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Article 14

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Abstract

A generalization of Langmuir adsorption isotherm is proposed. Langmuir model with its main assumptions was developed by assuming that multilayer adsorption can occur. Some particular cases for new equation are discussed and results obtained are verified for experimental data.

I. Introduction

Analysis of gas-solid physical adsorption equilibrium is important to design separation and purification processes as well as heterogeneous chemical reactors. The equilibrium between the fluid phase and the adsorbent phase is expressed by adsorption isotherms. The first classification of physical adsorption isotherms was presented by Brunauer *et al*¹. In 1985 the IUPAC Commission on Colloid and Surface Chemistry proposed modification of this classification by addition to the original five types of Brunauer *et al.* a sixth type, the stepped isotherm². Type I (the Langmuir isotherm) is typical of microporous adsorbents (activated carbons, zeolites). Next two are typical of nonporous materials with strong (type II) and weak (type III) fluid-surface forces. Types IV and V are characteristic for mesoporous materials when capillary condensation occurs (these types exhibit hysteresis loop). Type VI occurs for materials with relatively strong fluid-surface forces, usually when the temperature is near the melting point for the adsorbed gas.

Many theories and models have been presented in the literature to describe these different types of isotherms. Gregg and Sing³ have given a detailed discussion of the various models used to interpret each type of the isotherms.

The derivation of a scientifically based adsorption isotherm was first achieved by Langmuir (1918). The Langmuir isotherm model assumes monolayer adsorption on a homogeneous surface. Originally based on a kinetic basis, the model is thermodynamically consistent as it reduces to Henry's law at low pressures. The model was also derived based on statistical thermodynamics. Although the Langmuir isotherm was introduced more than 80 years ago, it still remains the most commonly used adsorption isotherm equation. Its success undoubtedly reflects its ability to fit a wide variety of adsorption data quite well, but it may also partly reflect the appealing simplicity of the isotherm equation and the ease with which its adjustable parameters can be estimated.

By using more realistic assumptions, many modifications have been made to the Langmuir isotherm, which are well summarized in the monographs of Ruthven⁴, Yang⁵, Adamson⁶, Rudzinski and Everett⁷.

The purpose of this study is to propose some generalization of Langmuir isotherm, which will give the possibility to extend the description for multilayer adsorption.

II. Basic considerations



[Assumptions](#)



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Assumptions


Here we consider Langmuir model with its main assumptions:

- Adsorption takes place only at specific localized sites on the surface and the saturation coverage corresponds to complete occupancy of these sites.
- Each site can accommodate one and only one molecule or atom.
- The surface is energetically homogeneous, and there is no interaction between neighboring adsorbed molecules or atoms.
- There are no phase transitions.

Next, we derive modified Langmuir adsorption isotherm on the following additional assumptions:

- We assume formation of a few adsorption layers, each layer being adsorbed on the preceding one according to Langmuir equation. The adsorbed molecules in one layer can act as adsorption sites for molecules in the next layer. Clearly then, prior to complete surface coverage the formation of second and higher layers will commence. This means that, where the surface is covered with only one layer of adsorbate, an equilibrium exist between that layer and the vapor, and where to layers are adsorbed, the upper one is in equilibrium with the vapor, and so forth. Since the equilibrium is dynamic, the actual location of the surface sites covered by one ore more layers may vary but the number of molecules in each layer remains constant.
- Adsorption energy in the first layer is a constact ($E_1 = constant$) and in the each of the following layers the adsorption energy E_n and is equal to the energy of liquefaction ($E_n = E_L$).
- The effective surface area for a given layer is equal of the surface coverage of the preceding layer.

Derivation of isotherm

The monomolecular adsorption is described by  **Equation 1** :

$$V = S \cdot \Gamma(p) \quad \Gamma(p) = \frac{bp}{b+a_1} \quad b = \frac{V_m}{S} \quad V(p) = V_m \cdot \frac{p}{b+a_1} \quad \text{Equation 1}$$

where S is the surface area, $\Gamma(p)$ is the absolute isotherm (expressed per unit of the surface area), b is the temperature dependent parameter, a_1 is the intensive parameter connected with adsorption energy in the first layer: $a_1 = a_0 \cdot \exp(-E_a/RT)$, and V_m is the monolayer capacity.

The polimolecular adsorption is given as

$$\Gamma(p) = \Gamma_1(p) + \Gamma_2(p) + \dots + \Gamma_n(p) = \sum_{j=1}^n \Gamma_j(p) \quad \text{Equation 2}$$

where $\Gamma_j(p)$ is the amount adsorbed in the j^{th} layer on the unit of the surface area of adsorbent.

For the following layers:

$$\Gamma_1(p) = \frac{b_1 p}{p+a_1} \quad \Gamma_2(p) = \frac{p}{p+a_1} \cdot \frac{b_2 p}{p+a_2} \quad \Gamma_3(p) = \frac{p}{p+a_1} \cdot \frac{p}{p+a_2} \cdot \frac{b_3 p}{p+a_3} \quad \text{Equation 3}$$

where $\frac{p}{p+a_1}$ and $\frac{p}{p+a_1} \cdot \frac{p}{p+a_2}$ are the surface area accessible (surface coverage) for 2nd and 3rd layer, respectively.

The general expression is then

$$\Gamma_j(p) = b_j \prod_{i=1}^j \frac{p}{p+a_i} \quad \Gamma(p) = \sum_{j=1}^n b_j \prod_{i=1}^j \frac{p}{p+a_i} \quad \text{Equation 4}$$

$$\Gamma(p) = \frac{b_1 p}{p+a_1} + \frac{p}{p+a_1} \cdot \frac{b_2 p}{p+a_2} + \frac{p}{p+a_1} \cdot \frac{p}{p+a_2} \cdot \frac{b_3 p}{p+a_3} + \dots + b_n \prod_{i=1}^n \frac{p}{p+a_i} \quad \text{Equation 5}$$

where b_j corresponds to the maximum amount adsorbed in the given layer on the absolute isotherm.

Assuming that $b_1 = b_2 = \dots = b_n = b$ and for $i > 1$: $a_2 = a_3 = \dots = a_n = a_L$

where a_L is the intensive parameter connected with the heat of liquefaction E_L ,



[Equation 5](#) we obtain

$$\begin{aligned} \Gamma(p) &= b \cdot \frac{p}{p+a_1} + b \cdot \frac{p}{p+a_1} \cdot \frac{p}{p+a_1} + b \cdot \frac{p}{p+a_1} \cdot \left(\frac{p}{p+a_1}\right)^2 + \dots + b \cdot \frac{p}{p+a_1} \cdot \left(\frac{p}{p+a_1}\right)^{n-1} = \\ &= b \cdot \frac{p}{p+a_1} \cdot \left[1 + \frac{p}{p+a_1} + \left(\frac{p}{p+a_1}\right)^2 + \dots + \left(\frac{p}{p+a_1}\right)^{n-1} \right] \end{aligned}$$



Equation 6

where

$$\frac{p}{p+a_L} + \left(\frac{p}{p+a_L}\right)^2 + \dots + \left(\frac{p}{p+a_L}\right)^{n-1}$$

is decreasing geometric series in which any term has a form:

$$W_n = \frac{\frac{p}{p+a_L} \left[1 - \left(\frac{p}{p+a_L}\right)^{n-1} \right]}{1 - \frac{p}{p+a_L}}$$



Equation 7

After adding up the terms of this geometric series we obtain

$$\Gamma(p) = \frac{bp}{p+a_1} \left[1 + \frac{\frac{p}{p+a_L} - \left(\frac{p}{p+a_L}\right)^n}{1 - \frac{p}{p+a_L}} \right] = \frac{bp}{p+a_1} \cdot \frac{1 - \left(\frac{p}{p+a_L}\right)^n}{1 - \frac{p}{p+a_L}}$$




Equation 8

[Assumptions](#)

[Final form of modified Langmuir adsorption isotherm](#)

Final form of modified Langmuir adsorption isotherm


From  [Equation 8](#), the final form of the modified Langmuir adsorption isotherm can be obtained

$$V = V_m \cdot \frac{p}{p + a_1} \cdot \frac{1 - \left(\frac{p}{p + a_L} \right)^n}{1 - \frac{p}{p + a_L}}$$

 **Equation 9**

where V_m , a_1 , a_L , and n are adjustable parameters.

III. Discussion of modified Langmuir isotherm

The final form of the modified Langmuir adsorption isotherm ( [Equation 9](#)) under certain circumstances takes the same form as several well-known isotherms. Analysis of these circumstances as the relation between adjustable parameters is given below as **Case 1 - Case 7**.

$$n=1$$

Langmuir isotherm

Case 1

$$a_I = a_L = a \quad (E_a = E_L)$$

$$V = V_m \cdot \frac{p}{p + a}$$



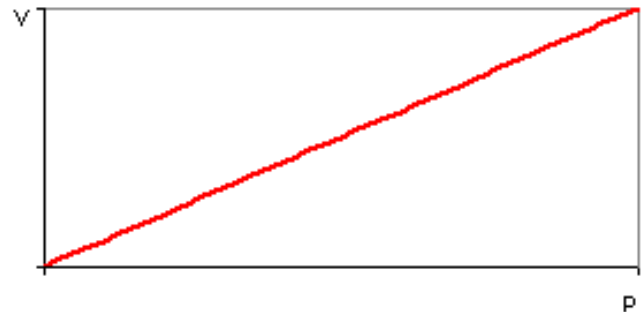
$$n \rightarrow \infty$$

Henry isotherm

Case 2

$$a_I = a_L = a \quad (E_a = E_L)$$

$$V = \frac{V_m}{a} \cdot p$$



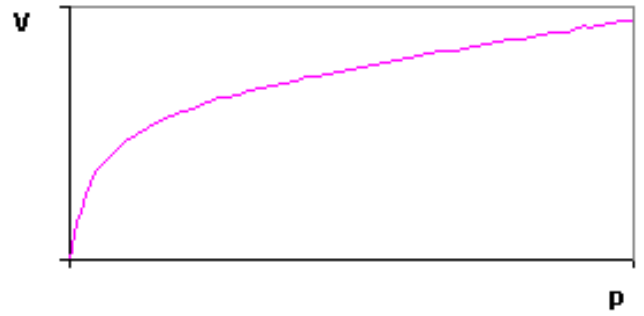
$$n \rightarrow \infty$$

Hüttig isotherm

Case 3

$$a_1 < a_L (E_a > E_L)$$

$$V = \frac{V_m}{a_L} \cdot p \cdot \frac{p + a_L}{p + a_1}$$



$$n \rightarrow \infty$$

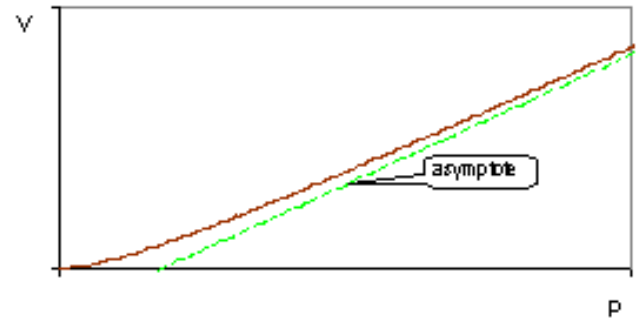
Case 4
III type according IUPAC

$$a_1 > a_L (E_a < E_L)$$

$$V = \frac{V_m}{a_L} \cdot p \cdot \frac{p + a_L}{p + a_1}$$

Asymptote:

$$V = \frac{V_m}{a_L} \cdot p + V_m \cdot \left(1 - \frac{a_1}{a_L}\right)$$



n - finite value

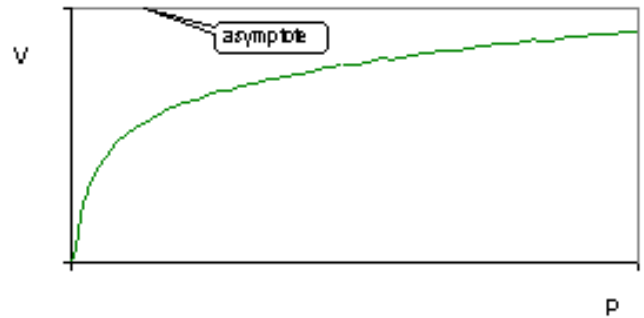
Case 5
BET type of isotherm for 2 layers

$$a_1 < a_L (E_a > E_L)$$

$$V = V_m \cdot \frac{p}{p + a_1} \cdot \left(1 + \frac{p}{p + a_L}\right)$$

Asymptote:

$$p \rightarrow \infty \quad V \rightarrow 2V_m$$



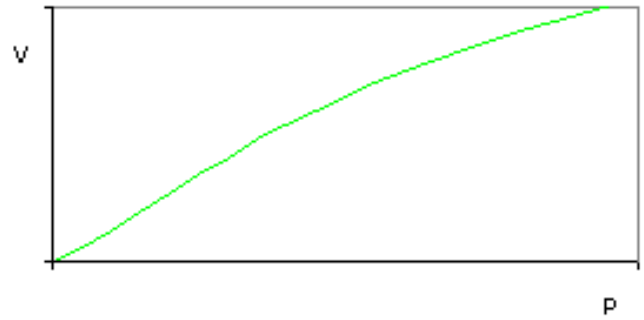
n - finite value

Case 6
"sigmoid" isotherm

For instance: $n=4$

$$a_I > a_L \quad (E_a < E_L)$$

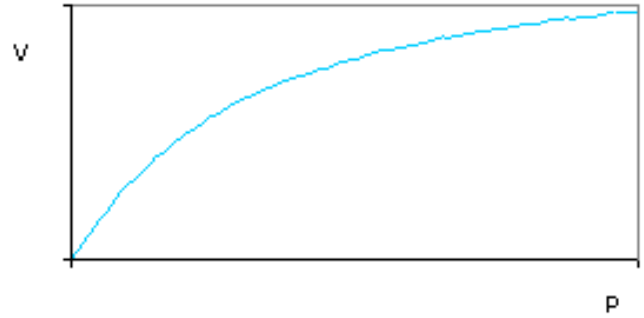
$$V = V_m \cdot \frac{p}{p+a_1} \cdot \frac{1 - \left(\frac{p}{p+a_L}\right)^4}{1 - \frac{p}{p+a_L}}$$



n - finite value

Case 7

$$a_I = a_L = a \quad (E_a = E_L) \quad V = \frac{V_m}{a} \cdot p \cdot \left[1 - \left(\frac{p}{p+a} \right)^n \right]$$



➡ [Final form of modified Langmuir adsorption isotherm](#)

[IV. Verification of modified Langmuir isotherm for experimental data](#) ➡

IV. Verification of modified Langmuir isotherm for experimental data

We consider three examples to compare the proposed equation with experiment. In each case the fitting of the experimental data was carried out by a non-linear least square optimization procedure.



[Adsorption of argon on non-porous silica](#)



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[Dispersion of Fitting Error for Langmuir Generalized Isotherm](#)



[Best-fit Parameters and Properties of System Active Carbon - Methane Calculated from Langmuir Generalized Equation](#)

Adsorption of argon on non-porous silica

Argon adsorption data at 87K on the reference silica (*Lichrospher Si-1000*) reported in [10](#) were used for



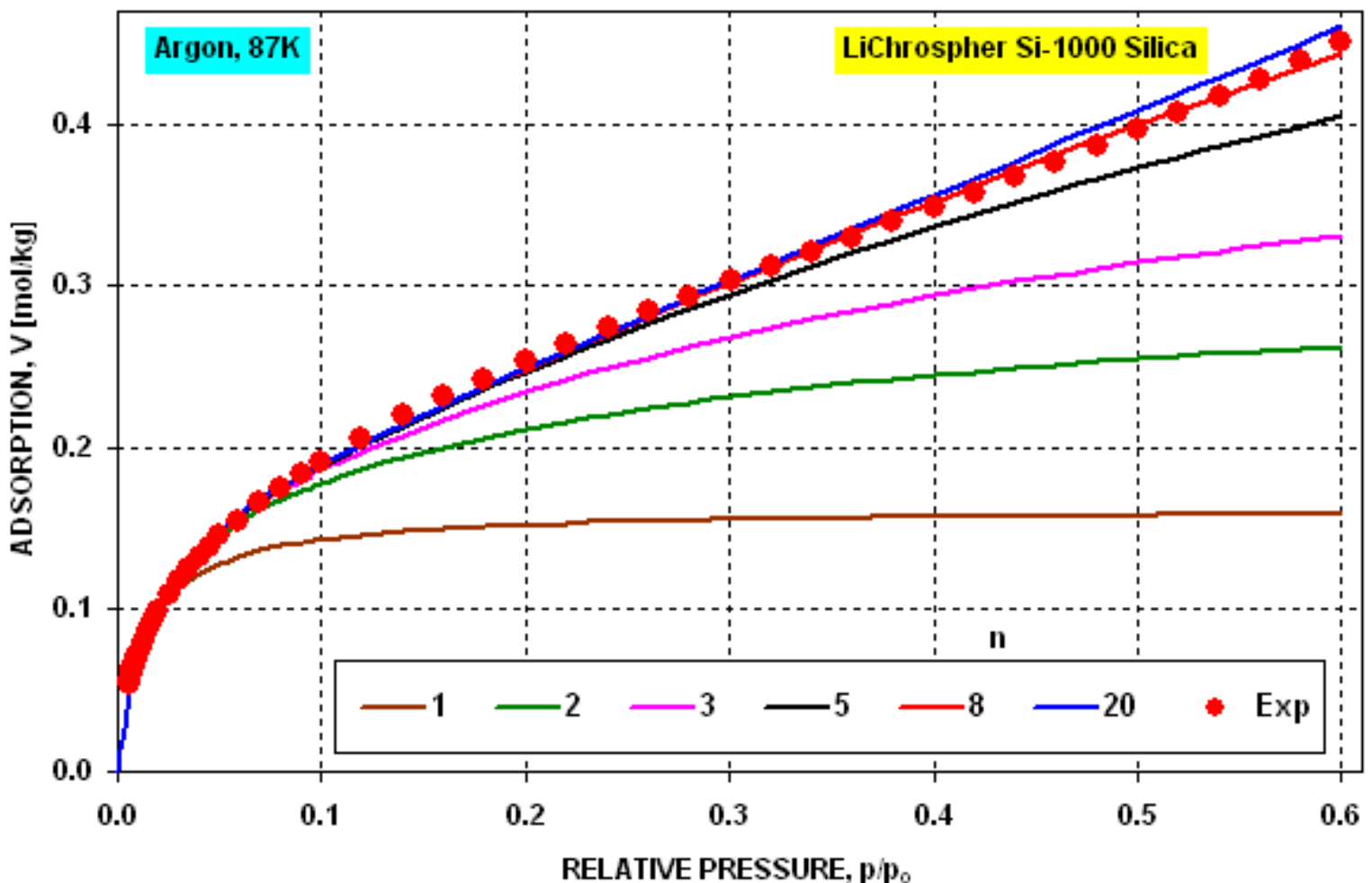
analysis of the  [Equation 9](#).  [Figure 1](#) illustrates the behavior of the equation proposed for various values of n . In the relative pressure range 0.005 - 0.6 the best fit was obtained for $n = 8$. The surface area of silica calculated for this relative pressure range from 42 experimental points was $18.2 \text{ m}^2/\text{g}$. It is in good agreement with value obtained in the previous work, [10](#) $19.3 \text{ m}^2/\text{g}$ in the relative pressure interval 0.04 - 0.2 from 13 experimental points. It can be assumed that the equation proposed is a useful tool for estimation the surface area of adsorbents. It is recommended that about 20 data points should be taken for careful surface area work.



Figure 1 Behaviour of the Proposed Isotherm Equation

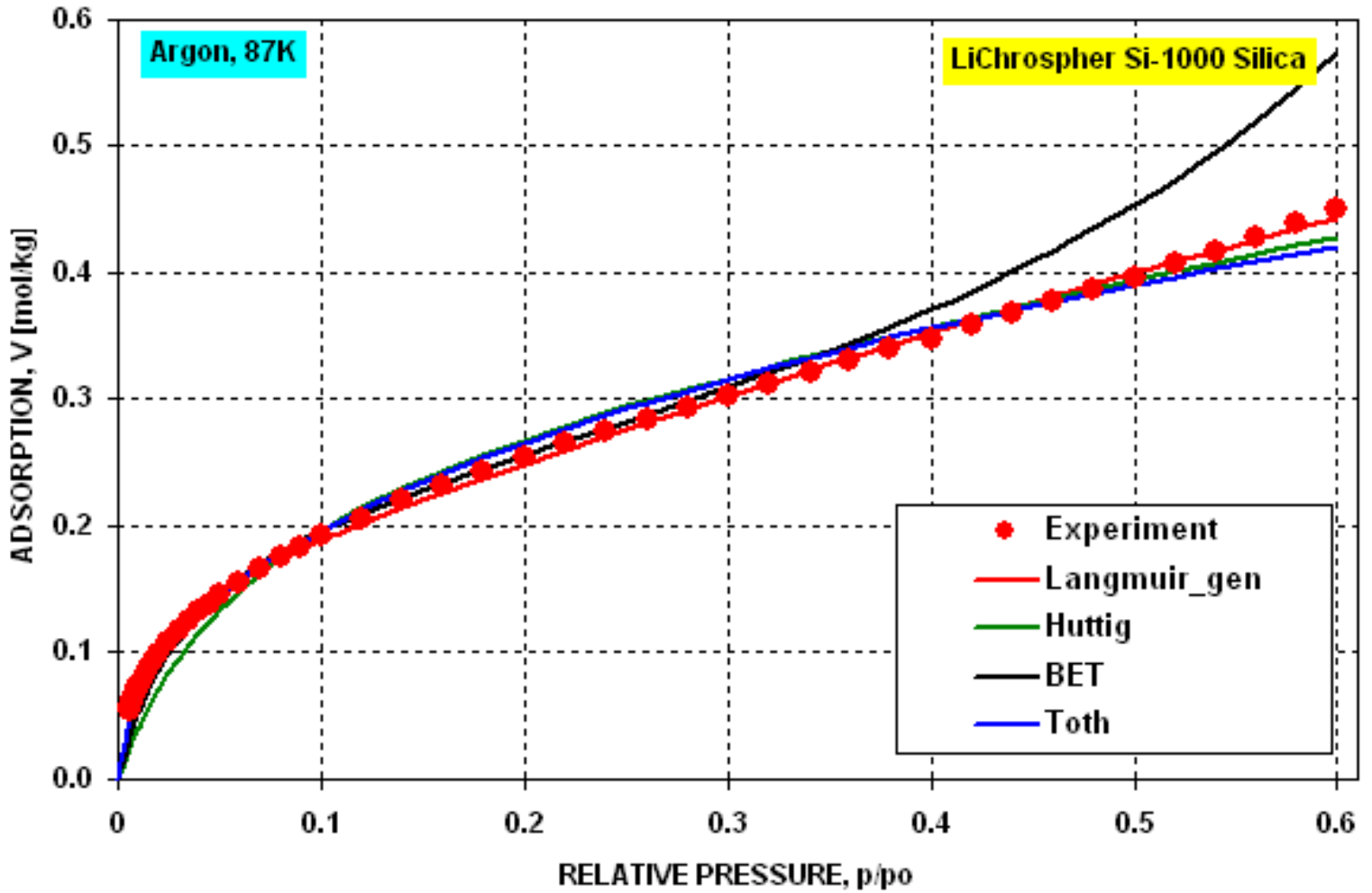




[Figure 2](#) shows the comparison of above data fitting using [Equation 9](#) and the other adsorption models (Hüttig, BET, and Toth). It was found that the modified Langmuir isotherm in the pressure range under investigation is sufficiently flexible to give a good representation of data.




Figure 2 Comparison of the Behaviour of the Various Isotherm Equations





[IV. Verification of modified Langmuir isotherm for experimental data](#)

[Estimation of surface area for carbonaceous adsorbents](#)

Estimation of surface area for carbonaceous adsorbents

While the validity of the surface area determination for microporous solids has been questioned,² it can be used as a parameter for comparison of different samples. We applied  [Equation 9](#) for estimation of surface area of two types of carbonaceous adsorbents (active carbon and activated carbon cloth).

Experimental data of nitrogen adsorption at 77K are presented in  [Figure 3](#). In  [Table 1](#) the


values calculated from  [Equation 9](#) and BET theory are reported. It can be seen that for a much wider relative pressure interval, reliable values are obtained.



Figure 3 Adsorption Data of Nitrogen (77K) on Active Carbon and Active Carbon Cloth

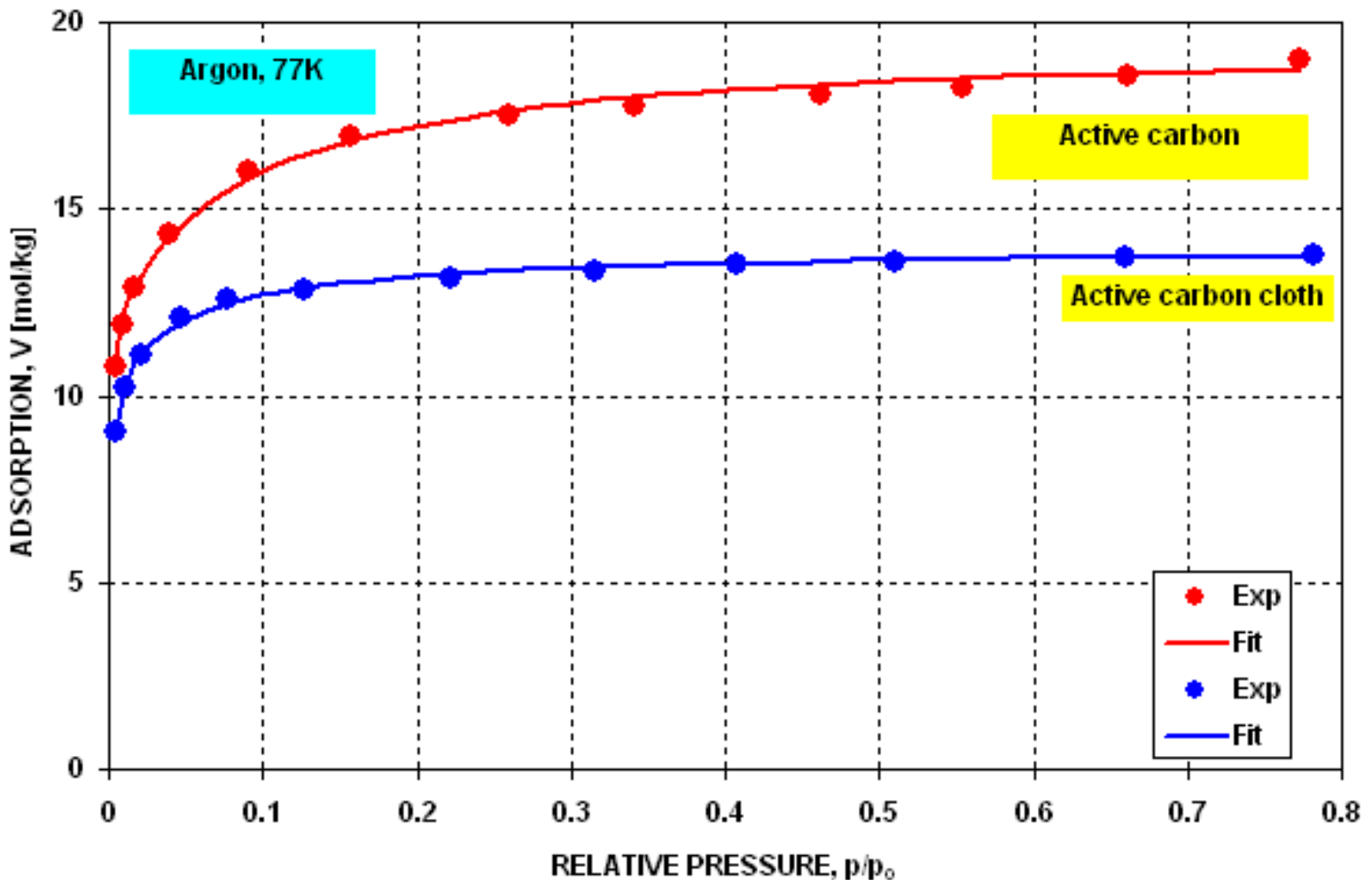




Table 1 Values of Surface Area Calculated from BET and Langmuir Generalized Equations

S [m ² /g]	Range of p/p _o	Active carbon	Active carbon cloth
BET	0.05 - 0.35	1130 ± 5%	970 ± 5%
Langmuir generalized	0.005 - 0.60	1210 ± 5%	1035 ± 5%


[➡ Adsorption of argon on non-porous silica](#)

[Supercritical adsorption of methane on active carbon ➡](#)



Supercritical adsorption of methane on active carbon

The applicability of the proposed adsorption isotherm equation was tested for high - pressure adsorption isotherms of methane on active carbon *Norit R2*, measured in our laboratory. ⁸ It was found that the isotherms for this system could not be described by classical Langmuir equation in the entire pressure and temperature ranges of the experimental data. Similar likes in Sircar's work ⁹ linearized Langmuir plots exhibit considerable

departure from linearity. It is caused by heterogeneity of the carbon surface.  **Figure 4** shows the results of fitting using Langmuir isotherm equation. The circles and the solid lines represent the experimental points and the model calculations, respectively. The goodness-of-fitting was also determined by consideration the


dispersion of residuals in fitting experimental data.  **Figure 5** depicts the dispersion of errors for experimental points.



Figure 4 Best-fit Curves for Langmuir Isotherm

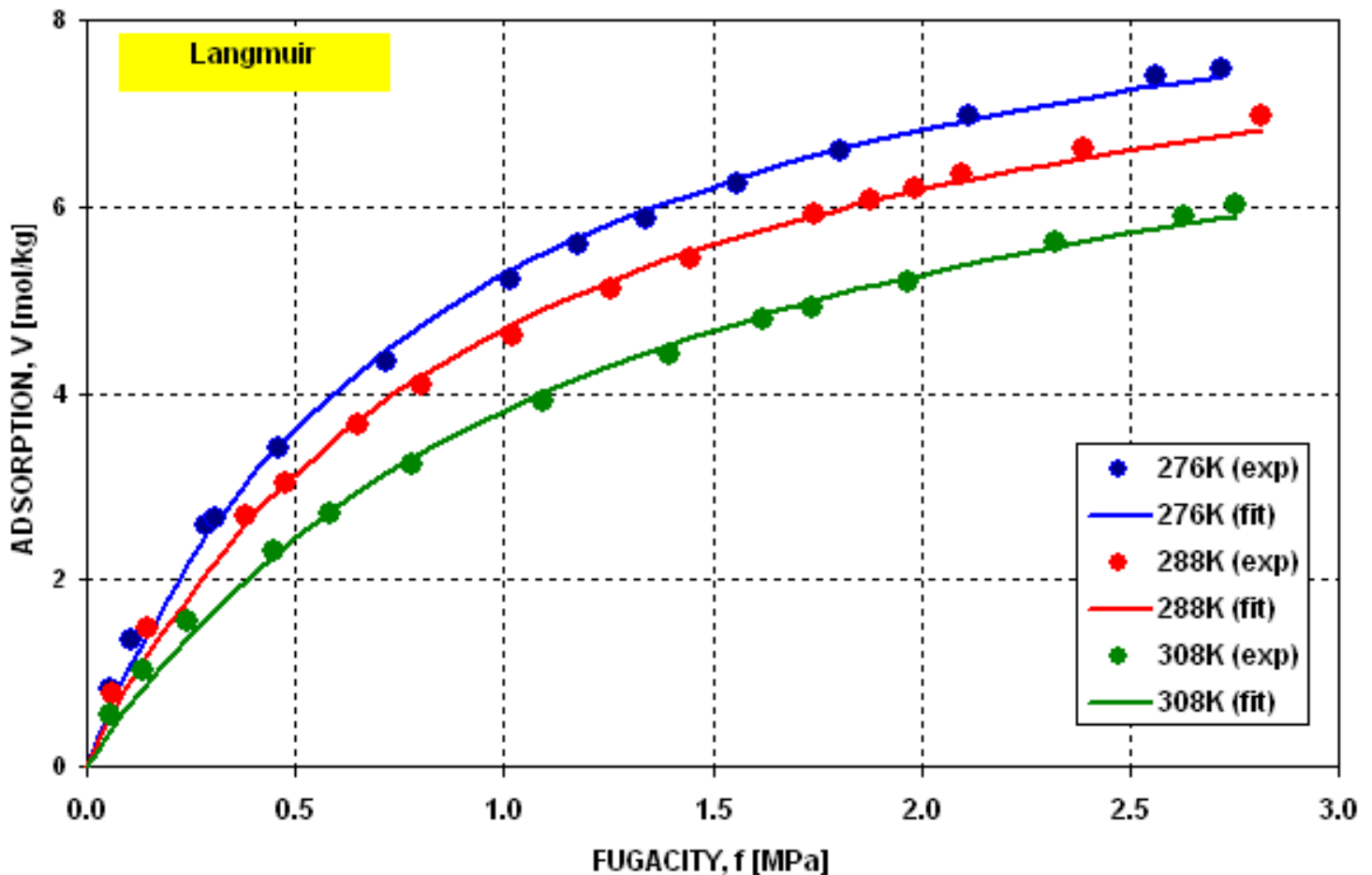
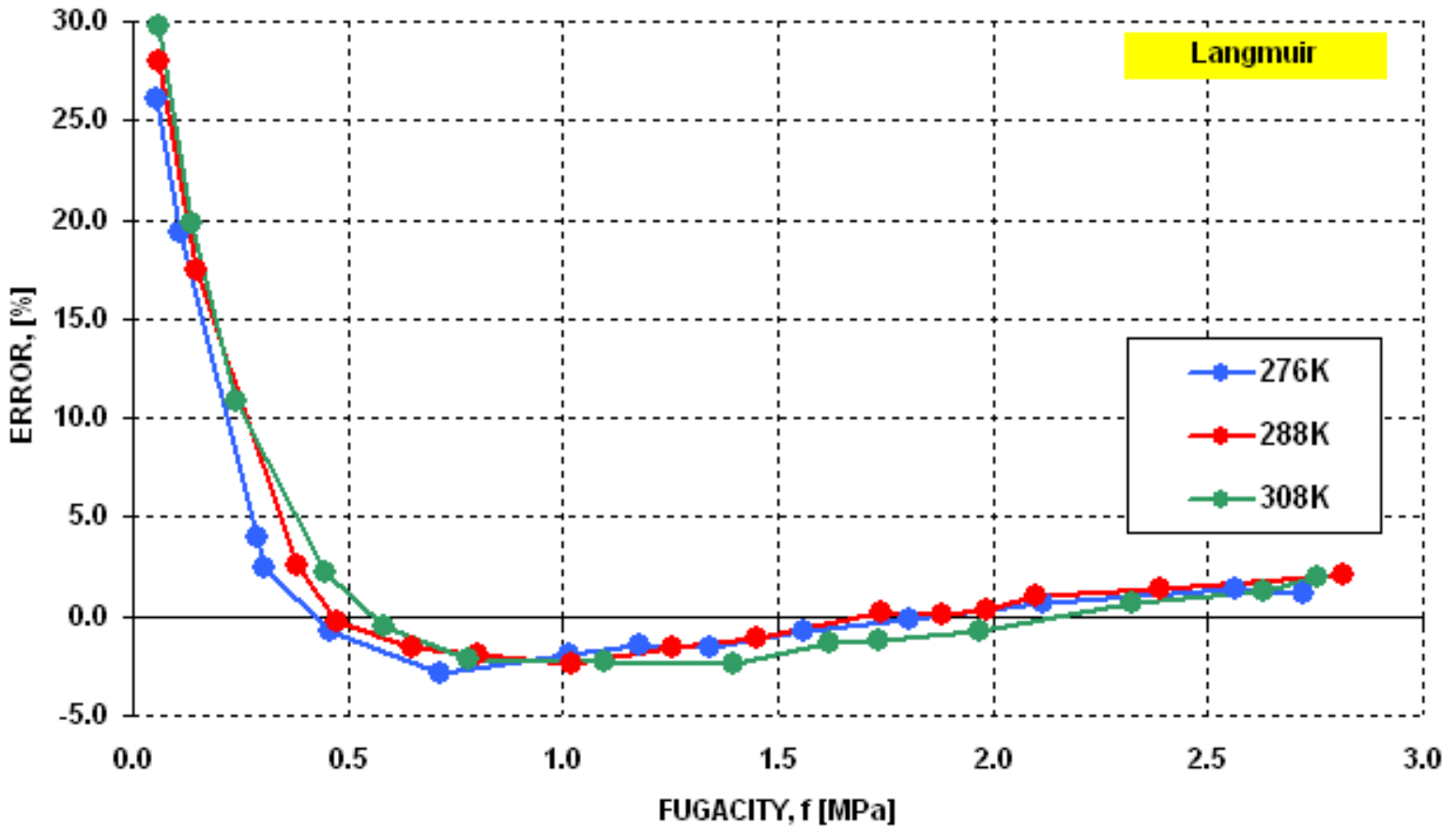




Figure 5 Dispersion of Fitting Error for Langmuir Isotherm



The modified Langmuir equation was then evaluated to determine how well it represents the gas - solid



equilibria. The results are presented in  [Figure 6](#) and  [Figure 7](#) . It may be seen that in the last case the dispersion of error is statistically random and the error does not exceed the limit of 1.5%.



Figure 6 Best-fit Curves for Langmuir Generalized Isotherm

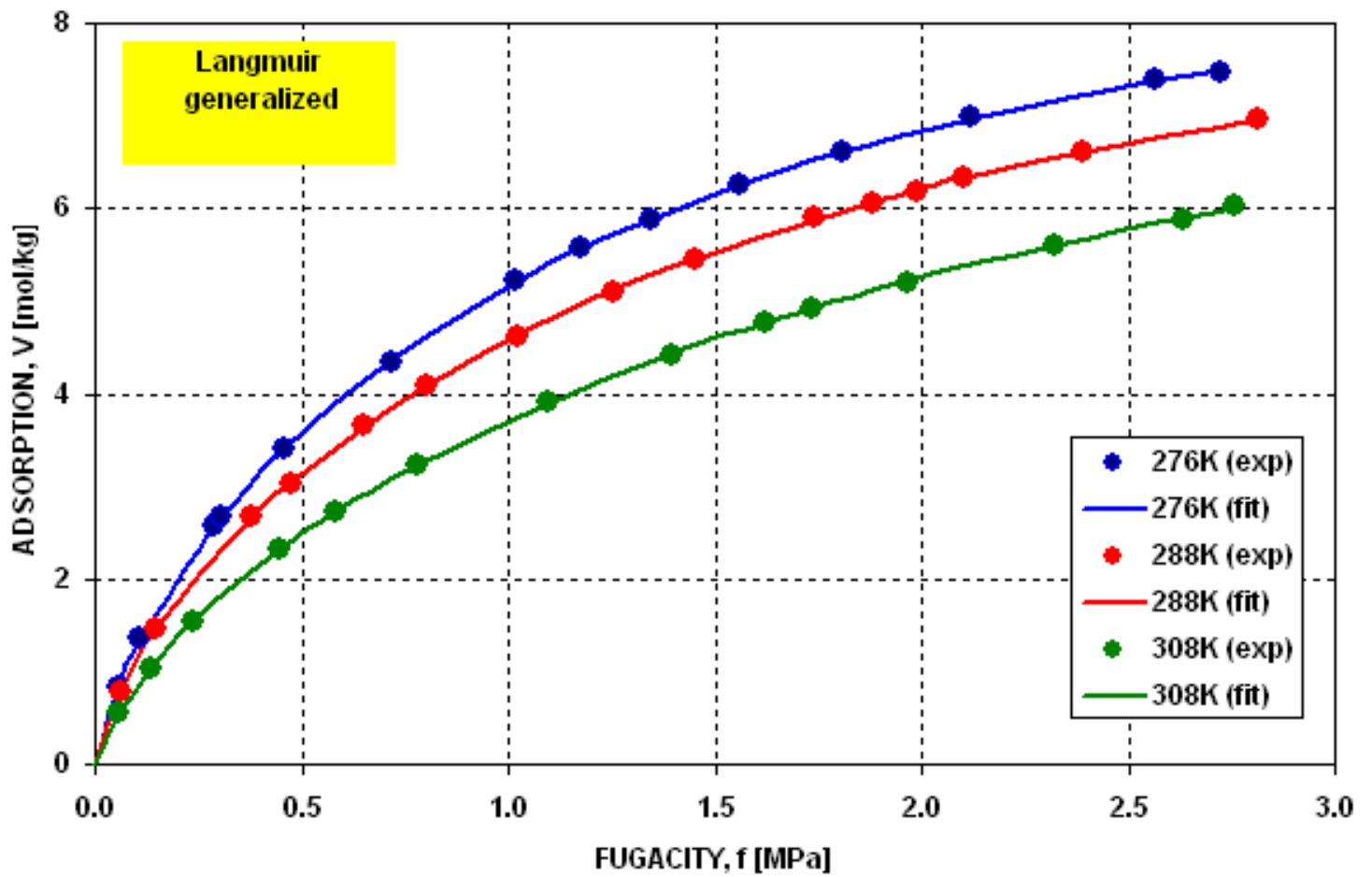
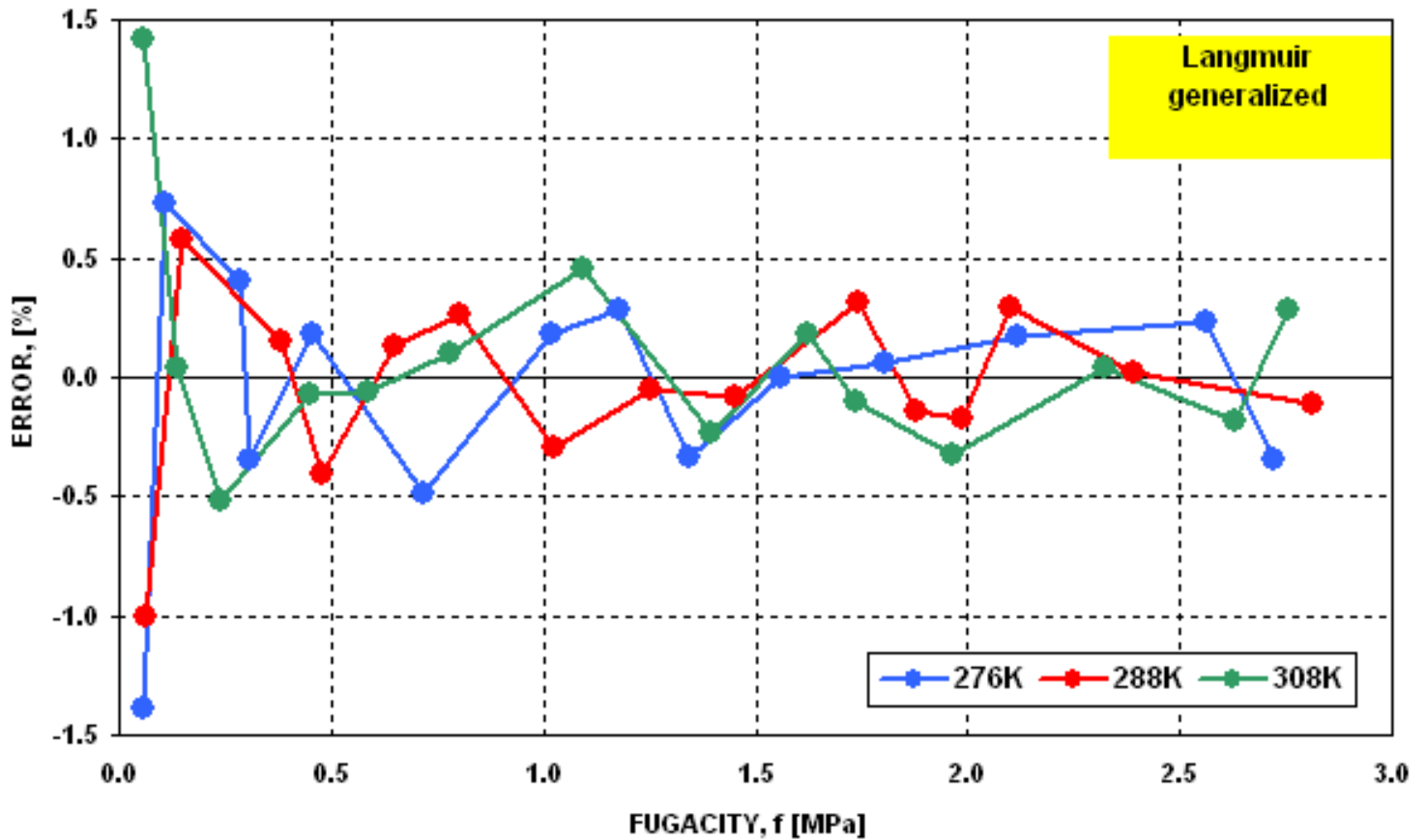





Figure 7 Dispersion of Fitting Error for Langmuir Generalized Isotherm



 **Table 2** summarizes the best-fit parameters for systems under investigation. Henry's-law constants at different temperatures ($K_H = V_m/a$) and isosteric heat of adsorption at zero coverage calculated from the

Henry's-law constants ($K_H = K_0 \cdot \exp(q^0/RT)$) are also listed in  **Table 2**

 **Table 2** Best-fit Parameters and Properties of System Active Carbon - Methane Calculated from Langmuir Generalized Equation

Best-fit parameters	T = 276K	T = 288K	T = 308K
V_m , [mol/kg]	2.459	2.430	2.381
$a_1 \cdot 10^{-5}$	1.25	1.46	2.15
$a_L \cdot 10^{-5}$	5.55	6.95	9.89
n	4.2	4.1	4.1
Standard error of fit	0.0166	0.0120	0.0116
Henry's-law constant, $K_H \cdot 10^5$ [mol/(kg Pa)]	1.97	1.66	1.11
Henry's-law constant at $T \rightarrow \infty$, $K_0 \cdot 10^8$ [mol/(kg Pa)]	6.53		

The results presented show that the equation proposed can describe the isotherm data quantitatively. The parameter V_m varies slightly with temperature, which is consistent with the Langmuir model. The value of isosteric heat of adsorption at zero coverage is higher than the heat of condensation and is enough to be characterized as physical adsorption.

[← Estimation of surface area for carbonaceous adsorbents](#)

[V. Conclusions →](#)

V. Conclusions

It may be concluded from the above observations that adsorption data are well analyzed by using the modified Langmuir adsorption isotherm. The parameters of the equation have the physical meaning and are found to be related to the Henry's law constant. Because of model proposed obeys Henry's law in the low-pressure region, it can be considered to be thermodynamic in nature regardless of the origin of the derivation. On the other hand it can be treated as a semi-empirical model with a good ability to fit isotherm data. The model can be applied to:

- the modeling and design of adsorption processes (separation of gaseous mixtures, storage of gases),
- the calculation of thermodynamic properties of adsorption system,
- the estimation of surface area of solids,
- developing analytical equations for characterization of adsorbents heterogeneity,
- the prediction of mixture equilibria.

Acknowledgments

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