



Understanding the mechanism of monolayer adsorption from isotherm

Elena Butyrskaya¹

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Abstract

A new approach for understanding the mechanism of monolayer adsorption is proposed. The Langmuir model, which does not take into account sorbate-sorbate bonds, is the most common one for interpreting monolayer adsorption. When using it, the assumption about the absence of sorbate-sorbate interactions between the sorbate molecules of the first layer is never checked. However, the sorbate-sorbate interactions can make an important contribution to the adsorption energy at physical adsorption. In this case, the formation of sorbate clusters in first layer is an energetically preferable process compared to the process of individual molecules adsorption. The monolayer cluster adsorption model, which takes into account sorbate-sorbate interactions, was introduced in our previous works. In present work, based on the experimental isotherms analysis, a criterion for the mechanism of monolayer adsorption (cluster or adsorption of individual molecules) is proposed. Examples are given of the this criterion application to the study of the mechanism of carbon dioxide adsorption by IRMOF-6, IRMOF-11 and IRMOF-1, ethane by highly activated carbon Saran and methane by mica. This work develops a new approach to the interpretation of monolayer adsorption mechanism.

Keywords Adsorption mechanisms · Isotherms · Sorbent-sorbate interaction · Monolayer cluster adsorption · Langmuir model validity

1 Introduction

Understanding the mechanism of sorption interaction is important for the targeted development of sorption technologies. A significant number of sorption technologies are based on the adsorption phenomenon, which is according to IUPAC “increase in the concentration of a dissolved substance at the interface of a condensed and a liquid (gas) phase due to the operation of surface forces”. Information about adsorption mechanism can be obtained from the isotherms analysis, which also allows you to obtain data on the specific surface and porosity of the sorbent, the structural characteristics of the sorbate and accumulate a experimental and calculated database for the effective use of adsorption methods.

A large number of adsorption models are presented in the literature [1–16], which can be divided into empirical, semi-empirical and theoretical (chemical, physical and ion exchange) models [3, 4]. The equations of empirical models (Freundlich, Sips, etc.) describe experimental isotherms well, but they are not derived analytically, the meaning of their parameters is unclear, and they cannot be used to study interactions in a adsorption system. Theoretical (physical, chemical, ion exchange) models are based on understandable assumptions about the mechanism of adsorption, their parameters have a clear physico-chemical meaning, which allows for a deep interpretation of adsorption interactions based on isotherm analysis. Examples of the most common theoretical models are the Langmuir model (chemical and physical adsorption) [17], the BET model [18] and its modifications (physical adsorption), interesting theoretical models are Buttersack [8, 9], Shimizu and Matubayasi [10] models. The ion exchange theoretical isotherms of Kenya and Navy describe the ion exchange adsorption process [3, 11, 12].

In our works [1, 2, 13–16], a physical model of adsorption has been developed that takes into account intermolecular

✉ Elena Butyrskaya
bev5105@yandex.ru

¹ Department of Chemistry, Voronezh State University, Universitetskaya pl. 1, Voronezh 394006, Russia

interactions between sorbate molecules. Taking into account the sorbate-sorbate interactions leads to the formation of sorbate clusters on the sorbent. The physicochemical validity of adsorption in the form of clusters is presented in work [2]. Adsorption in the form of clusters provides greater adsorption energy compared to the fixation of individual molecules due to the contribution of sorbate-sorbate interactions to reducing the energy of the system and is energetically preferable [1, 2, 13–16].

The equation for the cluster adsorption isotherm was obtained analytically [1, 2], its parameters have a clear physico-chemical meaning. These parameters are the equilibrium coefficients of sorbate cluster formation, the capacity of the monolayer and the structural characteristics of the clusters. The latter is an important feature of the cluster adsorption equation, since it also allows us to determine the structure of sorbate clusters based on the experimental isotherm analysis. Knowledge of the sorbate clusters structure is important, for example, for catalysis reactions, where the structure of the sorbed catalyst is crucial for understanding its action; as well as in surface chemistry and physics as a tool for studying chemical processes occurring on the surface, etc.

The formation of sorbate clusters on the sorbent during adsorption has been noted in many works [4, 18–21], however, not all models are theoretical, and the method for determining the sorbate structure from an experimental isotherm is not presented in the literature.

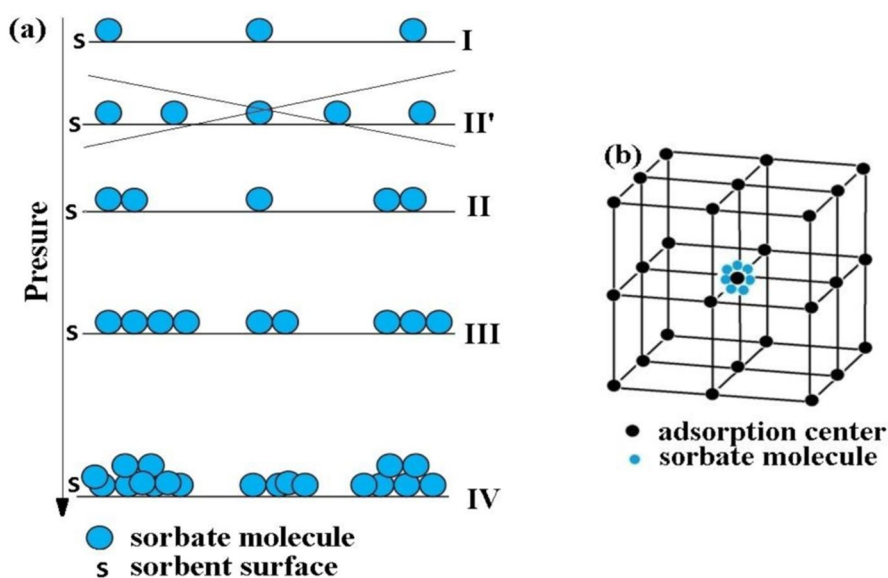
An important special case of cluster adsorption is single-layer cluster adsorption, when all sorbate clusters are located in the first layer of the sorbent. The fixation of sorbate in the form of associates reflects a broader picture of monolayer adsorption compared to the Langmuir model.

The physico-chemical differences between monolayer cluster adsorption and the Langmuir model are as follows [2]:

1. The monolayer cluster model takes into account sorbate-sorbate interactions between molecules of the first layer, which are not taken into account in the Langmuir model.
2. In the single-layer cluster model, the sorbent surface is assumed to be piecewise homogeneous (homogeneous in the Langmuir model).
3. In the Langmuir model, adsorption is localized on separate adsorption centers, each of which interacts with 1 adsorbate molecule. In the model of a single-layer cluster, one adsorption center can interact with several sorbate molecules, which, for example, occurs in porous systems (Fig. 1b) and is due to the presence of free space around their centers.

An example of proven single-layer cluster adsorption is the adsorption of CO_2 by a number of metal-organic frameworks [2]. Metal-organic frameworks (MOFs) are highly symmetrical porous structures consisting of metal-containing clusters organized to crystal structures by organic linkers [22–26]. Zinc-oxygen tetrahedra (Zn_4O) are metal-containing clusters of the IRMOF-1, IRMOF-6 and IRMOF-11 sorbents analyzed in this work, SI, 1. Four identical angular regions surround these tetrahedra, and CO_2 clusters are located in the first layer of these regions, which is confirmed by quantum chemistry methods [2] and corresponds to the results of molecular dynamics calculations [27]. CO_2 molecules are fixed in the first layer of sorbents IRMOF-1, IRMOF-6, IRMOF-11 as the monomers and clusters of 3(4) molecules [2]. The surface area of these MOFs is sufficient for a single-layer cover, SI, 1 [2]. .

Fig. 1 Cluster adsorption on nonporous (a) and porous (b) sorbents [2]. S is non-porous sorbent surface (in general non-planar). The crossed out structure II' is energetically less favorable in comparison with the II structure



The reversibility of desorption isotherms observed for these MOFs [28, 29] can serve as experimental confirmation of the monolayer nature of adsorption. Indeed, during monolayer adsorption, the first layer of sorbate is desorbed during desorption, and it is also formed first during adsorption, which may be the reason for reversibility. In multilayer adsorption, the upper layers are desorbed first, but in adsorption, the first layer is filled first, which can lead to a difference in adsorption and desorption (hysteresis).

The presented work is a logical continuation of the works [1, 2, 13–16]. *The novelty of this study* lies in the proposed fundamentally new method for establishing the mechanism of monolayer adsorption, based either only on the analysis of experimental isotherms, or on finding equilibrium coefficients of adsorption reactions using the graphical method and the least squares method. The proposed method is justified analytically in this work and confirmed by concrete examples. Thus, this paper shows how to determine whether the mechanism of monolayer adsorption is Langmuir (adsorption of individual molecules) or cluster (i.e. sorbate clusters are formed in the first layer of the sorbent).

2 Methods

2.1 The cluster adsorption model

This model [1, 2, 13–16] describes both monolayer and multilayer adsorption, which consists in the formation of monomers, dimers, ..., clusters from n -molecules on the sorbent from monomeric sorbative. According to [2], the concept of cluster adsorption follows from the analysis of the sorbate structure at the most energetically advantageous adsorption process. At the beginning of the physical adsorption process, sorbate molecules are independently fixed on the surface of the sorbent (Fig. 1a, I). However, with increasing pressure, new sorbate molecules will attach to already adsorbed molecules (Fig. 1a, II), that increases the adsorption energy due to the contribution of the energy of sorbate-sorbate bonds to it. Structure II is energetically preferable to structure I' due to the contribution of intermolecular interactions to reducing the energy of the system during adsorption.

The presence of intermolecular interactions in the sorbate cluster is also the diffusion driving force of a single sorbate molecule to a neighboring monomer (or cluster). As a result, the sorbent is covered with sorbate clusters located in the first layer, Fig. 1a, III [2]. Individual molecules are fixed in the first layer only due to the sorbent-sorbate interaction, the cluster in the first layer is fixed both due to the sorbent-sorbate interactions and due to intermolecular interactions in the sorbate cluster, which increases the adsorption energy. Consequently, the formation of clusters provides a greater

energy reduction during adsorption compared to the fixation of individual molecules. The cluster model takes into account that several molecules can be sorbed into the first layer of one sorption center (Fig. 1b). This is due to the presence of free space around sorption centers. The molecules of second layer will be fixed over the 1st layer clusters if all sorbent reaction centers are occupied, that leads to multilayer cluster adsorption (Fig. 1a, IV), the corresponding isotherm equation is presented in [1, 2, 13–16]. The reaction equations for cluster adsorption of molecules A on sorbent S have the form



Note that (1) are the resulting equations of adsorption reactions, which consist in the transformation of sorbative molecules of the external environment into the sorbate cluster SA_i . These can be complex reactions occurring in several stages in the general case.

The equation of the isotherm of multilayer cluster adsorption corresponding to reactions (1) is presented in work [1]. Its special case is the equation of the isotherm of monolayer cluster adsorption (all sorbate clusters SA_i lie in 1 layer), which has the form [2], SI, 2:

$$q = q_m \frac{K_1 P + K_2 P^2 + \dots + K_i P^i + \dots + K_n P^n}{1 + K_1 P + K_2 P^2 + \dots + K_i P^i + \dots + K_n P^n}. \quad (2)$$

q_m is the monolayer capacity, P is the equilibrium pressure, K_i are the equilibrium coefficients of the adsorption reactions (1), $i = 1, 2, \dots, n$ is the number of monomers in the sorbate clusters, n is the maximum cluster size ($n > 1$). The magnitudes $K_1, \dots, K_i, \dots, K_n$ can be considered dimensionless if you enter a dimensionless pressure SI, 2 (S8). If Eq. (1) correspond to adsorption occurring in several elementary stages and are equations of complex reactions, then the K_i in (2) are the product of the equilibrium constants of the corresponding elementary reactions. "This corresponds to the conclusion of the theory of chemical kinetics, according to which the equilibrium constant of the total process is a product of the equilibrium constants of elementary reactions" [1]. An example of such a situation is the cluster formation on the surface by sequential addition of one molecule to already sorbed ones.

For $n = 1$ of (2), we obtain the Langmuir model.

When multilayer clusters are formed on the sorbent surface, the coefficients before $K_i P^i$ in the numerator of Eq. (2) are different from 1 [1]. They are equal to the ratio of

the number of molecules in the cluster (i) to the number of molecules in the cluster first layer (m_i) [1], that is, they are determined by the structure of the cluster. For monolayer adsorption $i = m_i$ ($i/m_i = 1$) and Eq. (2) is valid [1, 2, 13–16].

2.2 Analytical bases of the criterion of the monolayer adsorption mechanism

In this investigation, we write down the equation of monolayer cluster adsorption (2) in the form

$$q = q_m \frac{K(P)P}{1 + K(P)P}, \quad (3)$$

where

$$K(P) = K_1 + K_2P + \dots + K_iP^{i-1} + \dots + K_nP^{n-1}, \quad (4)$$

and K_i are the equilibrium coefficients of the adsorption reactions (1).

Equation (3) has the form of the Langmuir equation. However, the Langmuir equilibrium coefficient K_L is replaced in (3) by the pressure function $K(P)$ (4), which we will call the concentration function. The coefficients K_1, K_2, \dots, K_n of the function $K(P)$ (4) have a clear physico-chemical meaning: they are the equilibrium coefficients of reactions (1), that follows from the analytical derivation of Eq. (2), SI, 2. Thus, at monolayer cluster adsorption, the function $K(P)$ increases according to a power law with increasing P . With Langmuir adsorption, $K(P) K_L$ is constant and does not depend on pressure.

$$q = q_m \frac{K_L P}{1 + K_L P} \quad (5)$$

For the goals of this article, we propose to express $K(P)$ and K_L from (3) and (5) as

$$K(P) = \frac{q}{q_m - q} \frac{1}{P} \quad (6)$$

$$K_L = \frac{q}{q_m - q} \frac{1}{P} = \text{const} \quad (7)$$

It is important that the function $K(P)$ (6) and the equilibrium coefficient K_L (7) can be calculated tabularly from the experimental isotherm if the capacity of the monolayer q_m is known. The q_m parameter, at monolayer adsorption, is approximately determined as the adsorption value on a capacitive plateau.

2.3 Simplified equation of single-layer cluster adsorption

Equation (2) was applied to the interpretation of experimental isotherms and it is shown that experimental isotherms are often well described by a simplified equation [2, 14–16]:

$$q = q_m \frac{K_1 P + K_n P^n}{1 + K_1 P + K_n P^n}. \quad (8)$$

Equation (8) describes the fixation of monomers and clusters of the maximum possible size in the first layer of the sorbent. The formation of clusters of the maximum possible size leads to a maximum reduction in the energy of the system during adsorption, since these clusters have a greater number of sorbate-sorbate interactions, which contribute to the adsorption energy. Clusters can form on less reactive sorbent sites where the adsorption potential is insufficient to fix monomers or small clusters, however, adsorption in the form of large clusters is possible due to the contribution of sorbate-sorbate bonds to the adsorption energy if their number is large enough [13–16]. Monomers are often sorbed at more reactive sites of the sorbent (for example, at the end sites or defects).

2.4 Graphical determination of the parameters of the simplified equation

The significance of Eq. (8) is that it can be written in linear form and its parameters can be determined graphically from the experimental adsorption isotherm [2], which makes it easier to use in practice. This work proposes an approach to the linearization of Eq. (8) different from those set out in work [2], which allows us to compare (8) with the Langmuir model. In present work, we introduce the concentration function $K(P)$ in accordance with (4) into the simplified Eq. (8):

$$q = q_m \frac{K_1 P + K_n P^n}{1 + K_1 P + K_n P^n} = q_m \frac{K(P)P}{1 + K(P)P}, \quad (9)$$

which is defined by the expression

$$K(P) = K_1 + K_n P^{n-1}. \quad (10)$$

The coefficients K_1 and K_n of this function have a clear physico-chemical meaning: K_1 is the equilibrium coefficient of the reaction $S + A = SA$, describing the formation of monomers on the sorbent, K_n is the equilibrium coefficient of the reaction $S + nA = SA_n$, describing the formation of clusters of n molecules in 1 layer of the sorbent. Thus, both

equilibrium coefficients K_1 and K_n contribute to $K(P)$, (the first with weight 1, the second with weight P^{n-1}).

The monolayer capacity q_m at monolayer adsorption can be determined approximately from the experimental isotherm. The equilibrium coefficient K_1 in the case of the applicability of Henry’s law is determined by the formula [2]

$$K_1 = \frac{\Gamma}{q_m},$$

Γ is the Henry constant, determined from the initial section of the isotherm.

Thus, from (10) we have.

$$K(P) - K_1 = K(P) - \frac{\Gamma}{q_m} = K_n P^{n-1}, \text{ or} \\ \lg \left(K(P) - \frac{\Gamma}{q_m} \right) = \lg K_n + (n - 1) \lg P. \tag{11}$$

The function $K(P)$ can be given in tabular form from relation (6).

Taking into account $K(P)$ from (6), the expression (11) takes the form

$$\lg \left(\frac{q}{q_m - q} \frac{1}{P} - \frac{\Gamma}{q_m} \right) = \lg K_n + (n - 1) \lg P, \tag{12}$$

The function $Y = \lg \left(\frac{q}{q_m - q} \frac{1}{P} - \frac{\Gamma}{q_m} \right)$ linearly depends on $\lg P$, similar to that obtained in work [2] and the parameters n and K_n can be determined graphically (Fig. 2).

When graphically determining the parameters of isotherms, it is important to keep in mind the following [2]:

- i) $q - q_m \rightarrow 0$, if $q \rightarrow q_m$, but the magnitude $q - q_m$ is included in the denominator of the left-hand side of (12);
- ii) $\frac{q}{q_m - q} \frac{1}{P} - \frac{\Gamma}{q_m} \rightarrow 0$ at low P and $\lg \left(\frac{q}{q_m - q} \frac{1}{P} - \frac{\Gamma}{q_m} \right) \rightarrow -\infty$;

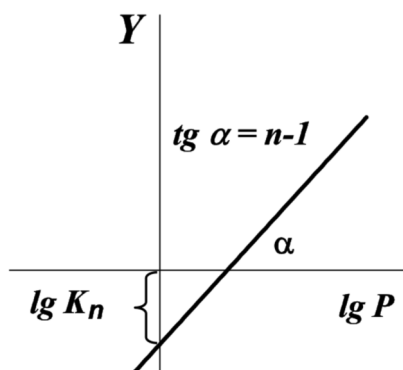


Fig. 2 Determination of parameters n and K_n by linearisation method [2]

- iii) The value of q_m cannot be determined very accurately from the experimental isotherm without additional research;
- iv) Sorbents have the most reactive sites (defects, end sites where bonds are broken, etc.) almost always, the rest of the surface has no broken bonds and is less reactive for adsorption; at low concentrations, the sorbate is fixed in more reactive areas, therefore, the values of $K(P)$ (6) may not reflect the properties of the entire surface at $P \sim 0$;

Consequently, a small error in determination of the q and P values in the regions $P \sim 0$ and $q \sim q_m$ can lead to a significant error in determining the linear function (12) in these areas. Therefore, if the function (12) is observed to deviate from the linear function in the low-pressure or capacitive plateau regions, these regions should be excluded when graphically determining the parameters.

Note that the error at approximating experimental data by a function depends both on the error of experimental data (direct errors) and on the type of approximating function (indirect errors). As a result, the magnitude of the error functions used to estimation of the model (R^2 in our work) depends on the type of functions of the linearized and initial forms [30–32]. Therefore, the parameters describing the linearized isotherm (Fig. 2, (12)) with a certain degree of accuracy do not necessarily describe the original isotherm (9) with the same accuracy. As a result, in order to obtain the correct value of the error function, a nonlinear regression analysis must be performed.

Nonlinear modeling is more significant than linearized models because it reflects experimental results much better. However, a significant difference in the initial values of the parameters from the optimal ones during nonlinear regression analysis may lead to divergence of its algorithm. Therefore, the parameters found by linearization can serve as a zero approximation for nonlinear modeling, that is essential for practice.

2.5 Experimental criterion for a monolayer adsorption mechanism

It follows from (4) and (10) that in the case of cluster formation in the first sorbent layer, the function $K(P)$ increases according to a power law with increasing P . If the Langmuir model is applicable, $K(P) \equiv K_L$ is a constant and is independent of pressure. If the tabular definition (6) of the $K(P)$ function leads to the conclusion that it practically does not depend on pressure, then the Langmuir model is a good approximation of the analyzed isotherm. If the function $K(P)$ increases with increasing P , which follows from (12), then the single-layer adsorption is clustered, which is important

for the interpretation of the adsorption mechanism. If the $K(P)$ function changes with increasing pressure in a manner different, the adsorption mechanism is more complex.

3 Results and discussion

Let's consider the application of this criterion on specific examples.

3.1 Cluster adsorption

In this section, we present the pressure dependences of the concentration function $K(P)$ calculated by formulas (6) and (10) for the case of monolayer adsorption of carbon dioxide by metal-organic frameworks IRMOF-11, IRMOF-6 and IRMOF-1. Experimental isotherms were obtained by A. R. Millward and O. M. Yaghi [29] (SI, 1) and are presented in Fig. 3 by a point curve (no experiment to obtain isotherms was performed in the present work).

The monolayer character of CO₂ adsorption on these sorbents is confirmed by a sufficient surface area of the studied sorbents for a monolayer coating (SI, 1), as well as by quantum chemistry methods [2]. According to them, each sorbent reaction center is surrounded by clusters of 3–4 CO₂ molecules located in 1 layer, which corresponds to the cluster adsorption model. At the same time, the adsorption energy of a cluster of 4 CO₂ molecules on a representative fragment of the studied sorbents is $E_{\text{ads}} = -35.0$ kcal/mol [2], which is greater than the kinetic energy of the thermal motion of CO₂ molecules ($5/2 RT \sim 1.5$ kcal/mol), therefore, clusters will not be destroyed by the thermal motion

of molecules. Equations (2) and (8) are obtained under the condition that all clusters lie in the first layer, therefore their excellent compliance with experimental isotherms also indicates in favor of a single-layer coating. The possibility of formation of (CO₂)_n clusters was confirmed experimentally and theoretically [13, 33–35].

At graphical determination of the q_m , K_1 , K_n and n parameters (Fig. 2) the q_m value is taken from the experiment (maximum experimental loading). In addition, the parameters q_m , K_1 , K_n and n are also found by the least squares method from the condition of the best agreement of the simplified Eq. (8) with experimental isotherms for the entire region [2]. Thus, the calculation of $K(P)$ according to the formula (6) was carried out for two values of the monolayer capacity q_m :

- 1) $q_{m1} = q_{\text{max}}$ is the maximum experimental loading corresponding to the achievement of a capacitive plateau by the isotherm, SI, 1;
- 2) $q_{m2} = q_{\text{mLSF}}$ is calculated by the least squares fitting (LSF) from the condition of the best experimental isotherm agreement with Eq. (8) for the entire region.

The obtained parameters are presented in Table 1 (the graf and LSF rows of the Table 1, respectively) and used to construct the dependence $K(P)$ according to formulas (6) and (10).

Figure 4 shows the dependences of $K(P)$ obtained by formulas (6) and (10) for the pressure region bounded by vertical lines in Fig. 3. Figure 4a, c and e show the dependencies of $K(P)$ calculated by formula (6) using the values of the maximum experimental loading $q_{m1} = q_{\text{max}}$, as well

Fig. 3 Experimental (points) [29] and calculated by formula (9) (solid lines) isotherms of carbon dioxide adsorption on metal-organic frameworks IRMOF-11, IRMOF-6 and IRMOF-1 (when calculating the isotherm by formula (9), the functions $K(P)$ (10) calculated in this paper are used, the isotherms parameters are defined graphically)

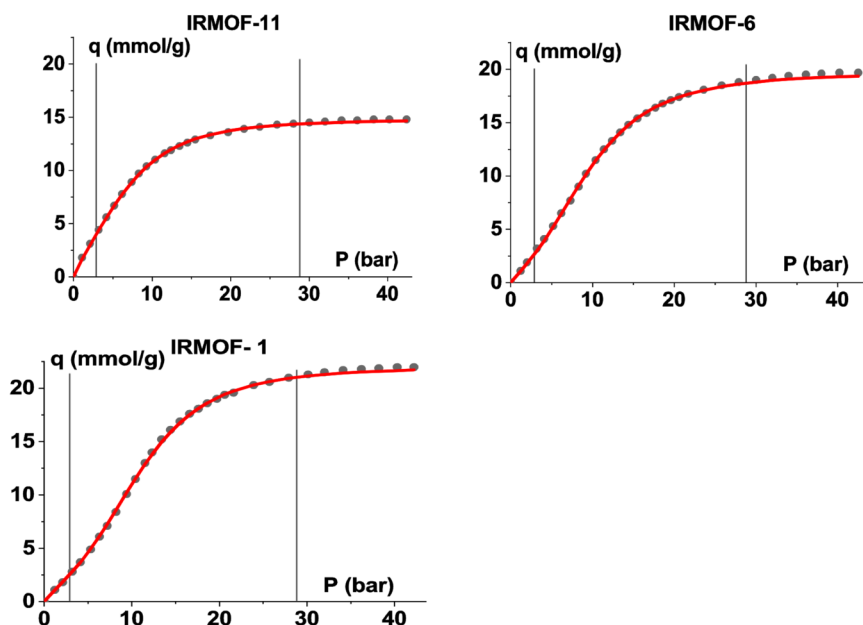


Table 1 The adsorption isotherm parameters for cluster adsorption model

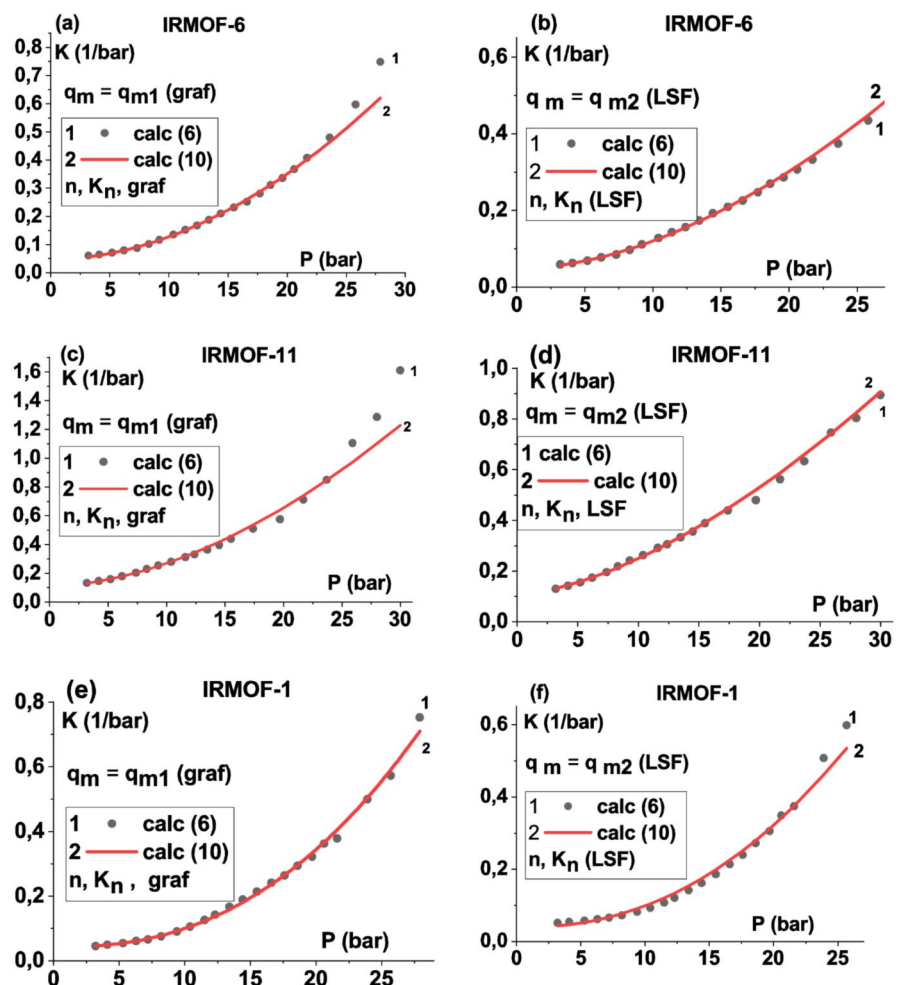
	q_m , mmol/g	n	K_1	K_n	R^2
<i>IRMOF – 11</i>					
graf*	14.80	2.782	0.1106	$2.612 \cdot 10^{-3}$	0.9995
LSF**	15.04	2.580	0.1085	$3.698 \cdot 10^{-3}$	0.9998
<i>IRMOF – 6</i>					
graf*	19.7	2.908	$4.653 \cdot 10^{-2}$	$1.000 \cdot 10^{-3}$	0.9992
LSF**	20.15	2.790	$4.658 \cdot 10^{-2}$	$1.194 \cdot 10^{-3}$	0.9999
<i>IRMOF – 1</i>					
graf	22.00	3.378	$4.167 \cdot 10^{-2}$	$0.245 \cdot 10^{-3}$	0.9995
LSF	22.27	3.245	0.03878	$0.339 \cdot 10^{-3}$	0.9998

* Linearization (12) in the area between vertical lines, Fig. 3

** LSF method for the entire region [2]

as by formula (10) using the parameters found graphically (the graf row of the Table 1). In Fig. 4b, d and f this dependence is obtained for the value of the monolayer capacity and the parameters found by the LSF method (the LSF row of the Table 1). The parameters found graphically (Table 1) slightly differ from those found in the work [2]. This is due to the fact that in [2] a less wide of the isotherm between vertical lines was used to determine them.

Fig. 4 Dependencies of $K(P)$ calculated using formulas (6) (points) and (10) (lines) for two values of q_m : a, c, e: $K(P)$ was calculated by formula (6) using the values of the maximum experimental loading $q_{m1} = q_{max}$, as well as by formula (10) using the parameters found graphically (the graf row of the Table 1); b, d, f: calculation according to formulas (6) with $q_m = q_{m2}$ (LSF) and (10) using data from the “LSF” row of the Table 1



The obvious conclusion from the graphs in Fig. 4 is a significant increase (\sim by an order of magnitude) in the value of $K(P)$ with pressure increasing. This indicates that Langmuir’s approximation (the absence of interactions between the sorbate molecules of the first layer) is incorrect. The good agreement of the $K(P)$ functions calculated by formulas (6) and (10) indicates the cluster nature of adsorption. The discrepancy between some functions in Fig. 4 in the region of high pressures indicates a significant dependence of the $K(P)$ on q_m value in the region of the capacitive plateau when calculated using the formula (6). The use of the maximum experimental loading ($q_m = q_{m1} = q_{max}$) in the calculation according to formula (6) allows us to make the right conclusion about the nature of adsorption and can be used to clarify the mechanism.

3.1.1 Comparison of the cluster model with the Sips model

The experimental isotherm is also well described by the Sips model, which was introduced as an empirical model [36]:

Table 2 The Sips isotherm parameters calculated by LSF method

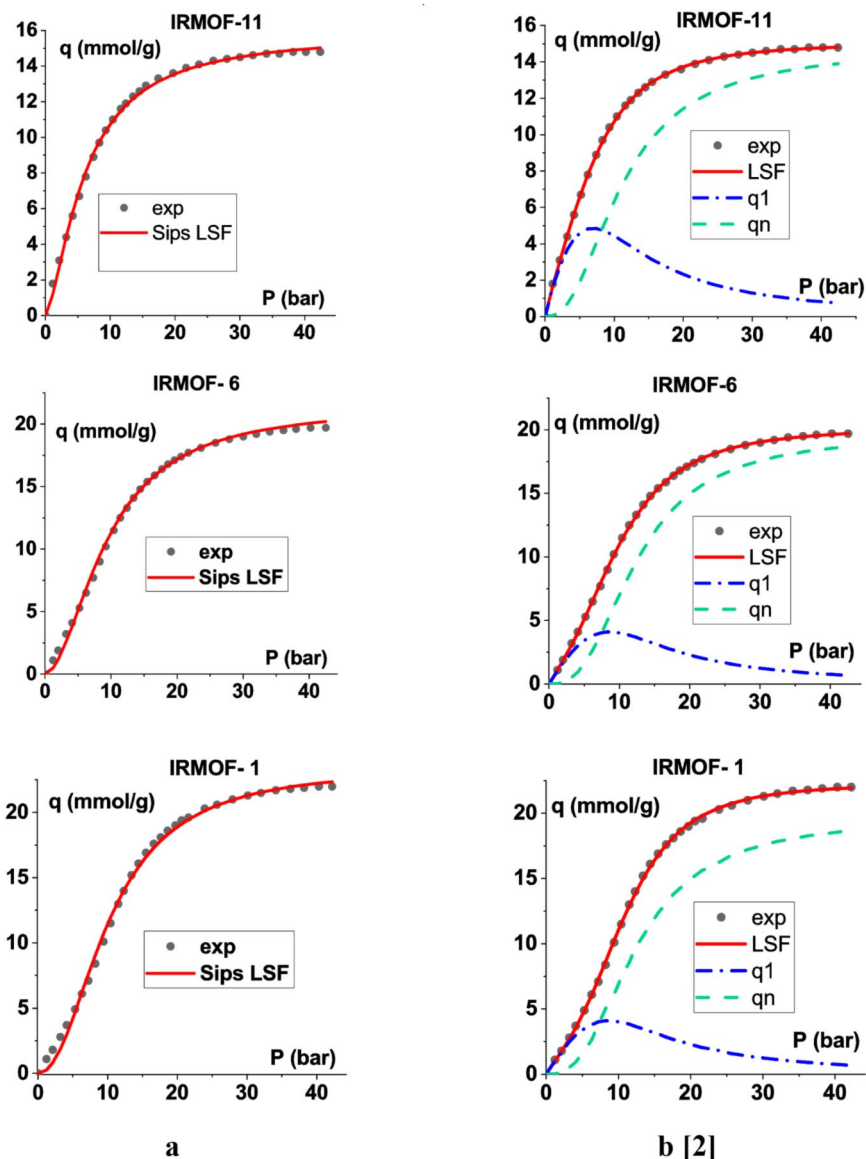
	q_{ms} , mmol/g	K_{ns} , bar ⁻¹	n_s	R^2
IRMOF-11	15.863	0.0685	1.487	0.9979
IRMOF-6	21.464	0.0162	1.840	0.9980
IRMOF-1	23.481	0.0074	2.111	0.9966

$$q = q_{ms} \frac{K_{ns} P^{n_s}}{1 + K_{ns} P^{n_s}} \quad (13)$$

q_{ms} , K_{ns} , n_s - parameters of the Sips model. It is easy to see that Eq. (13) is a special case of Eq. (2). According to (1) and (2), the Sips model (13) describes the formation of clusters of n_s molecules on the sorbent, q_{ms} is the capacity of the monolayer, K_{ns} is the equilibrium coefficient of the adsorption reaction $S + n_s A = SA_{n_s}$. Since the coefficient before K_{ns} in the numerator (13) is 1, this equation corresponds to

monolayer adsorption (see all comments to Eq. (2)). In the Sips model, there is no adsorption of monomers and sorbate clusters from $n \neq n_s$ molecules. Thus, the proposed cluster model (2) makes it possible to understand the adsorption mechanism of the Sips model and the physico-chemical meaning of the its model parameters. The parameters of the Sips model for the systems under study are calculated by the LSF method (Table 2). A comparison of the Sips isotherm (13) and the cluster adsorption isotherm (8) is shown in Fig. 5. The isotherm of cluster adsorption can be decomposed into contributions to the adsorption of monomers and clusters SI, 3. In Fig. 5b the dash dot line (q1) represents the contribution to the adsorption of monomers, the dash line (qn) represents the contribution of clusters. The n_s values for the studied systems (Table 2) allows us to conclude that

Fig. 5 Experimental (points) [29] and calculated adsorption isotherm (solid lines) of carbon dioxide on metal-organic frameworks IRMOF-11, IRMOF-6 and IRMOF-1. **a** The Sips model (13), **b** The cluster adsorption model (8), q1, qn is the contribution to the adsorption of monomers and clusters (SI, 3), the isotherm parameters in (8) and (13) are calculated by the LSF method [2]



clusters of ~2 molecules are formed on the sorbent according to Sips model.

According to the cluster adsorption model (8), monomers and associates of 3–4 molecules are formed on the sorbent (*n* value in Table 1), and at low pressures the contribution to the adsorption of monomers prevails, at high pressures prevails clusters contribution Fig. 5b, curves q1, qn. Contribution to the adsorption of clusters (qn curve, Fig. 5b) there is less in the cluster model than in the Sips model (Fig. 5a). As a result, the monolayer capacity in the Sips model is overestimated, which raises the isotherm at all pressure values in order to obtain agreement between the model and the experiment for the entire region *P*. The Sips isotherm indistinctly reaches the capacitive plateau, unlike the experimental isotherm (Fig. 5a).

With an increase in the value of *n_s* (Table 2) The Sips model is more concave at low pressures, and its discrepancy with the experiment increases (Fig. 5a). Nevertheless, the Sips model, as follows from the above, allows us to conclude about the cluster nature of adsorption and is useful for evaluating the mechanism of adsorption. In our model, the agreement of theory and experiment at low pressures is ensured by the contribution to the adsorption of monomers (q1). Both the Sips model and (8) describe the experiment well (see R² in Tables 1 and 2). Thus, the correspondence of the model and the experimental isotherm is not a criterion for the adequacy of the model [4, 37].

3.2 Langmuir adsorption

When applying the Langmuir equation to the interpretation of adsorption isotherms, the condition of uniformity of reaction centers (7) is never checked. One of the ways of such verification is to control the fulfillment of the condition *K_L*

= const from the experimental isotherm (7). Let's take an example of experimental isotherms for which the concentration function *K(P)* (6) depends weakly on pressure, i.e. *K(P) = K_L ≈ const* (7) and Langmuir's model is valid. Two examples of such adsorption are the adsorption of ethane at 400 K on highly activated Saran carbon [38] and the adsorption of methane on mica at 90 K [17] (no experiment to obtain isotherms was performed in the present work). The adsorption data [17, 38] and the results of our *K(P)* calculation are shown in Figs. 6a and 7a. Equilibrium pressures *P* are shown in column 1, loading values *q* are shown in column 2 [17, 38]. Column 3 presents the *K(P)* data calculated using formula (6) for *q_m = q_{m1} = q_{max}(exp)*, column 4 shows the ones calculated for *q_m = q_{m2} = q_{mLSF}*. Figures 6b and 7b show the corresponding experimental isotherms (dots) [17, 38], and Langmuir isotherms (solid line), where *q_m* and *K_L* are found by LSF method.

The corresponding *K(P)* dependences are presented in Fig. 8.

Although the *K* value in the considered examples is not a strictly constant value its deviation from the constant is not very significant if we do not take into account the region of low pressures and the region close to the capacitive plateau. These values are highlighted in bold in columns 3 and 4 (Figs. 6 and 7). The weak dependence on pressure is confirmed by the slope coefficients of the linear *K(P)* regression which close to 0, Figure 8.

It is shown that for the systems studied, the maximum value of the experimental loading can be used to calculate the concentration function *K(P)* from the adsorption data if the middle part of the isotherm is used. However, the experimental isotherm in the area of high concentrations must be close to or reach the capacitive plateau so that the

Fig. 6 C₂H₆ adsorption on highly activated carbon Saran at 400 K [38], **a** adsorption data and results of the *K(P)* calculation by the formula (6), **b** adsorption isotherm and Langmuir's LSF parameters

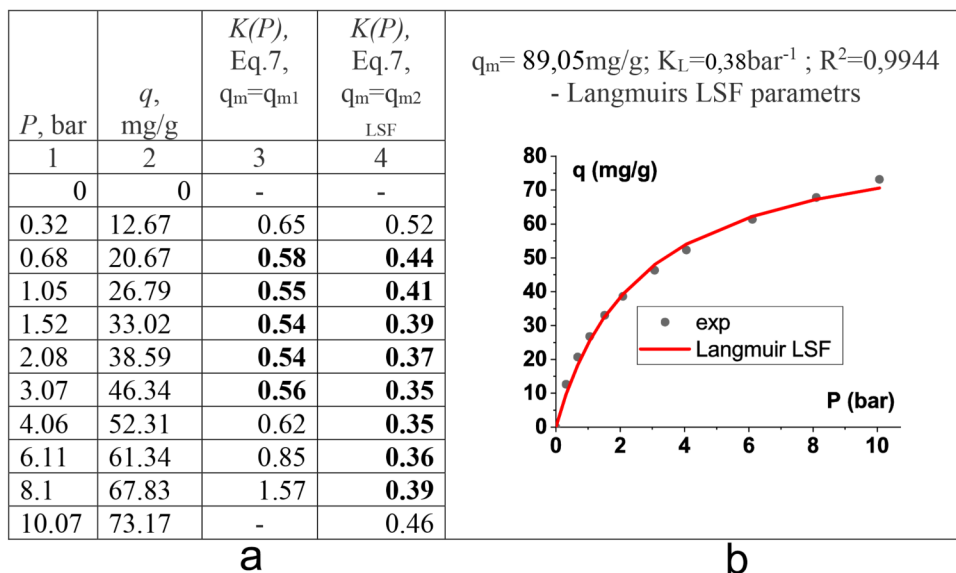


Fig. 7 CH₄ adsorption on mica at 90 K [17]. **a** adsorption data and results of the $K(P)$ calculation by the formula (6); **b** adsorption isotherm and Langmuir LSF parameters. (* - the loading value $q = q_{\text{obs}}$ in [17] is expressed by volume in cu. mm. absorbed by a strip of mica with a surface area of 5750 cm² and weighing 24.3 g)

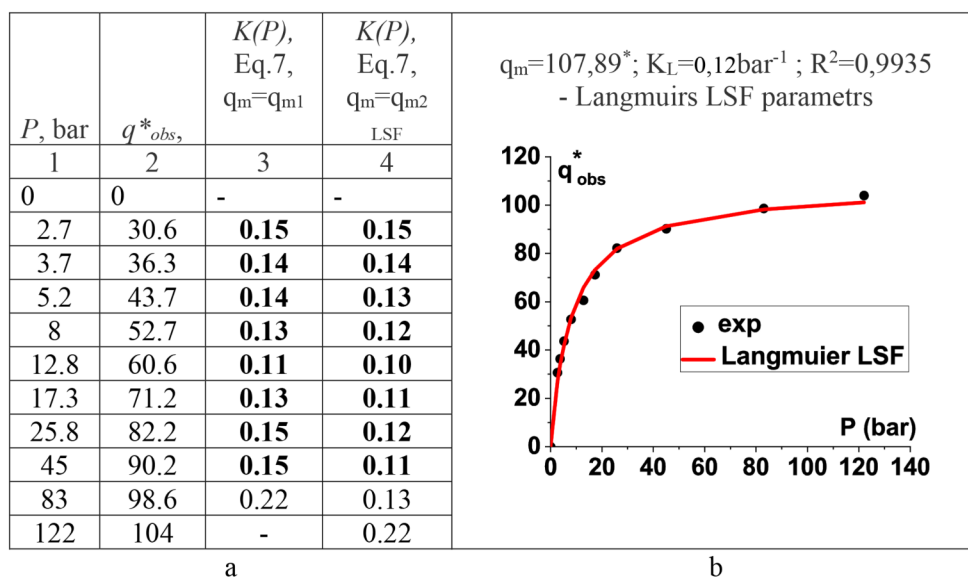
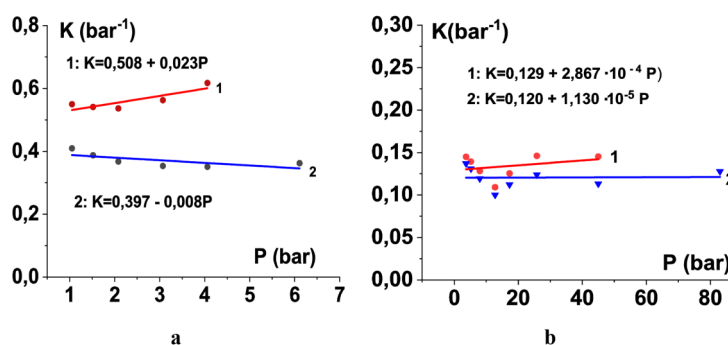


Fig. 8 Dependences $K(P)$. calculated by formula (6); **a** Ethane adsorption on highly activated Saran carbon at 400 K; **b** Methane adsorption on mica at 90 K. Dependence 1 is calculated for $q_m = q_{m1}$. dependency 2 is calculated for $q_m = q_{m2}$



experimental maximum loading is close to the capacity of the monolayer.

4 Conclusion

This work develops a new approach to mechanism interpreting of monolayer adsorption isotherms. It is shown how to determine the presence or absence of interactions between first-layer sorbate molecules using only monolayer adsorption isotherm data. The investigation was carried out by comparing Langmuir monolayer adsorption models, which do not take into account the sorbate-sorbate bonds, and the cluster adsorption model, which takes them into account. It is shown that the mechanism of monolayer adsorption (cluster or Langmuir) can be established by the analysis of the function $K(P)$ introduced in the work, and a method for determining it from the experimental isotherm is proposed. It has been analytically proven that in the case of cluster adsorption, this function increases significantly with increasing pressure; in the case of Langmuir adsorption, this function does not depend on pressure and transforms to the equilibrium coefficient of the Langmuir model. The

proposed criterion was applied to identify the mechanism of monolayer adsorption of carbon dioxide by IRMOF-6, IRMOF-11, IRMOF-1, ethane by highly activated Saran carbon and methane by mica. It has been shown that the adsorption of CO₂ on MOFs has a cluster character, while during the adsorption of ethane and methane, Langmuir adsorption of individual molecules on the sorbent takes place.

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Declarations

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