

Computation of diffusion coefficient dependence upon concentration from sorption experiments*

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The direct evaluation of the internal diffusion coefficient from experimental adsorption kinetic curve is possible, only when this coefficient is constant. In such a case, the known analytical solution of the 2nd Fick's law may be used. However, this assumption is not mostly satisfied. Then the concentration dependence of diffusion coefficients is to be evaluated. So far, only graphical methods for a plane sheet have been published.

In this paper a computer-suitable iteration method for deducing concentration dependence of diffusion coefficient from the sorption data is described. The idea is based on the Crank's method for progressing sorption experiments.

На основе экспериментально полученных адсорбционных кинетических кривых можно прямо оценить внутренние коэффициенты диффузии только в том случае, если они являются константами. В этом случае можно применять второй закон Фика. Однако это предположение в большинстве случаев недостаточно. В некоторых случаях необходимо определить зависимость коэффициентов диффузии от концентрации. До сих пор были опубликованы только плоскостные графические методы.

В этой статье и расчетах на основе подходящего итерационного метода для выбранных концентраций приводится зависимость коэффициента диффузии от сорбционных данных. Метод основывается на теории Кранка, которая применяется для современных сорбционных экспериментов.

One of the most important factors exerting influence upon the performance of any adsorption device appears to be the mass transfer rate. If the resistance of interface and of the adsorption on the active centres is negligible, only transport of molecules of adsorbate from the bulk liquid to the interface (external diffusion) and from the interface into the inside of particle (internal diffusion) has to be considered. For the description of the external diffusion only the rate equation

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$$\bar{r} = k_g(p - p_r), \quad (1)$$

is commonly used; on the other hand several mathematical models for the description of the internal diffusion can be used. The physically justified one is the 2nd Fick's law

$$\frac{\partial C}{\partial t} = \text{div}(D \text{ grad } C). \quad (2)$$

If the particle of a sorbent is isotropic (with no prevailing orientations of pores), the diffusion coefficient is a scalar.

Since, in general, the diffusion coefficient is concentration dependent, it is insufficient to know only its value at given conditions, but it is necessary to know the concentration dependence of the diffusion coefficient in the whole concentration interval. The aim of this paper was to develop the computer-suitable method for deducing diffusion coefficient—concentration dependence on the basis of results of the so-called “progressing sorption experiments” (in the subsequent experiments we move forward step by step in concentration, each new sorption process starting at the concentration where the previous one finished).

If the diffusion coefficient is constant and the particle has a simple geometrical shape (plane sheet, infinite cylinder, their intersections, or a sphere), there exists an analytical solution of eqn (2)

$$q = f(Fo). \quad (3)$$

For the actual forms of relation (3) for the geometries mentioned above see [2]. For each experimental point (t^j, q^j) it is possible to calculate the corresponding value of $Fo(q^j)$ by numerical solution of eqn (3) and hence of D_{ix}^j .

$$D_{ix}^j = l^2 \frac{Fo(q^j)}{t} \quad (4)$$

For $D = \text{constant}$, the whole kinetic curve is characterized by a single value of the diffusion coefficient D_{ex} calculated on the basis of the half-time values (*i.e.* time corresponding to $q = 0.5$), or from the initial gradient of relation $q = f(\sqrt{t})$ [1].

If D is not constant, there is no analytical solution of eqn (2) and the shape of the kinetic curve at given diffusion coefficient—concentration dependence can be obtained only by numerical integration of eqn (2). Therefore a direct computation of diffusion coefficient—concentration dependence is not possible and some iteration method has to be used. The values of the diffusion coefficients obtained from the values of the half-time or the initial gradient according to the equations valid for a constant diffusion coefficient are to be interpreted as mean values for the given concentration interval.

The main idea of the iterative method described in this paper is based on the method published by *Crank* [1] for “progressing sorption experiments” Its basical logical scheme is as follows:

1. For each concentration interval $\langle C_{k-1}, C_k \rangle$, the mean value of the diffusion coefficient $(\bar{D}_k)_{ex}$ is calculated in a suitable way from the experimental kinetic curve.

2. The first approximation of the relation

$$I(C) = \int_{C_0}^C D \, dC \quad (5)$$

for concentrations C_1, C_2, \dots is estimated by means of the equation

$$I_1(C_k) = \sum_{n=1}^k (\bar{D}_k)_{ex} (C_k - C_{k-1}). \quad (6)$$

3. The i -th approximation of the dependence of D on C is obtained by differentiation of the relation (5)

$$D_i(C) = \frac{dI_i(C)}{dC}. \quad (7)$$

4. The "theoretical" kinetic curves (8) are calculated by numerical integration of eqn (2) using concentration dependence $D_i(C)$ obtained in the previous step

$$q_{ki} = f_{ki}(t). \quad (8)$$

5. The mean diffusion coefficients for all intervals $(\bar{D}_k)_i$ are calculated in the same way as in step 1. If a satisfactory agreement between the values $(\bar{D}_k)_i$ and $(\bar{D}_k)_{ex}$ has been achieved, the computation process is finished. Otherwise we proceed as follows:

6. Relation is assembled

$$I_i = \varphi_i((\bar{D}_k)_i) \quad (9)$$

by means of which the next approximation of the relation $I(C)$ is estimated as

$$I_{i+1} = \varphi_i((\bar{D}_k)_{ex}) \quad (10)$$

and the calculation proceeds starting from step 3 (Fig. 1).

Crank [1] suggested to calculate $(\bar{D}_k)_{ex}$ from the half-time or initial gradient using

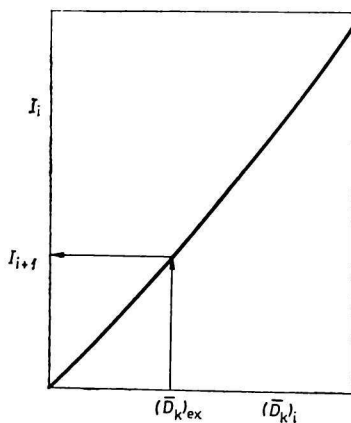


Fig. 1. Determination of the new approximation of the relation $I(C)$ according to point 6.

the formulas for constant diffusion coefficient and corresponding geometry. This way of estimation of $(\bar{D}_k)_{ex}$, however, does not profit from all information contained in the experimental kinetic curve. This is unfavourable mainly in the case of a very fast adsorption when there are only few experimental points on the kinetic curve. In this case it is impossible to estimate half-time or initial gradient with a sufficient accuracy and for estimation of $(\bar{D}_k)_{ex}$ the following procedure is recommended.

a) The value of D_{ex}^i is calculated according to eqn (3) and (4) for each experimental point.

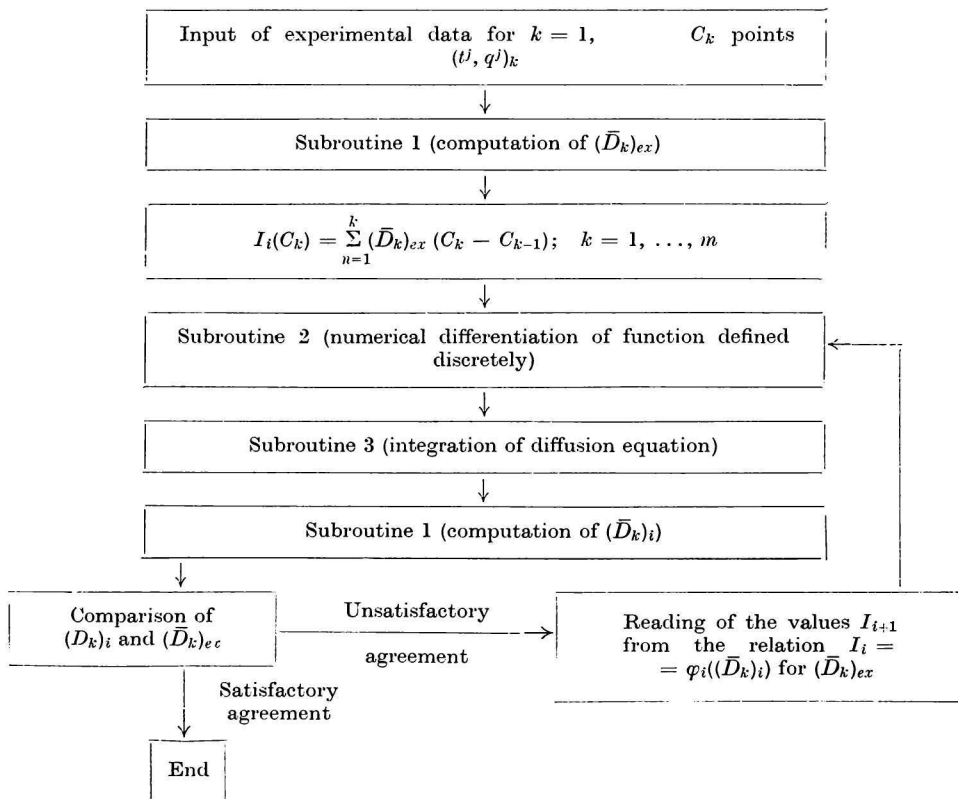
b) $(\bar{D}_k)_{ex}$ is evaluated as the integral mean of $D_{ex}(q)$ over the whole concentration interval

$$(\bar{D}_k)_{ex} = \frac{1}{\alpha_k - \beta_k} \int_{\alpha_k}^{\beta_k} D_{ex} dq. \quad (11)$$

The integration limits are chosen according to the distribution of experimental points along the kinetic curve.

Table 1

Flow chart of the program



Description of the program

Flow chart of the program is in Table 1. The program contains three subroutines:
 Subroutine 1: Computation of the mean value of diffusion coefficients from the kinetic curve.

Subroutine 2: Numerical differentiation of the discretely defined function.

Subroutine 3: Integration of diffusion equation (2).

This general scheme can be used for particles of any shape. For spherical particles the following scheme is valid.

Subroutine 1

The analytical solution of eqn (2) for constant diffusion coefficient can be expressed in the form of the infinite series

$$q = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-D n^2 \pi^2 t/l^2). \quad (12)$$

For each point (t^j, q^j) the corresponding value of D_{ex}^j is computed from (12) using Newton's method numerically. The mean diffusion coefficient for the corresponding kinetic curve in the k -th concentration interval is computed from eqn (11). The integration is performed using the trapesoid rule.

Subroutine 2

Since the measured values are influenced by experimental errors, differentiation is performed according to the method published by Lanczos [3], which makes it possible to eliminate the influence of random errors to some extent. The derivative at the point (x_i, y_i) is computed as the derivative of a parabola, which is computed from the points (x_{i-2}, y_{i-2}) , (x_{i-1}, y_{i-1}) , (x_i, y_i) , (x_{i+1}, y_{i+1}) , and (x_{i+2}, y_{i+2}) by the least-squares method.

Subroutine 3

The eqn (2) for spherical particles and spherically symmetric coordinate field has the form

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \left\{ \frac{\partial}{\partial r} \left(D(C) r^2 \frac{\partial C}{\partial r} \right) \right\}. \quad (13)$$

This partial differential equation was interpreted by the finite difference method.

Since an incorrect choice of time interval results in numerical instability of the computation process, the choice of its correct value is included in the subroutine 3. In the first case, the value selected was too high and when numerical instability appeared, computation was repeated with the half value.

The agreement of $(\bar{D}_k)_i$ and $(\bar{D}_k)_{ex}$ was considered to be satisfactory, if for at least $m(1 - \delta)$ values the inequality

$$\left| \frac{(\bar{D}_k)_i - (\bar{D}_k)_{ex}}{(\bar{D}_k)_{ex}} \right| < \varepsilon \quad (14)$$

was satisfied. The values δ and ε were chosen with respect to the accuracy of experimental data.

The values of I_{i+1} were estimated according to relation (10) by linear interpolation.

Symbols

C	concentration of adsorbate in adsorbent
D	diffusion coefficient
\bar{D}	mean value of diffusion coefficient
$Fo = \frac{D t}{l^2}$	Fourier number
I	value defined by eqn (5)
k_g	gas film mass-transport coefficient
l	characteristic linear dimension
	number of kinetic curves (concentration steps) during a progressing sorption experiment
p	partial pressure in the bulk of gas
p_f	partial pressure on the interface
q	relative amount adsorbed in time t
r	spherical coordinate
\bar{r}	mass transfer rate
t	time

Subscripts

	experimental value
	the value is related to the i -th iteration
j	the value is related to the j -th point of kinetic curve
k	the value is related to the k -th kinetic curve

References

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2. Crank, J., *The Mathematics of Diffusion*. Oxford University Press, 1964.
3. Lanczos, C., *Applied Analysis*. Prentice-Hall, Englewood Cliffs, N. Y., 1956.

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