

UNIVERSAL FUNCTION FOR THE DESCRIPTION OF MULTI-LAYER ADSORPTION ISOTHERMS

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In describing multi-layer adsorption it is common to use standard isotherms. To establish such isotherms experimental data are required at a wide range of adsorptive pressure. This paper presents the theoretical and experimental analysis of the new t_{δ} -method, which is suitable to predict type II multi-layer adsorption isotherms on the basis of only two adsorption values, measured in the area of mono- and multi-layer saturation and of the surface fractal dimension of the adsorbent.

Keywords: BET theory, multi-layer adsorption, Pickett equation, Polányi theory, universal function

Introduction

Standard isotherms are used for analysing the isotherms and different aspects of the adsorbate–adsorbent interaction of multi-layer adsorption. Discrete values of the measured isotherm are plotted vs. values of the standard isotherm at the same adsorptive pressure in t -graphs (where t stands for the thickness of a layer of adsorbed molecules), α_s -graphs and f -graphs [1–3]. Such comparative graphs reveal correspondence of the extent of adsorption on one adsorbent to that of the other adsorbent under similar conditions [4]. However, the standard isotherm analysis does not permit us to select adsorption isotherms theoretically, i.e. to establish it without or with only few experimental data.

The present paper aims to develop a universal function suitable for the calculation of adsorption isotherms with a minimum of experimental data. The universal function is obtained here by means of special transformation in the co-ordinates of the equation, describing the measured isotherm. Thus if we know the equation reliably describing the definite multi-layer adsorption isotherm we can establish the universal function for multi-layer adsorption for any isotherm of this type, for example for isotherms of type II according the IUPAC classification.

Theory

Standard isotherms provide a good analysis of measured isotherms by means of α_s - and t -methods only in the region of relative adsorbate pressures $0 < x \leq 0.35$ [1], which is described well by the two-parameter BET equation [5]:

$$a = a_m \left[\frac{Cx}{(1-x)(1-x+Cx)} \right] \quad (1)$$

where a – adsorption, a_m – the monolayer capacity, C – the adsorption equilibrium constant, and x – the relative vapour pressure.

For isotherm description in a wider range of the values of x the three-parameter BET equation is usually applied:

$$a = a_m \left[\frac{Cx}{1-x} \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (C-1)x - Cx^{n+1}} \right] \quad (2)$$

where n – the maximum number of layers in saturation. The main drawback of this equation is the fact that it does not describe the isotherm at $x \rightarrow 1$ and is complex enough for practical use.

More convenient for practical use is the three-parameter Pickett equation [6]:

$$a = a_m \left[\frac{Cx(1-x^n)}{(1-x)(1-x+Cx)} \right] \quad (3)$$

As Eq. (3) describes the isotherm only in the area of multi-layer saturation [7] it was modified to account for the surface heterogeneity [8]:

$$a = a_m \frac{Cx(1-x^n)(1+x^n)^{1/[3+(2-d_{fs})]}}{(1-x)(1-x+Cx)} \quad (4)$$

where d_{fs} – surface fractal dimension. In this form Eq. (4) lets us describe the multi-layer adsorption isotherm in the area $0 < x \leq 0.97$.

To derive the universal function we transform the Eq. (4) as follows

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$$\frac{a}{a_m \delta} = \frac{Cx}{(1-x)(1-x+Cx)} \quad (5)$$

where δ is the phenomenological amendment, introduced by us to take into account the adsorption layer thickness when the adsorption space is being filled.

The value of δ is defined as follows:

$$\delta = (1-x^n)(1+x^n)^{1/[3+(2-d_s)]} \quad (6)$$

Then the universal adsorption isotherm can be shown by a graph of the type:

$$t_\delta = \frac{a}{a_m \delta} = f(x) \quad (7)$$

and the universal function for the multi-layer adsorption isotherm is defined by Eq. (7). It is clear that when $\delta=1$ formula (7) turns into the equation which is used for t -graphs [1] i.e. the suggested method is an extension of the t -method accounting for the change in adsorption layer thickness when the adsorption space is being filled.

Results and discussion

Let us make a detailed analysis of the application of Eq. (7) for the prediction of multi-layer adsorption isotherms. Figure 1 shows the universal function of experimental water vapour adsorption isotherms on washed raw wool, woman's hair [9, 10] and of chemisorption isotherms of different counter-ions on VION KH-1 fibres [8]. Despite the evident differences in the structure of the adsorbents investigated the transformation of the individual isotherms by means of Eq. (7) made it possible to combine all the studied isotherms into one curve.

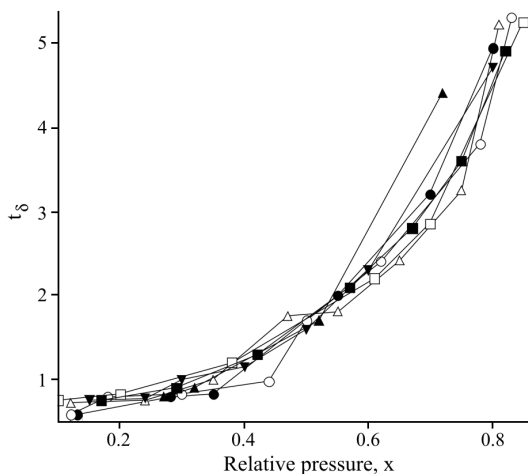


Fig. 1 The universal function built with the experimental isotherms of water vapour adsorption on \circ – washed raw wool, Δ – women's hair and chemisorptive fibre VION KN-1 with counter-ions; \bullet – Ni^{2+} , \blacktriangledown – Fe^{3+} , \square – Zn^{2+} , $+$ – Al^{3+} and \blacktriangle – Cu^{2+}

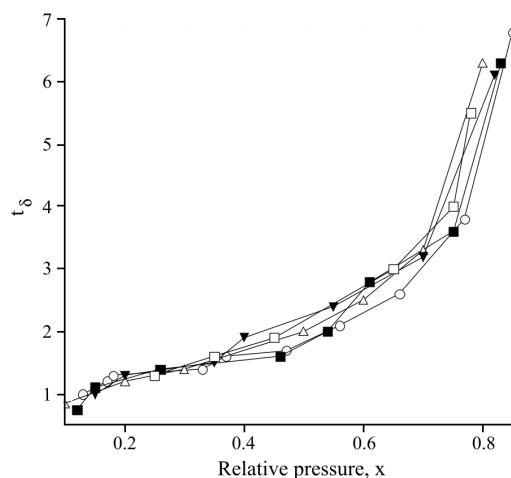


Fig. 2 The universal function built with the experimental isotherms of nitrogen adsorption on hardened cement paste of several types: \circ , $+$, Δ , \blacktriangledown and \square

Figure 2 shows the universal function of experimental nitrogen adsorption isotherms on hardened cement paste of different types [9]. As in the case of water vapour the individual isotherm transformation by means of Eq. (7) allows for the combination of all the studied isotherms into one curve.

It is interesting to compare the universal dependencies derived from experimental water vapour and nitrogen adsorption isotherms. It turned out that in combining the studied universal dependencies they coincide in the area of relative adsorptive pressures $0.5 < x < 0.97$ (Fig. 3) and deviate in the area $0 < x < 0.5$ (Fig. 4).

This fact can be explained in the following way. The area available for adsorption varies in the range of the relative adsorptive pressures $0 < x < 0.5$ corresponding to the degree of coverage $0 < \theta < 1.5$. When $\theta \geq 1.5$, i.e. in building-up of the second and

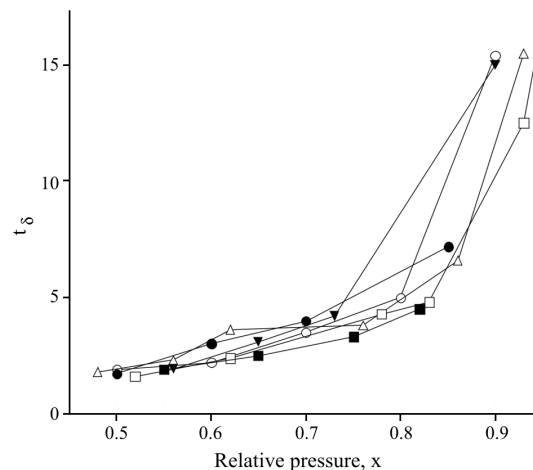


Fig. 3 The universal function built with the experimental isotherms of nitrogen adsorption on hardened cement paste of types \circ – A and \blacktriangledown – B and water vapour adsorption on these cement paste of types \square – A and $+$ – B and chemisorptive fibre VION KN-1 with counter-ion \bullet – Na^+ in area $x > 0.5$

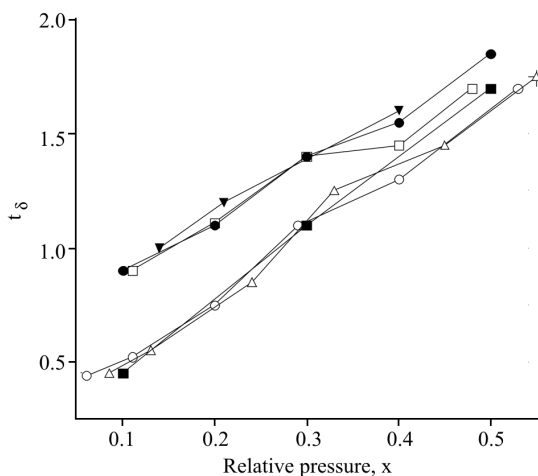


Fig. 4 The universal function built with the experimental isotherms of nitrogen adsorption on hardened cement paste of types \blacktriangledown – A, \square – B and \bullet – C and water vapour adsorption on \circ – washed raw wool, \triangle – women's hair and chemisorptive fiber VION KN-1 with counter-ion $+ - \text{Ca}^{2+}$ in area $x < 0.5$

following layers the interaction of the adsorbate molecules is determinative in the multi-layer film formation. Here both horizontal interactions within each layer and the vertical interactions between the layers are important. Both these interactions are defined by the parameters of Eq. (4). When, i.e. in formation of the first layer the determinant is the contribution of the adsorbate–adsorbent interaction, the type and value of which depending on both on the nature of the adsorbent and of the adsorbate.

To deal with the interaction of different adsorbates with the adsorbent surface we use the Polanyi potential theory [11]. According to this theory the adsorption potential in the adsorption space cell is connected either with the van der Waals force constant or with the value of polarisability (α) and the adsorbate ionisation potential (I). Because for water the dispersion contribution within the total interaction energy is small in comparison with the polar interactions it is expedient to connect it with its polarisability and ionisation potential. On the other hand the adsorption value in Polanyi theory is the adsorption potential function which has a single meaning. Hence the adsorption value can be also connected to the polarisability and the adsorbate ionisation potential. Then to take into account the different types universal dependencies of water and nitrogen in the area of small space fillings it is possible to assume that the values of t for water and nitrogen will be a definite function of $(\alpha_{\text{N}_2} I_{\text{N}_2}) / (\alpha_{\text{H}_2\text{O}} I_{\text{H}_2\text{O}})$, decreasing with increasing x value.

The ionisation potential and the molecular values of nitrogen and water were taken from [12]. The numerical analysis of the two universal

dependencies in the area of small fillings made it possible to obtain the following formula:

$$t_{\text{H}_2\text{O}} = t_{\text{H}_2\text{O}} \left[\frac{(I\alpha)_{\text{N}_2}}{(I\alpha)_{\text{H}_2\text{O}}} \right]^2 (1 - x^{1.15}) \quad (8)$$

Taking into account amendment (8) this allows us to combine water and nitrogen universal functions by means of the Eq. (7) in the area of small fillings $x < 0.5$.

In the general Eq. (5) we see the analytical form of the universal function. It is formally an analogue of the two-parameter BET Eq. (1). We use Eq. (5) in the form:

$$\frac{x}{(1-x)t_\delta} = \frac{1}{C_u} + \frac{C_u - 1}{C_u} x \quad (9)$$

where C_u is a constant which logically coincides with the local equilibrium constant in the BET theory.

To calculate value of C_u the universal function for water and nitrogen adsorption isotherms in co-ordinates of Eq. (9) was used.

It is seen from Fig. 5 that on the universal function graph the values for water and nitrogen coincide in the areas of high filling and slightly disperse in the area of the small ones. As by the introduction of amendment in Eq. (8) the universal function for water was reduced for the nitrogen universal function the latter will now be described analytically.

In Fig. 5 it is seen that the universal function can be linearised in Eq. (9) in the area $0 < x \leq 0.8$. Then we may write the following equation for the universal function in this area:

$$t_\delta = \frac{35x}{(1-x)(1-x+35x)} \quad (10)$$

To account for non-linearity in the area $x > 0.8$ the function $x/[t(1-x)] = f(x)$ may be accomplished by

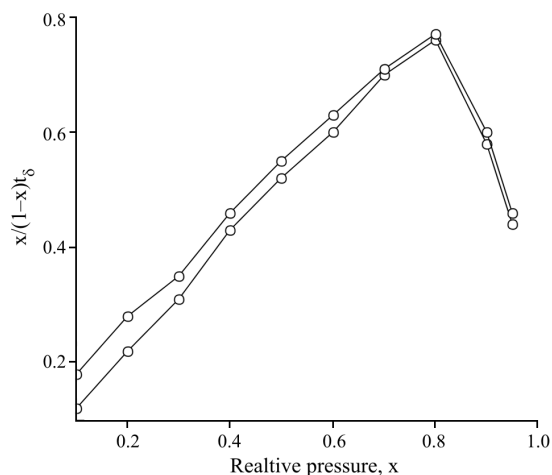


Fig. 5 The universal function built with the experimental isotherms of \circ – nitrogen and \triangle – water vapour adsorption on hardened cement paste of type A in Eq. (9) co-ordinates

introducing into Eq. (10) and we get the following amendment:

$$t = \frac{35x(1+x^{19})}{(1-x)(1-x+35x)} \quad (11)$$

Equation (11) can be used as the universal function describing multi-layer adsorption of all systems characterised by S-shaped isotherms.

Now let us show how the universal function (11) can be used for the reverse task-construction of universal isotherms with a minimum of experimental data. The individual isotherm of multi-layer adsorption is described by Eq. (4). To use this equation we must have four parameters: a_m , C , n and d_{fs} which can be defined in the following way.

First we should experimentally define one adsorption value a for the chosen adsorbent and adsorbate at a given temperature in the area of application of the two-parameter BET equation. Of course the area of the relative adsorptive pressure, in which the two-parameter BET equation is valid, depends on the nature of the adsorbent. In general this area is restricted to $0 < x < 0.3$ [1, 7, 8].

From Eq. (6) it is easy to see that for all reasonable numbers of layers n the value of $\delta \rightarrow 1$ in the area $0 < x < 0.3$. Then calculating the value of t_δ for the given value x by means of the universal function (11) and the corresponding value of a of the same value of x in the area $0 < x < 0.3$ we can calculate the monolayer capacity a_m in the following way:

$$a_m = \frac{a}{t} \quad (12)$$

Now we can calculate the value of C for the isotherm using the two-parameter BET equation as follows:

$$C = \frac{a(1-x)^2}{x[a_m - a(1-x)]} \quad (13)$$

It should be noted that the values of a , which are used in calculation by means of Eqs (12) and (13) are the same.

The next parameter to be defined is the number of layers of the multi-layer filling n . To calculate it we should obtain the adsorption value in the multi-layer filling experimentally. This area for the majority of adsorption systems described by S-shaped isotherm is in the range of the adsorptive relative pressures $0.5 < x < 0.8$ [6–8]. In this area the second term in Eq. (6) tends to one. Then we can calculate the value of n from Eq. (6) according the following equation:

$$n = \frac{\ln\left(1 - \frac{a_m t_\delta}{a}\right)}{\ln x} \quad (14)$$

The value of d_{fs} is defined by the surface structure of the adsorbent. For the majority of micro- and macroporous adsorbents $d_{fs} = 2.3–2.8$ [13, 14], but the definite choice of the values of d_{fs} should be made in relation to structural data given in the literature.

Conclusions

Our theoretical investigations show the possibility of a universal function for describing the multi-layer adsorption isotherms of type II in the IUPAC classification. As a matter of fact this method is the expansion of the famous t -method taking into account the variation of the adsorption layer thickness during the adsorption process, so it can be called t_δ -method. The suggested method allows us to predict the individual adsorption isotherm on the basis of only two adsorption values measured in the areas of mono- and multi-layer saturation. The applicability of the suggested method is demonstrated by the analyses of experimental water and nitrogen adsorption isotherms on different adsorbents.

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