

Kinetics of sorption in a stirred semiflow adsorber*

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In this paper a method for evaluating the kinetic data obtained in a stirred semiflow adsorber is proposed. It is shown how it is possible on the basis of an analysis of the exit flow to calculate the time variations in the amount adsorbed, concentration in the gaseous phase in the adsorber, and diffusion coefficient. These data may be used for the calculation of sorption devices of this type as well as the characterization of catalyysts.

В статье описывается способ расчета кинетических данных, полученных в полупроточном перемешивающемся адсорбере. На основе анализа выходного тока приводится метод расчета адсорбции со временем, концентрации газообразной фазы адсорбера и диффузионного коэффициента. Полученные результаты можно применить при расчете сорбционных аппаратур этого вида, а также при оценке катализаторов.

There are many mathematical models in literature which describe the kinetics of sorption in different types of sorption devices [1–10]. The major part of these papers is concerned with the problems of the kinetics of sorption in fixed bed adsorbers. In this study we payed attention to an isothermal stirred semiflow adsorber with the adsorbent deposited on stirrer blades. The number of revolutions of the stirrer was chosen in such a way that the following conditions were fulfilled:

1. The concentration of adsorbate on different particles of adsorbent at a certain time is equal.

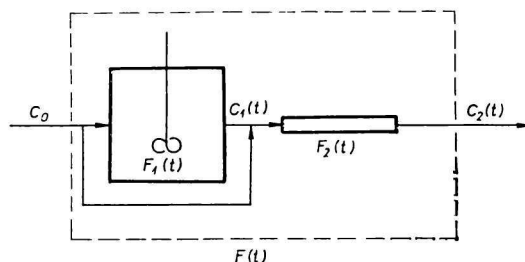
2. The gaseous phase passing through the adsorber is ideally mixed [11]. Its composition is uniform in the whole volume of adsorber and is identical with the composition of exit flow.

In order to describe the processes in the above adsorber we must know the concentration of adsorbate in the gaseous phase inside the adsorber as well as the amount adsorbed at a given time.

In order to determine the concentration of adsorbate in the gaseous phase inside the adsorber including the exit, $C_1(t)$ at the time t , we started from the scheme shown in Fig. 1.

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Fig. 1. Block diagram of the adsorber with analyzer.



The adsorbate of the concentration C_0 enters the adsorber in a stream of inert gas. Its concentration at the exit from the adsorber is $C_1(t)$ while this concentration is $C_2(t)$ at the entrance into analyzer (gas chromatograph). Between the adsorber and analyzer there is a dosing tap and capillary which are characterized by a measured residence time distribution function $F_2(t)$ (Fig. 2). At the beginning of measurements the adsorber is filled with activated adsorbent and inert gas while the adsorbate of the concentration C_0 in a stream of inert gas flows through the lower branch outside the adsorber and enters the analyzer through a dosing tap and the capillary. At the time $t = 0$ the lower branch is closed and the adsorbate of the concentration C_0 enters the adsorber.

On the basis of the definition of the residence time distribution function $F(t)$ [11] the relation between $C_1(t)$ and $C_2(t)$ can be written

$$C_0 - C_2(t) = \int_0^t (C_0 - C_1(s)) F_2'(t - s) ds, \quad (1)$$

where $(C_0 - C_2(t))$ is a convolution of $F_2'(t)$ and $(C_0 - C_1(t))$. For the Laplace images of these functions it holds

$$L(C_0 - C_2(t)) = L F_2'(t) L(C_0 - C_1(t)). \quad (2)$$

By introducing the relative concentrations $c(t) = C(t)/C_0$ we obtain

$$L(1 - c_2(t)) = L F_2'(t) L(1 - c_1(t)). \quad (3)$$

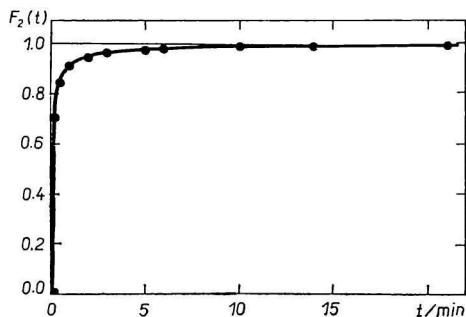


Fig. 2. Residence time distribution function $F_2(t)$.

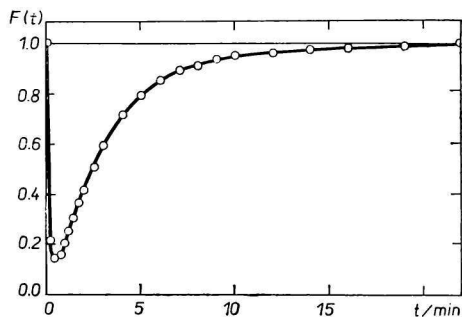


Fig. 3. Residence time distribution function $F(t)$.

At the time $t = 0$ the concentration at the entrance into the analyzer is $c_2(0) = 1$ and at the exit from the adsorber it is $c_1(0) = 0$.

The concentration $c_1(t)$ is obtained by solving the eqn (3)

$$c_1(t) = \frac{1}{p} + \frac{L c_2(t) - \frac{1}{p}}{L F_2'(t)} \quad (4)$$

Since the eqn (4) is to be subjected to a reverse transformation, the experimentally determined function $F_2(t)$ was smoothed by replacing it by an exponential function

$$F_2(t) = 1 - 0.100 e^{-0.351t} - 0.900 e^{-4.533t}, \quad (5)$$

i.e.

$$F_2'(t) = 0.0351 e^{-0.351t} + 4.0797 e^{-4.533t} \quad (6)$$

and hence

$$\begin{aligned} L c_1(t) &= \frac{1}{p} + \frac{L c_2(t) - \frac{1}{p}}{\frac{0.0351}{p + 0.351} + \frac{4.0797}{p + 4.533}} = \\ &= \frac{1}{p} + 0.243 L c_2(t) \frac{p^2}{p + 0.3867} + 1.187 L c_2(t) \frac{p}{p + 0.3867} + \\ &+ 0.3867 L c_2(t) \frac{1}{p + 0.3867} - \frac{0.243 p^2 + 4.884 p + 1.591}{p + 0.3867} \end{aligned} \quad (7)$$

By reverse transformation of eqn (7) we obtain the concentration $c_1(t)$ at the exit from the adsorber

$$\begin{aligned} c_1(t) &= 1.093 c_2(t) + 0.243 c_2'(t) - 0.093 e^{-0.3867t} - \\ &- 0.0360 \int_0^t e^{-0.3867(t-s)} c_2(s) ds. \end{aligned} \quad (8)$$

Equation (8) was solved numerically using a digital computer. The value of the derivative of $c_2'(t)$ was determined by the *Lanczos* method [12].

The amount adsorbed $A(t)$ at the time t is to be obtained by numerical solution of the equation

$$A(t) = \int_0^t (\dot{G}_0(t) - \dot{G}(t)) dt, \quad (9)$$

where

$$\dot{G}(t) = \frac{C(t) \dot{Q}}{q - C(t)}. \quad (10)$$

$\dot{G}(t)$ is the mass flow of adsorbate at the exit from the adsorber at the time t and

$\dot{G}_0(t)$ is the mass flow of adsorbate at the exit from the adsorber at the time t supposing no adsorption takes place. The values of $\dot{G}_0(t)$ may be obtained from the measured residence time distribution in the system $F(t)$ (Fig. 3). The symbol ρ stands for the density of gas in the adsorber and \dot{Q} for the mass flow of inert gas.

Under isothermal conditions, the diffusion in homogeneous spherical particles of adsorbent is governed by the diffusion equation [13]

$$\frac{\partial C(t, r)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ D(C) r^2 \frac{\partial C(t, r)}{\partial r} \right\}, \quad (11)$$

where $C(t, r)$ is the concentration of adsorbate at time t in a spherical particle of adsorbent at a distance r from the centre of the particle and $D(C)$ is the diffusion coefficient which is a function of concentration. This equation was used for the determination of the values of diffusion coefficients. The calculation procedure was as follows:

1. For a given diffusion coefficient the concentration in individual points of the particle of adsorbent was determined by numerical solution of eqn (11) (by the method of nets).

2. On the basis of the concentration field obtained in this way the total amount adsorbed at the time t , $A(t)$ was calculated by means of the equation

$$A(t) = 4\pi \int_0^a C(t, r) r^2 dr, \quad (12)$$

where a is the radius of the particle.

3. The calculated amount adsorbed was compared with the experimentally determined value. If no sufficient agreement was attained, a new value of $D(C)$ was chosen and the operation was repeated.

For the solution of the diffusion equation the following initial and boundary conditions were used

$$C(0, r) = 0, \quad 0 < r < a, \quad t = 0, \quad (13)$$

$$C(t, a) = \varphi(t), \quad r = a, \quad t > 0, \quad (14)$$

i.e. at the beginning of the measurement, there was a zero concentration inside the particle while the surface concentration $\varphi(t)$ was in equilibrium with the concentration in the gaseous phase $C_1(t)$. The concentration $\varphi(t)$ was to be determined from the adsorption isotherm.

Experimental

The kinetic sorption data were measured using an isothermal stirred adsorber presented in Fig. 4. The isothermal regime at temperatures ranging from 40 to 410°C was ensured accurate to 0.4% by means of an automatic control system. The particles of adsorbent (molecular sieve Calsit 5) were placed in the rotating part of the adsorber. The hydrodynamic regime in the adsorber was simulated by a convenient choice of the stirrer revolutions.

The concentration of adsorbate (*n*-heptane) in the stream of inert gas (nitrogen of electric bulb industry deprived of humidity and oxygen) was determined by means

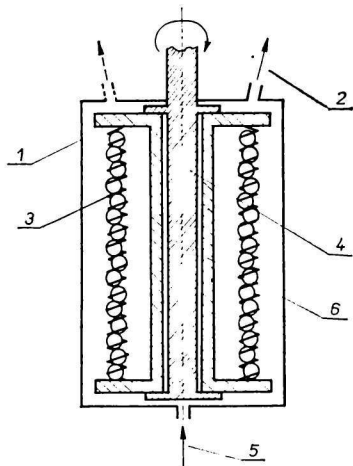


Fig. 4. Diagram of the adsorber and position of sample.

1. Thermostated jacket of the adsorber (inside diameter 40 mm, height 60 mm); 2. outlet flow (two possible ways); 3. bed of the sample; 4. axis of the rotor of adsorber; 5. inlet flow of gas; 6. supporting basket of the bed of sample.

of a gas chromatograph CHROM 3 with the residence time in the column kept at the bottom limit. The sample was dosed into the chromatograph by means of a graduated gauge (1 ml) and a 6-way dosing cock with two optional positions. The degree of purity of the *n*-heptane used was higher than 99.5%. After dosing the analyzed gas from the graduated gauge the instrument immediately performs the analysis on a ionization flame detector and an instantaneous deflection of recording pen of the recorder appears. The magnitude of the deflection recorded is directly proportional to the partial pressure of hydrocarbon in the gaseous phase which is determined by means of a calibration curve.

For the measurement of the residence time distribution function the particles of adsorbent were replaced by glass spheres of an equal size. At the time $t = 0$ a step change of the concentration of *n*-heptane at the entrance was made ($C(t) = 0$ for $t < 0$ and $C(t) = C_0$ for $t > 0$) and the exit concentration $C_2(t)$ was investigated as a function of time. Then it holds

$$F(t) = \frac{C_2(t)}{C_0} \quad (15)$$

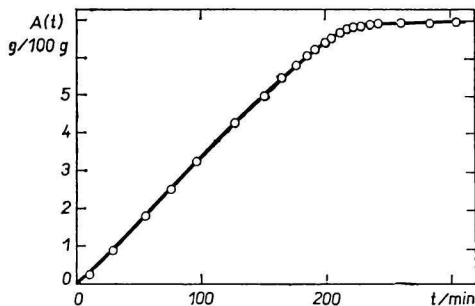


Fig. 5. Amount adsorbed as a function of time.

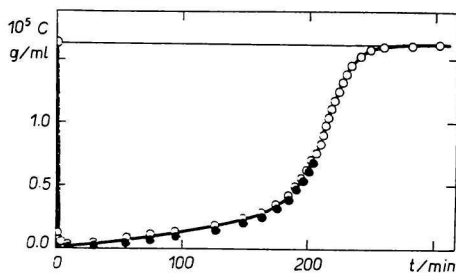


Fig. 6. Concentrations $C_1(t)$ and $C_2(t)$ as function of time.
● $C_1(t)$; ○ $C_2(t)$.

For the measurement of the function $F_2(t)$ the section between the adsorber and analyzer was filled with an inert gas and at the time $t = 0$ *n*-heptane was introduced through the lower branch (Fig. 1) in a constant concentration C_0 . The function $F_2(t)$ was calculated from eqn (15).

Since an ideal mixing was assumed in the calculation, it was necessary to choose high revolutions of the stirrer (420 rev./min). The residence time distribution function $F(t)$ measured at these revolutions was confronted with the residence time contribution obtained by replacing $F_1(t)$ by the residence time distribution function of an ideally mixed system [11]. For these revolutions the agreement was within experimental error.

These sorption measurements as well as the measurements of the distribution of residence time were carried out at 150°C, the concentration of *n*-heptane at the entrance into the adsorber was $C_0 = 1.62 \times 10^{-5}$ g ml⁻¹ (partial pressure 569.2 Pa), the weight of the sample of the molecular sieve after activation was 1.2934 g and the flow of inert gas was 29.1 ml/min. The amount adsorbed $A(t)$ as a function of time obtained by numerical solution of eqn (9) is shown in Fig. 5. The concentrations of the gaseous phase measured by the analyzer, $C_2(t)$, and the concentrations at the exit from the adsorber, $C_1(t)$, as functions of time were obtained by numerical solution of eqn (8) and are presented in Fig. 6. The adsorption isotherm measured using the above stirred adsorber, which is necessary for the determination of the concentration $\varphi(t)$, is illustrated in Fig. 7. The dependence of diffusion coefficient on the amount adsorbed is shown in Fig. 8.

Discussion

In this paper a method for measuring the sorption kinetics in a stirred semiflow adsorber and evaluating the respective experimental data is presented. The results may be used for both the theoretical study of adsorption and the design of industrial adsorbers.

The dependence of the diffusion coefficient on the amount adsorbed (Fig. 8) shows that at the beginning the value of diffusion coefficient increases; after achieving a maximum value it decreases and later it starts to rise substantially. (The high values of diffusion coefficient in this region correspond to the equilibrium adsorption.) The physical sense of the maximum may be attributed to the presence of different active centres.

The above course indicates a possibility of using this method in the characterization of active centres of adsorbents and catalysts. This study will be followed on.

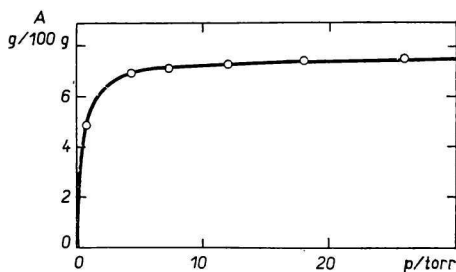


Fig. 7. Adsorption isotherm of *n*-heptane for molecular sieve Calsit 5 at 150°C.

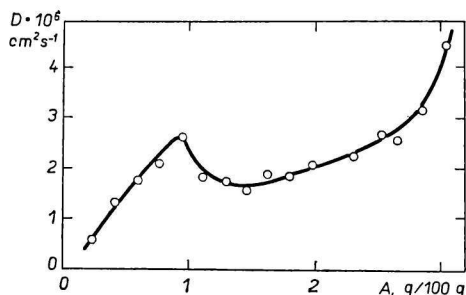


Fig. 8. Diffusion coefficient as a function of the amount adsorbed.

Symbols

A	amount adsorbed
a	radii of a spherical particle of adsorbent
C	concentration
c	relative concentration
D	diffusion coefficient
$F(t)$	residence time distribution function
\dot{G}	mass flow of adsorbate
\dot{Q}	mass flow of inert gas
r	radial coordinate
s	integration variable
t	time
$L f(t)$	Laplace image of the function $f(t)$
φ	concentration on the surface of adsorbent
ρ	density of gas in adsorber

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