EVALUATION OF THE DIFFUSION COEFFICIENT FROM EXPERIMENTAL DATA ON DYNAMIC SORPTION IN A CONTINUOUS STIRRED TANK REACTOR

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A method for the estimation of the diffusion coefficient from the sorption measurements in an isothermal continuous stirred tank reactors has been described. Experimental results have been presented and the diffusion coefficient has been evaluated.

A generally valid model of internal diffusion is the second Fick's law

$$\partial c/\partial t = \nabla . (D \nabla c) .$$

Its application, however, to adsorption units mandates knowledge of the diffusion coefficient D. Direct evaluation of the diffusion coefficient from sorption measurements is possible only with the assumption of its constancy (from the analytical solutions of diffusion equations). Unfortunately, as it is well known, the diffusion coefficient in sorption experiments is a function of concentration[2,3]. An iterative method to estimate the diffusion coefficient from kinetic measurements of sorption has been worked out by Crank[2]. Its use, though is limited to batch systems, small concentration changes, *etc.* In our previous work[1], an algorithm has been developed to estimate $D(c)$, possessing a broader applicability. This algorithm has been tested on numerous measurements both in batch and continuous reactors and it has turned out that the resultant $D(c)$ is independent of the experimental system. The function $D(c)$ was here expressed in the so-called nonparameteric form, *i.e.* in the form of a linear fractional function specified by values $D(c_i)$ in selected equidistant points spanning the investigated concentration interval.

The aim of this work is to express the diffusion coefficient $D(c)$ on the basis of a physical model to be derived below. Although the agreement between the experimental and theoretical amount adsorbed, as computed from the model, is less favourable compared to the mentioned algorithm[1], as a definite advantage of the model approach remains physical interpretability of its parameters and its simplicity.

THEORETICAL

Mathematical Model of Internal Diffusion

The density of diffusional flux of adsorbate within a sorbent particle is given by the first Fick's law

$$\bar{J} = -[D_1 \nabla(c - \varepsilon\varphi) + D_2 \nabla\varphi] . \tag{1}$$

If $\varepsilon\varphi \ll c$, Eq. (*1*) may be simplified to

$$\bar{J} = -[D_1 \nabla c + D_2 \nabla\varphi] . \tag{2}$$

Assuming local equilibrium within the particle, the relationship between concentrations c and φ (c is the mean concentration within the solid and the gas phase, φ is the concentration in the gas phase within the pores of the sorbent) is given by the adsorption isotherm $c = c(\varphi)$ and

$$\nabla\varphi = \nabla c \frac{\mathrm{d}\varphi}{\mathrm{d}c} . \tag{3}$$

The density of the diffusional flux may then be expressed in terms of a single gradient

$$\bar{J} = -D \,.\, \nabla c = -\left(D_1 + D_2 \frac{\mathrm{d}\varphi}{\mathrm{d}c}\right) . \nabla c , \tag{4}$$

where

$$D = D_1 + D_2 \frac{\mathrm{d}\varphi}{\mathrm{d}c} \tag{5}$$

and the second Fick's law (the model of internal diffusion) may be written in the form

$$\frac{\partial c}{\partial t} = \nabla . (D \nabla c) . \tag{6}$$

For spherical particles of the sorbent the last equation reduces to

$$\frac{\partial c(t, r)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D(c) \frac{\partial c(t, r)}{\partial r} \right] \tag{7}$$

with the initial and boundary conditions

$$\begin{aligned} &c(0, r) = 0\,, \\ &\frac{\partial c(t, 0)}{\partial r} = 0 \quad \text{for} \quad t > 0\,, \quad r = 0 \\ &c(t, a) = c^*(\varphi) \quad \text{for} \quad t > 0\,, \quad r = a\,. \end{aligned} \tag{8}$$

Assuming validity of the Langmuir adsorption isotherm in the form

$$c^*(\varphi) = \frac{A\,\varphi(t)}{1 + B\,\varphi(t)} \tag{9}$$

Eq. (5) yields

$$D(c) = D_1 + D_2 \frac{\mathrm{d}\varphi}{\mathrm{d}c} = D_1 + D_2 \frac{A}{(A - Bc)^2}\,. \tag{10}$$

The function $D(c)$ makes use of four parameters, namely two constants of the adsorption isotherm, which can be evaluated from sorption equilibria, and two coefficients D_1, D_2, which shall be determined from kinetic measurements or the dynamic of sorption.

Method of Evaluation of D_1, D_2

The purpose of this method is to assess the values of the coefficients D_1, D_2, minimizing the criterion of agreement between the experimental and calculated amounts. For the criterion of agreement we took the following objective function

$$Y(D) = \int_0^{t^*} [M_D(t) - M(t)]^2\,\mathrm{d}t\,, \tag{11}$$

where $M(t)$ is the experimental and $M_D(t)$ computed (for given D_1, D_2) adsorbed amount per particle. For spherical particles of the sorbent we may write

$$M(D) = 4\pi \int_0^a r^2 c(t, r)\,\mathrm{d}r\,. \tag{12}$$

The problem of determination of D_1 and D_2 leads thus to one of minimizing the objective function $Y(D)$. In order to locate this minimum the simplex method has been employed[4].

In the calculation of the function $Y(D)$ the procedure was as follows:

1) For preselected values D_1, D_2, Eq, (*7*) was solved numerically using the initial and boundary conditions (*8*) by the predictor-corrector[1] method. The equations for the predictor

$$\frac{\bar{c} - c^{\mathrm{j}}}{\Delta t} - \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \, D(c^{\mathrm{j}}) \frac{\partial}{\partial r} \left(\frac{\bar{c} + c^{\mathrm{j}}}{2} \right) \right] = 0 \quad \text{for} \quad r \in (0, a\rangle \tag{13}$$

$$\frac{\bar{c} - c^{\mathrm{j}}}{\Delta t} - 3D(c^{\mathrm{j}}) \frac{\partial^2}{\partial r^2} \left(\frac{\bar{c} + c^{\mathrm{j}}}{2} \right) = 0 \quad \text{for} \quad r = 0 \tag{14}$$

and for the corrector

$$\frac{c^{\mathrm{j}+1} - c^{\mathrm{j}}}{\Delta t} - \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \, D \left(\frac{c^{\mathrm{j}} + \bar{c}}{2} \right) \frac{\partial}{\partial r} \left(\frac{c^{\mathrm{j}} + \bar{c}}{2} \right) \right] = 0 \quad \text{for} \quad r \in (0, a\rangle \tag{15}$$

$$\frac{c^{\mathrm{j}+1} - c^{\mathrm{j}}}{\Delta t} - 3D \left(\frac{c^{\mathrm{j}} + \bar{c}}{2} \right) \frac{\partial^2}{\partial r^2} \left(\frac{c^{\mathrm{j}} + \bar{c}}{2} \right) = 0 \quad \text{for} \quad r = 0\,, \tag{16}$$

where j designated the time increment and $\bar{c}$ is an auxiliary function (predictor). Eq (*13*)–(*16*) have been rewritten into the finite-difference form.

2) Based on the computed concentration field, numerical integration of Eq. (*12*) was used to compute the amount adsorbed on a single particle, $M_{\mathrm{D}}(t)$ for $t \in \langle 0, t^* \rangle$.

3) Numerical integration of Eq. (*11*) yielded the value of $Y(D)$.

RESULTS AND DISCUSSION

The dynamics of sorption was examined in a laboratory isothermal continuous stirred tank reactor, with the sorbent being placed in a rotating basket, described in one of our earlier papers[5]. The speed of revolution of the rotor was chosen so as to equalize the gas phase concentration in the whole reactor (and hence to achieve identical distribution of the concentration $c(t, r)$ in all sorbent particles) and to permit one to neglect external diffusion. The volume of the gas phase was 60 cm^3; the concentration of the adsorbate in the flowing inert gas (nitrogen) at the reactor exit $\varphi(t)$ was checked throughout the experiment by the chromatographic method (the method of sampling has been described in ref.[5]). The overall amount adsorbed was determined from the mass balance; the amount adsorbed per particle, $M(t)$, was obtained by dividing the overall quantity by the number of particles present in the reactor.

Fig. 1 and 2 show graphically the courses of concentrations $\varphi(t)$ and the adsorbed amount, $A(t)$ (g/100 g), for the system n-heptane–molecular sieve CALSIT 5A at the temperature 50 and 120°C. The adsorption isotherms, measured in the de-

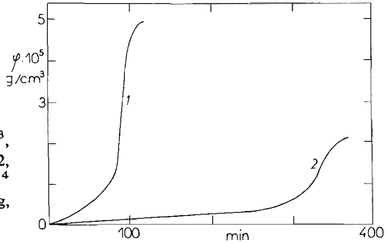

FIG. 1

Course of Concentration $\varphi(t)$

Measured at *2* ($\varphi_0 = 0{\cdot}214 \,.\, 10^{-4}$ g/cm³, $\dot{V} = 21{\cdot}75$ cm³/min, $m = 1{\cdot}2842$ g, $N = 92$, $a = 0{\cdot}145$ cm) and *1* ($\varphi_0 = 0{\cdot}497 \,.\, 10^{-4}$ g/cm³, $\dot{V} = 26{\cdot}46$ cm³/min, $m = 1{\cdot}2521$ g, $N = 89$, $a = 0{\cdot}145$ cm).

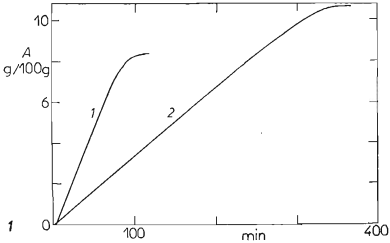

FIG. 2

Course of Adsorbed Amount $A(t)$ at *2* and *1*

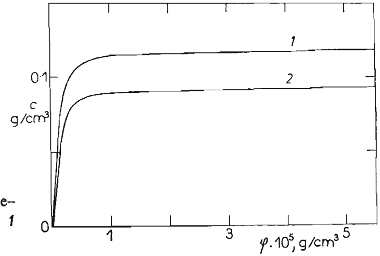

FIG. 3

Adsorption Isotherms for the n-Heptane–-Molecular Sieve CALSIT 5A System at *1* and *2*

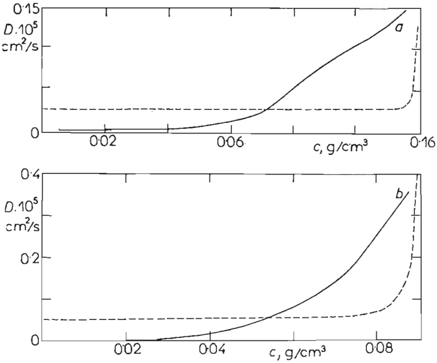

FIG. 4

Course of $D(c)$

——— Algorithm from ref.[1], ---- this work *a*) 50°C, *b*) 120°C.

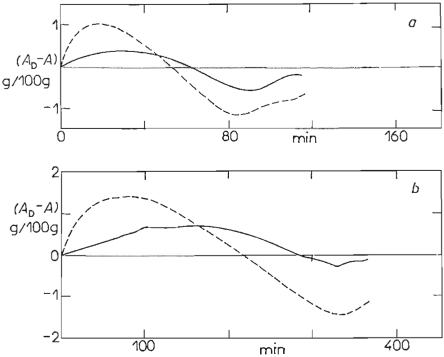

FIG. 5

The Deviation of the Experimental and Computed Adsorbed Amount

——— Algorithm from ref.[1], ---- This Work *a*) 120°C, *b*) 50°C.

scribed CSTR, are shown in Fig. 3. The values of the constants of the adsorption isotherm (*9*) (concentrations c and φ in (g/cm^3) units) are:

$$50°\text{C}: \quad A = 0{\cdot}2222 \,.\, 10^6\,, \quad B = 0{\cdot}1861 \,.\, 10^7$$
$$120°\text{C}: \quad A = 0{\cdot}1509 \,.\, 10^6\,, \quad B = 0{\cdot}1616 \,.\, 10^7\,,$$

The values of the coefficients D_1 and D_2 (cm^2/s) found by the simplex method are:

$$50°\text{C}: \quad D_1 = 0{\cdot}2859 \,.\, 10^{-6}\,, \quad D_2 = 0{\cdot}5798 \,.\, 10^{-5}$$
$$120°\text{C}: \quad D_1 = 0{\cdot}5088 \,.\, 10^{-6}\,, \quad D_2 = 0{\cdot}6035 \,.\, 10^{-3}\,.$$

The dependences $D(c)$ are shown in Fig. 4 showing also corresponding dependences $D(c)$ obtained by the algorithm described in ref.[1]. Fig. 5 shows the differences of the experimental and theoretical adsorbed amounts for the two methods. Numerical values of the objective function achieved with the aid of the presented method are:

$$50°\text{C}: \quad Y(D) = 8{\cdot}570 \,.\, 10^{-6}\,\text{g}^2\,\text{min}$$
$$120°\text{C}: \quad Y(D) = 1{\cdot}686 \,.\, 10^{-6}\,\text{g}^2\,\text{min}$$

while the algorithm from ref.[1] yielded following values of the objective function:

$$50°\text{C}: \quad Y(D) = 0{\cdot}281 \,.\, 10^{-6}\,\text{g}^2\,\text{min}$$
$$120°\text{C}: \quad Y(D) = 0{\cdot}259 \,.\, 10^{-6}\,\text{g}^2\,\text{min}\,.$$

It is apparent that for the presented method the achieved agreement between the theoretical and experimental amounts adsorbed is inferior to that provided by the algorithm from ref.[1]. The agreement has deteriorated especially for the 50°C measurements, which can be attributed to the excessively steep slope of the adsorption isotherm. The presented method as such, however, is substantially simpler, and and its parameters possess a definite physical meaning. In addition, the $D(c)$ curves are obtained in a simple parametric form well suited for further calculations. An appropriate expression of the temperature dependence of the parameters D_1 and D_2 could generalize this method to one yielding the concentration and temperature dependence of the diffusion coefficient.

LIST OF SYMBOLS

A	constant of Langmuir's isotherm
$A(t)$	experimental adsorbed amount (g/100 g)
$A_D(t)$	adsorbed amount for given $D(c)$

a	particle radius
B	constant of Langmuir's isotherm
c	concentration of adsorbate within particle
c^*	equilibrium concentration of adsorbate on the surface of the particle
D	diffusion coefficient
J	density of diffusional flux
M	experimental adsorbed amount per particles
M_{D}	adsorbed amount per particle for given $D(c)$
m	weight of sorbent in reactor
N	number of sorbent particles in reactor
r	radial coordinate
t	time
t^*	duration of experiment
$\dot{V}$	volume feed rate
$Y(D)$	objective function
φ	concentration of adsorbate in gas phase in reactor
φ_0	concentration of adsorbate in gas phase at inlet
ε	particle porosity

REFERENCES

1. Brunovská A., Brunovský P., Ilavský J.: Chem. Eng. Sci. *32*, 717 (1977).
2. Crank J.: *The Mathematics of Diffusion.* Oxford University Press, London 1964.
3. Garg D. R., Ruthven D. M.: Chem. Eng. Sci. *27*, 417 (1972).
4. Parkinson J. M., Hutchinson D.: *Proceedings of the Conference Numerical Methods for Non-Linear Optimilization*, p. 99. Academic Press, London 1972.
5. Ilavský J., Longauer J.: Chem. Zvesti *32*, 145 (1978).

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