



Multilayer adsorption on fractal surfaces[☆]

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ABSTRACT

Multilayer adsorption is often observed in liquid chromatography. The most frequently employed model for multilayer adsorption is the BET isotherm equation. In this study we introduce an interpretation of multilayer adsorption measured on liquid chromatographic stationary phases based on the fractal theory. The fractal BET isotherm model was successfully used to determine the apparent fractal dimension of the adsorbent surface. The nonlinear fitting of the fractal BET equation gives us the estimation of the adsorption equilibrium constants and the monolayer saturation capacity of the adsorbent as well. In our experiments, aniline and proline were used as test molecules on reversed phase and normal phase columns, respectively. Our results suggest an apparent fractal dimension 2.88–2.99 in the case of reversed phase adsorbents, in the contrast with a bare silica column with a fractal dimension of 2.54.

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1. Introduction

The adsorption theory derived by Brunauer et al. [1] was a milestone in the adsorption studies. The isotherm equation they derived was an extension of the Langmuir [2] theory to multilayer adsorption, where the adsorbed molecules interact with each other and sub-layers are forming on the top of the adsorbed layer. Partially based on this theory, low temperature nitrogen adsorption [3–5] is a powerful method to characterize packing materials used as adsorbents in the practice of liquid chromatography.

It has been thoroughly discussed by Fripiat [6,7] that the number of the molecules that can be adsorbed inside the pores is significantly affected by the geometric structure of the surface, and the assumption of a flat surface can result in oversimplified interpretations.

The conventional multilayer isotherm models – such as the BET equation which is often used to interpret adsorption isotherm data in liquid chromatography – assume a two-dimensional flat surface. The fractal dimension of the flat surface is $D=2$. The problem arising from this simplification is that this model does not take into account the effects caused by the rugged, near three-dimensional pore surface. With the increase of the fractal

dimension from 2 to 3, the adsorbed layers can accommodate fewer and fewer molecules as we depart from the surface. The first adsorbed layer of molecules smoothes a bit the surface ruggedness. Therefore in the second layer of adsorbed molecules, we will find fewer molecules than in the first one. With a similar reasoning one can demonstrate that the third and subsequent layers will contain still fewer and fewer molecules.

The number of molecules possibly adsorbed in the pore structure of a porous adsorbent is determined by the roughness of the pore surface in the case of gas adsorption on a solid surface. In liquid–solid adsorption, the fine details are more complex. In the practice of liquid chromatography, the test molecule is in solution, where the applied solvent is usually a binary mixture of an organic modifier and water. Therefore, more factors than simply the geometry of the adsorbent surface will affect the building up of a multilayer in the pores. The estimated fractal dimension of the surface in liquid–solid adsorption is not resulted only by the geometry of the surface, but it is due to a number of phenomena and all those effect will be present in the case of adsorption isotherm measurements in liquid chromatography.

1. The surface geometry. The architecture of the adsorbed multilayer on a flat surface is completely different from the one on a rugged, fractal-like surface. This difference is demonstrated in Fig. 1A and B. On a flat surface – in good agreement with the original BET theory – the molecular layers are highly ordered and accommodate identical number of molecules. On the other hand, if one looks at a fractal-like rough surface, the structure of the adsorbed multilayer above the surface will change, and the saturation capacity of the sub-layers further

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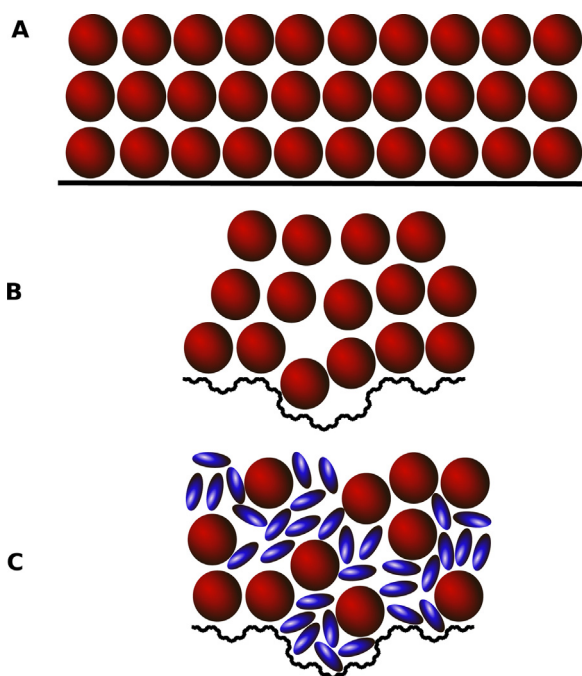


Fig. 1. The effects of the surface ruggedness and solvent co-adsorption on the architecture of the adsorbed multilayer. The lines are of same length and represent the cross section of a plain and a rough fractal-like surface. While on the flat surface (A) the adsorbed layers are highly ordered, the roughness of the surface (B) changes the ordered build-up of the sub-layers. Subsequent sub-layers can accommodate fewer molecules. In liquid chromatography, the adsorption of the solute molecules is always simultaneously occurs with a co-adsorption of solvent molecules (C). This phenomenon reduces the number of the adsorbed solute molecules above the adsorbent surface.

away from the adsorbent surface depends on the surface roughness.

2. The adsorption of the test compound is always a co-adsorption with solvent molecules. The adsorbed multilayer is not clearly built up from the studied solute itself – as it happens in the case of gas–solid adsorption – but the adsorbed layers is a mixture of the solute molecules and solvent clusters. This phenomenon reduces the theoretically possible number of molecules that can be adsorbed on the surface without taking into account the adsorption of solvent molecules. Fig. 1C gives a graphical overview of this phenomenon.
3. The available pore volume for adsorption in some cases of liquid chromatography is reduced by the chemical modification of the surface. The usually attached alkyl chains in reversed phase liquid chromatography set up a size–exclusion barrier for the test molecules, and reduce the surface of the original silica. In this case, the adsorption in the pores is not lessened just because of the surface roughness, but also because of the space required for the attached ligands.

The adsorption isotherm equations often used in liquid chromatography do not consider how the geometrical disorder of the surface affects the adsorption process. To take this and all the above mentioned phenomena into account, an isotherm equation that models the adsorption process on rough surfaces should be established.

In this study, we introduce an isotherm equation based on the BET theory to describe the fractal properties of the adsorption surfaces. To test the model, adsorption isotherms of aniline in reversed phase columns and the adsorption isotherm of proline on bare silica stationary phase were recorded. In the foregoing sections we

show the consequences of the roughness of the adsorbent surface on the adsorption properties of these compounds.

2. Theory

2.1. Frontal analysis for isotherm determination

Frontal analysis is widely used and the most accurate method to characterize the physico-chemical properties of chromatographic adsorbent beds [8]. Detailed methodology can be found in the literature [9–11]. The calculation of the solute concentration on the stationary phase q at a given mobile phase concentration C is given by the equation [12]:

$$q_{i+1} = q_i + \frac{(C_{i+1} - C_i)(V_{F,i+1} - V_0)}{V_a} \quad (1)$$

where q_i and q_{i+1} are the adsorbed concentration of the analyte when the stationary phase is in equilibrium with the solute mobile phase concentrations C_i and C_{i+1} at the i th and $(i+1)$ th step. $V_{F,i+1}$ is the inflection point of the breakthrough curve at the $(i+1)$ th step, V_0 is the void volume of the system and, V_a is the volume of the adsorbent.

2.2. BET isotherm for multilayer liquid adsorption

To derive the BET equation for a finite number of adsorbed layers of a single component system, we follow the pseudo-steady-state approach published by Gritti et al. [13]. When the adsorption surface is empty, the solute molecules interacts with the surface, what process is described by the following interaction constant

$$b_s = \frac{k_s^a}{k_s^d} \quad (2)$$

where k_s^a and k_s^d are the kinetic rate constants for surface adsorption and desorption, respectively. After the formation of a monolayer on the surface, the solute molecules start to interact with the molecules already adsorbed on the adsorbent surface, and the formation of subsequent layers can be observed in the case of BET type multilayer adsorption. The adsorbate–adsorbate interaction constant that describes this process is the following:

$$b_L = \frac{k_L^a}{k_L^d} \quad (3)$$

where k_L^a and k_L^d are the kinetic rate constants for adsorption and desorption within the adsorbed layer, respectively. If we assume the formation of n subsequent layers, the surface coverage fractions of the corresponding layers are

$$\theta_0, \theta_1, \theta_2, \dots, \theta_n \quad (4)$$

The sum of the surface coverage fractions is unity

$$\theta_0 + \theta_1 + \theta_2 + \dots + \theta_n = \sum_{i=0}^n \theta_i = 1 \quad (5)$$

For the free surface fraction θ_0 , the equilibrium steady-state is written as

$$\frac{d\theta_0}{dt} = 0 = k_s^d \theta_1 - k_s^a C(1 - \theta_1 - \theta_2 - \dots - \theta_n) \quad (6)$$

Rearranging Eq. (6) gives

$$\theta_1 = b_s C(1 - \theta_1 - \theta_2 - \dots - \theta_n) \quad (7)$$

When molecules tend to form a multilayer above the surface, interaction occurs between the adsorbed molecules, and a sub-layer is formed. For the first sub-layer we can write

$$\frac{d\theta_1}{dt} = 0 = k_s^a C(1 - \theta_1 - \theta_2 - \dots - \theta_n) - k_s^d \theta_1 - k_L^a C \theta_1 + k_L^d \theta_2 \quad (8)$$

Rearranging Eq. (8) yields

$$-[k_s^a \theta_1 - k_s^a C(1 - \theta_1 - \theta_2 - \dots - \theta_n)] + k_L^d \theta_2 = k_L^a C \theta_1 \quad (9)$$

Since the first term of the left hand side is 0 according to Eq. (6), we will get

$$\theta_2 = \frac{k_L^a}{k_L^d} C \theta_1 = b_L C \theta_1 \quad (10)$$

We can express θ_3 in a similar manner

$$\theta_3 = b_L C \theta_1 b_L C = (b_L C)^2 \theta_1 = b_L C \theta_2 \quad (11)$$

Thus a general relationship is found as

$$\theta_n = (b_L C)^{n-1} \theta_1 = b_L C \theta_{n-1} \quad (12)$$

The total amount adsorbed on the adsorbent surface is given as

$$q = q_s(\theta_1 + 2\theta_2 + 3\theta_3 + \dots + n\theta_n) \quad (13)$$

The total adsorbed amount can be re-expressed as

$$q = q_s \sum_{i=1}^n i \theta_i = q_s \theta_1 \sum_{i=1}^n i (b_L C)^{i-1} \quad (14)$$

θ_1 can be derived by substituting Eq. (12) into Eq. (7). The result is

$$\theta_1 = b_s C(1 - b_L C \theta_1 - (b_L C)^2 \theta_1 - \dots - (b_L C)^{n-1} \theta_1) \quad (15)$$

We can rearrange Eq. (15) as

$$\theta_1 = \frac{1}{(1/b_s C) + \sum_{i=1}^n (b_L C)^{i-1}} \quad (16)$$

Substituting Eq. (16) into Eq. (14) results in the BET isotherm for n adsorbed layers

$$q = \frac{q_s \sum_{i=1}^n i (b_L C)^{i-1}}{(1/b_s C) + \sum_{i=1}^n (b_L C)^{i-1}} \quad (17)$$

The classical BET isotherm equation for liquid phase adsorption is obtained from Eq. (17) when $n = \infty$

$$q = \frac{q_s b_s C}{(1 - b_L C)(1 - b_L C + b_s C)} \quad (18)$$

2.3. Fractal BET isotherm for multilayer liquid adsorption

As we have seen so far, the original BET isotherm equation was derived for flat surfaces. A fundamental measure of surface roughness is the fractal dimension. Fripiat et al. [6] extended the BET model for fractally rough surfaces. When S_r denotes the surface of the adsorbent measured on a length scale r , the fractal dimension of the surface can be defined as

$$D = \lim_{r \rightarrow 0} \frac{\ln S_r}{\ln r} \quad (19)$$

Thus the surface measured on a length scale r will fulfill the condition $S_r \propto r^D$. In multilayer adsorption, the second layer builds up on the first adsorbed layer. The molecules adsorbed in the first layer smooth the roughness of the surface, thus the second adsorbed layer will accommodate fewer molecules than the first layer. This progressive smoothing will go on as the number of adsorbed layers

increases. Fripiat et al. [6] used a numerical simulation and determined that the capacity of the i th layer (N_i) relative to that of the first layer (N_1) is

$$f_i = \frac{N_i}{N_1} = i^{-(D-2)} \quad (20)$$

Levitz et al. presented a mathematical justification for the above relationship [14]. Eq. (20) permits the calculation of the number of molecules in a multilayer adsorbed on a fractal surface. Fripiat et al. derived an isotherm equation for multilayer gas adsorption on fractal surfaces. In the following, we extend that approach to liquid adsorption. The BET isotherm for gas adsorption has two parameters: the monolayer saturation capacity and the BET constant. The adsorption equilibrium constant between the adsorbed layer is not explicitly present in the classical BET equation due to assumptions that are only valid for gas adsorption. When the BET isotherm is derived for liquid adsorption, that parameter should also be part of the model.

For a flat surface Eq. (13) gives total amount adsorbed. When the surface of the adsorbent is rough, the total amount adsorbed in a multilayer is expressed as

$$q = q_s [f_1 \theta_1 + (f_1 + f_2) \theta_2 + (f_1 + f_2 + f_3) \theta_3 + \dots + (f_1 + \dots + f_n) \theta_n] \quad (21)$$

The above equation can be rewritten using Eq. (20)

$$q = q_s \theta_1 \sum_{i=0}^n i^{2-D} \sum_{j=i}^n (b_L C)^{j-1} \quad (22)$$

Thus, the n -layer fractal BET isotherm is expressed as

$$q = q_s \frac{\sum_{i=0}^n i^{2-D} \sum_{j=i}^n (b_L C)^{j-1}}{(1/b_s C) + \sum_{i=1}^n (b_L C)^{i-1}} \quad (23)$$

When $n = \infty$, the fractal BET isotherm is obtained for liquid adsorption

$$q = \frac{q_s b_s C}{b_L(1 - b_L C + b_s C)} \text{Li}_{D-2}(b_L C) \quad (24)$$

where $\text{Li}_\alpha(z)$, the polylogarithm function of order α and argument z is defined as:

$$\text{Li}_\alpha(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^\alpha} \quad (25)$$

The polylogarithm function takes simple forms for $\alpha = 0$ and $\alpha = 1$.

$$\text{Li}_0(z) = \frac{z}{1-z}; \quad \text{Li}_1(z) = -\ln(1-z) \quad (26)$$

For a two-dimensional flat surface, where $D=2$, Eq. (24) gives the conventional BET isotherm equation (Eq. (18)). In the case of an extremely rugged, three-dimensional surface, where $D=3$, Eq. (24) simplifies to

$$q = \frac{-q_s b_s \ln(1 - b_L C)}{b_L(1 - b_L C + b_s C)} \quad (27)$$

The above isotherm model is the 3D equivalent of the BET isotherm equation.

3. Experimental

3.1. Instruments

The frontal analysis experiments were all acquired using an Agilent (Palo Alto, CA, USA) 1100 liquid chromatograph. This instrument includes a binary-solvent delivery system, an auto-sampler

Table 1

The physico-chemical properties of the columns used in this study. The table lists the geometrical volume of the stainless steel tube V_G , the coverage density of the octadecyl ligands $\alpha_{C_{18}}$ on the silica surface, the volume of the mobile V_m , and the adsorbent V_{ads} .

Column code	V_G (cm ³)	$\alpha_{C_{18}}$ ($\mu\text{mol}/\text{m}^2$)	V_m (cm ³)	V_{ads} (cm ³)
327	2.08	3.27	1.21	0.87
295	2.08	2.95	1.20	0.88
168	2.08	1.68	1.36	0.72
111	2.08	1.11	1.47	0.61
Silica	2.49	0.00	2.10	0.39

with a 100 μL sample loop, a diode-array UV-detector, a column thermostat and a data acquisition station.

3.2. Materials and reagents

Four reversed phase endcapped chromatographic columns with different surface coverage, and a bare silica column were tested. The surface coverage of the octadecyl bonded ligands of the reversed phase adsorbents were $\alpha_{C_{18}} = 3.27, 2.95, 1.68$ and $1.11 \mu\text{mol}/\text{m}^2$, respectively. All the reversed phase columns were prepared by the modification of the same batch of $5 \mu\text{m}$ average particle diameter and 100 \AA average pore diameter Kromasil 100 silica gel (Akzo Nobel, Bohus, Sweden). The silica column was a Water Atlantis column packed with $5 \mu\text{m}$ average particle diameter and 100 \AA average pore diameter stationary phase. The main physico-chemical properties of the columns is listed in Table 1. Acetonitrile was HPLC "isocratic grade", purchased from Sigma–Aldrich (Steinheim, Germany). Water was purified using Milli-Q system (Millipore, El Paso, TX, USA). Aniline and proline was purchased from Sigma–Aldrich (Steinheim, Germany).

4. Results and discussion

4.1. Fractal dimension of a chemically modified C_{18} adsorbents

The adsorption isotherm data points on the four reversed phase adsorbent was experimentally determined using step-wise frontal analysis. After the record of the chromatograms, the elution volume of the fronts was calculated according to the equal area method [13]. The adsorption isotherm data points were calculated at each equilibrium mobile phase concentration of aniline using the elution volumes of the fronts and the physical properties of the columns according to Eq. (1).

To determine the fractal dimension of the adsorbent, Eq. (24) was fitted to the experimental isotherm data points. The nonlinear fit was performed using a fixed value of the fractal dimension D , and the three estimated parameter were q_s , b_s , and b_L . The value of

Table 2

Best fitted isotherm parameters of Eq. (24) at the minimum of the RSS vs. D curve in the case of proline on bare silica and aniline on octadecyl-modified silica. The table gives a comparison between the isotherm parameters estimated assuming 2D or nearly 3D surfaces.

Column, analyte	q_s (g/dm ³)	b_s (dm ³ /g)	b_L (dm ³ /g)	D
<i>Silica-C₁₈, aniline</i>				
<i>3D surface</i>				
327	92.42 ± 0.64	0.0789 ± 0.0013	0.0266 ± 0.0001	2.88
295	97.71 ± 0.73	0.0784 ± 0.0015	0.0271 ± 0.0001	2.97
168	111.2 ± 0.47	0.0643 ± 0.0007	0.0276 ± 0.0001	2.92
111	140.4 ± 0.72	0.0509 ± 0.0006	0.0280 ± 0.0001	2.99
<i>2D surface</i>				
327	78.55 ± 1.576	0.1039 ± 0.0050	0.0207 ± 0.0002	2.00
295	82.30 ± 1.859	0.1050 ± 0.0057	0.0205 ± 0.0002	2.00
168	89.66 ± 1.935	0.0911 ± 0.0047	0.0218 ± 0.0002	2.00
111	110.1 ± 2.684	0.0736 ± 0.0039	0.0220 ± 0.0002	2.00
<i>Bare silica, proline</i>				
	141.8 ± 0.60	0.2808 ± 0.0017	0.1751 ± 0.0003	2.54

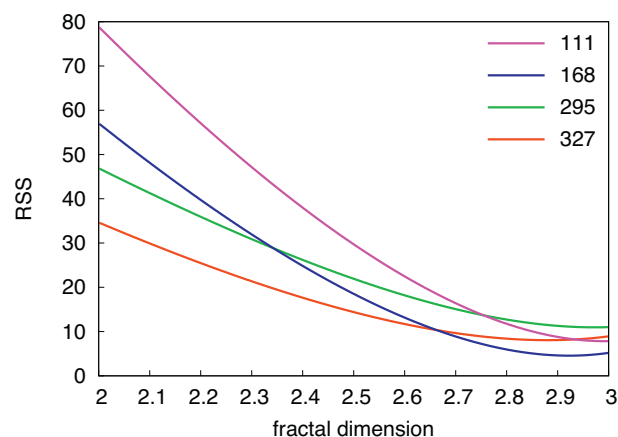


Fig. 2. The change of the sum of squares of the residuals with the change of the fractal dimension of the adsorbent. Results for four reversed phase endcapped chromatographic stationary phases with different surface coverage are presented. The surface coverage of the octadecyl bonded ligands of the reversed phase adsorbents are $\alpha_{C_{18}} = 3.27, 2.95, 1.68$ and $1.11 \mu\text{mol}/\text{m}^2$, respectively. The RSS value describes the agreement between the experimental isotherm data points and the fitted Eq. (24).

parameter D was increased from the lower border 2 to the upper limit 3 with a step size of 0.001. At each fractal dimension value, a nonlinear fit was performed, and the parameters were estimated. The goodness of the fit at each step was described by the residual sum of squares, RSS. Fig. 2 shows a comparison of the goodness of the fit of the fractal BET equation to the experimental isotherm data points in the case of the four reversed phase columns.

The fit of the isotherm model shows the worst agreement on all adsorbents when we assume flat surface, i.e. $D=2$. The disagreement between the fitted and measured isotherm is decreasing as the fractal dimension approaches the value of $D=2.9$. Above this threshold – depending on the surface coverage – a slight increase in the RSS value can be observed.

Fig. 3 gives an overview of the change of the estimated parameters with the change of the fractal dimension between values of $D=2$ and 3. The estimated monolayer saturation capacity q_s of the stationary phases show an increasing trend with the increase of the fractal dimension of the adsorbent. Similar trend can be observed in the case of the equilibrium constant of the interaction between the adsorbed layers b_L . The adsorption equilibrium constant with the surface b_s shows an opposite trend, it decreases with the increase of the fractal dimension.

The adsorption isotherm data points and the best fitted isotherm models at the minima of the RSS vs. D plot can be seen in Fig. 4.

The fractal dimension of the reversed phase adsorbents were determined according to the location of the minimum of the

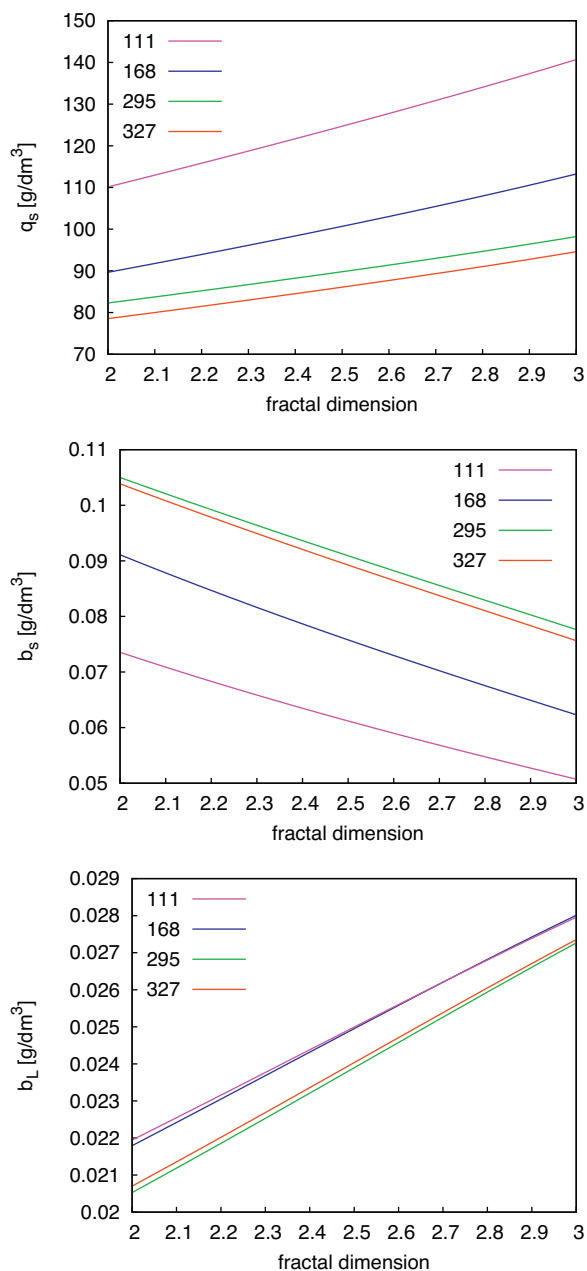


Fig. 3. The change of the estimated isotherm parameters during the nonlinear fit of Eq. (24) to the experimental isotherm data points with the change of the fractal dimension of the adsorbent. Results are reported for the same set of stationary phases as in Fig. 2.

RSS vs. D plot. The fractal dimension and the best fitted parameters corresponding to the optimum D are listed in Table 2. The change of each parameter with the surface coverage follows the previously observed trends [15,16]. The monolayer saturation capacity increases in parallel with the b_L parameter, and the b_s parameter decreases with the decrease of the surface coverage of the adsorbent.

4.2. Fractal dimension of an unmodified silica adsorbent

The solubility and adsorption properties of proline give the opportunity to measure its adsorption isotherms under HILIC (hydrophilic interaction chromatography) conditions [17]. With the aid of the BET-type isotherm of proline we can make a

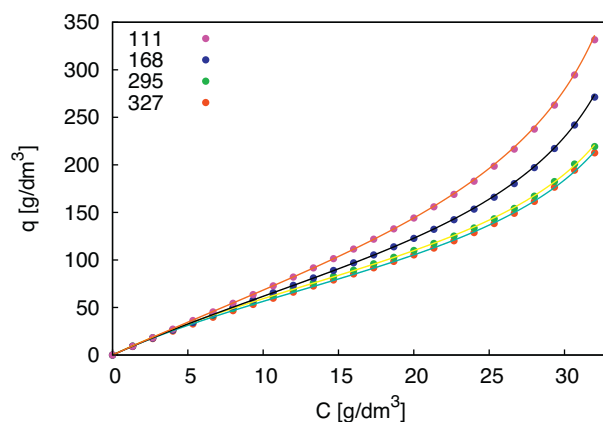


Fig. 4. The adsorption isotherm data points of aniline and best fitted fractal BET isotherm equation on the four reversed phase columns. The fits were performed using the optimum D value found on the RSS vs. D curves. Results are reported for the same set of stationary phases as in Figs. 2 and 3.

comparison between the fractal dimension of a chemically modified and an unmodified silica adsorbent. The adsorption isotherm of proline was recorded from 85% acetonitrile/15% water (v/v) mixture. The applied concentration range of proline was 0–4 g/cm³.

Using the same treatment as it was described in the previous section, the change of the isotherm parameters and the quality of fit were determined with the change of the fractal dimension. Fig. 5 shows the dependence of the estimated isotherm parameters on the fractal dimension. The trends are similar to the one observed in the case of aniline on the reversed phase columns. The best-fit parameters at the minima of the RSS are listed in Table 2.

The effect of the surface modification on the fractal dimension of the adsorbent is presented in Fig. 6. In the case of bare silica adsorbent the RSS vs. D curve shows a clear minimum at 2.54 value of the fractal dimension. In the comparison with the chemically modified reversed phase adsorbent a clearly decrease in the apparent fractal dimension can be observed.

4.3. Comparing the two-dimensional and three-dimensional BET isotherms

The determination of the fractal dimension and the comparison of the isotherm models fitted to the same set of experimental data was based on the sum of squares of the residuals. The comparison of the sum of squares of the residuals may give important information about model discrimination, i.e. which model (which fractal dimension) describes best the adsorption isotherm data points, but it does not indicate the accuracy of the models.

Since the fractal dimension of the surface of the C₁₈ packing material was found to be in the range of $D=2.88$ – 2.99 , we compared how accurately the original 2D and the newly derived 3D BET isotherm equations follow the experimental data.

The comparison between the best-fitting 2D and 3D models for the case of aniline as test analyte on the stationary phase with surface coverage of $\alpha_{C_{18}} = 1.11 \mu\text{mol}/\text{m}^2$ can be seen in Fig. 7. The 2D and 3D models (Eqs. (18) and (27), respectively) were fitted to the experimental data for the entire concentration range, up to $C = 33 \text{ g}/\text{dm}^3$. In Fig. 7, only the beginning of the isotherm is plotted in order to visually demonstrate the difference in the accuracy of the 2D and 3D models. The experimental error for the determination of the retention times of the fronts was assumed to be 1%. The experimental determination of those data, however, was done with significantly lower error – the day-to-day repeatability was below 0.5%. This higher value makes more clear that the use of the 2D model results in higher disagreement, an error that is

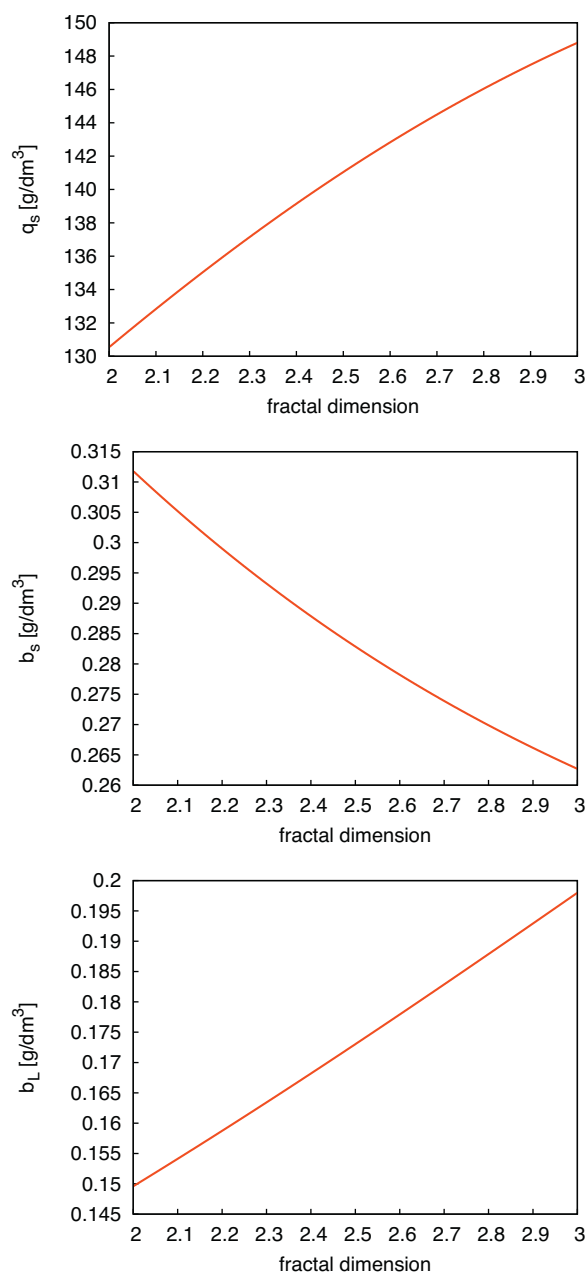


Fig. 5. The dependence of the estimated isotherm parameters of proline on unmodified silica adsorbent used in HILIC mode vs. the change of the fractal dimension of the stationary phase.

beyond the experimental error range for the entire concentration range.

The adsorption of aniline on an octadecyl modified adsorbent with low coverage of the bonded ligands is governed by a number of interactions. The chemical nature of this test compound allows strong interaction with both of the polar and apolar adsorption centers. This heterogeneous adsorption makes the built-up of the adsorbed multilayer of aniline molecules solvated with solute molecules a highly complicated example. In Fig. 8 we compare the experimental and calculated overloaded elution bands of aniline. A two-minute long plug was injected into the column with an initial concentration of 33 g/dm^3 . The numerical simulation was carried out as it was described elsewhere [18]. The inlet profile of the plug was modeled using an exponentially modified Gaussian function [19]. The band calculated assuming a two-dimensional

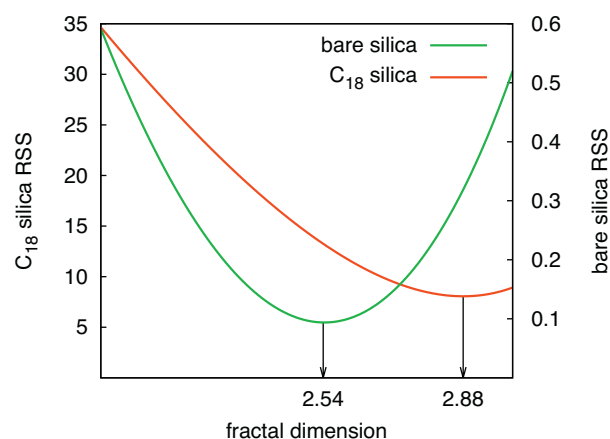


Fig. 6. Comparison of the RSS vs. D curves of aniline and proline on modified C_{18} and bare silica adsorbents, respectively. On the horizontal axis, the location of the minima of both curves are indicated.

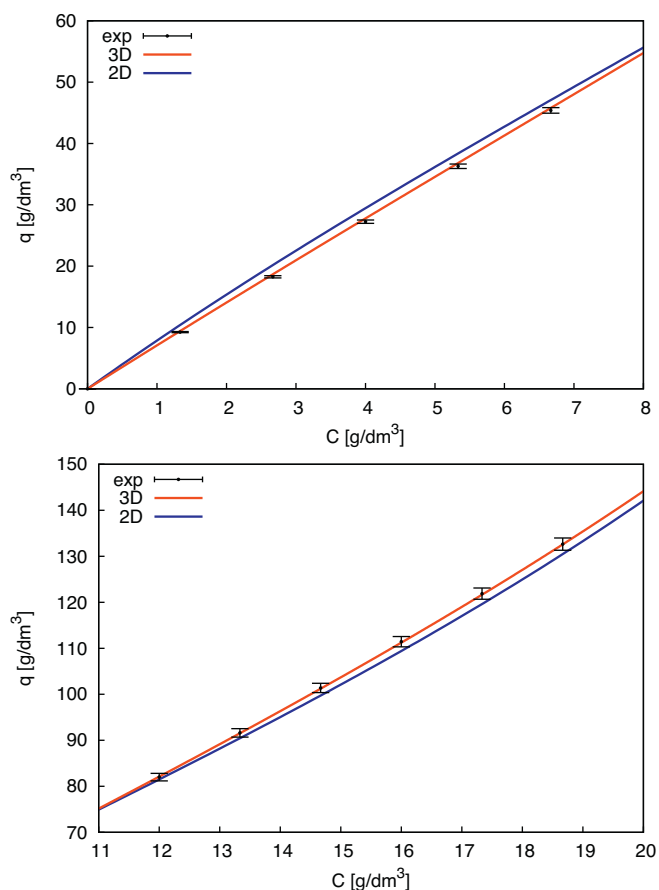


Fig. 7. Comparison of the two isotherm models assuming two-dimensional (2D) and three-dimensional surfaces (3D) with the experimental isotherm data points of aniline on the $\alpha_{C_{18}} = 1.11 \mu\text{mol/m}^2$ column with 1% experimental error displayed on the graph. The two isotherms are compared at lower (upper) and at higher (lower) equilibrium concentration of aniline.

adsorbent surface gives worse agreement with the experimental band. The improvement observed assuming a three-dimensional surface during the numerical simulation is pronounced for the entire concentration range. The overall shape of the calculated band is closer to the experimental one when a three-dimensional adsorbent surface was assumed, and the isotherm equation was chosen accordingly.

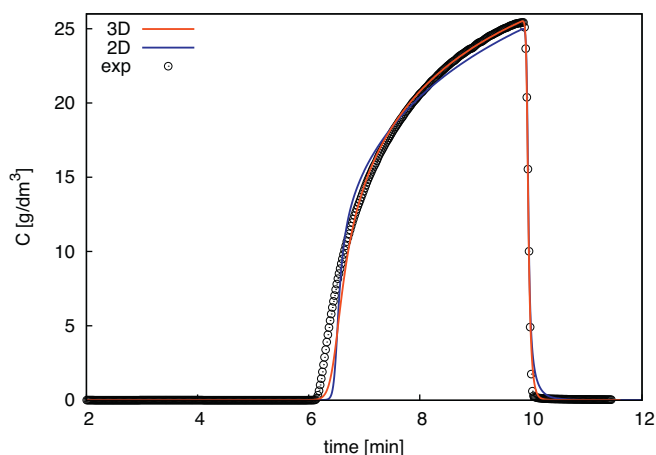


Fig. 8. Comparison of experimental and calculated overloaded elution bands of aniline on the $\alpha_{C_{18}} = 1.11 \mu\text{mol}/\text{m}^2$ column. The graph compares the calculated elution bands assuming three- or two-dimensional surfaces.

5. Conclusions

In this study, we derived an isotherm equation for multilayer adsorption based on the BET theory, taking account the surface geometry, and the disorder that arises from it. By the nonlinear fit of this equation to the adsorption isotherm data points derived from frontal analysis experiments allowed us to determine the crucial adsorption isotherm parameters, and the apparent fractal dimension of the adsorbent surface.

Using the fractal BET isotherm equation, the adsorption behavior of aniline was described, and the geometric characterization of the reversed phase packing materials were done. Our results suggest that the apparent fractal dimension of the octadecyl bonded silica is in the range of 2.9–3.0. The estimated monolayer saturation capacity q_s of the adsorbent grows with the decrease of surface coverage of the octadecyl chains, good correlation with the more pore volume availability for the adsorption. The adsorption equilibrium constant with the adsorbent surface b_s is decreasing with the decrease of the surface coverage, with the lower possible hydrophobic interaction possible on the adsorbent surface. The equilibrium constant of the interaction between the adsorbed layers b_L shows slight increase with the decrease of the surface coverage, what parallel results the more interaction with the residual silanol groups what supports the formation of the multilayer adsorption.

We used proline as test compound in the case of unmodified silica adsorbent. In this case, the fractal dimension was found to be

around 2.5, a significantly lower value than in the case of aniline on modified surface.

We found that the fractal or 3D BET (Eq. (27)) isotherm equation fits better the experimental data than the classical 2D BET equation. The reader should be reminded, however, that with liquid/solid adsorption, one is unable to obtain the real fractal dimension of the adsorbent surface. Fig. 1 illustrates an important detail for liquid/solid adsorption. We may expect that when multilayer adsorption takes place, not only solute, but also solvent molecules are found in the adsorbed layers. Thus the adsorbed layers are progressively thinner in solute molecules even on a flat surface. The nature of surface roughness and solute–solvent interactions lead to similar consequences: fewer molecules are found in the adsorbed layers as we depart from the surface.

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