Calculation of nonlinearly placed parameters by the method of planned experiment

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This paper deals with a new method for calculating the parameters placed nonlinearly in mathematical relationships by using a set of experimental data the number of which is greater than the number of the parameters sought for. In this method the planned experiment is used for selecting the points in which the values of an optimization criterion are calculated. From these values the coefficients of response function are determined. The optimum values of parameters are related to the minimum of the response function. This method is illustrated by some examples concerning evaluation of the parameters of equations of adsorption isotherms.

В статье описывается новый метод расчета нелинейно расположенных параметров в математических зависимостях на основе экспериментальных данных, количество которых больше, чем количество определяемых параметров. В методе используется планированный эксперимент так, что в соответствии с ним выбираются точки, в которых рассчитываются значения специального критерия. На основе значений критерия устанавливаются коэффициенты функции регрессии. Оптимальные значения параметров для данного критерия расчитываются из минимума функции регрессии. Применимость метода демонстрируется на примере расчета параметров уравнений изотерм адсорбции.

In research work, we frequently have to determine from a set of data some nonlinearly placed parameters occurring in a functional relationship between measured quantities. As a rule, we try to solve a nonlinear problem by using such analytical operation which transforms the nonlinear problem into a linear one. It is known from literature and it results from our calculations as well that the values of parameters thus obtained are usually less precise. This problem cannot be satisfactorily solved even by introducing statistical weights.

In the relationships which cannot be linearized, the approximate values of parameters can be determined from selected points by solving the necessary number of transcendental equations.

The approximate values of parameters thus obtained must be improved in accuracy, in a certain sense they must be optimized. For this purpose, the linearization by means of an expansion into the Taylor series is frequently used. This procedure may lead to complicated expressions and a great number of cycles is necessary for achieving the required precision.

The development of machine-computing technique brought further methods for the calculation of parameters such as simplex method, random search method, *etc.* If the simplex method is used in solving an n-dimensional nonlinear problem, the values of the purpose function are to be determined in $n+1$ points of a spatial polyhedron. By turning over this polyhedron about all edges, we seek for such new position in which the purpose function exhibits less value. After reaching the optimum position, we go on calculating with a polyhedron having smaller length of edges [1]. If the method of random search is used, the intervals in which the optimum values of parameters occur are to be determined. The values of parameters are selected by chance from these intervals and subsequently the values of purpose function are calculated for them. According to the obtained values of purpose function, the intervals of the values of parameters are gradually contracted [2]. Both these methods require a great number of steps and the use of high-speed computers. Besides this, their convergence in the final stage of calculation is relatively slow.

Description of the calculation of parameters by the method of planned experiment

The requirement to investigate the whole region of the assumed occurrence of the values of parameters sought for and on the other hand, the demand for reduction of the number of cycles in the method of random search led us to the idea of a more systematic selection, of the values of parameters. For this aim, we may take advantage of the computing procedures of planned experiment.

The problem to determine the unknown values of parameters is usually formulated so that we must determine the values of parameters $a_1, a_2, \ldots, a_m$ of the relationship

$$y = \mathrm{f}(x; a_1, a_2, \ldots, a_m) \qquad (1)$$

from a set of measured data $\{x_i, y_i\}$, $i = 1, 2, \ldots, n$. The algorithm of the proposed method can be made up as follows:

1. To estimate the values of parameters in eqn (*1*) by some approximate method or from their physical meaning. These estimates are denoted $a_{10}, a_{20}, \ldots, a_{m0}$.

2. To ascertain the intervals in which the occurrence of the optimum values of parameters is expected. It proved to be convenient to use the procedure in which

the degree of approximation of the estimates to the optimum values is expressed by standard deviation

$$s_0^2 = \frac{\sum_{i=1}^{n} [y_i - f(x_i; a_{10}, a_{20}, \ldots, a_{m0})]^2}{n} \qquad (2)$$

In order to respect the influence of the values y_i and estimates a_{i0}, the following expression was chosen for the determination of the values of intervals

$$\Delta a_{i0} = L_i \frac{s_0}{\bar{y}} a_{i0} \qquad (3)$$

where $\bar{y}$ is the arithmetic mean of the measured values, y_i and L_i is a suited coefficient. The intervals in which the occurrence of the optimum values of parameters is expected are $\langle a_{i0} - \Delta a_{i0}; a_{i0} + \Delta a_{i0} \rangle$.

Further possibility of determining Δa_{i0} ensues from the expression

$$\Delta a_{i0} = a_{i0} L_i \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left[\frac{y_i + f(x_i; a_{10}, a_{20}, \ldots, a_{m0})}{y_i} \right]^2} \qquad (4)$$

3. To select the criterion K (purpose function) that will be used for finding out the optimum values of parameters, for instance the sum of squares of the deviations between the measured and calculated values

$$K_j(a_1^j, a_2^j, \ldots, a_m^j) = \sum_{i=1}^{n} [y_i - f(x_i; a_1^j, \ldots, a_m^j)]^2 \qquad (5)$$

4. To select the regression equation of planned experiment

$$K = f(X_1, X_2, \ldots, X_m) \qquad (6)$$

and determine the values of its coefficients. For this purpose, it is necessary:

a) To form dimensionless expressions

$$X_i = \frac{a_i - a_{i0}}{\Delta a_{i0}} \qquad i = 1, 2, \ldots, m \qquad (7)$$

which in a planned experiment are called factors. It holds

$$\begin{array}{ll} a_i = a_{i0} - \Delta a_{i0} & X_i = -1 \\ a_i = a_{i0} & X_i = \ \ 0 \\ a_i = a_{i0} + \Delta a_{i0} & X_i = +1 \end{array} \qquad (8)$$

Individual combinations of the levels of the factors $X_1, \ldots, X_m$ are distinguished from each other by the index j in eqn (5).

b) To calculate the values of purpose function K_j, $j = 1, 2, \ldots, N$ in the points corresponding to the mentioned levels of factors in the specification of planned experiment. One calculation of the value of purpose function corresponds to one point in the planned experiment. It is profitable to use a central orthogonal composition plan in which the number of experiments is given by the relation

$$N = 2^m + 2\,m + p \tag{9}$$

where p is the number of experiments in the centre of plan.

c) To calculate the coefficients of the chosen regression equation (*6*) for particular planned experiment.

5. To calculate the values of factors X_i which correspond to the minimum of function (*6*). It results from the postulate of the existence of minimum of eqn (*6*) that we must select at least a quadratic regression equation

$$K = b_0 + b_1X_1 + b_2X_2 + \ldots + b_mX_m + b_{12}X_1X_2 + b_{m-1,\,m}X_{m-1}X_m + \\ + b_{11}X_1^2 + \ldots + b_{mm}X_m^2 \tag{10}$$

6. To determine the values of parameters a_i, denoted a_{i1}, from the values of factors X_i calculated according to item 5 by means of transformation according to eqn (*7*).

7. To calculate the value of criterion $K(a_{11}, \ldots, a_{m1})$ and to compare it with the value $K(a_{10}, \ldots, a_{m0})$ according to the inequality

$$\left| \frac{K(a_{11}, \ldots, a_{m1}) - K(a_{10}, \ldots, a_{m0})}{K(a_{10}, \ldots, a_{m0})} \right| < \varepsilon \tag{11}$$

where ε is a small number fixed beforehand. Provided inequality (*11*) is fulfilled, the calculation is finished and the obtained values of parameters are optimal ones for a given criterion. Provided inequality (*11*) is not fulfilled, the values $a_{11}, \ldots, a_{m1}$ become a centre of a new plan ($a_{i1} \rightarrow a_{i0}$) and the calculation is to be repeated from item 2.

Verification of the method

The proposed method for calculating the parameters by means of planned experiment was verified by the calculation of parameters of adsorption isotherms. The used set of experimental equilibrium data of the system carbon dioxide—Calsit 5 at 373 K given in Table 1 has been taken from paper [3]. From this set of equilibrium data, two parameters of the Langmuir adsorption isotherm have been calculated

$$a = a_1 \frac{a_2 p}{1 + a_2 p} \tag{12}$$

where a is the relative fraction of adsorbate, p is the vapour pressure of adsorptive, and a_1, a_2 are the parameters sought for. In order to verify the possibility of

Table 1

Experimental and calculated equilibrium data of the system CO_2—Calsit 5 at 373 K

No.	Experimental		Calculated	
	$\frac{a_i \cdot 10^2}{\text{g g}^{-1}}$	$\frac{p_i}{\text{Pa}}$	$a_i \cdot 10^2/\text{g g}^{-1}$ from eqn (*12*)	$a_i \cdot 10^2/\text{g g}^{-1}$ from eqn (*13*)
1	0.241	101	0.037	0.050
2	0.447	680	0.243	0.312
3	0.849	1 592	0.553	0.676
4	1.412	3 349	1.107	1.271
5	2.276	7 066	2.120	2.262
6	3.432	13 599	3.509	3.533
7	5.275	27 864	5.509	5.370
8	6.693	42 930	6.806	6.683
9	8.290	68 128	8.113	8.232

calculating three parameters, we have used the Peterson—Redlich equation of adsorption isotherm

$$a = a_3 \frac{p}{1 + a_4 p^{a_5}} \qquad (13)$$

where a_3, a_4, and a_5 are parameters.

Calculation of parameters of the Langmuir equation of adsorption isotherm

From the linearized form of eqn (*12*)

$$\frac{p}{a} = \frac{1}{a_1} p + \frac{1}{a_1 a_2} \qquad (14)$$

we calculated the first estimates of the parameters $a_{10} = 9.7036 \times 10^{-2}$ g g^{-1} and $a_{20} = 5.750 \times 10^{-5}$ Pa^{-1} by means of the method of least squares. Then

$$s_0 = \sqrt{\frac{\sum_{i=1}^{9} \left(a_i - 0.097036 \frac{5.75 \times 10^{-5} p_i}{1 + 5.75 \times 10^{-5} p_i} \right)^2}{9-2}} = 5.175 \times 10^{-3} \text{ g g}^{-1}$$

$$\Delta a_{10} = 0.5 \frac{5.1757 \times 10^{-3}}{3.213 \times 10^{-2}} 9.7036 \times 10^{-2} = 0.00781 \text{ g g}^{-1}$$

$$\Delta a_{20} = 0.5 \frac{5.1757 \times 10^{-3}}{3.213 \times 10^{-2}} 5.750 \times 10^{-5} = 0.463 \times 10^{-5} \text{ Pa}^{-1}$$

The intervals of numerical values of the parameters are: $a_1 \in \langle 8.9226 \times 10^{-2}; 10.4846 \times 10^{-2} \rangle$, $a_2 \in \langle 5.287 \times 10^{-5}; 6.213 \times 10^{-5} \rangle$.

For finding out the optimum values of parameters, we chose the criterion of type (5) given by the equation

$$K_j = \sum_{i=1}^{9} \left(a_i - a_1^j \frac{a_2^j p_i}{1 + a_2^j p_i} \right)^2 \qquad (15)$$

The regression equation of planned experiment for two factors has the form

$$K = b_0 + b_1 X_1 + b_2 X_2 + b_{12} X_1 X_2 + b_{11} X_1^2 + b_{22} X_2^2 \qquad (16)$$

For determining the regression coefficients in eqn (*16*), there are $N = 2^2 + 2 \times 2 + 2 = 10$ experiments necessary. The specification of experiments as well as the corresponding levels of parameters are given in Table 2. The values of criteria calculated from eqn (*15*) for the corresponding levels of parameters are quoted in the last column of Table 2.

Table 2

Specification of experiments, calculated values of parameters, and calculated values of criteria for particular experiments

Number of experiment	Factor		Parameter		Criterion
j	X_1	X_2	$\frac{a_1^j \cdot 10^2}{\text{g g}^{-1}}$	$\frac{a_2^j \cdot 10^5}{\text{Pa}^{-1}}$	$\frac{K_j \cdot 10^4}{\text{g}^2 \text{g}^{-2}}$
1	−1	−1	8.9226	5.287	2.154679
2	+1	−1	10.4846	5.287	2.599730
3	−1	+1	8.9226	6.213	2.023522
4	+1	+1	10.4846	6.213	5.711161
5	−1.077	0	8.8622	5.750	2.045218
6	+1.077	0	10.5450	5.750	4.298461
7	0	−1.077	9.7036	5.251	1.294945
8	0	+1.077	9.7036	6.249	2.762544
9	0	0	9.7036	5.750	1.875173
10	0	0	9.7036	5.750	1.875173

The numerical values of coefficients of regression equation (*16*) (in $\text{g}^2\,\text{g}^{-2}$) calculated according to [4] are

$$b_1 = \frac{\sum_{j=1}^{10} X_{1j} K_j}{\sum_{j=1}^{10} X_{1j}^2} = \frac{5.629442 \times 10^{-4}}{6.319858} = 0.89075 \times 10^{-4}$$

$$b_2=\frac{\sum_{j=1}^{10} X_{2j}K_j}{\sum_{j=1}^{10} X_{2j}^2}=\frac{4.560878\times10^{-4}}{6.319858}=0.72167\times10^{-4}$$

$$b_{12}=\frac{\sum_{j=1}^{10} X_{1j}X_{2j}K_j}{\sum_{j=1}^{10} (X_{1j}X_{2j})^2}=\frac{3.242588\times10^{-4}}{4}=0.81067\times10^{-4}$$

$$b_{11}=\frac{\sum_{j=1}^{10} X'_{1j}K_j}{\sum_{j=1}^{10} (X'_{1j})^2}=\frac{3.0108965\times10^{-4}}{2.69696}=1.11640\times10^{-4}$$

$$b_{22}=\frac{\sum_{j=1}^{10} X'_{2j}K_j}{\sum_{j=1}^{10} (X'_{2j})^2}=\frac{0.3589162\times10^{-4}}{2.69696}=0.13304\times10^{-4}$$

$$b_0=b'_0-b_{11}\overline{X_1^2}-b_{22}\overline{X_2^2}=2.66406\times10^{-4}-1.11640\times10^{-4}\times0.632-$$
$$-0.13304\times10^{-4}\times0.632=1.87439\times10^{-4}$$

The used values of the quantities according to Table 2 are:

$$\overline{X_1^2}=\frac{1}{10}\sum_{j=1}^{10} X_{1j}^2=\frac{1}{10}\times6.3199\doteq0.632$$

$$\overline{X_2^2}=\frac{1}{10}\sum_{j=1}^{10} X_{2j}^2=\frac{1}{10}\times6.3199\doteq0.632$$

$$X'_{1j}=X_{1j}^2-\overline{X_1^2}=X_{1j}^2-0.632$$

$$X'_{2j}=X_{2j}^2-\overline{X_2^2}=X_{2j}^2-0.632$$

$$b'_0=\frac{1}{10}\sum_{j=1}^{10} K_j=\frac{1}{10}\times26.6406\times10^{-4}=2.66406\times10^{-4}$$

The real specified form of regression equation (*16*) is

$$K=1.87439\times10^{-4}+0.89075\times10^{-4}\cdot X_1+0.72167\times10^{-4}\cdot X_2+$$
$$+0.81067\times10^{-4}\cdot X_1X_2+1.11640\times10^{-4}\cdot X_1^2+0.13304\times10^{-4}\cdot X_2^2 \quad (17)$$

The minimization of function (*17*) gives a system of equations

$$\begin{aligned}0.81067\,X_2+2\times1.11640\,X_1&=-0.89075\\2\times0.13304\,X_2+0.81067\,X_1&=-0.72167\end{aligned}\quad (18)$$

By solving eqns (*18*), we obtain: $X_1 = 5.53119$; $X_2 = 14.13555$.

The calculated values of the factors X_1 and X_2 occur outside the region of values for which eqn (*17*) has been derived. On the basis of the postulate that the values of criterion should be improved in each cycle of calculation we can decide whether the values of parameters ascertained from the minimum values of X_1 and X_2 according to eqn (*7*) are to be used for further cycle of calculation.

The minimum values of the factors X_1 and X_2 can be used for calculating the values of parameters $a_{11} = 5.3837 \times 10^{-2}$ g g^{-1} and $a_{21} = 1.2295 \times 10^{-4}$ Pa^{-1} by means of eqn (*7*). The corresponding value of criterion calculated from eqn (*15*) is $K_1 = 1.8147 \times 10^{-3}$ g^2 g^{-2}. By comparing this value with the value of criterion corresponding to the first estimates of parameters as quoted in the last two lines of Table 2, we can observe a significant deterioration of the value of the criterion after the first cycle of calculation.

We can continue in calculation and adjust the intervals of particular parameters by a new choice of the values of L_i or a new choice of the values of parameters a_1 and a_2 while this procedure remains preserved. For further calculation, the second variant was used while the values of criteria from the specification of experiments presented in Table 2 were applied. It is obvious that the value of criterion corresponding to the seventh point of planned experiment with parameters $a_1 = 9.7306 \times 10^{-2}$ g g^{-1} and $a_2 = 5.251 \times 10^{-5}$ Pa^{-1} is lower than the value of criterion corresponding to the first estimates of parameters (the last two experiments). The calculation was repeated from item 2 with the values of parameters resulting from experiment 7. The results of calculations are given in Table 3. The calculated relative fractions of adsorbate presented in Table 1 correspond to the optimum values of parameters of eqn (*12*) which are quoted in the last line of Table 3.

Table 3

Values of parameters of eqn (*12*) and values of the criterion corresponding to particular planned experiments

Number of plan	$\frac{a_1 \cdot 10^2}{\text{g g}^{-1}}$	$\frac{a_2 \cdot 10^4}{\text{Pa}^{-1}}$	L_i	$\frac{K \cdot 10^4}{\text{g}^2\,\text{g}^{-2}}$	$\frac{\varepsilon}{\%}$
0	9.7036	0.5750	0.5	1.873	—
1	9.7036	0.5251	0.5	1.297	30.75
2	9.7036	0.4873	0.5	1.122	13.49
3	11.1270	0.3205	0.5	0.842	24.96
4	11.7464	0.3202	0.5	0.399	52.61
5	12.0255	0.3029	0.5	0.393	1.50
6	12.0593	0.3018	0.5	0.393	0.00

Calculation of parameters of the Peterson—Redlich equation of adsorption isotherm

The estimates of parameters of eqn (*13*) were performed as follows: We chose the values of parameter a_5 to be equal to 0.8, 0.9, and 1.0. We calculated the values of parameters a_3 and a_4 from the linearized form of eqn (*13*) with constant value of parameter a_5 by means of the method of least squares. The values of parameters $a_{30} = 6.7900 \times 10^{-6}$ g g^{-1} Pa^{-1}, $a_{40} = 6.5900 \times 10^{-4}$ Pa$^{-a_5}$, $a_{50} = 0.8000$ which gave the least sum of squares of the differences between experimental and calculated values of relative fractions of adsorbate were used as the first estimates. Then we may write

$$s_0 = \sqrt{\frac{\sum_{i=1}^{9}\left(a_i - 6.79 \times 10^{-6}\frac{p_i}{1 + 6.59 \times 10^{-4}\, p_i^{0.8}}\right)^2}{9-3}} =$$

$$= 3.5446 \times 10^{-3}\ \text{g g}^{-1}$$

and for $L_i = 0.1$, $\Delta a_{30} = 7.5 \times 10^{-8}$ g g^{-1} Pa^{-1}, $\Delta a_{40} = 7.3 \times 10^{-6}$ Pa$^{-a_5}$, $\Delta a_{50} = 8.8 \times 10^{-3}$. The intervals of the numerical values of parameters are: $a_3 \in \langle 6.705 \times 10^{-6};\ 6.865 \times 10^{-6} \rangle$; $a_4 \in \langle 6.517 \times 10^{-4};\ 6.663 \times 10^{-4} \rangle$; $a_5 \in \langle 0.7912;\ 0.8088 \rangle$.

The criterion of optimization was chosen in the form

$$K_j = \sum_{i=1}^{9}\left(a_i - a_3^j \frac{p_i}{1 + a_4^j p_i^{a_5^j}}\right)^2 \qquad (19)$$

For three factors, the regression equation of planned experiment has the following form [4, 5]

$$K = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + \\ + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \qquad (20)$$

The needed number of experiments for the determination of regression coefficients in $N = 2^3 + 2 \times 3 + 1 = 15$. The plan of experiments and the calculated values of criterion for particular experiments are given in Table 4. The numerical values of the coefficients of regression equation (*20*) (dimension g^2 g^{-2}) calculated from the equations presented in papers [4, 5] are

$$b_0' = \frac{\sum_{j=1}^{15} K_j}{N} = \frac{20.520508 \times 10^{-4}}{15} = 1.36803 \times 10^{-4}$$

$$b_1 = \frac{\sum_{j=1}^{15} X_{1j}K_j}{\sum_{j=1}^{15} X_{1j}^2} = \frac{0.766599 \times 10^{-4}}{10.952} = 6.99963 \times 10^{-6}$$

$$b_2=\frac{\sum_{j=1}^{15} X_{2j}K_j}{\sum_{j=1}^{15} X_{2j}^2}=\frac{-0.275282\times10^{-4}}{10.952}=-2.51353\times10^{-6}$$

$$b_3=\frac{\sum_{j=1}^{15} X_{3j}K_j}{\sum_{j=1}^{15} X_{3j}^2}=\frac{-1.054597\times10^{-4}}{10.952}=-9.62927\times10^{-6}$$

$$b_{12}=\frac{\sum_{j=1}^{15} X_{1j}X_{2j}K_j}{\sum_{j=1}^{15} (X_{1j}X_{2j})^2}=\frac{-0.242025\times10^{-4}}{8}=-3.02531\times10^{-6}$$

$$b_{13}=\frac{\sum_{j=1}^{15} X_{1j}X_{3j}K_j}{\sum_{j=1}^{15} (X_{1j}X_{3j})^2}=\frac{-2.023627\times10^{-4}}{8}=-2.52953\times10^{-5}$$

$$b_{23}=\frac{\sum_{j=1}^{15} X_{2j}X_{3j}K_j}{\sum_{j=1}^{15} (X_{2j}X_{3j})^2}=\frac{1.521517\times10^{-4}}{8}=1.90189\times10^{-5}$$

$$b_{11}=\frac{\sum_{j=1}^{15} X'_{1j}K_j}{\sum_{j=1}^{15} (X'_{1j})^2}=\frac{0.093308\times10^{-4}}{4.360732}=2.13975\times10^{-6}$$

$$b_{22}=\frac{\sum_{j=1}^{15} X'_{2j}K_j}{\sum_{j=1}^{15} (X'_{2j})^2}==\frac{0.124062\times10^{-4}}{4.360732}=1.24911\times10^{-6}$$

$$b_{33}=\frac{\sum_{j=1}^{15} X'_{3j}K_j}{\sum_{j=1}^{15} (X'_{3j})^2}=\frac{3.534064\times10^{-4}}{4.360732}=8.104291\times10^{-5}$$

$$b_0=b'_0-b_{11}\overline{X_1^2}-b_{22}\overline{X_2^2}-b_{33}\overline{X_3^2}=1.368034\times10^{-4}-$$
$$-2.139753\times10^{-6}\times0.730-1.249108\times10^{-6}\times0.730-$$
$$-8.104296\times10^{-5}\times0.730=7.51682\times10^{-5}$$

Table 4

Plan of experiments for the calculation of parameters of eqn (*13*) and calculated values of the criterion for particular experiments

Number of experiment	Factor			Parameter			Criterion
j	X_1	X_2	X_3	$\frac{a_3^j \cdot 10^6}{\text{g g}^{-1}\,\text{Pa}^{-1}}$	$\frac{a_1^j \cdot 10^4}{\text{Pa}^{-a_5}}$	a_5^j	$\frac{K_j \cdot 10^4}{\text{g}^2\,\text{g}^{-2}}$
1	−1	−1	−1	6.7150	6.5170	0.7912	1.541109
2	+1	+1	−1	6.8650	6.5170	0.7912	2.272236
3	−1	+1	−1	6.7150	6.6630	0.7912	1.174159
4	+1	+1	−1	6.8650	6.6630	0.7912	1.761547
5	−1	−1	+1	6.7150	6.5170	0.8088	1.493470
6	+1	−1	+1	6.8650	6.5170	0.8088	1.190057
7	−1	+1	+1	6.7150	6.6630	0.8088	1.864552
8	+1	+1	+1	6.8650	6.6630	0.8088	1.462853
9	−1.215	0	0	6.6989	6.5900	0.8000	0.720594
10	+1.215	0	0	6.8811	6.5900	0.8000	0.846681
11	+0	−1.215	0	6.7900	6.5013	0.8000	0.787568
12	0	+1.215	0	6.7900	6.6787	0.8000	0.753394
13	0	0	−1.215	6.7900	6.5900	0.78931	2.079443
14	0	0	+1.215	6.7900	6.5900	0.81069	1.818967
15	0	0	0	6.7900	6.5900	0.8000	0.753880

$$\overline{X_1^2}=\overline{X_2^2}=\overline{X_3^2}=\frac{1}{15}\sum_{j=1}^{15}X_{kj}^2=\frac{1}{15}\times 10.952\approx 0.730$$

$$X'_{kj}=X_{kj}^2-\overline{X_{kj}^2}=X_{kj}^2-0.730; \qquad k=1, 2, 3$$

The minimization of the regression equation

$$\begin{aligned}K\cdot 10^6 = 75.16819 + 6.99963\ X_1 - 2.51353\ X_2 - 9.62927\ X_3 - \\ - 3.02531\ X_1X_2 - 25.29534\ X_1X_3 + 19.01894\ X_2X_3 + \\ + 2.13975\ X_1^2 + 1.24911\ X_2^2 + 81.04291\ X_3^2\end{aligned} \tag{21}$$

gives the system of equations

$$\begin{aligned}2\times 2.13975\ X_1 - 3.02531\ X_2 - 25.29534\ X_3 = -6.99963 - \\ -3.02531\ X_1 + 2\times 1.24911\ X_2 + 19.01894\ X_3 = 2.51353\end{aligned} \tag{22}$$

$$25.29534\ X_1 + 19.01894\ X_2 + 2\times 81.04291\ X_3 = 9.629266$$

the solution of which is $X_1=-16.269841$, $X_2=1.700444$, $X_3=-2.679216$.

The corresponding values of parameters of eqn (*13*) calculated according to eqn (*7*) are: $a_{31} = 5.5698\times 10^{-6}$ g g^{-1} Pa^{-1}, $a_{41} = 6.7141\times 10^{-4}$ Pa$^{-a_5}$, $a_{51} = 0.77642$.

The value of criterion corresponding to these values of parameters is $K_1 = 2.861\times 10^{-5}$ g^2 g^{-2}. When comparing this value of criterion with the value $K_0 = 7.539\times 10^{-5}$ g^2 g^{-2} corresponding to the first estimates of parameters we can see that the value of criterion has been improved and the calculated values of parameters a_{i1} can be, therefore, used as input estimates for subsequent cycle. The

Table 5

Values of parameters of eqn (*13*) and values of the criterion corresponding to particular planned experiments

Number of plan	Parameter				Criterion	
	$\frac{a_3\cdot 10^6}{\text{g g}^{-1}\ \text{Pa}^{-1}}$	$\frac{a_4\cdot 10^4}{\text{Pa}^{-a_5}}$	a_5	L_i	$\frac{K\cdot 10^4}{\text{g}^2\ \text{g}^{-2}}$	$\frac{\varepsilon}{\%}$
0	6.7900	6.5900	0.80000		0.7539	—
1	5.5698	6.7141	0.77642	0.1	0.2861	62.05
2	5.3410	6.8576	0.76624	0.1	0.1540	46.17
3	5.1775	6.9199	0.76122	0.1	0.1343	12.79
4	5.0951	0.9694	0.75837	0.1	0.1293	3.70
5	5.0516	7.0129	0.75664	0.1	0.1280	1.01
6	5.0287	7.0531	0.75550	0.1	0.1277	0.23

calculating cycle thus repeat from item 2. The obtained results of calculation are summarized in Table 5. The values of relative fractions of adsorbate calculated from eqn (*13*) with the optimum values of parameters quoted in the last line of Table 5 are listed in the last column of Table 1.

Discussion

The verification of this method has shown that the course of calculation depends on the form of eqn (*1*). A successful calculation of two parameters does not usually require precise input estimates of parameters. For quite nonlinear functions [1] with more than two parameters, for instance if the parameters sought for are in exponents, we need relatively precise input values of parameters with quite narrow intervals ($L_i \in (0.05, 0.1)$). The problem is evidently connected with the fact that the used quadratic regression equation describes the dependence of the used criterion on parameters only in a relatively narrow region of the minimum with sufficient accuracy. The proposed method can be successfully applied in these cases, too. However, we must use a more reliable method for determining the input values of parameters or search systematically the region about the approximate values of parameters by means of the proposed method. In a planned search of the region round the approximate values, we usually choose wider intervals of parameters, $L_i \in (0.5, 1)$ in the initial phase of calculation.

The method of calculation of parameters by means of a planned experiment is not exacting from the view-point of computation and enables us to carry out calculations in reasonable time by means of table calculators.

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