

RESTRAINS IN GAB EQUATION FOR DETERMINING ABSORBENT STRUCTURE

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Abstract. The target of this publication is to present the restrains in the GAB model as a result of mathematical approach to the absorption process. In this study some difficulties in determining the structural characteristics of porous products with the use of the GAB model are presented. The problem to be solved can be used for cognitive and for application purposes as well.

Keywords: hygroscopic products, parameters of structure, mathematical approach to the sorption process

INTRODUCTION

Structure and chemical composition play an important role in various physical and chemical surface processes which affect surface behavior under miscellaneous conditions.

The surface of solids is heterogeneous, which is caused by its roughness. Moreover, its heterogeneity is affected by chemical composition which influences the adsorption processes [4,7,9,10,11].

In the quantitative approach, the surface structure as well as the chemical composition may be determined using the various methods for surface testing. For this purpose, a method consisting in atomic excitation (molecules) within the superficial layers of the solid by the use of electrons, ions, molecules, photons, electric-and magnetic field etc. is advisable.

The monitoring and analysis of substance atom response (molecules), makes it possible to determine the surface characteristics [4,15].

In spite of the fact that the adsorption-based methods are improved all the time and may be even characterized by high resolution [4,9,10,17], the determination of the surface structure through the gas adsorption method assures a very general view of surface structure.

The measurements of water vapour sorption, their graphic and model approach, may be used for:

- designing the conditions under which food can be stored,
- determining the food shelf life,
- determining the functional characteristics for dehydrated food [16].

However, when determining the structure of porous solids through the sorption methods, the characteristics of such solids, due to the absorbent selectiveness in relation to the substances undergoing adsorption [10,20], must be taken into consideration.

In the case of research of the structure of porous solids which are characterized by hygroscopic properties, using the method of water vapour adsorption is essential for testing the functional solids properties which derive from their hygroscopicity.

No mathematical equation for common use which could be plotted as a sorption curve for any product within the entire range of water activity has been developed hitherto. The sorption results do not form mostly lines with typical shapes which could be easily quantified in the form of mathematical equation. Therefore, the target to be achieved is to determine an equation which is the best possible solution and to map the point pattern obtained experimentally.

Bearing in mind the current knowledge about sorption, the determining of coefficients of chemical equilibrium equations cannot be based on the adsorbate and adsorbent properties data only. The coefficients of chemical equilibrium equations are determined by matching them with the data obtained experimentally (the sorption isotherm equations which are mostly described by the professional literature). It is obvious that most sorption isotherm equations allow us to fit the empirical data better if compared with data obtained by the use of the GAB model. Nevertheless, the parameters of the said equations are deemed to be characteristic constants only and thus having no physical dimension and, consequently, make it impossible for us to make a thermodynamic analysis of the sorption. The GAB model transforms empirical data and subsequently makes it possible to make calculations so that both adsorbent structure and changes in energy state of adsorbent-adsorbate during the sorption process can be determined.

MATERIAL

One of the models which are widely applicable for the mapping of sorption isotherms in the range of multilayer adsorption is the GAB model [4]:

$$\frac{v}{v_m} = \frac{c_e k a_w}{(1 - k a_w)(1 - k a_w + c_e k a_w)} \quad (1)$$

where: a_w – water activity, v – adsorbed gas volume, v_m – maximum adsorbed gas volume at total surface coverage, k – parameter, c_e – energy constant which is the difference between the heat of adsorption in the 1st layer $\Delta h_{a,1}$, and the heat of condensation Δh_k quantifiable as the following relationship $c_e = e^{-(\Delta h_{a,1} - \Delta h_k) / kT}$ on the assumption that an entropic agent, which is situated before the exponential function, equals 1.

The GAB model includes the modified adsorbent properties in the range of multilayer adsorption. In addition, it reflects the run of water sorption isothermal lines for foods within the range of α_w from 0 to 0.90. It may be applied for determining the monomolecular layer volume as well as energetic processes which occur during sorption. Also, extrapolation to other temperatures from the results obtained is possible. The transformation of GAB is characterized by a wider application range (compared with that of the BET model) if the mapping degree of empirical data is satisfactory [8,18,19].

METHODS

The equation of GAB (1) is transformed into trinomial square $y = ax^2 + bx + c$. The (a , b , c) parameters of this equation are expressed by the relationships between the parameters c_e, k, a_w of the basic equation (1). The change in form is made using the identity transformations. The application of the identity transformation of the basic form of the GAB equation into the form of trinomial square made it possible to maintain the relationship between the parameters c_e, k, a_w , which are set in the initial form of the equation.

RESULTS AND DISCUSSION

Dividing equation (1) on both sides by $c_e k a_w$, we obtain the following:

$$\frac{v_m \cdot c_e \cdot k \cdot a_w}{v} = (1 - k \cdot a_w)(1 - k \cdot a_w + c_e \cdot k \cdot a_w) \quad (2)$$

and dividing equation (2) by $v_m c_e k$ we obtain:

$$\frac{a_w}{v} = \frac{k \cdot a_w^2 (1 - c_e) + a_w (c_e - 2)}{v_m \cdot c_e} + \frac{1}{v_m \cdot c_e \cdot k} \quad (3)$$

in which:

$$\frac{k(1 - c_e)}{v_m c_e} = a \quad (4)$$

$$\frac{c_e - 2}{v_m \cdot c_e} = b \quad (5)$$

$$\frac{1}{v_m \cdot c_e \cdot k} = c \quad (6)$$

When determining the parameter k out of the equations (4) and (6), the following mutual comparisons should be made:

$$\frac{av_m \cdot c_e}{1 - c_e} = \frac{1}{c \cdot v_m \cdot c_e} \quad (7)$$

Out of equation (5) we determine $v_m c_e$:

$$v_m \cdot c_e = \frac{c_e - 2}{b} \quad (8)$$

And out of (7) we determine the following:

$$c \cdot a(v_m \cdot c_e)^2 = 1 - c_e \quad (9)$$

And by putting $v_m c_e$, determined on the basis of equation (8), in the equation (9) we obtain the following:

$$c \cdot a\left(\frac{c_e - 2}{b}\right)^2 = 1 - c_e \quad (10)$$

The parameters a , b , and c are numerical values which are determined using the method of the least squares on the basis of empirical data and, on the assumption that the criterion of choosing parameters for the adsorption equilibrium equations is to achieve a minimum value by the following:

$$S(k) = \sum_{i=1}^N [Y_i - \hat{Y}_i(x_i, k)]^2$$

where $k = [k_1, k_2, \dots, k_L]^T$ = vector of parameters, $x = [x_1, x_2, \dots, x_M]$ = vector of independent variables, Y = adsorption data a^* obtained experimentally or pressure p or adsorptive volume: W , determined from the adsorption equilibrium equation, M – number of independent variables, N – number of experiment stands, L – number of parameters in the adsorption equilibrium equation.

From the equation (10) the parameter c_e (energetic constant) is determined. For this purpose (10) is subjected to the following identity transformations:

$$c \cdot a(c_e - 2)^2 = (1 - c_e) \cdot b^2 \quad (11)$$

$$c \cdot a(c_e^2 - 4 \cdot c_e + 4) = b^2 - b^2 \cdot c_e \quad (12)$$

$$c_e^2 - 4 \cdot c_e + 4 = \frac{b^2}{c \cdot a} - \frac{b^2 \cdot c_e}{c \cdot a} \quad (13)$$

$$c_e^2 - 4 \cdot c_e + \frac{b^2 \cdot c_e}{c \cdot a} + 4 - \frac{b^2}{c \cdot a} = 0 \quad (14)$$

$$c_e^2 + c_e \left(\frac{b^2}{c \cdot a} - 4 \right) + 4 - \frac{b^2}{c \cdot a} = 0 \quad (15)$$

As a result of which we can come to the conclusion that a discriminant of trinomial in the form of (15) is:

$$\Delta = \left(\frac{b^2}{c \cdot a} - 4 \right)^2 - 4 \cdot \left(4 - \frac{b^2}{c \cdot a} \right) \quad (16)$$

$$x_1 = \frac{-\left(\frac{b^2}{c \cdot a} - 4 \right) - \sqrt{\left(\frac{b^2}{c \cdot a} - 4 \right)^2 - 4 \cdot \left(4 - \frac{b^2}{c \cdot a} \right)}}{2} \quad (17)$$

or

$$x_2 = \frac{-\left(\frac{b^2}{c \cdot a} - 4 \right) + \sqrt{\left(\frac{b^2}{c \cdot a} - 4 \right)^2 - 4 \cdot \left(4 - \frac{b^2}{c \cdot a} \right)}}{2} \quad (18)$$

and a square root of (17) or (18) of the equation of (15) equals the energetic constant c_e .

If two solutions are possible, than the physical nature of the effect determines the right one. It is physically impossible for c_e to be negative, so only x_2 may be considered as the right solution. Moreover:

$$\sqrt{\left(\frac{b^2}{c \cdot a} - 4 \right)^2 - 4 \cdot \left(4 - \frac{b^2}{c \cdot a} \right)} > \left(\frac{b^2}{c \cdot a} - 4 \right)$$

and it results in a simple criterion that $\frac{b^2}{c \cdot a} > 4$. If this condition is not fulfilled, the

description of isotherm with the use of GAB equation is not possible.

The remaining physical quantities are to be determined assuming that the volume of the monomolecular layer is as follows:

$$v_m = \frac{c_e - 2}{b \cdot c_e} \quad (19)$$

and the k parameter equals:

$$k = \frac{1}{a \cdot v_m \cdot c_e} \quad (20)$$

In the empirical world there is surely nothing that could be beyond the possibility of being plotted by mathematical relationships. There are obviously some phenomena whose mathematical description is too complicated for us to be able to make analyses or calculations for practical reasons. However, all physical phenomena could be described using the mathematical formalism, e.g. differential equations, taking into account the initial and boundary conditions, or up-to-date formalism, in which there are representations between multidimensional or infinite dimensional nonlinear differentiable manifolds.

In spite of the fact that the GAB transformation is a physical improvement of description of the sorption phenomenon, it is characterized by some constrains, resulting from its mathematical nature. A reduction form of the GAB equation is a trinomial square function.

There may be such experimentally obtained data sets for which a discriminant of the trinomial square (16) is of a negative value, which is an evidence for a specific location of a parabola (no zero points). Consequently, it is not possible to determine univocally the root (17) or (18) of such an equation like that, which is a basis for the calculation of the remaining parameters of the structure. The only solution to the said equation could be based on a complex number set which, according to the latest knowledge, makes it impossible for us to make univocally a physical interpretation of the equation. In addition, to establish a criterion of the change in location of the function subject to approximation, which is necessary to find one of the best infinite solutions, is impossible.

CONCLUSIONS

To sum up what is said above, we can arrive at the conclusion that:

1. Characteristics of solids surface (that is roughness and chemical heterogeneity) affect the sorption process whose target is aiming at the balance of the active forces which are satisfactorily described in the GAB model.
2. Sorption effect may be described using the mathematical formalism jointly with the physical interpretation.
3. The GAB equation, by its mathematic-physical nature, is formally constrained as far as determining of sorption of specific surface, volume and diameter of the pores of micro-porous materials, on the basis of the isotherm line obtained empirically, are concerned.

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OGRANICZENIA RÓWNANIA GAB W OKREŚLANIU PARAMETRÓW STRUKTURY ADSORBENTÓW

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Streszczenie. Celem publikacji było przedstawienie ograniczeń modelu GAB wynikających z matematycznego ujęcia zjawiska sorpcji. W pracy zaprezentowano trudności w określaniu charakterystyk strukturalnych produktów porowatych z wykorzystaniem modelu GAB. Postawiony problem może posłużyć nie tylko celom poznawczym, ale również aplikacyjnym.

Słowa kluczowe: produkty higroskopijne, parametry struktury, matematyzacja zjawiska sorpcji