A METHOD OF OBTAINING THE EQUATIONS OF MOISTURE ADSORPTION AND DESORPTION ISOTHERMS

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A new method is suggested which can be used to obtain the approximate equations of adsorption and desorption isotherms using the error functions.

Because of the theoretical and practical importance of adsorption and desorption phenomena for many fields of knowledge and technological applications, the search for the equations of adsorption and desorption isotherms is started again from time to time. The equations should describe the isotherms over the whole range of relative humidity of the environment and equilibrium moisture content of the material. It is very difficult to find these equations by strictly analytical methods [1-4]. That is why the researchers usually try to get empirical isothermal equations by the mathematical processing of experimental data. There are a lot of such equations obtained at different times which are used in practice [2-7], and some reviews analyzing the strengths and weaknesses of the approximate equations were published. The equations most frequently reduce to the form $W = W(\varphi)$ or $\varphi = \varphi(W)$.

The objective of this study was to find from the form of the equation such an approximate adsorption equation which would be based on the tabulated function, and the equation itself would be compact and contain parameters that can be calculated in the simplest way.

The problem can be solved for any shape of the isotherm, but the S-curves have been chosen from the whole diversity of shapes. The adsorption isotherms of the majority of colloid and colloid capillary-porous physical bodies are of this very shape [8, 9]. This shape suggests the formation of a polymolecular adsorption layer and of different forms of bond between moisture and material. Note that, depending on the relative humidity of the environment φ, the sections with domination of a particular bond form can be distinguished in the moisture curve $W = E(\varphi)$ [1, 9].

Studies of the features characterizing the empirical curves can provide experimental data to be generalized subsequently which will compensate, to some extent, for the absence of a strict analytical theory of adsorption processes.

To save space, in what follows we will only dwell on adsorption, but in most cases all that will be said can be extended to desorption.

An analysis of many S-shaped isotherms has shown that mathematically they can be expressed, particularly, in terms of the error function (erf-function) as

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2)\, dt.$$

The plot of the function has two parallel asymptotes and is similar in its shape to the adsorption curve at a constant temperature of the medium. The processing of numerous experimental curves for their description yielded the following equation

$$\varphi = a \operatorname{erf}(p(W - W_0)) + b. \tag{1}$$

In most cases the above equation satisfactorily describes the whole isotherm from the beginning to the end over a wide temperature range and throughout the whole range of W and φ. The erf-function tables facilitate the calculation of the parameters of the equation and of its predicted quantities [10]. The empirical adsorption curve is obtained in the same rectangular coordinate system as is the experimental curve.

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TABLE 1. Experimental and Calculated Data on Adsorption on Writing Paper

φ, %	10	20	30	40	50	60	70	80	90	100
$\tilde{\varphi}$, %	12	22	31	39,5	49,2	59,5	71,2	82,3	90,3	—
W, %	0,030	0,043	0,0525	0,0615	0,072	0,084	0,100	0,120	0,142	—
$\tilde{W}$, %	0,027	0,041	0,052	0,062	0,073	0,085	0,098	0,115	0,141	—
$x = \sqrt{W}$	0,1732	0,2074	0,2291	0,2480	0,2683	0,2898	0,3162	0,3464	0,3768	—

$$\tilde{\varphi} = + 50\,\mathrm{erf}\,(8{,}6\,(x - 0{,}27)) + 50;\quad \sigma^2 = 2{,}12;\quad \sigma = 1{,}46\%;\quad \tilde{x} = 0{,}27 + $$
$$+ 0{,}1163\,\mathrm{erf}^{-1}\left(\frac{\varphi - 50}{50}\right);\quad \tilde{W} = (\tilde{x})^2;\ \sigma^2 = 0{,}0001;\ \sigma = 0{,}01\%.$$

TABLE 2. Experimental and Calculated Data on Desorption from Peat

φ, %	10	20	30	40	50	60	70	80	90
$\tilde{\varphi}$, %	10,3	18,7	29,7	40	51	59,8	70,4	79,4	88,8
W, %	0,035	0,063	0,096	0,126	0,160	0,190	0,232	0,277	0,345
$\tilde{W}$, %	0,033	0,066	0,096	0,126	0,157	0,191	0,231	0,282	0,359
$x = \sqrt{W}$	0,1871	0,2510	0,3098	0,3550	0,4	0,4359	0,4817	0,5263	0,5874

$$\tilde{\varphi} = + 50\,\mathrm{erf}\,(4{,}4\,(x - 0{,}4)) + 51;\quad \sigma^2 = 0{,}6088;\quad \sigma = 0{,}78\%;\quad \tilde{x} = 0{,}4 - $$
$$- 0{,}23\,\mathrm{erf}^{-1}\left(\frac{\varphi - 51}{50}\right);\quad \tilde{W} = (\tilde{x})^2;\ \sigma^2 = 0{,}000036;\ \sigma = 0{,}0055\%.$$

The relation of the empirical formula with the differential equation which could express the phenomena studied in a certain mathematical form is always of great value for mathematical modeling. Therefore, it should be emphasized that the function (1) is a general solution of the differential equation

$$\frac{d^2\varphi}{dW^2} + 2p^2(W - W_0)\frac{d\varphi}{dW} = 0. \tag{2}$$

That can be checked easily if we bear in mind that

$$\frac{d\varphi}{dW} = -\frac{2ap}{\sqrt{\pi}}\exp(-p^2(W - W_0)^2), \tag{3}$$

$$\frac{d^2\varphi}{dW^2} = \frac{4ap^3}{\sqrt{\pi}}(W - W_0)\exp(-p^2(W - W_0)^2). \tag{4}$$

Generally speaking, the fact that the differential equation formally relates the quantities used in experiment does not certainly mean that the equation is fully adequate for the real physical process. It only provides a suitable mathematical model for the isotherm, and formulas (3) and (4) may be useful in deep research of adsorption.

It will be shown in a general form how we suggest to determine a, b, W_0, and p in Eq. (1) by using experimental data, i.e., by having the adsorption isotherm.

When the inflection point divides the curve into two symmetrical or nearly symmetrical parts, the parameters a and b can be calculated from the expressions

$$a = 0{,}5(\varphi_F - \varphi_I),\quad b = 0{,}5(\varphi_F + \varphi_I). \tag{5}$$

These quantities depend on random experimental conditions and, to a certain extent, on the researcher's intuition. The error due to the approximations (5) will be of the same order of magnitude as the measurement error of φ. The parameter W_0 is the abscissa of the inflection point whose ordinate is $\varphi_0 = b$.

The parameter p is found as follows: we fix two or three test points in the experimental curve at both sides of the inflection point and write their coordinates (W_i; φ_i), where i is the point number. Substituting the found values of a, b, W_0 and coordinates W_i, φ_i into

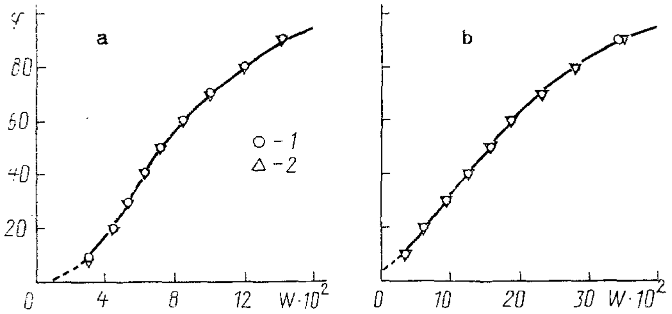

Fig. 1. Adsorption (a) and desorption (b) isotherms for Examples 1 and 2: 1) experimental points; 2) predicted points. φ, W, %.

$$\operatorname{erf}(u) = \operatorname{erf}(p(W - W_0)) = \frac{\varphi - b}{a} \tag{6}$$

gives as many equations (6) as the number of fixed experimental points. Using the table of erf-functions, from each of the equations (6) we evaluate the argument $p(W_i - W_0) = u_i$, from which $p = p_i = u_i/(W_i - W_0)$ is found. The arithmetic mean of all p_i values is assumed to be the value of unknown parameter p [11].

It can be seen that the three parameters (a, b, W_0) can be calculated in the simplest way from visual estimations of the extremal values in the empirical curve, excepting the parameter p although its calculation is also not very complicated in a general case due to the tables. The above procedure of calculating p is suitable for processing the curves, both symmetrical and almost symmetrical relative to the inflection point. Another method can be suggested for the former: as the inverse of the error function can be linearized, two experimental points are sufficient to find p from the formulas

$$p = \frac{u_1 - u_2}{W_1 - W_2} \quad \text{or} \quad p = \frac{u_1 - u_2}{x_1 - x_2}, \tag{7}$$

where u_1 and u_2 were calculated preliminarily from (8) using the table of erf-function, $x = \sqrt{W}$. So, if in Example 1 given later we take two points, $M_1(0.2480; 40)$ and $M_2(0.2898; 60)$, of the adsorption isotherm in the coordinates $x-\varphi$, where $x = \sqrt{W}$, we obtain $u_1 = 0.179$, $u_2 = -0.179$, and then $p = -8.56$ (in the first procedure $p = -8.6$).

The parameters can be corrected if that improves the approximation estimated in terms of inadequacy variance. In some cases the improvement can be markedly better if two values of p are obtained, one for the curve before the inflection, the other after the inflection. Each part of the curve will be described by its own equation. However, a single general equation seems preferable.

Essential asymmetry can be eliminated by using Kapteyn equation [12]. A nonsymmetrical curve very often reduces to a suitable symmetrical one by using a logarithmically normal distribution [2, p. 37] or by replacing the argument by a suitable function, for example, its square root. Thereafter the isotherm equation is found following the above procedure.

From Eq. (1) the adsorption equation easily follows as a function of the argument φ:

$$W = W_0 + \frac{1}{p} \operatorname{erf}^{-1}\left(\frac{\varphi - b}{a}\right), \tag{8}$$

where $\operatorname{erf}^{1}((\varphi - b)/a)$ are also evaluated with the table of the erf-function, but as a function which is the inverse of the initial one, i.e., when the argument is found from the function value.

The equations (1) and (8) appear useful, for example, for calculating the specific surface area and the moisture-material binding energy during adsorption, chemical μ and experimental θ_e potentials of mass transfer in the hygroscopic region, true specific and isothermal mass capacity c_m, and other thermodynamic properties [2, 5, 7, 8]. Their values are necessary to choose the methods and regimes for drying and moistening new materials that are promising for advanced technologies.

The sorption dynamic problem cannot also be solved without the sorption isotherm in any form. It is necessary together with the balance equation, the kinetic equation, and the boundary conditions [4, 13].

To conclude the article, we give examples of adsorption and desorption isotherm equations obtained by following the suggested technique with concrete experimental data (Tables 1 and 2).

The first and the third lines of each table give experimental φ and W, the second and the third, those calculated from the equations written beneath the tables. The corresponding inadequacy variances are shown next to every equation.

The formulas available in Examples 1 and 2 predict $\tilde{\varphi}$ and $\tilde{W}$ in the case of their direct or inverse relation. If the table of erf(x) is entered into the computer storage, the calculation efficiency increases and the approximation improves.

Example 1. Writing paper. Adsorption isotherm, T = 297 K [8, No. 43] (see Figure 1a).

If the adsorption isotherm is plotted in the coordinates $W-\varphi$, one can immediately see that the S-curve is not centrally symmetric. Its asymmetry is almost fully eliminated by the substitution of the variable $x = \sqrt{W}$ for W. Further data processing following the suggested method in the coordinates $x-\varphi$ gives the predicted adsorption equations presented in Table 1 and satisfactory predicted values of φ and W contained in the same table.

Example 2. Peat. Desorption isotherm, T = 303 K [8, No. 1102] (see Figure 1b). The calculation results are summarized in Table 2. Evidently, the proposed method can be applied to obtain the adsorption equations not only in moisture absorption but also in other cases when experimental adsorption curves for gases, acid vapors, etc. are sigmoid with two parallel asymptotes.

The mathematic model suggested can be based on the probability integral in any analytical form, i.e.,1 it can be normalized in any way. This may be convenient because for some normalizations there are tables of both the direct and inverse functions [14, p. 374].

NOTATION

W, equilibrium moisture content of material, %; φ, relative humidity of air or gas medium, %; φ_I, φ_F, initial and final relative air (gas) humidities, respectively, %; a, b, W_0, p, parameters to be found from the experimental data; u, erf-function argument; x, new variable in Kapteyn transform; μ, the chemical potential of mass transfer, temperature function and material moisture; θ_e, experimental potential of mass transfer in arbitrary mass transfer degrees, ^{0}M; c_m, mass capacity, kmole/J; σ^2, inadequacy variance; σ, root mean square deviation.

LITERATURE CITED

1. A. Adamson, Physical Chemistry of Surfaces [Russian translation], Moscow (1979).
2. S. D. Greg and K. S. Sing, Adsorption, Specific Surface, Porosity [Russian translation], Moscow (1970).
3. P. G. Romankov, N. B. Rashkovskaya, and V. F. Frolov, Mass Transfer Processes in Chemical Engineering [in Russian], Leningrad (1975).
4. V. V. Rachinskii, Elements of the General Theory of Dynamics of Sorption and Chromatography [in Russian], Moscow (1964).
5. V. M. Kisarov, Zhurn. Fiz. Khim., **43**, No. 4, 1037-1039 (1964).
6. A. S. Ginzburg and I. M. Savina, Mass Moisture Transfer Characteristics of Food Products [in Russian], Moscow (1982).
7. N. E. Gorobtseva, Intensification of Thermal Drying Processes [in Russian], Minsk (1986), pp. 30-40.
8. L. M. Nikitina, Thermodynamic Parameters and Mass Transfer Coefficients in Moist Materials [in Russian], Moscow (1963).
9. A. V. Lukov, Transfer Phenomena in Capillary-Porous Bodies [in Russian], Moscow (1964).
10. Handbook of Special Functions, ed. by M. Abramovitz and I. Stagun [Russian translation], Moscow (1979).
11. M. S. Smirnov, V. L. Yarovenko, and V. I. Lysenko, Mikrobiol., **56**, No. 5, 812-815 (1987).
12. G. Korn and T. Korn, Mathematical Handbook for Researchers and Engineers [in Russian], Moscow (1970).
13. N. V. Kel'tsev, Fundamentals of Adsorption Engineering [in Russian], 2nd ed., Moscow (1984).
14. V. Yu. Urbakh, Biometric Methods [in Russian], Moscow (1964).