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ZLC Response for Systems with Surface Resistance Control

DOUGLAS RUTHVEN* AND FEDERICO BRANDANI
Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstrasse 5, 04103 Leipzig, Germany

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Abstract. The forms of the ZLC response for surface resistance and internal diffusion control are compared and it is suggested that for linear or nearly linear systems, these two patterns of behavior can be distinguished experimentally by examining the ratio of slope to intercept of the ZLC response plotted in log-linear coordinates.

Keywords: ZLC, diffusion, surface resistance

It has been widely assumed that, under conditions such that all extracrystalline resistances to mass and heat transfer are eliminated, the kinetics of sorption in zeolite crystals are controlled by intracrystalline diffusion. A wide range of experimental techniques including frequency response, zero length column (ZLC) and single crystal membrane permeation have been developed to determine intracrystalline diffusivities from measurements of the sorption (or permeation) rates under well defined conditions. Recent experimental studies have, however, shown that in many systems the sorption kinetics are in fact controlled by surface resistance to mass transfer rather than by intracrystalline diffusion (Lehmann et al., 2003; Geier et al., 2003). It is therefore pertinent to examine in detail the form of the ZLC response under conditions of surface resistance control and to enquire whether it is possible in practice to distinguish between intracrystalline diffusion control and surface resistance control from the experimental response curves.

Linear Systems

When the equilibrium relationship is linear the situation is straightforward. For a diffusion controlled system the response is given by Kärger and Ruthven (1992):

$$C = \frac{c}{c_0} = 2L \sum_{n=1}^{\infty} \frac{e^{-\beta_n^2 \tau}}{\beta_n^2 + L(L-1)} \tag{1}$$

$$\beta_n \cot \beta_n + L - 1 = 0 \tag{2}$$

where c_0 is the sorbate concentration in the gas phase with which the sample is initially equilibrated and

$$L = \frac{1}{3} \cdot \frac{FR^2}{KV_s D} \tag{3}$$

The parameter L can be considered as the ratio of the time constants for diffusion (R^2/D) and convective desorption (KV_s/F). When L is small the adsorbed phase is essentially at equilibrium and the desorption rate is controlled entirely by convection. β is small and $\beta_n \cot \beta$ may be replaced by the first term in the series expansion of this function, leading to $L \approx \beta^2/3$ and thus reducing Eq. (1) to the simple exponential form:

$$C = \exp(-Ft/KV_s) \tag{4}$$

In this situation the ZLC desorption curve, plotted as $\ln(c/c_0)$ vs. Ft, becomes simply a straight line of slope $-1/KV_s$, through the origin, invariant with flow rate.

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*Permanent address: Department of Chemical Engineering, University of Maine, Orono, ME, 04469-5737, USA.

Under conditions of kinetic control (large L) Eq. (1) yields the long time asymptote:

$$C \approx \frac{2}{L-1} e^{-\pi^2 \tau} \approx \frac{2}{L} e^{-\pi^2 \tau} \tag{5}$$

The intercept of a plot of $\ln(c/c_0)$ vs. t clearly varies inversely with the purge flow rate while the slope remains constant. Invariance of the slope of such a plot with purge rate thus provides a convenient experimental test for kinetic control.

For surface resistance control the governing equations for a spherical adsorbent particle are:

$$-Fc = V_s \frac{\mathrm{d}\bar{q}}{\mathrm{d}t} \tag{6}$$

$$k(\bar{q} - q_{\mathrm{surf}}) = -\frac{R}{3} \frac{\mathrm{d}\bar{q}}{\mathrm{d}t} \tag{7}$$

Assuming (linear) equilibrium at the particle surface ($q_{\mathrm{surf}} = Kc$) these equations yield:

$$\frac{\mathrm{d}\bar{q}}{\mathrm{d}\tau^1} = \frac{-\bar{q}}{1+\alpha} \tag{8}$$

where $\alpha = \frac{3KV_s}{F} \cdot \frac{k}{R}$ and $\tau^1 = \frac{3kt}{R}$.

Integrating and inserting the initial condition ($\bar{q} = q_o = Kc_o$ at $t = 0$) yields:

$$Q = \frac{\bar{q}}{q_0} = \exp\left(-\frac{\tau^1}{1+\alpha}\right) \tag{9}$$

and hence:

$$C = \frac{c}{c_0} = \frac{\alpha}{1+\alpha} \exp\left(-\frac{\tau^1}{1+\alpha}\right) \tag{10}$$

In the equilibrium control limit (α large corresponding to low flow rate and/or high mass transfer coefficient) Eq. (10) reduces to:

$$C = e^{-\tau^1/\alpha} = \exp(-Ft/KV_s) \tag{11}$$

which is, as expected, identical with Eq. (4).

If α is small (kinetic control) Eq. (10) reduces to:

$$C \approx \alpha e^{-\tau^1} \tag{12}$$

which may be compared with Eq. (5). Although Eqs. (12) and (5) are of the same general form they are in fact easily distinguishable since the ratio of intercept/slope (for a plot of $\ln(c/c_0)$ vs. t) is KV_s/F for the surface barrier model (Eq. 12) and 0.6 KV_s/F for the diffusion control model (Eq. (5)). Such a test is of course only valid if independently measured values of KV_s/F are available. The recommended procedure would be to measure KV_s from the ZLC response at very low flow rates under conditions of equilibrium control (Eq. (4)) and then to use the values so obtained to check the consistency of the kinetic measurements at high purge flow rates.

Non-Linear Systems

An analysis of a non-linear (Langmuirian) diffusion controlled system has been presented by Brandani (1998). The main conclusion is that although the intercept of the long time asymptote decreases with increasing non-linearity, the slope is unaffected by non-linearity so it is still possible to determine the diffusional time constant from the slope of long time asymptote, even under non-linear conditions.

For a Langmuirian system with surface resistance the governing differential mass balance equation (Eqs. (6) and (7)) become:

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}\tau^1}\right)^2 + \left(Q - \frac{1+\alpha}{\alpha\lambda}\right)\frac{\mathrm{d}Q}{\mathrm{d}\tau^1} - \frac{Q}{\alpha\lambda} = 0 \tag{13}$$

with $Q = 1$ at $\tau^1 = 0$. Since this equation is non-linear it must be integrated numerically. The response in terms of the dimensionless effluent concentration is then found from Eq. (6) which becomes:

$$C = -\alpha(1-\lambda)\frac{\mathrm{d}Q}{\mathrm{d}\tau^1} \tag{14}$$

Representative results are shown in Fig. 1 for several different degrees of isotherm non-linearity (measured by λ). It may be seen that for $\alpha < 1.0$ (kinetic control) the response curve, in coordinates of $\ln(c/c_0)$ vs. τ^1, remains essentially linear with the same slope as for a linear equilibrium system ($\lambda = 0$) but with a decreasing intercept. It is remarkable that, despite the non-linearity of Eq. (14), the solution remains close to a simple exponential decay for a wide range of parameters. Only as equilibrium control is approached ($\alpha \gg 1.0$) do the response curves deviate significantly from a simple exponential form, approaching for high values of α the limiting form for complete equilibrium control (Brandani and Ruthven, 2003), which may be

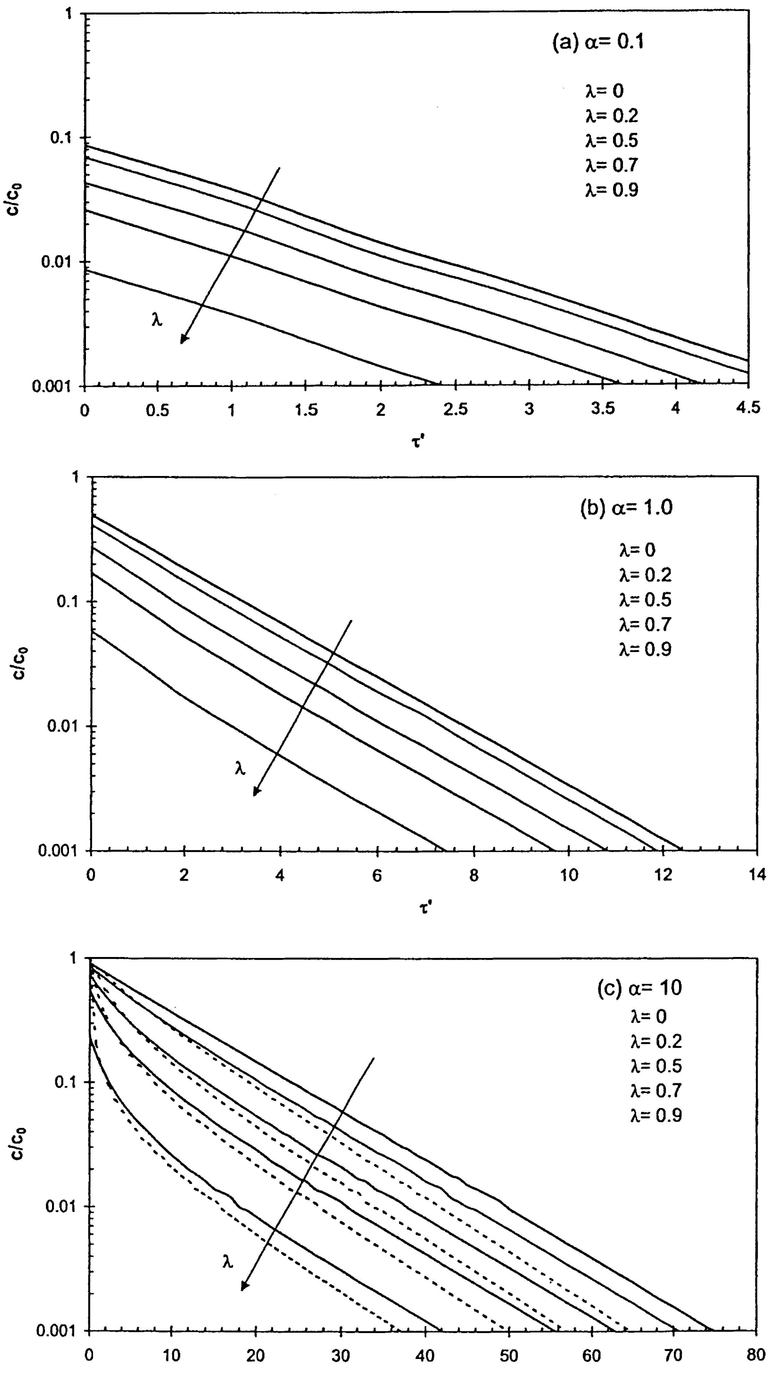

Figure 1. Theoretical ZLC desorption curves for a surface barrier controlled system (calculated by integration of Eq. (13)) showing the effects of parameters α and λ, (a) $\alpha = 0.1$ (kinetic control); (b) $\alpha = 1.0$ (intermediate case); (c) $\alpha = 10$ (approaching equilibrium control); - - - - curves for equilibrium control calculated from Eq. (15).

Table 1. Variation of ratio intercept/slope for surface barrier control ($\alpha \ll 1.0$).

λ	0	0.2	0.5	0.9
$\frac{\text{Int}}{\text{Slope}}$	$\frac{KV_s}{F}$	$0.77\ \frac{KV_s}{F}$	$0.47\ \frac{KV_s}{F}$	$0.1\ \frac{KV_s}{F}$

expressed:

$$\ln C = -\tau^1/\alpha - \frac{\lambda(1-\lambda)(1-C)}{1-\lambda(1-C)} + \ln[1-(1-C)\lambda] \qquad (15)$$

As with a diffusion controlled system the mass transfer coefficient may therefore be found from the slope of a plot of $\ln C$ vs. t, even when the isotherm is substantially non-linear, provided that the condition for kinetic control ($\alpha < 1.0$) is fulfilled.

The ratio of intercept/slope for such plots however decreases with increasing isotherm non-linearity as may be seen from Table 1.

This means that the test proposed to check whether surface barrier or intracrystalline diffusional resistance is dominant is valid only when the isotherm is linear or close to linear. A non-linear system with barrier control can mimic a diffusion controlled linear system for which the Int/Slope ratio should be about $0.6\ KV_s/F$.

Nomenclature

b	Langmuir equilibrium constant
c	sorbate concentration in fluid phase
c_0	initial value of c (during equilibration)
C	c/c_0—dimensionless fluid phase concentration
D	intracrystalline diffusivity
F	purge flow rate
k	surface mass transfer coefficient
L	dimensionless parameter defined by Eq. (3)
q	sorbate concentration in adsorbed phase
$\bar{q}$	value of d averaged over a crystal
q_o	value of q at equilibrium with c_0
q_s	saturation capacity (Langmuir model)
Q	dimensionless adsorbed phase concentration $\bar{q}/q_0$
R	equivalent radius of zeolite crystal
t	time
V_s	volume of adsorbent (in ZLC)
α	dimensionless parameter $\frac{3VK_s}{F}\cdot\frac{k}{R}$
β_n	parameter in Eq. (2)
τ	dimensionless time parameter Dt/R^2
τ^1	dimensionless time parameter $3kt/R$
λ	non-linearity parameter $= q_0/q_s$

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