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An Analytical Study of Molecular Transport in a Zeolite Crystallite Bed

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Abstract. Analytical solutions of the diffusion equations to obtain the diffusant concentrations in the macro- and micropores which constitute the pore system of a zeolite bed are presented. The parameter which determines the influence of each pore type on the evolution of the adsorbate/adsorbant system towards the equilibrium state is described. Examples are given to illustrate a qualitative and quantitative study based on the curves obtained from these equations.

Keywords: mathematical models, transport diffusion, intracrystallite diffusion, intercrystallite diffusion, zeolites

Introduction

The transport of molecules in the pore system of zeolites and other solids has been extensively studied by several authors (Barrer, 1979; Kärger and Ruthven, 1992; Chen et al., 1994). When a bed of zeolite crystallites is considered, it can be accepted that molecular transport involves two important processes: diffusion in the macropores formed by the space between the crystallites (intercrystallite diffusion) and diffusion in the micropores within the crystallites (intracrystallite diffusion). To determine the contribution of each of these processes to the overall diffusion process, one has to know the values of certain parameters, such as the diffusion coefficients, the pressure in the gas phase, the dimensions of the crystallite bed, the adsorption isotherm, etc.

The relationship between these different parameters and the concentration profiles can be established after having chosen a diffusion model and resolved the equations which describe it. In a previous article by Magalhães et al. (1997) the competitive effects of inter- and intra-crystallite diffusion were analysed semi-quantitatively on the basis of the concentration profiles obtained by a numerical method. In the present work, analytical solutions of the diffusion equations are presented both for the macropores and the micropores. In this way the parameter which allows an evaluation of the relative importance of inter- and intracystalline diffusion is clearly identified.

Mathematical Model

Several models have been developed to study the diffusion of molecules in zeolites (Barrer and Jost, 1949; Barrer, 1963; Younquist, 1970; Ruckenstein et al., 1971). The model developed here is analogous to the bipore model of Ruckenstein (Ruckenstein et al., 1971; Ma and Lee, 1976; Lee, 1978) where a spherical pellet consisting of microporous spherical crystallites is exposed to a constant concentration of adsorbate in the gas phase. In our model the spherical pellet is replaced by a rectangular parallelipipedal or cylindrical bed one face of which is permeable (Fig. 1). In this case one can consider that diffusion is linear in the macropores (the length of the bed) and radial in the micropores. The transport diffusion coefficient in the macropores, D_{inter}, is usually several orders of magnitude greater than that in the micropores, D_{intra}. In this simple "isothermal non-uniform" model, we have made the following assumptions: (i) during the evolution of the system towards equilibrium there has to be a concentration gradient in the macropores and/or in the micropores; (ii) the effect of heat is negligible; (iii) the diffusion coefficients are independent of the concentration; (iv) diffusion occurs in the Henry's Law region of

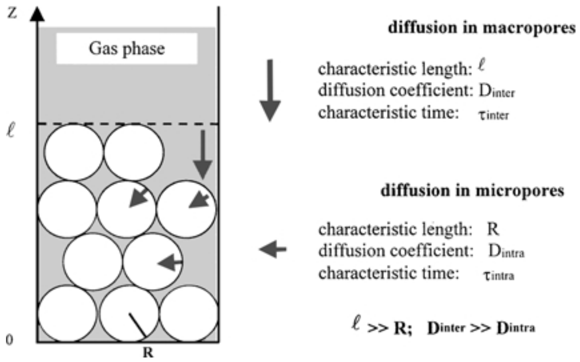

Figure 1. Schematic representation of the diffusion processes.

the adsorption isotherm; (v) there is a local equilibrium at the surface of the crystallites.

The diffusion equations are given by the mass balances in the macropores and the micropores, following (Magalhães et al., 1997; Ruckenstein et al., 1971; Ma and Ho, 1974):

$$\varepsilon_{\text{inter}}\frac{\partial c}{\partial t} = D_{\text{inter}}\,\varepsilon_{\text{inter}}\frac{\partial^2 c}{\partial z^2} - 3(1-\varepsilon_{\text{inter}})\frac{D_{\text{intra}}}{R}\left(\frac{\partial q}{\partial r}\right)_{r=R} \qquad (1)$$

$$\frac{\partial q}{\partial t} = D_{\text{intra}}\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \qquad (2)$$

All notations are explained in the Nomenclature section.

Initial and limiting conditions are given by:

$$\begin{array}{rr} c(z, t=0) = 0 & q(r, z, t=0) = 0 \\ c(z=\ell, t) = c_\infty & q(r=R, z, t) = Kc(z,t) \\ \dfrac{\partial c(z=0,t)}{\partial z} = 0 & \dfrac{\partial q(r=0,z,t)}{\partial r} = 0 \end{array} \qquad (3)$$

Using dimensionless quantities, except for time, Eqs. (1) and (2) become:

$$\tau_M\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial Z^2} - \Gamma\left(\frac{\partial Q}{\partial X}\right)_{X=1} \qquad (4)$$

$$\tau_m\frac{\partial Q}{\partial t} = \frac{\partial^2 Q}{\partial X^2} + \frac{2}{X}\frac{\partial Q}{\partial X} \qquad (5)$$

where

$$\left.\begin{array}{lll} C = \dfrac{c}{c_\infty} & Q = \dfrac{q}{q_\infty} & K = \dfrac{q_\infty}{c_\infty} \\ Z = \dfrac{z}{\ell} & X = \dfrac{r}{R} & \Gamma = \dfrac{3}{p_{\text{inter}}}\dfrac{\tau_M}{\tau_m} \\ \tau_M = \dfrac{\ell^2}{D_{\text{inter}}} & \tau_m = \dfrac{R^2}{D_{\text{intra}}} & p_{\text{inter}} = \dfrac{\varepsilon_{\text{inter}}c}{\varepsilon_{\text{inter}}c + (1-\varepsilon_{\text{inter}})q} \\ & & \qquad \approx \dfrac{\varepsilon_{\text{inter}}}{(1-\varepsilon_{\text{inter}})K} \end{array}\right\} \qquad (6)$$

The adsorption constant value, K, is usually high for hydrocarbons in zeolites, therefore $\varepsilon_{\text{inter}}$ is much smaller than $(1-\varepsilon_{\text{inter}})\,K$ and can be neglected in the expression of the relative amount of Xe atoms in the intercrystallite space, p_{inter}.

Γ characterizes the behavior of the system; this is the ratio between the time scales for transport in the intercrystallite gas phase and that in the intracrystallite pores. $\Gamma \ll 1$ implies that intracrystallite diffusion is the controlling process and the opposite for $\Gamma \gg 1$.

The resolution of the differential Eqs. (4) and (5) is given in the appendix and leads to the concentration profiles of the diffusant in the bed (macropores), $C(Z,t)$, and in the crystallites (micropores) situated in the bed at a height Z, $Q(X,Z,t)$:

$$C(Z,t) = 1 + \frac{6\pi}{\Gamma p_{\text{inter}}}\sum_{n=1}^{\infty}\sum_{k=1}^{\infty}\frac{(2n-1)\cos\left(\frac{2n-1}{2}\pi Z\right)\exp\left(-\frac{\beta_{kn}^2}{\tau_m}t\right)}{(-1)^n\beta_{kn}^2\left[\frac{3}{p_{\text{inter}}}\left(\frac{1}{\sin^2(\beta_{kn})} - \frac{\cot(\beta_{kn})}{\beta_{kn}}\right) + 2\right]} \qquad (7)$$

$$Q(X,Z,t) = 1 + \frac{6\pi}{X\Gamma p_{\text{inter}}}\sum_{n=1}^{\infty}\sum_{k=1}^{\infty}\frac{(2n-1)\sin(\beta_{kn}X)\cos\left(\frac{2n-1}{2}\pi Z\right)\exp\left(-\frac{\beta_{kn}^2}{\tau_m}t\right)}{(-1)^n\sin(\beta_{kn})\beta_{kn}^2\left[\frac{3}{p_{\text{inter}}}\left(\frac{1}{\sin^2(\beta_{kn})} - \frac{\cot(\beta_{kn})}{\beta_{kn}}\right) + 2\right]} \qquad (8)$$

where β_{kn} is the kth root of the nth transcendental equation (see the appendix):

$$\beta_{kn}\cot\beta_{kn} - \frac{P_{\text{inter}}}{3}\beta_{kn}^2 = 1 - \frac{\left(n-\frac{1}{2}\right)^2\pi^2}{\Gamma} \qquad (k \text{ and } n = 1, 2, 3, \ldots) \qquad (9)$$

Let us consider finally the total amounts adsorbed, defining the quantities M_t and M_∞ by:

$$\begin{aligned} M_t &= M_m(t) + M_M(t) \\ &= \int_0^t \varepsilon_{\text{inter}} D_{\text{inter}} \left(\frac{\partial C}{\partial Z} \right)_{Z=1} dt \end{aligned} \tag{10}$$

$$\begin{aligned} M_\infty &= M_m(t_\infty) + M_M(t_\infty) \\ &= \int_0^\infty \varepsilon_{\text{inter}} D_{\text{inter}} \left(\frac{\partial C}{\partial Z} \right)_{Z=1} dt \end{aligned} \tag{11}$$

The ratio M_t/M_∞ is given by:

$$\frac{M_t}{M_\infty} = \frac{\sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n-1)^2 \left[1-\exp\left(-\frac{\beta_{kn}^2}{\tau_m} t\right)\right]}{\beta_{kn}^4 \left[\frac{3}{p_{\text{inter}}} \left(\frac{1}{\sin^2(\beta_{kn})} - \frac{\cot(\beta_{kn})}{\beta_{kn}}\right) + 2\right]}}{\sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n-1)^2}{\beta_{kn}^4 \left[\frac{3}{p_{\text{inter}}} \left(\frac{1}{\sin^2(\beta_{kn})} - \frac{\cot(\beta_{kn})}{\beta_{kn}}\right) + 2\right]}} \tag{12}$$

Discussion

Equations (7) and (8) give the dependence of the diffusant concentration in the macropores and the micropores, respectively, on the time and the spatial coordinates. Equation (12) gives the total quantity of the diffusant in all the pores at time t. Depending on the nature of the quantity measured, which depends on the technique employed, one can use one or other of these equations to simulate the experimental results, with τ_M and τ_m as adjustable parameters. The values of these parameters for which there is agreement between simulation and experiment can be used to calculate the diffusion coefficients D_{inter} and D_{intra}. We must remember that the values of these coefficients are not identical with those for the same system at equilibrium. The intracrystallite diffusion coefficient is usually corrected according to Eic and Ruthven (1988) and Kärger and Ruthven (1992):

$$D_{\text{intra}}^{n.\text{eq}} = D_{\text{intra}}^{\text{eq}} \times \frac{\partial \ln c}{\partial \ln q} \tag{13}$$

while the gas phase diffusion coefficient has rather to be corrected as (Reyes et al., 2000):

$$D_{\text{inter}}^{n.\text{eq}} = \frac{D_{\text{inter}}^{\text{eq}}}{1 + \alpha(dq/dc)} \tag{14}$$

where α is the average surface-to-volume ratio of the pores, D_i^{eq} and $D_i^{n.\text{eq}}$ are the diffusion coefficients at equilibrium (self-diffusivity) and out of equilibrium (transport diffusivity), respectively.

Table 1. Examples of parameters for the simulation of diffusion in an adsorbate/zeolite system.

Parameters	Case a	Case b	Case c
$\varepsilon_{\text{inter}}$	8×10^{-1}	8×10^{-1}	8×10^{-1}
K	1×10^{5}	1×10^{5}	1×10^{5}
ℓ (cm)	2	2×10^{-1}	2×10^{-1}
R (cm)	1×10^{-3}	1×10^{-3}	1×10^{-2}
D_{inter} (cm^2/s)	1×10^{-1}	1×10^{-1}	1×10^{-1}
D_{intra} (cm^2/s)	1×10^{-10}	1×10^{-10}	1×10^{-10}
τ_M (s)	40	4×10^{-1}	4×10^{-1}
τ_m (s)	1×10^{4}	1×10^{4}	1×10^{6}
τ_M/τ_m	4×10^{-3}	4×10^{-5}	4×10^{-7}
Γ	3×10^{2}	3	3×10^{-2}

The kinetic curves for adsorption (uptake curves) corresponding to the different theoretical cases of Table 1 are presented in Fig. 2. When the relative quantity adsorbed is plotted against time t (Fig. 2(a)), one observes that the system reaches equilibrium faster when the mean diameter of the crystallites or the bed length is smaller (keeping the other parameters constant).

It seems obvious that the size of the crystallites and the bed has an effect upon the evolution of the system towards equilibrium. However, it seems difficult to determine from these curves the step which controls the overall rate of diffusion. The setting-up of Eqs. (7), (8) and (12) has shown that the parameter Γ is correlated with the dimensions of the bed and the crystallites, with the porosity and the adsorption equilibrium constant (see Eq. (6)). This parameter can play an important part in the analysis of the evolution of the system towards equilibrium, because it is directly involved in the expressions for C and Q as well as that of the β_{kn} coefficients. Intuitively, one is tempted to evaluate the ratio of the diffusion times τ_M/τ_m to determine the relative importance of macropores and micropores in the control of diffusion; this procedure is not exact, since it does not take into account the population distribution between these two types of pore, as if the two diffusion steps were independent.

To be exact, one must evaluate Γ since this takes account of both the diffusion times and the relative populations p_{inter} and $p_{\text{intra}} (=1 - p_{\text{inter}})$ of the diffusant in each pore type. In the case of solids with a high adsorption capacity, generally $p_{\text{inter}} \ll p_{\text{intra}}$; it can be assumed that $p_{\text{intra}} \to 1$. Magalhães et al. (1997) have shown that control by the macropores is determined by

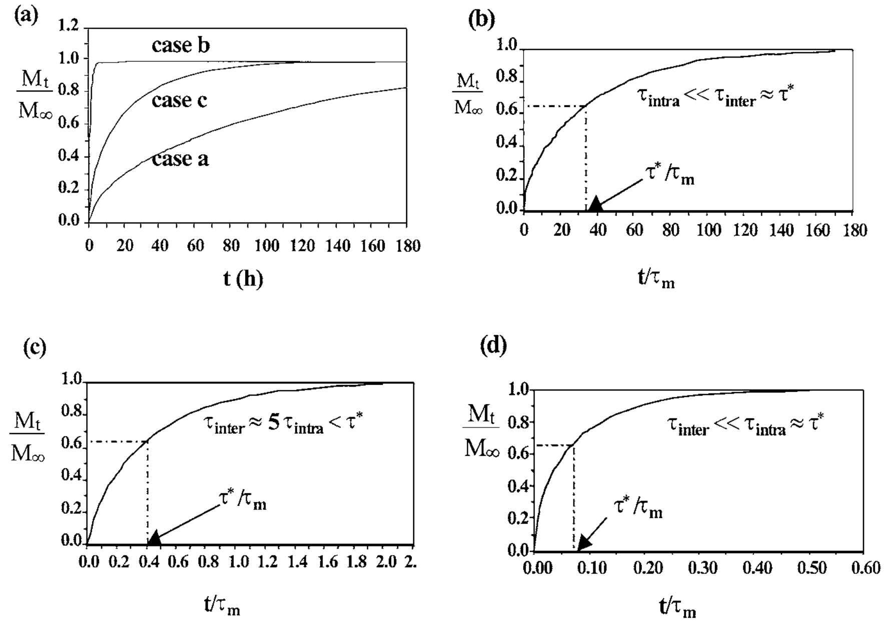

Figure 2. Plots of the uptake curves according to Eq. (36) in function of time, t (a), of the ratio t/τ_m for case a (b), case b (c), case c (d); (b)–(d) show the values of time constant of diffusion.

$\Gamma \gg 1$ and by the micropores by $\Gamma \ll 1$; between these limits both the macropores and the micropores control the overall diffusion rate. The validity of this criterion is confirmed when the concentration profiles and the kinetic curves for adsorption are analyzed for the three cases presented in Table 1. In Table 2 the roots β_{kn} of Eq. (9) are given for each case.

Case a, $\Gamma \gg 1$ (Table 1) Intercrystallite Diffusion Controls the Overall Diffusion Process

The kinetic curve for adsorption (uptake sorption curve) for this case is given in Fig. 2(b)). Considering that the system has attained quasi-equilibrium in time t_{eq} corresponding to $M_t/M_\infty \geq 0.95$, one can determine that $t_{\text{eq}}/\tau_m \approx 170$ (Fig. 2(b)). It can be seen that the intercrystallite concentration becomes uniform over the entire length of the bed for this same value of t/τ_m (Fig. 3(a)); on the other hand, the intracrystallite concentration is very quickly uniform over the entire crystallite (as soon as $t/\tau_m > 10$) but it does not reach its equilibrium value until a time which is more or less long depending on the position of the crystallite in the bed. For example, $t_{\text{eq}}/\tau_m \approx 30$ for a crystallite situated nearer the top of the bed (Fig. 3(b)) and $t_{\text{eq}}/\tau_m \approx 170$ for one further down (Fig. 3(c)).

Let us denote τ^* the overall diffusion time constant for the system. When the effect of the micropores is negligible this time is determined by the time constant for intercrystallite diffusion τ_{inter}. Assuming that the macropores can be considered as a cylinder, we obtain: (Kärger and Ruthven, 1992; M.-A. Springuel-Huet et al., 1996; Magalhães et al., 1997)

$$\tau_{\text{inter}} = \frac{\ell^2}{3D_{\text{inter}}p_{\text{inter}}} = \frac{\tau_M}{3p_{\text{inter}}} \cong \frac{\tau_M}{3}\frac{(1-\varepsilon_{\text{inter}})K}{\varepsilon_{\text{inter}}} \tag{15}$$

By using Eq. (15) one obtains for case (a), $\tau_{\text{inter}}/\tau_m \approx \tau^*/\tau_m \approx 33.3$ and $t_{\text{eq}} \approx 5\tau^*$. It follows that Eq. (12) leads to:

$$M_t/M_\infty = 0.64 \quad \text{for } t = \tau^* \tag{16}$$

The relation (16) can be generalized to the various adsorbate/adsorbent systems described by Eq. (12). In other words this expression allow to determine with a good approximation the diffusion time constant, τ^*, and the equilibrium time, t_{eq}, necessary to obtain a quasi-equilibrium in these systems.

Table 2. Some roots of the transcendental equation of the form: $\beta_{kn} \cot \beta_{kn} - \frac{p_{\text{inter}}}{3} \beta_{kn}^2 = 1 - \frac{(n-\frac{1}{2})^2 \pi^2}{\Gamma}$.

n	β_{1n}	β_{2n}	β_{3n}	β_{4n}	β_{5n}	β_{6n}	β_{7n}	β_{8n}	β_{9n}	β_{10n}
					Case a: $p_{\text{inter}} = 4 \times 10^{-5}$ and $\Gamma = 3 \times 10^2$					
1	0.1586	4.4952	7.7262	10.9047	14.0666	17.2210	20.3714	23.5195	26.6660	29.8115
2	0.4684	4.5098	7.7347	10.9107	14.0713	17.2248	20.3747	23.5222	26.6685	29.8137
3	0.7706	4.5390	7.7517	10.9228	14.0806	17.2325	20.3811	23.5279	26.6734	29.8181
4	1.0559	4.5828	7.7772	10.9409	14.0946	17.2439	20.3908	23.5363	26.6808	29.8247
5	1.3232	4.6404	7.8111	10.9649	14.1133	17.2591	20.4037	23.5474	26.6906	29.8335
6	1.5671	4.7111	7.8531	10.9949	14.1366	17.2782	20.4198	23.5614	26.7030	29.8445
7	1.7851	4.7932	7.9030	11.0307	14.1644	17.3010	20.4391	23.5781	26.7177	29.8577
8	1.9765	4.8843	7.9601	11.0719	14.1967	17.3275	20.4615	23.5976	26.7349	29.8731
9	2.1412	4.9815	8.0235	11.1184	14.2333	17.3576	20.4871	23.6198	26.7545	29.8907
10	2.2818	5.0815	8.0922	11.1697	14.2739	17.3911	20.5156	23.6446	26.7765	29.9104
					Case b: $p_{\text{inter}} = 4 \times 10^{-5}$ et $\Gamma = 3$					
1	1.4483	4.6742	7.8311	10.9792	14.1244	17.2682	20.4113	23.5541	26.6965	29.8388
2	2.7371	5.5669	8.4989	11.5028	14.5511	17.6266	20.7194	23.8239	26.9363	30.0544
3	2.9898	5.9859	8.9934	12.0150	15.0515	18.1022	21.1657	24.2402	27.3241	30.4159
4	3.0637	6.1283	9.1947	12.2636	15.3355	18.4110	21.4902	24.5734	27.6604	30.7513
5	3.0944	6.1890	9.2841	12.3797	15.4761	18.5734	21.6718	24.7714	27.8722	30.9744
6	3.1100	6.2201	9.3303	12.4406	15.5512	18.6622	21.7734	24.8851	27.9972	31.1097
7	3.1190	6.2380	9.3570	12.4761	15.5953	18.7146	21.8341	24.9537	28.0734	31.1934
8	3.1246	6.2492	9.3738	12.4985	15.6232	18.7479	21.8727	24.9976	28.1226	31.2476
9	3.1284	6.2567	9.3851	12.5135	15.6419	18.7703	21.8988	25.0273	28.1558	31.2844
10	3.1310	6.2620	9.3930	12.5240	15.6551	18.7861	21.9171	25.0482	28.1793	31.3104
					Case c: $p_{\text{inter}} = 4 \times 10^{-5}$ et $\Gamma = 3 \times 10^{-2}$					
1	3.1034	6.2069	9.3106	12.4146	15.5190	18.6240	21.7295	24.8358	27.9427	31.0505
2	3.1373	6.2747	9.4120	12.5494	15.6867	18.8241	21.9614	25.0988	28.2361	31.3735
3	3.1401	6.2801	9.4202	12.5603	15.7003	18.8404	21.9804	25.1205	28.2606	31.4006
4	3.1408	6.2816	9.4224	12.5632	15.7041	18.8449	21.9857	25.1265	28.2673	31.4081
5	3.1411	6.2822	9.4234	12.5645	15.7056	18.8467	21.9878	25.1290	28.2701	31.4112
6	3.1413	6.2826	9.4238	12.5651	15.7064	18.8477	21.9889	25.1302	28.2715	31.4128
7	3.1414	6.2827	9.4241	12.5655	15.7069	18.8482	21.9896	25.1309	28.2723	31.4137
8	3.1414	6.2828	9.4243	12.5657	15.7071	18.8485	21.9900	25.1314	28.2728	31.4142
9	3.1415	6.2829	9.4244	12.5658	15.7073	18.8488	21.9902	25.1317	28.2731	31.4146
10	3.1415	6.2830	9.4245	12.5659	15.7074	18.8489	25.1319	25.1319	28.2734	31.4149

Case c, $\Gamma \ll 1$ (Table 1), Intracrystallite Diffusion Controls the Overall Diffusion Process

The system reaches equilibrium after a time t_{eq} corresponding to $t/\tau_m = 0.4$ (Fig. 2(d)); it is also the time required for a uniform intracrystalline concentration (Fig. 4(b)), whereas the intercrystallite concentration becomes uniform in a very short time t (Fig. 4(a)). It should be noticed that regardless of the position of the crystallite in the bed, the intracrystalline concentration attains its equilibrium value at the same time t equal to t_{eq}. In this case (macropore effect negligible) τ^* is determined by the intracrystallite diffusion time constant τ_{intra}. It can be shown that for a spherical diffusional medium (Ruthven, 1984; Koresh and Soffer, 1981; Kärger, 1982):

$$\tau_{\text{intra}} = \frac{R^2}{15 D_{\text{inter}} p_{\text{intra}}} \cong \frac{\tau_m}{15} \tag{17}$$

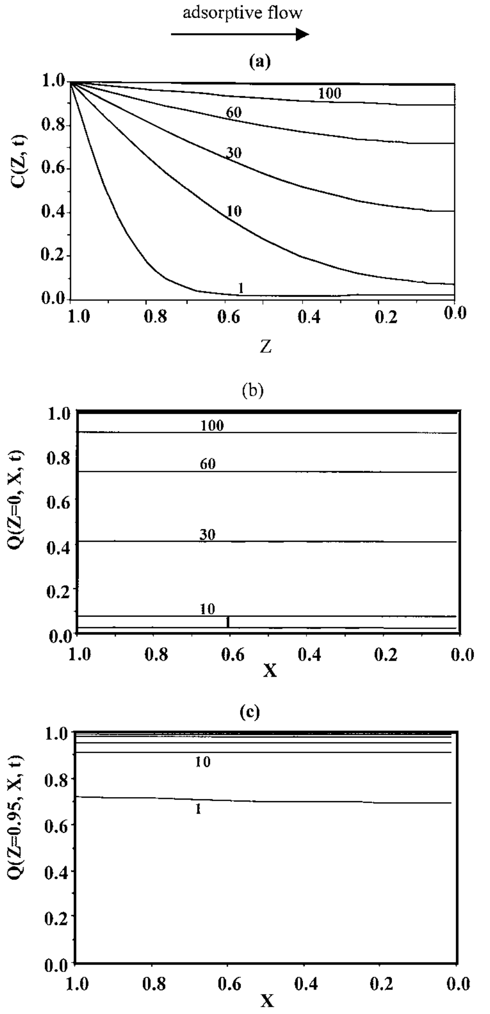

Figure 3. Concentration profiles of the adsorbate in case a, along the bed in macropores (a), in crystallites at the bottom of the bed (b) and in crystallites near the top of the bed (c). Numbers on graph are values of t/τ_m.

By using Eq. (17) one obtains for case (c) $\tau_{\text{intra}}/\tau_m \approx \tau^*/\tau_m \approx 0.07$ and $t_{\text{eq}} \approx 6\tau^*$. The substitution of t by $\tau_{\text{intra}}(\approx\tau^*)$ in Eq. (12) gives $M_t/M_\infty = 0.64$; which confirms the generality of the relation (16).

It results from the analysis of cases (a) and (c) that: (i) τ_{inter} and τ_{intra} have the physical meaning of mean lifetime of the diffusant in each type of pore; (ii) τ_M (or τ_m) does not represent the time required to attain equilibrium in the macropores (or micropores) but the time necessary for a molecule to diffuse from the top to the bottom of the bed (or from surface of the crystallite to its center).

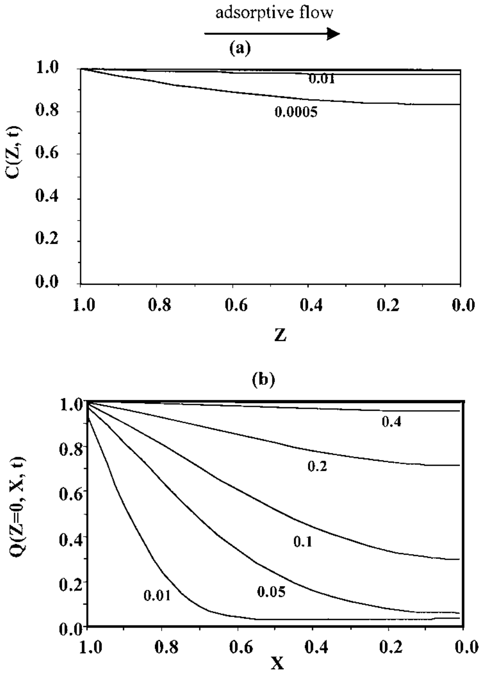

Figure 4. Concentration profiles of the adsorbate in case c, along the bed in macropores (a) and in crystallites at the bottom of the bed (b). Numbers on graph are values of t/τ_m.

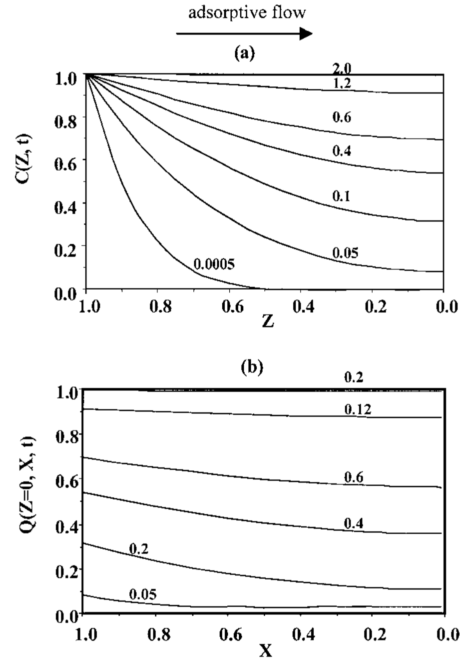

Figure 5. Concentration profiles of the adsorbate in case b, along the bed in macropores (a), in crystallites at the bottom of the bed (b). Numbers on graph are values of t/τ.

Case b, $\Gamma \approx 1$ (Table 1) Both Intra- and Intercrystallite Diffusion Control the Overall Diffusion Process

The system reaches equilibrium at a time t_{eq} corresponding to $t/\tau_m \approx 2$ (Fig. 2(c)). It can be seen that the concentration gradient in the two types of pore persists at times t close to equilibrium (Fig. 5). The time constant for overall diffusion τ^* can be evaluated using Fig. 2(c) and the relation (16); this gives $\tau^*/\tau_m \approx 0.4$ and $t_{\text{eq}} \approx 5 \times \tau^*$. This value of τ^* corresponds to the sum, $\tau_{\text{inter}} + \tau_{\text{intra}}$. Indeed, one can calculate $\tau_{\text{inter}} \approx 0.33 \times \tau_m$ and $\tau_{\text{intra}} \approx 0.07 \times \tau_m$ (Eqs. (15) and (17)).

It results from this analysis that τ^* has the same physical meaning as the time constant for long-range diffusion introduced by Kärger and Heink (1983), Kärger and Pfeifer (1987) and Kärger et al. (1988).

Conclusion

Analytical solution of the system of diffusion equations for a bipore solid gives solutions which make it possible to discern the parameters which determine the evolution of the system towards the equilibrium state. In this way one can define a dynamic parameter which allows us to evaluate the relative contributions of macropores and micropores to the overall diffusion rate.

Appendix

Putting $N = XQ$, Eqs. (4) and (5) simplify:

$$\tau_M \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial Z^2} - \Gamma\left[\left(\frac{\partial N}{\partial X}\right)_{X=1} - (N)_{X=1}\right] \quad (18)$$

$$\tau_m \frac{\partial N}{\partial t} = \frac{\partial^2 N}{\partial X^2} \quad (19)$$

In the same way as for Eqs. (1) and (2), using dimensionless quantities, Eq. (3) become:

$$\begin{array}{ll} C(Z, t=0) = 0 & N(X, Z, t=0) = 0 \\ C(Z=1, t) = 1 & N(X=1, Z, t) = C(Z, t) \quad (20) \\ \dfrac{\partial C(Z=0, t)}{\partial Z} = 0 & \dfrac{\partial^2 N(X=0, Z, t)}{\partial X^2} = 0 \end{array}$$

Solution: Concentration Profiles

Solutions for the time dependence of the concentrations C and Q and the spatial coordinates are obtained according to the procedure originally used by Ruckenstein et al. (1971): (a) first the Laplace transforms of the functions C and N are determined:

$$\bar{C} = \int_0^\infty C \exp(-pt)\, dt \quad \text{and}$$

$$\bar{N} = \int_0^\infty N \exp(-pt)\, dt \quad (21)$$

where p is a positive real variable sufficiently great to make the integral converge; (b) then the solutions, C and N, are obtained by using the inverse transform of the functions $\bar{C}$ and $\bar{N}$ with respect to the variable p.

Applying the Laplace transformation to Eqs. (7) to (9) one obtains:

$$\frac{\partial^2 \bar{C}}{\partial Z^2} = \tau_M p \bar{C} + \Gamma\left[\left(\frac{\partial \bar{N}}{\partial X}\right)_{X=1} - (\bar{N})_{X=1}\right] \quad (22)$$

$$\frac{\partial^2 \bar{N}}{\partial X^2} = \tau_m p \bar{N} \quad (23)$$

$$\bar{C}(Z=1) = \frac{1}{p} \quad (24a)$$

$$\frac{\partial \bar{C}(Z=0)}{\partial Z} = 0 \quad (24b)$$

$$\bar{N}(X=1) = \bar{C}(Z) \quad (24c)$$

$$\frac{\partial^2 \bar{N}(X=0)}{\partial X^2} = 0 = \bar{N}(X=0) \quad (24d)$$

The general solution of Eq. (12) is of the form:

$$\bar{N}(X) = A \cos(\beta X) + B \sin(\beta X) \quad (25)$$

where $\beta^2 = -\tau_m p$, A and B are the constants to be determined by means of conditions (24c) and (24d).

Thus, the particular solution of Eq. (23) is given by:

$$\bar{N}(X) = \bar{C} \frac{\sin(\beta X)}{\sin \beta} \quad (26)$$

Whence:

$$(\bar{N})_{X=1} = \bar{C} \quad (27)$$

$$\left(\frac{\partial \bar{N}}{\partial X}\right)_{X=1} = \beta \bar{C} \cot \beta \quad (28)$$

By substituting Eqs. (26) and (27) in Eq. (21), and p by β^2/τ_m. one obtains:

$$\frac{\partial^2 \bar{C}}{\partial Z^2} = -\bar{C}\left[\Gamma(1 - \beta \cot \beta) + \frac{\tau_M}{\tau_m}\beta^2\right] \quad (29)$$

Let:

$$\gamma^2 = \Gamma(1 - \beta\cot\beta) + \frac{\tau_M}{\tau_m}\beta^2 \tag{30}$$

Equation (29) becomes:

$$\frac{\partial^2\bar{C}}{\partial Z^2} = -\gamma^2\bar{C} \tag{31}$$

The solution of Eq. (22) is given by that of Eq. (31) satisfying the same conditions (24a) and (24b). The general solution of Eq. (31) is:

$$\bar{C}(Z) = a\cos(\gamma Z) + b\sin(\gamma Z) \tag{32}$$

γ is defined in Eq. (30); a and b are constants to be determined by means of conditions (24a) and (24b). Whence

$$\bar{C}(Z) = \frac{\cos(\gamma Z)}{p\cos\gamma} \tag{33}$$

Substituting Eq. (33) in Eq. (26), this latter becomes:

$$\bar{N}(X, Z) = \frac{\cos(\gamma Z)\sin(\beta X)}{p\cos\gamma\sin\beta} \tag{34}$$

According to Heavyside's theorem the original function of a Laplace transform function of the form $\bar{\mathrm{F}} = \frac{f(p)}{pg(p)}$ is (Turney, 1946):

$$\begin{aligned}\mathrm{F}(t) &= \int_0^\infty \frac{f(p)}{pg(p)}\exp(pt)\,dp \\ &= \sum_{k=1}^{\infty}\left\{\frac{f(p_k)}{[p_k g'(p_k) + g(p_k)]}\exp(p_k t)\right\}\end{aligned} \tag{35}$$

where p_k are the different positive roots of $g(p) = 0$ and $g' = \frac{dg}{dp}$.

This theorem is an application of the method for the calculation of a contour integral by means of "residuals," such that all the singular points of the integral are simple poles. If the integral has a pole at $p = 0$ and an infinity of poles at different $p = p_k \neq 0$, one can write.

$$F(t) = \frac{f(p=0)}{g(p=0)} + \sum_{k=1}^{\infty}\frac{f(p_k)}{p_k g'(p_k)}\exp(p_k t) \tag{36}$$

We look first for the original function $C(Z)$ whose Laplace transform is given by Eq. (33), that is:

$$\bar{C}(Z) = \frac{\cos\gamma Z}{p\cos\gamma} = \frac{f(p)}{pg(p)} \tag{37}$$

where $f(p) = \cos(\gamma Z)$ and $g(p) = \cos\gamma$

The roots of $g(p) = \cos\gamma = 0$ are given by:

$$\gamma = (2n-1)\frac{\pi}{2} \qquad (n = 1, 2, 3, \ldots) \tag{38}$$

$$\gamma^2 = \left(n - \frac{1}{2}\right)^2\pi^2 \qquad (n = 1, 2, 3, \ldots) \tag{39}$$

Replacing γ^2 by the expression of Eq. (30) and τ_M/τ_m by $\Gamma p_{\text{inter}}/3$ (Eq. (6)), one obtains:

$$\beta\cot\beta - \frac{p_{\text{inter}}}{3}\beta^2 = 1 - \frac{\left(n-\frac{1}{2}\right)^2\pi^2}{\Gamma} \qquad (n = 1, 2, 3\ldots) \tag{40}$$

Because Eq. (39) is transcendental, there must be a large number of roots for each value of n. Thus, we can write:

$$\beta_{kn}\cot\beta_{kn} - \frac{p_{\text{inter}}}{3}\beta_{kn}^2 = 1 - \frac{\left(n-\frac{1}{2}\right)^2\pi^2}{\Gamma} \qquad (k \text{ and } n = 1, 2, 3\ldots) \tag{41}$$

where β_{kn} is the kth root of the nth transcendental equation.

By applying the inverse transformation (Eq. (26)) to $\bar{C}(Z)$ and introducing Eq. (28), one obtains the concentration of the diffusant in the bed (macropores) at time t (Eq. (7)):

$$C(Z,t) = 1 + \frac{6\pi}{\Gamma p_{\text{inter}}}\sum_{n=1}^{\infty}\sum_{k=1}^{\infty}\frac{(2n-1)\cos\left(\frac{2n-1}{2}\pi Z\right)\exp\left(-\frac{\beta_{kn}^2}{\tau_m}t\right)}{(-1)^n\beta_{kn}^2\left[\frac{3}{p_{\text{inter}}}\left(\frac{1}{\sin^2(\beta_{kn})} - \frac{\cot(\beta_{kn})}{\beta_{kn}}\right) + 2\right]}$$

Now we look for the original function $N(X, Z)$ whose Laplace transform is given by Eq. (34), that is:

$$\bar{N}(X, Z) = \frac{\cos(\gamma Z)\sin(\beta X)}{p\cos\gamma\sin\beta} = \frac{u(p)}{pv(p)} \tag{42}$$

where $u(p) = \cos(\gamma Z)$ and $v(p) = \cos\gamma\sin\beta$.

By applying the inverse transformation (Eq. (26)) to $\bar{N}(X, Z)$, replacing N by XQ and introducing Eq. (28), one obtains at time t the diffusant concentration at a distance X (relative to the centre) in the crystallites situated in the bed at a height Z (Eq. (8)):

$$
\begin{aligned}
&Q(X, Z, t)\\
&\quad = 1 + \frac{6\pi}{X\Gamma p_{\text{inter}}} \sum_{n=1}^{\infty}\sum_{k=1}^{\infty}\\
&\quad \frac{(2n-1)\sin(\beta_{kn}X)\cos\left(\frac{2n-1}{2}\pi Z\right)\exp\left(-\frac{\beta_{kn}^2}{\tau_m}t\right)}{(-1)^n\sin(\beta_{kn})\beta_{kn}^2\left[\frac{3}{p_{\text{inter}}}\left(\frac{1}{\sin^2(\beta_{kn})}-\frac{\cot(\beta_{kn})}{\beta_{kn}}\right)+2\right]}
\end{aligned}
$$

Nomenclature

c	Adsorbate concentration in macropores (molecules/cm^3)
c_∞	Adsorbate equilibrium concentration in macropores (molecules/cm^3)
$C = c/c_\infty$	Nondimensional adsorbate concentration in macropores
D_{inter}	Macropore diffusion coefficient (cm^2/s)
D_{intra}	Micropore diffusion coefficient (cm^2/s)
K	Adsorption equilibrium constant
ℓ	Bed length (cm)
M_m	Micropore uptake
M_M	Macropore uptake
M_t	Total uptake at time t
M_∞	Total uptake at equilibrium
p_{inter}	Relative number of molecules in macropores in equilibrium condition
p_{intra}	Relative number of molecules in micropores in equilibrium condition
q	Adsorbate concentration in micropores (molecules/cm^3)
q_∞	Equilibrium adsorbate concentration in micropores (molecules/cm^3)
$Q = q/q_\infty$	Nondimensional adsorbate concentration in micropores
r	Distance from crystallite center (cm)
R	Mean crystallite radius (cm)
$X = r/R$	Nondimensional distance from crystallite center
z	Distance from bottom of the crystallite bed (cm)
$Z = z/\ell$	Nondimensional distance from bottom of the bed crystallites

Greek Letters

α	Average surface-to-volume ratio of the pores
$\varepsilon_{\text{inter}}$	Bed porosity
τ_M	Diffusion time required for a molecule to penetrate the bed crystallites from the top to the bottom (s)
τ_m	Diffusion time required for a molecule to penetrate a crystallite from external surface to the centre (s)
τ_{inter}	Time constant of diffusion in intercystalline space (s)
τ_{intra}	Time constant of diffusion in intracrystalline space (s)
τ^*	Effective time constant of the global process of diffusion in the system (s)
Γ	Dynamic parameter

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