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Analysis of the Piezometric Method for the Study of Diffusion in Microporous Solids: Isothermal Case

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Abstract. The piezometric method used for the measurement of diffusion coefficients in microporous solids is examined in an attempt to establish the limits of applicability. In the present study isothermal conditions are assumed. The theoretical model for the description of the transient behaviour is linearized and solved to yield analytical solutions. The effect of the physical parameters governing the system response is described. It appears that severe limitations must be considered for strongly adsorbed and fast diffusing species.

Based on the results it is possible to suggest improvements to the experimental technique and an alternative approach to analyze the experimental response curves, in which the only unknown parameter is the diffusional time constant.

Keywords: measurement method, mathematical model, intraparticle diffusion, zeolite

Introduction

The piezometric method, which involves following the transient pressure response when a sample of adsorbent is subjected to a change in sorbate pressure, has been widely applied to the measurement of intracrystalline diffusion in zeolites. In a recent review (Bülow and Micke, 1995) this approach was claimed to be superior to most other transient methods and to be applicable even to the most difficult systems involving rapidly diffusing, strongly adsorbed species. Indeed it has also been claimed to provide the required accuracy to allow measurements of combined processes such as intracrystalline diffusion accompanied by reaction (Bülow and Micke, 1994). The necessity for allowing for the time constant of the valve in the analysis of the experimental data was noted as the only significant disadvantage of this technique. The recommended approach is to use a numerical simulator (ZEUS), incorporating the time constant of the valve, to fit the experimental pressure response curves and to determine the time constant (R^2/D) for intracrystalline diffusion (Bülow and Micke, 1995). However, for systems such as benzene-NaX the diffusivities obtained from this technique (Bülow et al., 1983) differ substantially from the values obtained by several different experimental methods (Eic et al., 1988; Brandani et al., 1996). This observation led us to examine, in greater detail, the assumptions involved and the inherent limitations of the piezometric method.

In order to gain physical insight into the role played by the system parameters and the operational variables, we chose to derive an analytical solution to the model equations. To make the problem tractable we have used the isothermal approximation which is unlikely to be valid when diffusion is very rapid. Nevertheless, even with this limitation, the results of the analysis provide a useful insight into the system behavior and suggest that the limitations of the technique are in fact more severe than had been assumed. When the piezometric method is applicable, we suggest an alternative integral method to evaluate the diffusional time constant, which eliminates the need to describe the flow through the valve.

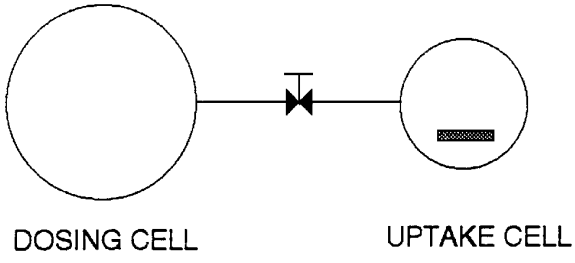

Figure 1. Schematic diagram of a piezometric setup.

Mathematical Model

The experimental apparatus can be considered as two volumes interconnected and separated by a valve (Bülow and Micke, 1995) as shown in Fig. 1. Initially the pressure in the dosing volume is raised to a specified value. At time zero the valve is opened and the pressure response is monitored. It is not clear why only the pressure in the dosing volume is measured (Bülow and Micke, 1995) and in fact we will return to this point later.

One of the basic problems that must be considered is the flow of the gas through the valve. The aim of the present approach is to obtain analytical solutions for the transient behaviour of this system. We therefore consider only small pressure differences, in order to obtain a linearized expression for the flow through the valve. This is experimentally valid, especially for very strongly adsorbed species, far from the Henry's law region where the initial pressure ratio between the dosing and the uptake volume can be quite large. Bülow and Micke (1994) consider the following equation for the flow through the valve

$$\frac{dn}{dt} = \chi_t \chi \left(P_d^2 - P_u^2\right) \tag{1}$$

where P_d and P_u are the pressures in the dosing and uptake volumes, χ is the valve constant and χ_t represents a time dependent function which describes the opening of the valve, being considered by Bülow and Micke (1994) a ramp function with an opening time of 0.5 s.

The sorbate pressure at the surface of the solid varies with time. The maximum uptake rate will occur under the limiting condition where the adsorption process is equilibrium controlled. In order to establish the limits of applicability of the piezometric technique, it is therefore possible to simplify the problem by considering the valve ideal, i.e., with a zero opening time. The system with the "real" valve will be closer to the equilibrium control limit, since the opening of the valve imposes a further limitation on the mass flow to the uptake volume. Considering a small pressure difference, Eq. (1) can be rewritten as

$$\frac{dn}{dt} \simeq \chi \left(P_d^0 + P_u^0\right)(P_d - P_u) = \bar{\chi}(P_d - P_u) \tag{2}$$

The following mass balance applies to the uptake volume (V_u)

$$V_s \frac{d\bar{q}}{dt} + \epsilon V_u \frac{dc}{dt} = \frac{dn}{dt} \tag{3}$$

while for the dosing volume (V_d)

$$\frac{dn}{dt} = -\frac{V_d}{\Re T_d} \frac{dP_d}{dt} \tag{4}$$

where ideal gas behaviour is assumed.

The solid phase mass balance, considering spherical particles, is given by

$$\frac{\partial q}{\partial t} = D\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{5}$$

and

$$\frac{d\bar{q}}{dt} = \frac{3D}{R}\left(\frac{\partial q}{\partial r}\right)_{r=R} \tag{6}$$

As boundary conditions on Eq. (5) we consider equilibrium at the surface between the adsorbed phase and the gas phase, and the symmetry condition

$$\left(\frac{\partial q}{\partial r}\right)_{r=0} = 0 \tag{7}$$

In order to obtain an analytical solution we also must assume a linear equilibrium relationship

$$q(R, t) - q_0 = H(c(t) - c_0) \tag{8}$$

Introducing the following dimensionless variables

$$\tau = \frac{tD}{R^2}; \quad Q = \frac{q - q_0}{q_\infty - q_0}; \quad C = \frac{c - c_0}{c_\infty - c_0};$$
$$\rho_d = \frac{P_d - P_u^0}{P_\infty - P_u^0}; \quad \rho_u = \frac{P_u - P_u^0}{P_\infty - P_u^0} \tag{9}$$

and the following dimensionless parameters

$$\gamma = \frac{1}{3}\frac{\epsilon V_u}{H V_s}; \quad \delta = \frac{1}{3}\frac{V_d}{H V_s}; \quad w = \frac{\Re T_d}{V_d}\frac{\bar{\chi} R^2}{D} \tag{10}$$

it is possible to obtain the analytical solution of this system of equations. Details are given in Appendix A.

The dimensionless pressure in the dosing volume is given by

$$\frac{\rho_d}{\rho_d^0} = \frac{3\delta}{1+3\delta+3\gamma} + \sum_{i=1}^{\infty} a_i \exp\left(-\beta_i^2 \tau\right) \tag{11}$$

where

$$a_i = \frac{2w^2\delta\beta_i^2}{2w^2\delta\beta_i^2 + \left(w-\beta_i^2\right)^2\left(\beta^2 + z_i^2 - z_i + 2\gamma\beta_i^2\right)} \tag{12}$$

$$z_i = 1 + \gamma\beta_i^2 + \frac{w\delta\beta_i^2}{w-\beta_i^2} \tag{13}$$

and β_i are the positive nonzero roots of

$$\beta_i \cot\beta_i - z_i = 0 \tag{14}$$

The dimensionless pressure in the uptake volume is given by

$$\frac{\rho_u}{\rho_d^0} = \frac{3\delta}{1+3\delta+3\gamma} + \sum_{i=1}^{\infty} a_i \left(1 - \frac{\beta_i^2}{w}\right) \exp\left(-\beta_i^2 \tau\right) \tag{15}$$

Form of the Response Curves

Let us consider first the response of the pressure in the dosing volume, i.e., the measured quantity (Bülow and Micke, 1995). The transient in presence of adsorbent is confined within a region bounded by the equilibrium control limit and the response in the absence of the adsorbent. The equilibrium control limit, for the dosing cell, is:

$$\frac{\rho_d}{\rho_d^0} = \frac{3\delta}{1+3\delta+3\gamma} + \frac{1+3\gamma}{1+3\delta+3\gamma} \times \exp\left(-\frac{1+3\delta+3\gamma}{1+3\gamma} w\tau\right) \tag{16}$$

while the pressure in the absence of the adsorbent is given by

$$\frac{\rho_d}{\rho_d^0} = \frac{\delta}{\gamma+\delta} + \frac{\gamma}{\gamma+\delta} \exp\left(-\frac{\gamma+\delta}{\gamma} w\tau\right) \tag{17}$$

The corresponding expressions for the uptake cell are:

$$\frac{\rho_u}{\rho_d^0} = \frac{3\delta}{1+3\delta+3\gamma} \times \left[1 - \exp\left(-\frac{1+3\delta+3\gamma}{1+3\gamma} w\tau\right)\right] \tag{18}$$

and, in the absence of adsorbent

$$\frac{\rho_u}{\rho_d^0} = \frac{\delta}{\delta+\gamma}\left[1 - \exp\left(-\frac{\delta+\gamma}{\gamma} w\tau\right)\right] \tag{19}$$

The curves calculated from Eq. (11), all decrease monotonically to the final equilibrium value. Qualitatively it is therefore difficult, if not impossible, to distinguish between kinetically and equilibrium controlled responses in the dosing cell. The curves calculated from Eq. (15), if far removed from the equilibrium control limit, may exhibit a maximum, allowing a clear qualitative indication of a kinetically controlled process when the pressure in the uptake cell is monitored.

In order to show some representative examples of the response curves we have chosen to fix $\gamma = \delta$, which means that the dosing and uptake cell volumes are assumed to be the same. This is similar to the usual situation. For example, in the system of Bülow and Micke (1994), $V_d/V_u = 1.5$.

Figures 2(a) and (b) show a set of response curves calculated from Eqs. (11)–(15) (with $\gamma = \delta = 0.01$ which is a typical value for a substance that is not strongly adsorbed) for a range of different values of the parameter w, which is essentially the ratio of the time constants for the valve opening and for intracrystalline diffusion. In Fig. 2(a), also shown are the limiting curves for equilibrium control and for empty cell, calculated from Eqs. (16) and (17). It is evident that, over a considerable range of values of w there are only minor differences between the kinetically controlled response and the limiting curves for equilibrium control. This is especially true for the pressure response of the doser vessel for values of w up to approximately 100. The difference from the equilibrium controlled curve is greater in the final stages of the approach to

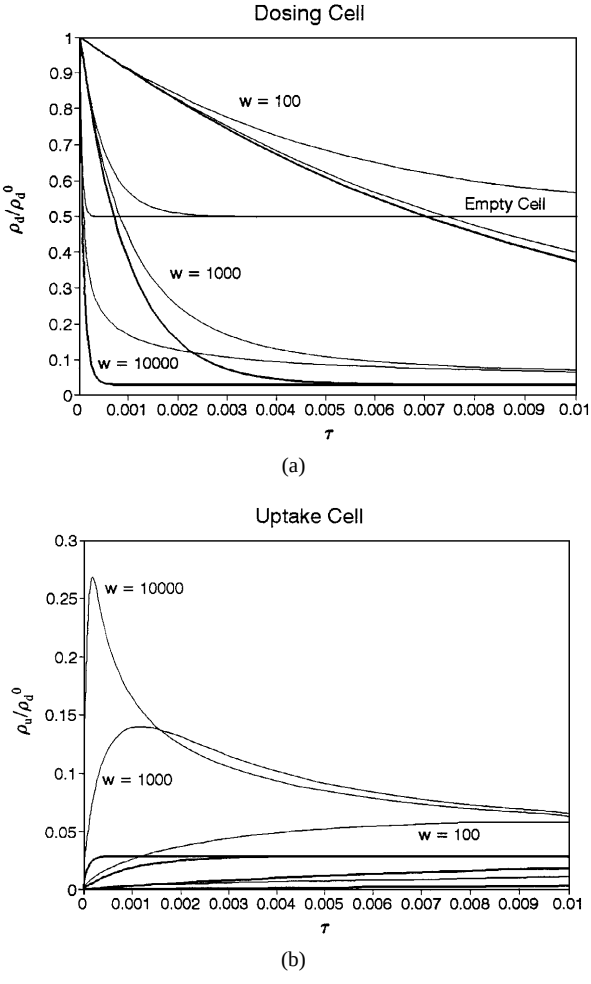

Figure 2. Curves corresponding to $\gamma = \delta = 0.01$ at different values of w: (a) pressure response in dosing cell; (b) pressure response in uptake cell. Heavy solid lines represent equilibrium control.

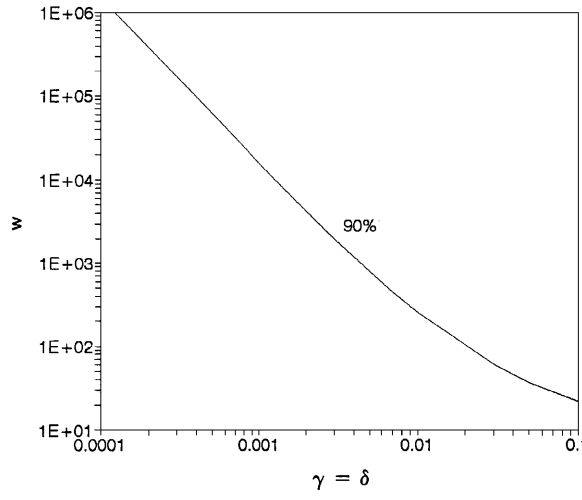

Figure 3. Parameter values required to obtain 90% fractional approach to equilibrium at the corresponding time for 95% fractional approach to equilibrium of the equilibrium controlled process.

equilibrium. However, it has been clearly shown that this portion of the response curve is strongly affected by heat effects (Lee and Ruthven, 1979; Grenier et al., 1994). It follows from this observation that the ability of the piezometric method to yield reliable intracrystalline diffusivity values is severely constrained, and with strongly adsorbed species, is restricted to systems for which the time constant (R^2/D) is relatively large.

To obtain a quantitative assessment of the range of parameter values over which reliable diffusivity data can be obtained when monitoring the pressure in the dosing cell, we have calculated the value of w which yields a 5% deviation from the equilibrium controlled curve at 95% approach to equilibrium of the pressure in the dosing cell (i.e., when at the same time the response has only reached 90% fractional approach to equilibrium). Although this choice is somewhat arbitrary it is logical since the region of the curve beyond 95% fractional approach to equilibrium is strongly influenced by heat effects. Figure 3 shows the values of w as a function of $\gamma = \delta$ for which this criterion is fulfilled. It is clear that the range of conditions over which reliable diffusivity values can be extracted is in fact quite restricted. Furthermore, the required w increases almost quadratically as the equilibrium constant increases, thus limiting the applicability to strongly adsorbed species. It appears that in these cases a possible approach could be that of an increase in temperature, since equilibrium is typically more strongly temperature dependent than the diffusional time constant.

Very little information concerning the diffusional time constant can be obtained from the initial portion of the sorption curve since, in this region, any small error in the experimental measurement leads to a large error in the estimated value for the diffusional time constant. There is therefore no need for, and essentially no benefit to be gained from, the use of a very fast response pressure transducer, since the initial portion of the curve does not contain useful information. The validity of this statement is even more obvious if one considers that the initial portion of the pressure response is also strongly affected by the precise way in which the valve is opened.

The half time has been often used to have an indication of the magnitude of the diffusional time constant

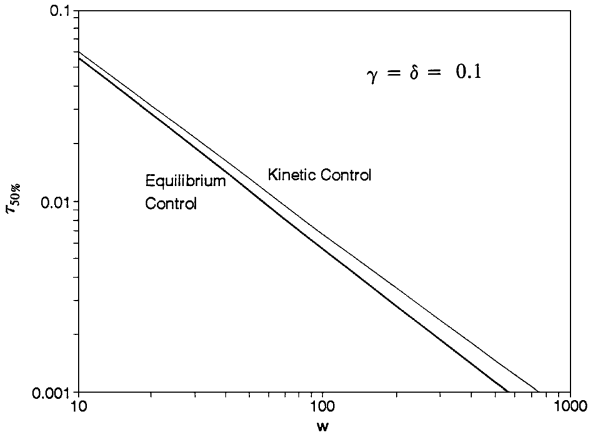

Figure 4. Comparison of the half time for equilibrium control and kinetic control for a favourable value of $\gamma = \delta = 0.1$.

(see for example (Do and Rice, 1995)). The present analysis shows that this quantity should certainly not be used for a piezometric system. To illustrate this point we show in Fig. 4 a plot of the sorption half-time (i.e., the time for the pressure change in the dosing cell to reach half its final value) as a function of the parameter w, for the kinetically controlled and the equilibrium controlled cases at a favourable value of $\gamma = \delta = 0.1$. If a linear scale is used for both $\tau_{50\%}$ and w there is essentially no distinguishable difference between the two curves.

Discussion

Provided that the process is not too fast to permit application of the piezometric method, monitoring the pressure in the uptake cell offers an important advantage which seems, so far, to have been overlooked. If the conditions are far removed from equilibrium control, the pressure in the uptake cell will exhibit a distinct maximum, rather than rising monotonically to its final equilibrium value, as illustrated in Fig. 2(b) for $w > 100$. By monitoring the pressure in the uptake cell it should be possible to detect this maximum and thus to obtain a reliable indication of mass transfer, rather than equilibrium control.

As a representative example we consider the sorption of benzene in large NaX zeolite crystals (120 μm diameter) under the experimental conditions employed by Bülow et al. (1983). All the relevant parameter values are given in Table 1 from which it is possible to estimate $\gamma \sim \delta \sim 6 \cdot 10^{-4}$. According to the criterion

Table 1.

Temperature[1]	353 K
Volume of dosing cell[1]	120 cm^3
Volume of uptake cell[1]	80 cm^3
H[2]	10^7
Intracrystalline diffusivity[1], D_0	$2 \cdot 10^{-7}$ cm^2 s^{-1}
Mass of solid[1]	8 mg
Radius of crystals[1]	60 μm
χ_2^3	1.3 10^{-8} mol Pa^{-2} s^{-1}
P_d^0	30 Pa
P_u^0	20 Pa
γ	0.0005
δ	0.00075
w	2860

[1]From Bülow et al. (1983).
[2]Estimated from Ruthven and Kaul (1993).
[3]From Bülow and Micke (1994).

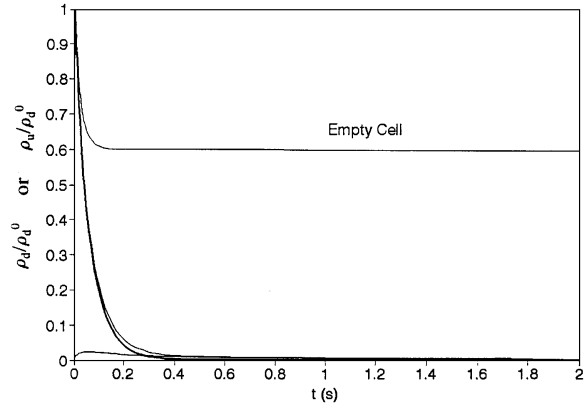

Figure 5. Curves calculated using the parameters reported in Table 1. Pressure response in dosing and uptake cells (solid lines). Equilibrium control limit in dosing cell (heavy solid line).

shown in Fig. 3, reliable diffusivity measurements can be made by following the pressure in the dosing volume only if $w > 10^5$, which translates to $D < 6 \cdot 10^{-9}$ cm^2/s. Pressure response curves for both doser and uptake cells calculated for this system under the specified conditions are shown in Fig. 5. It is quite clear that if the diffusivity is of the order of magnitude reported by Bülow et al. (1983), the uptake curve will be essentially indistinguishable from the equilibrium controlled limiting case and no useful information would be obtainable by the piezometric method. The process is practically complete in less than 1 s, therefore the measured response would essentially reflect the opening of

the valve, since the opening time was approximately 0.7 s (Bülow et al., 1983). To claim that the piezometrically observed behavior is consistent with the self-diffusivity values derived from PFG-NMR measurements is therefore misleading. Under the experimental conditions the pressure response in the doser cell must have been very close to the equilibrium control limit and therefore insensitive to the diffusivity value. Only by monitoring the pressure response in the uptake cell is it possible to obtain an experimental confirmation of the controlling mechanism. Bülow and co-workers, over the last fifteen years, have consistently monitored only the pressure in the dosing cell.

If the pressure in both cells is monitored an additional advantage is gained. It is possible to analyze the response curves without the need for an accurate description of the flow through the valve. This can be accomplished using an overall mass balance that allows to predict the pressure in the dosing cell from the experimentally determined pressure in the uptake volume. The only hypothesis needed is that the differential mass balance equation in the solid is linear, i.e., a concentration independent diffusivity. This is usually the case in experimental investigations. The mean adsorbed phase concentration can be evaluated from a convolution integral of the corresponding solution for a step boundary condition (Kuhfittig, 1978)

$$\bar{Q} = 6 \sum_{n=1}^{\infty} \int_0^{\tau} \exp[n^2 \pi^2 (u - \tau)] \rho_u(u)\, du \qquad (20)$$

The pressure in the dosing cell can be obtained from the overall mass balance

$$\frac{\rho_d}{\rho_d^0} = 1 - \frac{\gamma}{\delta} \frac{\rho_u}{\rho_d^0} - \frac{2}{\delta} \sum_{n=1}^{\infty} \int_0^{\tau} \exp[n^2 \pi^2 (u - \tau)] \frac{\rho_u(u)}{\rho_d^0}\, du \qquad (21)$$

where it is useful to point out that

$$\frac{\rho_u}{\rho_d^0} = \frac{P_u - P_u^0}{P_d^0 - P_u^0}; \quad \frac{1}{3\delta} = \frac{P_d^0 - P_u^0}{P_\infty - P_u^0} - \frac{\gamma}{\delta} - 1 \qquad (22)$$

and that the ratio δ/γ depends only on the geometry of the system.

Therefore, if the pressure in the uptake cell exhibits a distinct maximum, it is possible, using Eq. (21), to obtain the diffusional time constant which is the only unknown parameter. The calculated pressure in the dosing cell will only depend on the intracrystalline mass transfer, since the information regarding the flow through the valve is in the experimentally determined pressure in the uptake cell. This approach is more direct than the one suggested by Micke and Bülow and does not need any hypothesis on the equation governing the flow through the valve, and the actual valve opening. For the numerical integration of Eq. (20), since experimental data are usually collected at fixed time intervals, a simple method will suffice. Figure 6 shows the pressure response in the dosing cell, for $w = 500$ and $\gamma = \delta = 0.1$, calculated from the pressure in the uptake cell (Eq. (15)) using, for the evaluation of the integral, the numerical method reported in Appendix B.

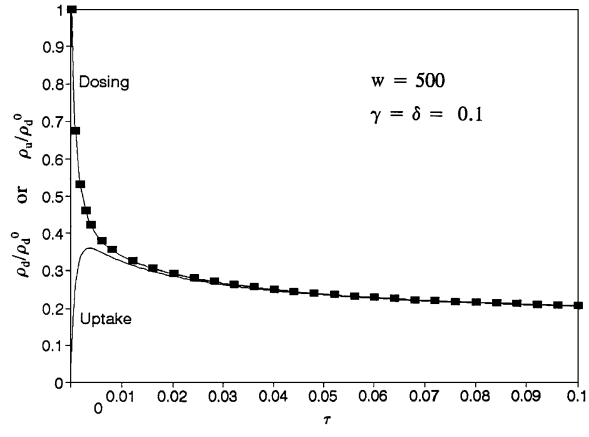

Figure 6. Comparison of the pressure response in the dosing cell calculated from Eq. (11) (continuous curve) and Eq. (21) (symbols) with the numerical integration described in Appendix B. $w = 500$; $\gamma = \delta = 0.1$.

Conclusions

The key features of the piezometric technique have been identified through a simplified analysis. This analysis can be used to establish when the response is kinetically controlled and therefore the technique is applicable to measure intracrystalline diffusivities. It is clear that the limitations on the method, when applied to rapidly diffusing and strongly adsorbed species, are severe. This point seems to have been overlooked by many of the experimenters who have used the piezometric technique. Based on the present approach, it is obvious that the experimentally monitored quantity should be the pressure in the uptake cell, which can provide clear experimental evidence of a kinetically controlled process. There appears to be no simple

approximate method to extract reliable diffusional time constants, due to the uncertainties introduced by the flow of the gas through the valve and the actual opening of the valve. However, it is possible to apply a curve fitting algorithm if the pressures in the dosing and the uptake cell are monitored simultaneously. In this case no previous information on the valve dynamics is required, and the only unknown parameter is the diffusional time constant, which can be varied in order to match the experimental pressure in the dosing cell.

We have therefore provided both theoretical and experimental means of establishing the limits of applicability of the piezometric technique. In light of the present study, all those measurements where only the pressure in the dosing volume has been monitored should be viewed critically, especially for fast diffusing and strongly adsorbed species, since no experimental evidence can support the assumption of a kinetically controlled system.

Appendix A

With the dimensionless variables and parameters defined in Eqs. (9) and (10) we can rewrite the governing equations in dimensionless form.

$$\frac{d\rho_d}{d\tau} = w(\rho_u - \rho_d) \tag{A1}$$

$$\gamma\frac{d\rho_u}{d\tau} + \delta\frac{d\rho_d}{d\tau} + \left(\frac{\partial N}{\partial \xi} - N\right)_{\xi=1} = 0 \tag{A2}$$

with $\xi = r/R$, $N = Q\xi$ and

$$\frac{\partial N}{\partial \tau} = \frac{\partial^2 N}{\partial \xi^2} \tag{A3}$$

with initial and boundary conditions given by

$$\rho_d(0) = \rho_d^0; \quad \rho_u(0) = 0; \quad N(\xi, 0) = 0;$$
$$N(0, \tau) = 0; \quad N(1, \tau) = \rho_u(\tau) \tag{A4}$$

This system of equations can be solved in the Laplace domain.

$$s\tilde{\rho}_d - \rho_d^0 = w(\tilde{\rho}_u - \tilde{\rho}_d) \tag{A5}$$

$$\gamma s\tilde{\rho}_u + \delta\big(s\tilde{\rho}_d - \rho_d^0\big) + \left(\frac{d\tilde{N}}{d\xi} - \tilde{N}\right)_{\xi=1} = 0 \tag{A6}$$

$$s\tilde{N} = \frac{d^2\tilde{N}}{d\xi^2} \tag{A7}$$

with

$$\tilde{N}(1) = \tilde{\rho}_u; \quad \tilde{N}(0) = 0 \tag{A8}$$

Equations (A5)–(A8) can be easily solved to yield the dimensionless pressure in the uptake cell

$$\frac{\tilde{\rho}_u}{\rho_d^0} = \frac{\delta w}{(s+w)\big(\sqrt{s}\coth\sqrt{s} - 1 + \gamma\big) + \gamma w s} \tag{A9}$$

and the dimensionless pressure in the dosing cell

$$\frac{\tilde{\rho}_d}{\rho_d^0} = \frac{\delta w + \sqrt{s}\coth\sqrt{s} - 1 + \gamma s}{(s+w)\big(\sqrt{s}\coth\sqrt{s} - 1 + \gamma\big) + \gamma w s} \tag{A10}$$

Inversion to the time domain can be obtained through the use of the method of residues (Crank, 1975). Equations (11)–(15) are obtained.

Appendix B

We assume that the pressures in the dosing and uptake cells are sampled simultaneously and at equal time intervals. It is necessary to calculate the following functions for each term, n, in the series

$$F_i = \exp(-n^2\pi^2\tau_i)\int_0^{\tau_i}\exp(n^2\pi^2 u)\rho_u(u)\,du \tag{B1}$$

It is simple to derive the following relationship

$$F_{i+1} = \exp(-n^2\pi^2\Delta\tau) \times\left[F_i + \int_{\tau_i}^{\tau_{i+1}}\exp[n^2\pi^2(u-\tau_i)]\rho_u(u)\,du\right] \tag{B2}$$

where $\Delta\tau$ is the time interval $\tau_{i+1} - \tau_i$. All the functions in the series can therefore be calculated iteratively. Assuming that the dimensionless pressure in the uptake cell can be well approximated by a linear function in each subinterval

$$\exp(-n^2\pi^2\Delta\tau)\int_{\tau_i}^{\tau_{i+1}}\exp[n^2\pi^2(u-\tau_i)] \times\left[\rho_u^i + \frac{\rho_u^{i+1} - \rho_u^i}{\Delta\tau}(u-\tau_i)\right]du$$
$$= \frac{\rho_u^i}{n^2\pi^2}[1 - \exp(-n^2\pi^2\Delta\tau)] + \frac{\rho_u^{i+1} - \rho_u^i}{n^4\pi^4\Delta\tau}[n^2\pi^2\Delta\tau - 1 + \exp(-n^2\pi^2\Delta\tau)] \tag{B3}$$

This equation has been used in the integration needed to plot Fig. 6. Equation (B2) can be applied also to higher order polynomial interpolations if higher accuracy is required.

Nomenclature

c Gas phase concentration, mol m^{-3}
C Dimensionless gas phase concentration, Eq. (9)
D Diffusivity, $m^2\ s^{-1}$
H Equilibrium constant
n Moles in dosing cell, mol
N $Q\xi$
P Pressure, Pa
q Adsorbed phase concentration, mol m^{-3}
$\bar{q}$ Average adsorbed phase concentration, mol m^{-3}
Q Dimensionless adsorbed phase concentration, Eq. (9)
r Radial coordinate, m
R Radius of crystals, m
$\Re$ Ideal gas constant, $J\ K^{-1}$
s Laplace domain variable
t Time, s
T Temperature, K
V Volume, m^3
w Ratio of the diffusional and the valve time constants, Eq. (10)

Greek Letters

β_i Eigenvalues of the system, roots of Eq. (14)
γ Ratio of the accumulation in the uptake cell and in the solid, Eq. (10)
δ Ratio of the accumulation in the dosing cell and in the solid, Eq. (10)
ϵ Void fraction in uptake cell
ξ Dimensionless radial coordinate
ρ Reduced pressure, Eq. (9)
τ Dimensionless time, Eq. (9)
χ Valve constant, mol $Pa^{-2}\ s^{-1}$
χ_t Functions describing valve opening
$\bar{\chi}$ Linearized valve constant, mol $Pa^{-1}s^{-1}$

Superscripts

0 Initial value
$\sim$ Function in the Laplace domain

Subscripts

d Dosing
s Solid
u Uptake
∞ Final value at equilibrium

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