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Note

ZLC diffusion measurements: Combined effect of surface resistance and internal diffusion

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The mathematical model for a zero length column (ZLC) system has been extended to the practically important situation in which the sorption kinetics are controlled by the combined effect of intracrystalline diffusion and surface resistance to mass transfer. The validity of the new model is demonstrated by application to experimental data for diffusion of ethane in DDR zeolite.

1. Introduction

The zero length column (ZLC) technique, first introduced in 1988, is now widely used as a simple way of measuring intraparticle (or intracrystalline) diffusion in adsorbent or catalyst particles. In the original development (Eic and Ruthven, 1988; Ruthven and Eic, 1988; Ruthven and Brandani, 2000) it was assumed that the desorption rate is controlled entirely by diffusion out of the particle, with equilibrium always maintained with the surrounding fluid at the external surface. For many systems this is a reasonable approximation but recent studies carried out by advanced optical techniques such as interference microscopy (IFM) or infrared microscopy (IRM) (Kortunov et al., 2005; Heinke et al., 2007; Ruthven et al., 2010) have revealed that, in many zeolite crystals, there is significant mass transfer resistance at the external surface so that the sorption rate is actually controlled by the combined effects of internal diffusion and surface resistance. The ZLC model has been modified for the extreme case in which surface resistance is rate controlling (Brandani and Ruthven, 2005) but the more important general situation in which both internal and surface resistances are important has not yet been addressed. It turns out that such an extension of the model is in fact straightforward and provides useful additional insight as well as enhancing the capabilities of the ZLC technique.

2. Theoretical model

In a ZLC experiment a small sample of adsorbent is pre-equilibrated with a stream containing a small concentration of an adsorbable species in an inert carrier (typically He) and then purged at a constant flow rate, monitoring continuously the sorbate concentration in the effluent stream. To model the system it is assumed that the ZLC cell is well mixed, with (linear) equilibrium between the fluid and adsorbed phases at the external surface of the particle. Desorption from the adsorbent particles (considered as an assemblage of identical spheres) is assumed to be controlled by intraparticle diffusion with a constant diffusivity

$$\frac{\partial q}{\partial t} = D\left(\frac{2}{r}\frac{\partial q}{\partial r} + \frac{\partial^2 q}{\partial r^2}\right) \tag{1}$$

$$\text{Initial condition:} \quad t<0: \quad q = q_0 = Kc_0 \text{ for all } r \tag{2}$$

$$\text{Boundary conditions:} \quad r=0, \quad \left(\frac{\partial q}{\partial r}\right)_{r=0} = 0 \tag{3}$$

$$r=R; \quad -D\left(\frac{\partial q}{\partial r}\right)_{r=R} = \frac{FR}{3KV_s}q_R = \frac{FR}{3V_s}c(t) \tag{4}$$

In dimensionless form these equations become

$$\frac{\partial Q}{\partial \tau} = \frac{2}{\eta}\frac{\partial Q}{\partial \eta} + \frac{\partial^2 Q}{\partial \eta^2} \tag{5}$$

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where $Q=q/q_0$, $\eta=r/R$, $\tau=Dt/R^2$.

$$\eta=1;\quad -\left(\frac{\partial Q}{\partial \eta}\right)_{\eta=1}=\frac{FR^2}{3KV_sD}Q_{\eta=1}=LQ_{\eta=1} \tag{6}$$

where

$$L=\frac{FR^2}{3KV_sD} \tag{7}$$

The solution for the ZLC response curve (c/c_o vs. t) is given by

$$\frac{c}{c_0}=2L\sum_{n=1}^{\infty}\frac{\exp(-\beta_n^2Dt/R^2)}{[\beta_n^2+L(L-1)]} \tag{8}$$

with β_n given by the roots of the transcendental equation:

$$\beta_n\cot\beta_n+L-1=0$$

$$L=\frac{F}{3KV_s}\frac{R^2}{D}=\frac{1}{3}\,\frac{\text{Purge flow rate}}{\text{Adsorbent vol.}}\,\frac{R^2}{D} \tag{9}$$

In the long time region only the first term of the summation is significant so Eq. (8) simplifies to

$$\ln\left(\frac{C}{C_0}\right)\approx\ln\left[\frac{2L}{\beta_1^2+L(L-1)}\right]-\beta_1^2\frac{Dt}{R^2} \tag{10}$$

which defines the log time asymptote. For large values of L there is a further simplification since $\beta_1\rightarrow\pi$. Under these conditions it is clear that a plot of $\log(c/c_0)$ vs. t should yield a linear long time asymptote with slope $-\pi^2D/R^2$ and intercept given by the first term on the right hand side of Eq. (10) with β_1 replaced by π. Changing the L value (for example by varying the purge rate) will change the intercept but the asymptotic slope should remain essentially constant.

Except at short times, when L is large, the response curve (Eq. (8)) is well approximated, over a wide range, by the simple expression (Brandani and Ruthven, 1996):

$$\frac{c}{c_0}=\frac{1}{L}\left(\sqrt{\frac{R^2}{\pi Dt}}-1\right) \tag{11}$$

Evidently a plot of c/c_0 vs. $1/\sqrt{t}$ should be linear with a constant x-axis intercept corresponding to $\sqrt{(\pi D/R^2)}$ and a negative intercept of $1/L$ on the y-axis, from which the values of D/R^2 and K are readily found.

If there is significant surface resistance to mass transfer Eqs. (1)–(3) remain the same but in place of Eq. (4) we have

$$r=R;\quad -D\left(\frac{\partial q}{\partial r}\right)_{r=R}=k(q_R-q_{surf})=\frac{FR}{3KV_s}q_{surf}=\frac{FR}{3V_s}c(t) \tag{12}$$

whence

$$Q_R=\frac{q_R}{q_{surf}}=1+\frac{FR}{3kKV_s} \tag{13}$$

In the dimensionless form Eq. (6) is replaced by

$$\eta=1;\quad -\left(\frac{\partial Q}{\partial \eta}\right)_{\eta=1}=L'Q_{\eta=1};\quad \frac{1}{L'}=\frac{1}{L}+\frac{D}{kR} \tag{14}$$

Since Eq. (14) is formally the same as Eq. (6) (with L replaced by L') the solutions (Eqs. (8)–(11)) remain the same with L replaced by L'. In the limit of high surface resistance D/kR becomes large and if the purge rate is high enough to satisfy the condition:

$$\frac{3k}{R}\ll\frac{F}{KV_s} \tag{15}$$

the concentration profile within the particle become flat and the response curve reduces to a simple exponential decay:

$$\frac{c}{c_0}=\frac{3kKV_s}{FR}\exp\left(-\frac{3kt}{R}\right) \tag{16}$$

This corresponds to the case of surface resistance control (Brandani and Ruthven, 2005).

It is evident (since L is proportional to F/K) that if a ZLC response curve for a system in which there is significant surface resistance is interpreted in accordance with the original model (assuming negligible surface resistance) the derived value of the parameter L' will be smaller than the true value of L (see Eq. (14)) with the result that the values of the apparent equilibrium constant (estimated assuming $L'=L$) will be erroneously large and will show an increasing trend with purge flow rate. In contrast the slope of the long time asymptote (provide that $L'>10$) is essentially independent of L, implying that the diffusional time constant (D/R^2) calculate from the asymptotic slope is not affected by the presence of moderate surface resistance.

3. Experimental verification

Precisely this pattern of behavior has been observed in a recent experimental study of diffusion of ethane in large crystals (40 μm diameter) of DD3R (the pure silica form of ZSM-58). The size distribution was narrow (approximately 38–42 μm). To improve the accuracy with which the equilibrium constants for weakly adsorbed gases such as methane and ethane could be measured, a somewhat larger than normal sample of adsorbent was used in the ZLC cell (22.1 mg). A series of measurements was also carried out with smaller samples (18, 6 and 4 mg) to confirm the absence of any significant extracrystalline resistances (Vidoni, 2011). Representative ZLC response curves measured at three different purge flow rates are shown in Fig. 1 in which the theoretical curves calculated in accordance with Eq. (8) with the given parameters are also shown. It is evident that the theoretical curves provide an excellent representation of the observed behavior. The parameters L' and D/R^2 were calculated from the slopes and intercepts of the long time asymptotes of Fig. 1a in accordance with Eq. (10) and from the c/c_0 and $1/\sqrt{t}$ intercepts of Fig. 1(b) in accordance with Eq. (11). The parameter values obtained in both ways were very similar; the average values are summarized in Table 1.

Note that the slopes of the long time asymptotes in Fig. 1(a) are essentially constant and the plots of c/c_0 vs. $1/\sqrt{t}$ (Fig. 1(b)) show a common intercept on the $1/\sqrt{t}$ axis implying that the diffusivity is independent of flow rate (as it should be).

The variation of L' with flow rate, shown in Fig. 2, conforms to Eq. (14), thus allowing the values of K and the surface rate coefficient (k) to be derived from the slope and intercept of such linear plots.

For comparison the ZLC data for CH_4 in the same sample of DDR crystals at 323 K are also included in Fig. 2. For that system the K values calculated from the traditional model (assuming intracrystalline diffusion control with negligible surface resistance) are independent of flow rate ($L'=L$) and the plot of $1/L'$ vs. $1/F$ passes through the origin. It appears that, although surface resistance is significant for ethane it is insignificant for the smaller methane molecule.

4. Conclusions

The new model provides a clear and consistent interpretation of the ZLC response curves for ethane in DDR. More importantly, it