

A Simple Procedure for Estimating the Diffusion Coefficient from Sorptive Experiments in the Infinite Bath

The sorption kinetics of penetrants (gas, vapor, dye) in an infinite polymeric cylinder with radius r (for example, the fiber) may be described by the Hill infinite series¹ as

$$R_t = \frac{M_t}{M_\infty} = 1 - \sum_{i=1}^{\infty} \frac{4}{q_i^2} \exp(-q_i^2 T) \quad (1)$$

where R_t is the relative amount of penetrant; M_t and M_∞ are the amounts of the penetrant in the fiber at time t and equilibrium ($t \rightarrow \infty$), respectively; $T (= Dt/r^2)$ is the dimensionless time; D is the diffusion coefficient; and q_i is the i th positive root of the Bessel function of first kind and order zero.

Provided that concentration of penetrant on the fiber surface (infinite bath) and D are kept constant, eq. (1) can be derived from Fick's second law of diffusion.

From the experimental data $(M_t, t)_{i=1 \dots n}$, it is necessary to estimate the diffusion coefficient D (generally also the equilibrium amount of penetrant M_∞). This is a rather complicated problem which is usually solved by means of nonlinear regression (after approximation of infinite series by several members is accomplished) with suitable criteria. In most cases the least-squares criterion is applied.²

A considerable simplification of the calculations is obtained by using the method of statistical moments.² Zikánová and Kočičík³ state that the first statistical moment M_1 of the kinetic curve (i.e., the dependence R_t versus t) may be expressed by the relationship

$$M_1 = \int_0^{\infty} t \frac{dR_t}{dt} dt = \int_0^{\infty} (1 - R_t) dt \quad (2)$$

Substitution of eq. (1) into eq. (2) gives the well-known expression

$$M_1 = \frac{r^2}{8D} \quad (3)$$

From eq. (2) it follows that M_1 is the area over the sorption curve confined by the line $R_t = 1$. By applying the numeric integration, it is possible to determine M_1 and then from eq. (3) the diffusion coefficient D .

However, there is a more simple method available to assess the first statistical moments M_1 by a suitable approximate function. In a number of works⁴⁻⁶ it has been verified that eq. (1) may successfully be approximated by simple kinetic equation:

$$R_t = \sqrt{1 - \exp(-Kt)} \quad (4)$$

where K is the apparent rate constant. Validity of this equation can be proved by plotting $-\ln(1 - R_t^2)$ vs. t_i for all experimental data. As a result, a straight-line is obtained passing through the origin. A number of simple methods for estimating the parameters K and M_∞ from eq. (4) are given in the literature⁶ (all for cases where C_∞ is not known beforehand).

Substituting from eq. (4) into eq. (2) leads to eq. (5):

$$M_1^* = 2(1 - \ln 2)K^{-1} \quad (5)$$

where M_1^* is the first statistical moment of the kinetic curve expressed by eq. (4).

In comparing the first moments M_1 with M_1^* , the following relationship results:

$$D = \frac{Kr^2}{16(1 - \ln 2)} = 0.2037Kr^2 \quad (6)$$

The above equation defines the relation between the constant K and the diffusion coefficient D .

By combining eq. (6) with eq. (4) and rearranging, the following equation may be derived:

$$T_i^* = -0.2037 \ln[1 - R_t^2] \quad (7)$$

Comparison of the values T_i determined from eq. (1) (40 members of infinite series) with the values

T_i^* computed from eq. (7) in the range $0.1 \leq R_t \leq 0.98$ gave relative errors $100(T_i - T_i^*)/T_i^*$ less than 5%. This demonstrates the applicability of eq. (4) for approximation of eq. (1). In estimating the diffusion coefficient D from experimental data, it is possible, for a given M_∞ , to determine the constant K as a slope of the dependence $-\ln(1 - R_t^2)$ vs. t_i and, subsequently, from eq. (6) the value D . In case M_∞ is not known, it is necessary to seek the parameters M_∞ and K by fitting experimental data using eq. (4).

Compared with other methods for approximate calculation of D in use (i.e., from the initial slope of the dependence R_t vs. \sqrt{t}), the one suggested here has the following merits: (1) it takes into account the whole course of sorption (all experimental points), and (2) it eliminates random errors of measured values $M_{t_i}(R_{t_i})$. Approximate eq. (4) was applied to determine the first statistical moment from experimental points (the area over sorption curve confined by the line $R_t = 1$). Equation (3) is not approximate. This means that resulting D values obtained by this method are very close to those computed from eq. (1) by nonlinear curve fitting.

To summarize, a very simple method for estimating the diffusion coefficient D based on eqs. (4) and (6) has been derived. This procedure provides very accurate estimates of D and can easily be applied for desktop as well as pocket calculators. The method enables rough validity testing of the Hill infinite series.

References

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