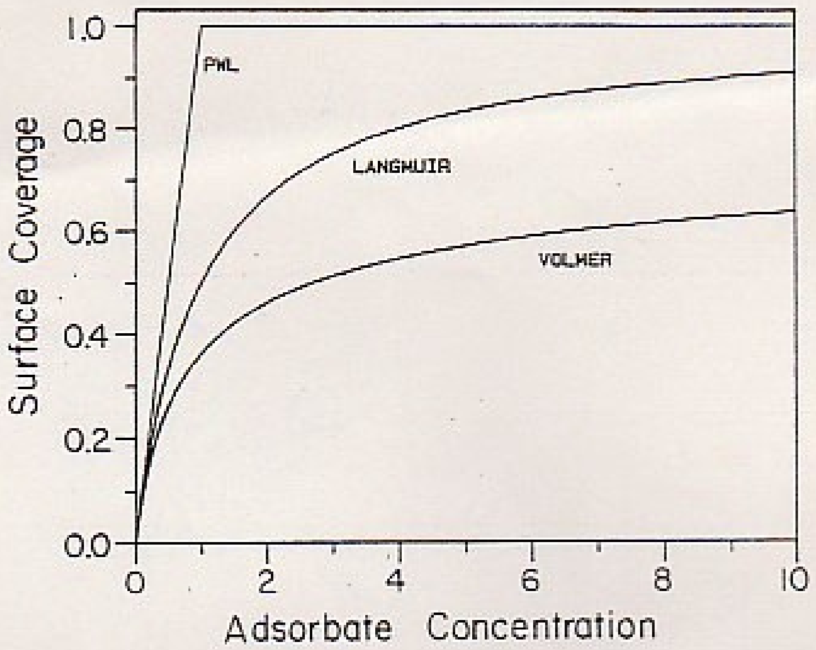
Figure 2. Gamma probability density function in its normalized form: at $\alpha/\beta = 1$ (or $\sigma/\mu = 1$). Parameter values are shown in the figure.

Figure 3. Normalized ($N' = 1$, $K' = 1$) overall isotherms for heterogeneous adsorption (panels A-C) and their secondary replots: θ/c versus θ (panels D-F). Plots were made for the forms: [16] - A, D; [17] - B, E; and [18]- C, F. Value of parameters μ and σ ($\mu = \sigma$) are shown in the figure. Plots of corresponding forms: [12], [13], and [14] for *energetic heterogeneity* ($\mu = \sigma \longrightarrow \infty$) are marked by INF.

Figure 4. Normalized ($N' = 1$, $K' = 1$) overall isotherms for heterogeneous adsorption (panels A-C) and their secondary replots: θ/c versus θ (panels D-F). Plots were made for the forms: [27] - A, D; [28] - B, E; and [29] - C, F. Value of parameters α and β ($\alpha = \beta$) are shown in the figure. Plots of corresponding forms: [23], [24], and [25] for *geometrical heterogeneity* ($\alpha = \beta \longrightarrow \infty$) are marked by INF.

Figure 5. The Volmer [30], Fowler [31] and Hill - de Boer [32] isotherms and their simulation by PWL model. The Volmer, Fowler (at $K_F = 1$), and Hill - de Boer (at $K_{HdB} = 1$) isotherms were plotted in (θ/c, θ) - coordinates (panel A). The corresponding overall isotherms in PWL model (panel B) were obtained for the Volmer isotherm at $\alpha = \beta = 0.3$, $\sigma = \mu = 1$, [27]; for the Fowler isotherm at $\alpha = \beta = 2$, $\sigma = \mu = 8.0$, [17]; and for the Hill - de Boer isotherm at $\alpha = \beta = 0.33$, $\sigma = \mu = 2$, [28].

Figure 6. The Toth isotherm [33] and its simulation by PWL model. The Toth isotherm was plotted in (θ/c, θ) - coordinates for four values of heterogeneity factor (n) as shown in panel A. The corresponding overall isotherms in PWL model were obtained by numerical integration of [7] at values $\alpha = \beta = \sigma = \mu$ shown in panel B.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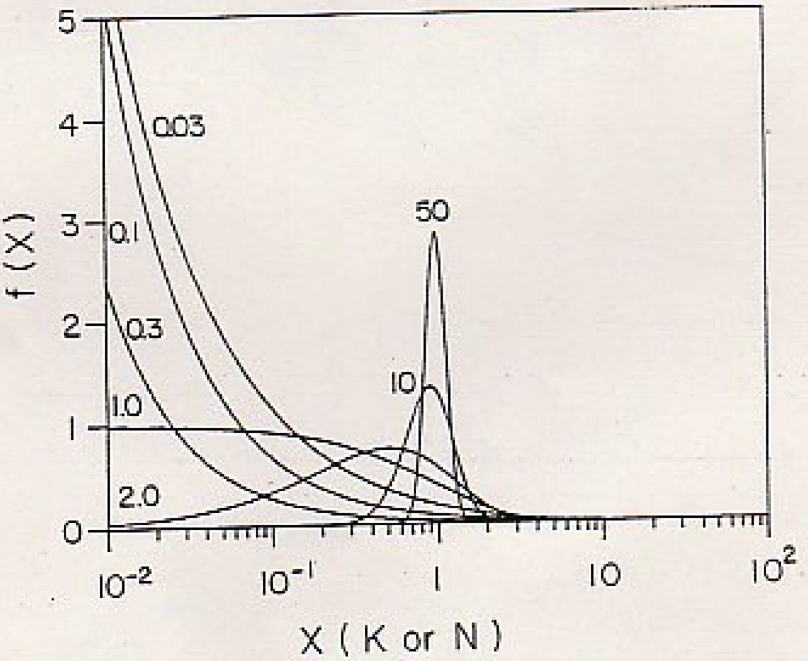
0.6
0.4
0.2
0.0
Surface Coverage
PWL
LANGMUIR
VOLMER
0
2
4
6
8
10
Adsorbate Concentration

Fig. 1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4
3
2
1
0
f (X)
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2.0
50
10
10^-2
10^-1
1
10
10^2
X (K or N)

Fig. 2

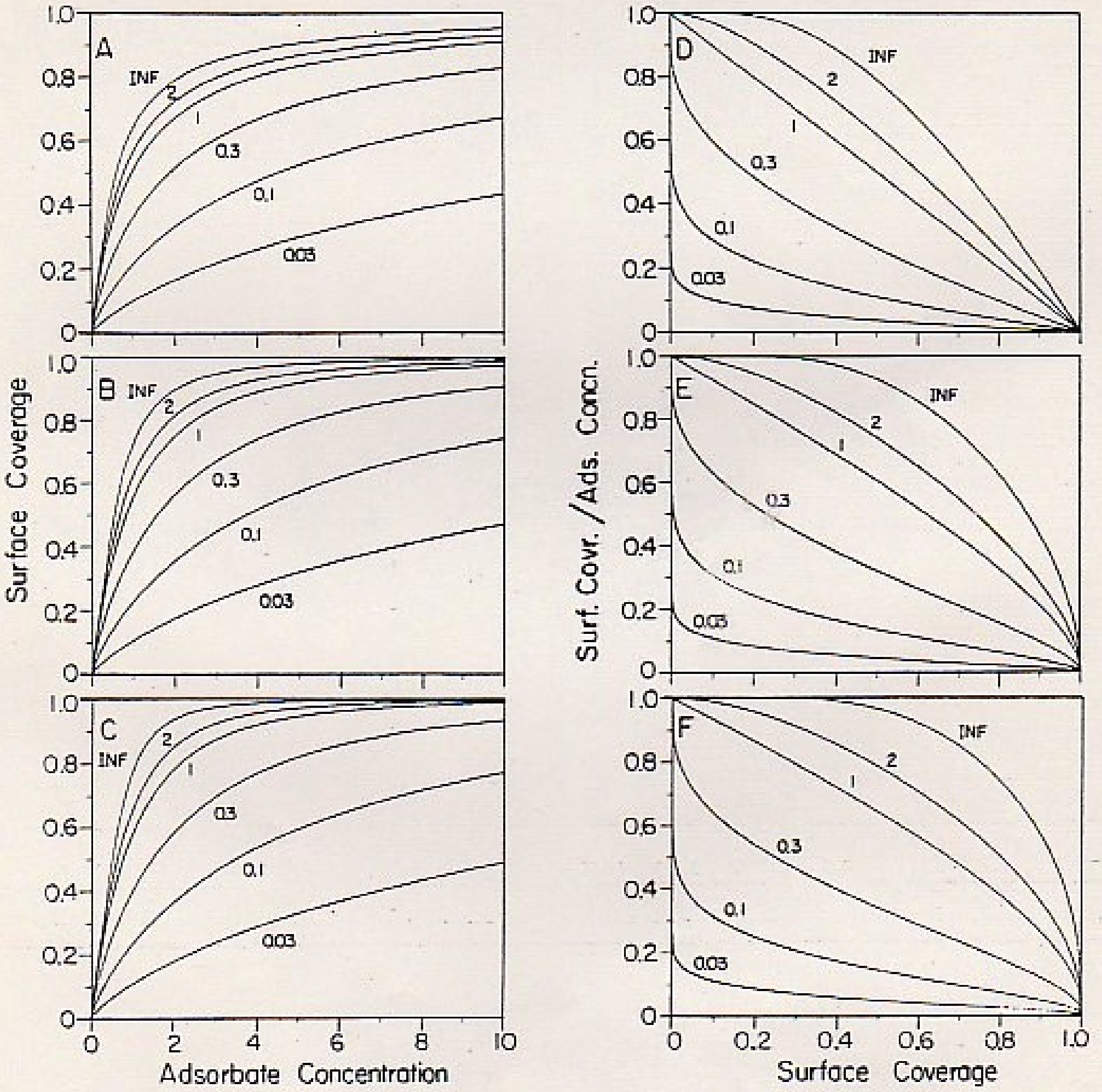
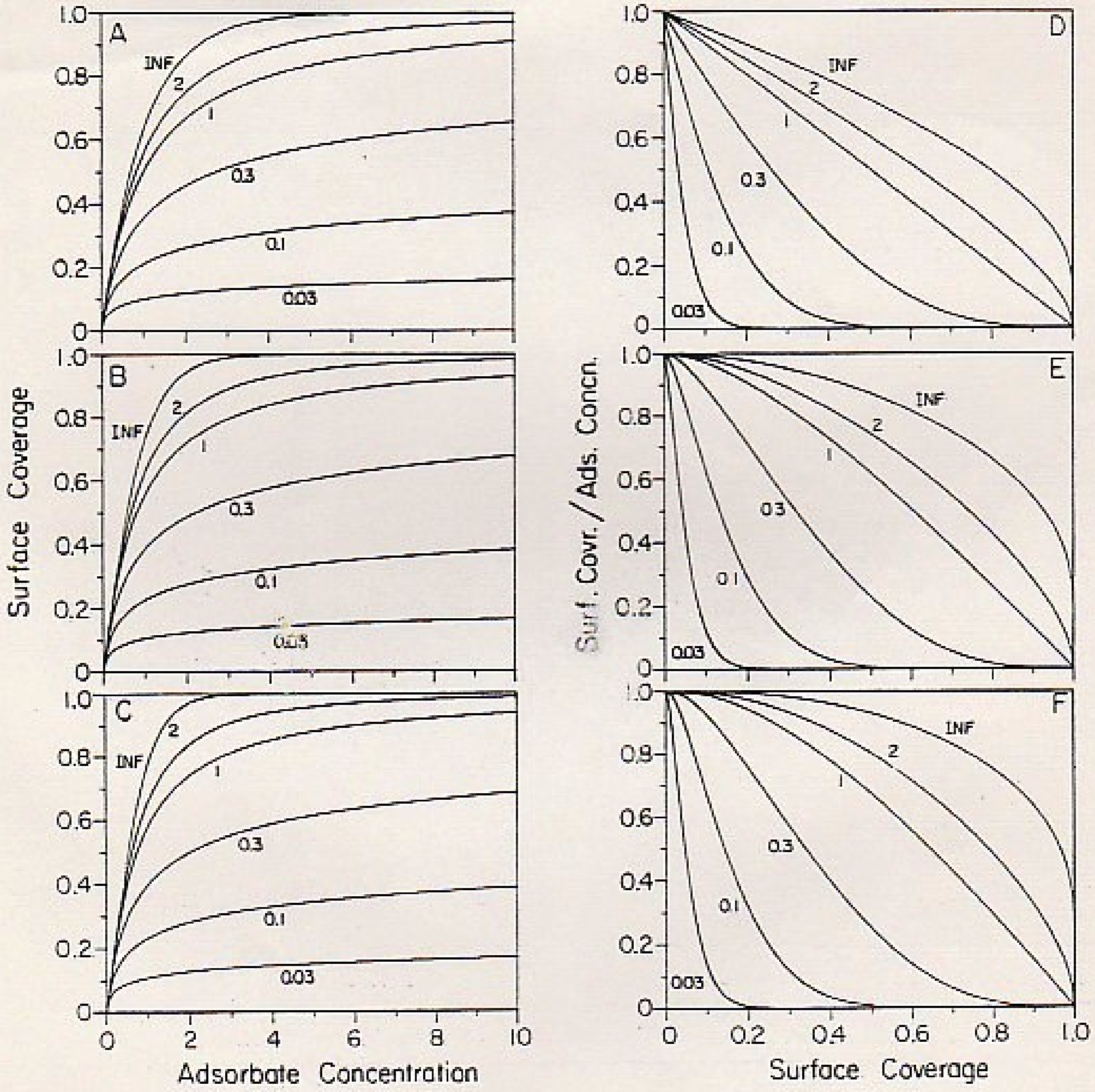

A
B
C
D
E
F
INF
2
1
0.3
0.1
0.03
Surface Coverage
Adsorbate Concentration
Surf. Covr. /Ads. Concn.
Surface Coverage
0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
10
0
0.2
0.4
0.6
0.8
1.0

Fig. 3


A
B
C
D
E
F
INF
2
1
0.3
0.1
0.03
Surface Coverage
Adsorbate Concentration
Surf. Covr. / Ads. Concn.
Surface Coverage
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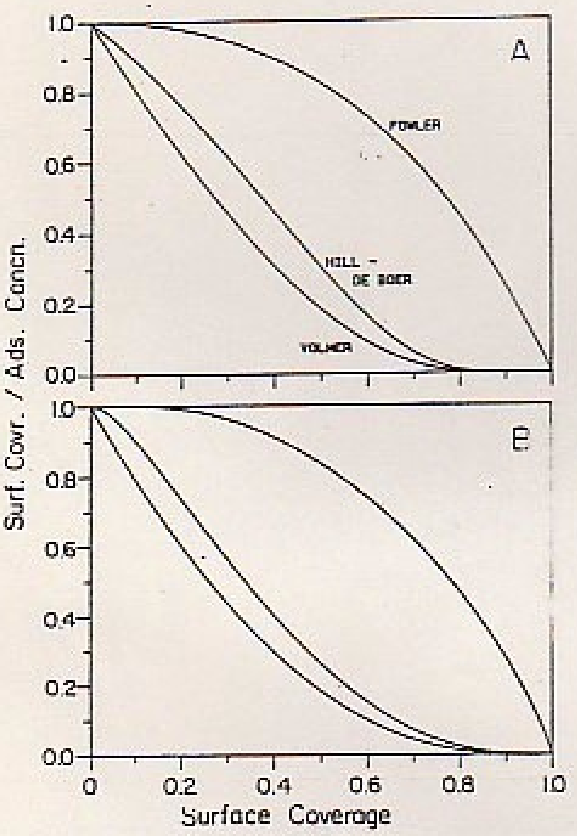
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
10

Fig. 4


A
B
FOWLER
HILL - DE BOER
VOLMER
Surf. Covr. / Ads. Concn.
Surface Coverage
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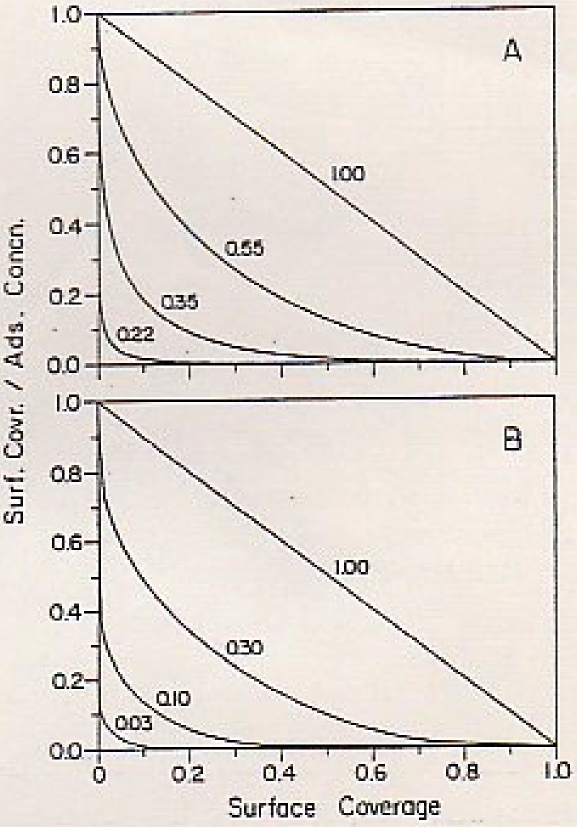
0.4
0.6
0.8
1.0
0

Fig. 5


A
B
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0.35
0.22
1.00
0.30
0.10
0.03
Surf. Covr. / Ads. Concn.
Surface Coverage
0.0
0.2
0.4
0.6
0.8
1.0
0

Fig. 6