Analysis of methane adsorption isotherms on active carbons

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An analytic equation to describe gas adsorption on energetically heterogeneous adsorbent is given. An approach proposed assumes that the overall isotherm could be presented as a sum of local isotherms with appropriate statistic weights. The parameters of equation are related to the Henry's-law constant. Adsorption of methane for various active carbons was successfully described by this equation.

Studies on the physical adsorption of methane on different types of adsorbents are stimulated both by theoretical and practical interest. For example, an analytical representation of adsorption equilibrium data is needed in natural gas storage and PSA separation/purification processes. Modelling methane isotherms provides a useful tool for studying adsorption mechanism, characterisation of porous solids and collecting useful information of adsorption systems.

Over the past century, many theories and models have been proposed to describe the physisorption of gases by different adsorbents. Gregg and Sing have given a detailed discussion of the various models used to interpret each type of the isotherms [1]. Many of these isotherm models are empirical in nature but some have been shown to have a thermodynamic basis. Generally, each isotherm model, which obeys Henry's law in the low-pressure region, is considered to be thermodynamic in nature regardless of the origin of the derivation. A second less widely applied criteria for thermodynamic

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consistency is that the amount adsorbed, equals the saturation limit, only at infinite pressure. Semi-empirical models are defined as those, which are derived from thermodynamic models but include the terms, which produce a model, which no longer meets the test for thermodynamic consistency. Empirical models are defined as those mathematical forms, which were derived only on the basis of their ability to fit equilibrium data.

The derivation of a scientifically based adsorption isotherm was first achieved by Langmuir at the beginning of the 20th century. Within the Langmuir viewpoint adsorption takes place at a fixed number of surface sites. As detailed elsewhere 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 summarised in monographs, for instance of Ruthven [2], Yang [3], Adamson [4], Rudziński and Everett [5].

Typically, for the analysis of experimental data the Langmuir equation is expressed in the linear form. Thus, if equation applies and values of p/a are plotted against p values, a straight line should result. It was shown that the Langmuir plot may have not a constant slope for the complete range of pressures, but may be subdivided into linear subsegments. This behaviour was attributed to surface heterogeneity. For instance, Sircar [6] describes the isotherm by two straight lines representing low-pressure and high-pressure regions.

In fact, to overcome these discrepancies between experimental and theoretical data, Langmuir proposed to represent overall isotherm as a sum of Langmuir-like terms with appropriate statistical weights. Unfortunately, in the next 20 years this paper was completely forgotten [1].

In this study we propose to return to this approach and we assume that the overall isotherm could be presented as a sum of local isotherms

$$a = a_m \cdot \sum_i f_i \cdot \frac{b_i p}{1 + b_i p}$$

where a_m is the saturation or monolayer capacity, b_i is an energetical constant and f_i is statistical weight of local isotherm.

It can be easily shown that in the limit zero pressure, the adsorption isotherm proposed obeys Henry's law ($K_H = a_m \cdot \sum_i f_i b_i$), as well as tends to a_m at the limit of $p \to \infty$.

The applicability of the approach proposed was tested for high-pressure adsorption isotherms of methane on active carbons, measured in our laboratory [7]. Figure 1 shows the linearised Langmuir plot.
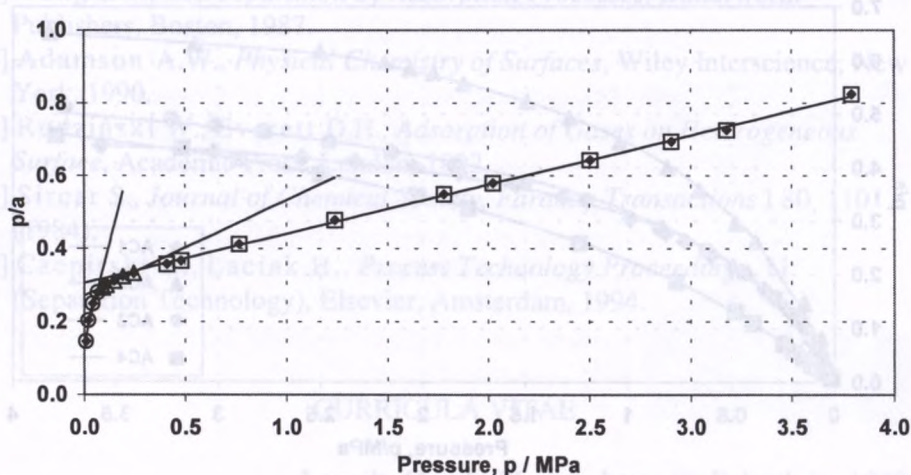

Fig. 1. Linearised Langmuir plot for system methane – active carbon

It can be seen that the data can be described by no more than 3 linear regions with different adsorption energy. According to this observation we limited ourselves to 3 terms of the equation proposed and its parameters were estimated with regression procedure.

Table below summarises the best-fit parameters for the three regions as well as values of Henry's-law constants.

Tab. 1. The best-fit parameters

Sample	AC1		AC2		AC3		AC4	
a_m (mmol/g)	5.459		8.467		6.780		6.231	
i	f_i	b_i	f_i	b_i	f_i	b_i	f_i	b_i
1	0.678	1.808	0.600	1.719	0.689	1.500	0.560	0.780
2	0.164	1.010	0.369	0.650	0.166	0.270	0.250	0.500
3	0.157	0.480	0.030	0.163	0.145	0.234	0.190	0.430
$K_H \cdot 10^6$ (mol/(kg Pa)	8.01		10.81		7.54		4.01	

Figure 2 describes the fit of the isotherms for methane by the equation proposed. The symbols and the solid lines represent the experimental points and the model calculations, respectively. The goodness-of-fitting was determined by considering the dispersion of residuals in fitting experimental data. It was found that the dispersion of error is statistically random and its value does not exceed the limit of 1.5%.
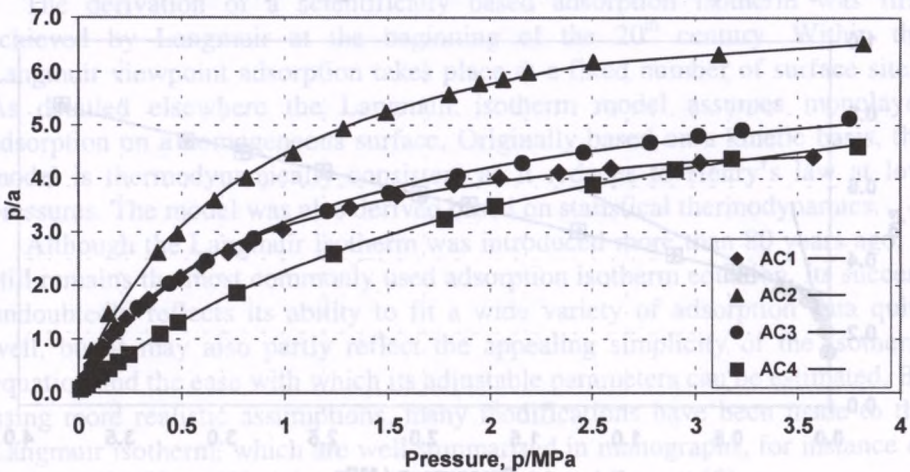

Fig. 2. Adsorption isotherms of methane on active carbons

It may be concluded from the above observations that adsorption data are well described by using the modified Langmuir approach. The parameters of the equation have the physical meaning and are found to be related to the Henry's law constant. Because the model proposed obeys Henry's law in the low-pressure region, it can be considered to be thermodynamic. 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 calculation of thermodynamic properties of adsorption system,
- the estimation of surface area of solids,
- developing analytical equations for characterisation of adsorbents heterogeneity,
- the prediction of mixture equilibria,
- the modelling and design of adsorptive separation processes and storage of gases.

A number of problems still remain to be explored and we do hope to discuss some of them in our next work.

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Leszek Czepirski was born in Poland in 1949. In 1972 graduated (M.Sc. in Chemistry) from the Faculty of Mathematics, Physics and Chemistry of the Jagiellonian University in Cracow. In 1979 received Ph.D degree in Technical University in Wroclaw. D.Sc. degree (Hab.) he received in 1990 in Maria Curie-Sklodowska University in Lublin. Starting from 1972 he has been working in University of Mining and Metallurgy (from 1994 until now as Associate Professor). In 1990-93 and 1996-99 he was Deputy Dean for Education in your Faculty. Since 1993 he has been Head of Department of Physicochemistry of Interfacial Phenomena.

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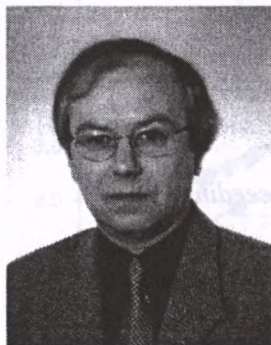
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