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A STEP-BY-STEP METHOD FOR THE CALCULATION OF THE CONCENTRATION DEPENDENCE OF THE DIFFUSION COEFFICIENT FROM A SINGLE (DE)SORPTION EXPERIMENT

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NOMENCLATURE

a,	activity of the sorbent;
D,	diffusion coefficient [m^2/s];
J,	mass flux [kg/m^2 s];
k_c,	continuous phase mass-transfer coefficient [m/s];
m,	mass concentration [kg/m^3];
n,	number of intervals;
t,	time [s];
z,	distance coordinate [m];
Δt,	time interval [s];
ρ_{bulk},	mass concentration of sorbent in the bulk of the continuous phase [kg/m^3];
ρ^*_{pure},	mass concentration of sorbent in the continuous phase in equilibrium with pure sorbent at the temperature of the dispersed phase [kg/m^3].

Subscripts

i,	at the interface between dispersed and continuous phase;
cr,	at the critical point;
0, 1, 2, 3,	indicate limits of concentration intervals.

INTRODUCTION

THE CONCENTRATION dependence of a diffusion coefficient can be obtained from a number of successive experiments at different concentration levels [1] or by interpretation of a single (de)sorption experiment. Some methods of the latter type require the assumption of a certain functional relation between diffusivity and concentration [2, 3]. Duda and Vrentas [4] developed a method in which such an assumption is not necessary. It makes use of an approximate solution of the diffusion equation for constant surface concentration. The present method which has been described by Schoeber [5] deals with diffusion with variable surface concentration. It shows some similarity to Prager's method [6] for the interpretation of successive sorption experiments.

APPROACH

In a (de)sorption experiment the surface flux is measured as a function of time. The surface concentration in the dispersed phase is calculated from the equation describing the sorption flux in the continuous phase:

$$J = k_c(a_i\rho^*_{\text{pure}} - \rho_{\text{bulk}}). \tag{1}$$

All variables in this equation can be measured experimentally except a_i, which can therefore be calculated from this equation. The sorption isotherm, i.e. the relation between the surface concentration m_i and the surface activity a_i, will then reveal the value of m_i.

In the present method we adopt a step-function approximation to the concentration dependence of the diffusion coefficient. The diffusion coefficient in a concentration interval $m_{j-1} > m > m_j$ is assumed to be constant and to be the value of D_j.

Successive concentration profiles during a desorption process, starting at a homogeneous initial concentration m_0, are drawn schematically in Fig. 1. In this example the system does not shrink upon desorption. After time t_1 the surface concentration equals m_1. By application of a single parameter estimation to the solution of the diffusion equation the diffusivity D_1 can be calculated from the experimental data. At time t_2 the surface concentration has reached m_2. Over the interval $m_1 < m < m_2$ the corresponding value of the diffusion coefficient, D_2, can now be calculated. In this calcu-

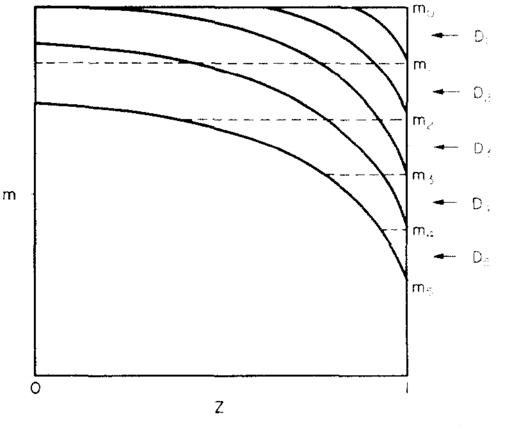

FIG. 1. Schematic representation of the change in concentration profile during a desorption process.

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lation of D_2 the known diffusivity value D_1 at concentrations between $m_0 > m > m_1$ is used. Once the diffusivities D_1 and D_2 are known, they are applied in the appropriate concentration intervals and D_3 can be calculated from the conditions at time t_3. In this way successive values of the diffusivity are obtained. The actual concentration dependence of the diffusion coefficient is approximated closely by taking sufficiently small concentration intervals.

Implementation of the calculation method is relatively easy when the diffusion equation is solved by a finite difference method. For the solution of the diffusion equation with known concentration dependence of the diffusivity the equation is discretized into a difference equation. The space parameter z is then divided into a number of intervals (n), which results into $n+1$ "grid points". Initially, the concentration at every point is known from the initial condition of the diffusion equation. By application of the difference equation, $n-1$ relations are found, which we use for the calculation of the concentration at every grid point after some time Δt. Together with two relations which follow from the two boundary conditions the concentration at the new value of t can be calculated by solving the complete set of $n+1$ equations with $n+1$ unknown concentrations. By taking small steps Δt the sorption process can be calculated.

In a similar way we calculate the concentration dependence of the diffusion coefficient from a (de)sorption experiment. Again the initial condition gives the concentration at $t = 0$ at every grid point. Again $n-1$ relations are found by application of the difference equation and 2 relations are obtained from the boundary conditions. However, only n concentrations at time t_1 are unknown since the surface concentration has been measured experimentally. Therefore, the parameter D_1 can be calculated by solving the complete set of $n+1$ equations with n unknown concentrations and one unknown diffusion coefficient. In the next step again $n+1$ relations follow from the difference equation with boundary conditions. Now the parameter D_2 can be solved. In this calculation the diffusivity D_1 is used in the concentration interval $m_0 > m > m_1$. In this way the whole concentration dependence of the diffusion coefficient can be calculated by moving step-by-step through the sorption history.

DISCUSSION

The present method has been applied successfully to a desorption curve which had been obtained by simulating the drying of a slab on a digital computer. The points in Fig. 2 have been calculated according to this method and are in good agreement with the concentration dependence of the diffusivity as used in the simulation of the desorption curve (solid line). This result shows that the method can be applied successfully if a sufficiently accurate (de)sorption curve is available.

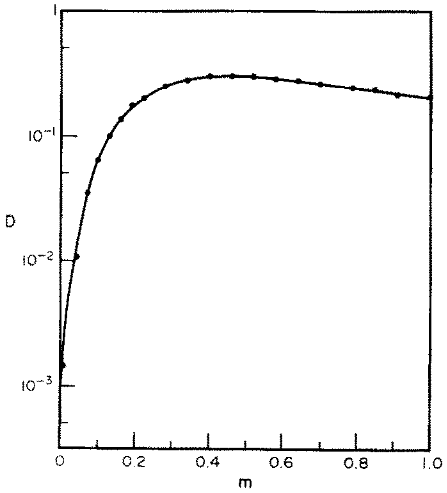

FIG. 2. Concentration dependence of the diffusion coefficient as used for testing the present method. The solid line represents the dependence used in the simulation. Points indicate values of the diffusion coefficient calculated from the simulated desorption curve by the present method.

However, the method is rather sensitive to inaccuracies in the measurements. Experimental noise interfering with the relation between surface concentration and time may have pronounced influence on the concentration dependence of the diffusion coefficient calculated in this way. The instability can be illustrated as follows. If D_1 is estimated too low, this must be compensated by D_2, which will therefore be estimated too high: D in relation to m tends to oscillate. This oscillation can effectively be suppressed by smoothing $D(m)$ during the calculation procedure. However, somewhat larger errors in the experimental value of $m_i(t)$ may cause serious problems. For instance, an increase of m_i with increasing time is "impossible" in a desorption process and might even result in a negative value of the local diffusion coefficient. Therefore, the input curve $m_i(t)$ also has to be smoothed.

Another aspect that needs attention stems from the fact that for highly concentration dependent diffusion coefficients the surface concentration hardly influences the sorption rate, unless the average concentration is close to the surface concentration. To ensure that this latter condition is satisfied during the experiment, the mass-transfer coefficient in the continuous phase must be such, that the concentration profile in the body remains rather flat. On the other hand, the sensitivity of the process to the value of the diffusion coefficient inside the body becomes too small if mass transfer is dominated by continuous phase mass transfer. For highly concentration dependent diffusivities a constant value of the gas phase mass transfer coefficient can never fulfil both requirements during the complete (de)sorption history. In such cases only part of the (de)sorption curve can be used or the mass-transfer coefficient in the continuous phase has to be varied during the process.

A third difficulty that might be encountered concerns the determination of the surface concentration m_i. If in a certain concentration interval the activity a varies only slightly with varying concentration ($da/dm \ll 1$), a small experimental error in a_i will cause a considerable error in m_i. In drying, for instance, the water activity is often approximately constant with varying concentration, if $m_i > m_{cr}$. Therefore, the present method can be applied only to experiments in which the concentration is below m_{cr}.

The method has not yet been tested on an experimentally determined (de)sorption history.

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