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Stefano Brandani
Scottish Carbon Capture and Storage, School of Engineering, The University Edinburgh, The King’s Buildings, Edinburgh, United Kingdom.

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A Simple Graphical Check of Consistency for Zero Length Column Desorption Curves

The mass balance for a zero length column (ZLC) system leads to a very simple check which can be used to ensure internal consistency of the experimental curves. This is based on reporting experiments run at different flow rates on a \( c/c_0 \) vs. \( Ft \) plot, where \( F \) is the volumetric flow rate. The proposed method is applied to two different sets of results from the literature and can be used to identify that in one case the data are inconsistent. The results lead to an important recommendation: any future contribution reporting ZLC curves should include the \( c/c_0 \) vs. \( Ft \) plot which can confirm the internal consistency of the results and indicate if the experiments are carried out under equilibrium or kinetic control.

Keywords: Consistency check, Equilibrium control, Kinetic control, Zero length column

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1 Introduction

The zero length column (ZLC) technique was first introduced in 1988 by Eic and Ruthven as a novel chromatographic technique to measure intra-crystalline diffusion using small samples of zeolite [1]. The validity of the basic assumptions of the theoretical model has been widely investigated and the simple model has been modified to be applicable for measurements under nonlinear conditions [2, 3], non-isothermal systems [4], for biporous adsorbents [5, 6], and for systems with crystal size distribution [7]. The technique was successfully applied to the determination of equilibrium isotherms [8, 9] by running the system under equilibrium control conditions. In this case, a plot of \( c/c_0 \) vs. \( Ft \) allows confirming that equilibrium is being measured when curves at different flow rates overlap [8]. The same plot permits to demonstrate that the system is under kinetic control. Even though the technique has been in use for over 25 years, there are still no simple checks for the consistency of ZLC experiments and if individual curves are analyzed separately this may lead to the incorrect interpretation of the results as reported by Mangano et al. [10]. In this contribution, a simple test is presented and applied to show how to recognize inconsistent results.

2 Theory

The overall mass balance for a chromatographic column with a single adsorbing component in an inert carrier gas can be written as:

\[
\frac{V_S}{dt} \frac{dc}{dt} + \frac{V_F}{dt} \frac{dc}{dt} = F(c_{IN} - c_{OUT})
\]  

Here, \( \bar{c} \) is the average fluid phase concentration; \( \bar{q} \) is the average adsorbed phase concentration; \( c_{IN} \) is the inlet concentration; \( c_{OUT} \) is the fluid phase concentration at the outlet; \( F \) is the volumetric flow rate; \( V_S \) is the volume of the solid in the column; and \( V_F \) is the volume of the fluid in the column.

The basis of the ZLC technique is that the axial dimension is reduced to the point where dispersion dominates and the fluid phase concentration is independent of position and equal to the average concentration. For the standard desorption experiment \( c_{IN} = 0 \) and \( c = c_{OUT} \). Therefore, the mass balance becomes:

\[
\frac{V_S}{dt} \frac{dq}{dt} + \frac{V_F}{dt} \frac{dc}{dt} = -F \bar{c}
\]  

The integral with respect to time will yield:

\[
V_S[q(t) - q(0)] + V_F[c(t) - c(0)] = - \int_0^t F \bar{c} dt
\]  

Rearranging and dividing by \( c(0) = c_0 \):

\[
\int_0^t \frac{F \bar{c}}{c_0} dt = \frac{\bar{q}(0) - \bar{q}(t)}{c_0} + V_F \left[ 1 - \frac{c(t)}{c_0} \right]
\]  

Wang et al. [11] have shown that the flow rate at the outlet of a ZLC can be approximated by:

\[
F = \frac{F_{Car} \gamma}{1 - \gamma + \Delta}
\]  

1) List of symbols at the end of the paper.
where $F_{\text{Car}}$ is the flow rate of the inert carrier gas, $y$ is the mole fraction of the adsorbate, and $\Delta$ is a flow rate correction term. If the system is close to linear and the dimensionless Henry law constant $K$ is greater than 100, then $\Delta$ can be neglected when $y < 0.2$. This indicates that if the experiments are run under dilute conditions, $y < 0.05$, the flow rate remains to an excellent approximation equal to the flow rate of the carrier gas and constant. In these conditions, Eq. (4) can be written as:

$$
\int_{0}^{t} \frac{c}{c_0} \, dt = V_S \left[ \frac{q(0) - \bar{q}(t)}{c_0} \right] + V_T \left[ 1 - \frac{c(t)}{c_0} \right]
$$

Eq. (6) shows that for dilute systems if the ZLC curves are plotted as $c/c_0$ vs. $t$, the area under the curves is independent of the flow rate and represents the sum of the normalized accumulation in the fluid and adsorbed phases. Eq. (6) results from a simple mass balance and the assumption that the system is dilute; therefore, it can be used to distinguish good data from clearly inconsistent data.

The general model of Brandani and Ruthven [12] can be applied to generate the theoretical curves to understand the behavior under kinetic control. This model includes mass transfer controlled by a diffusion process, a non-zero accumulation in the fluid phase, and a linear adsorption isotherm. For this model the controlling dimensionless groups are:

$$
L = \frac{1}{3} \frac{FR^2}{DKV_S}; \quad \gamma = \frac{1}{3} \frac{V_F}{KV_S}
$$

where $D$ is the diffusivity, $K$ is the dimensionless Henry law constant, and $R$ is the particle radius.

Fig. 1 ($\gamma = 0.01$) is representative of a gas system. The dimensionless time is:

$$
\tau = \frac{tD}{R^2}
$$

The short time solution to this model is given by [12]:

$$
\frac{c}{c_0} \approx 1 - \tau \frac{L}{\gamma} \approx \exp \left( -\tau \frac{L}{\gamma} \right) = \exp \left( \frac{-Ft}{V_F} \right)
$$

In the limit of low flow rates ($L \ll 1$), the system becomes equilibrium-controlled and the solution to the model reduces to a simple exponential [8]:

$$
\frac{c}{c_0} = \exp \left( -\tau \frac{3L}{1 + 3\gamma} \right) = \exp \left( -\frac{Ft}{KV_S + V_T} \right)
$$

The traditional way of reporting ZLC experiments is the $c/c_0$ vs. $t$ plot, which is presented in Fig. 1, where time is scaled by the dimensionless time constant.

As the flow rate increases and the system becomes kinetically controlled, the long-time asymptote has a slope that is then almost independent of flow rate and is used to determine the diffusion time constant [1].

From Eq. (10) it seems appropriate to plot $c/c_0$ vs. $\tau = \frac{3L}{1 + 3\gamma}$ as the dimensionless equivalent of the $c/c_0$ vs. $Ft$ plot. The choice of how to normalize $Ft$ is based on use of the total...
accumulation in the system divided by \( c_0 \). Fig. 2 illustrates the qualitative behavior that should be observed in a ZLC system complying with the correct mass balance when the system is dilute, and as a result the flow rate is assumed constant.

It is clear that for the integral given by Eq. (6) to remain constant with flow rate, an increase in flow rate corresponds to a more pronounced decrease in the fluid phase concentration followed by a long time asymptote that crosses the curves with lower flow rate. As the \( L \) value increases (increasing flow rate) in a kinetically controlled system there must always be a point where curves at two flow rates cross. The only exception is in the limit of equilibrium control where the curves overlap in the entire concentration range.

3 Applying the Test to Literature Data

Fig. 3 presents an example of a series of ZLC curves at different flow rates taken from Hu et al. [13]. The set of curves clearly complies with the qualitative behavior and is consistent with the mass balance, Eq. (6). Each curve at a higher flow rate crosses the ones at lower flow rates. The experiments were carried out with a single pellet, 6 mg of sample, and, having passed the consistency check, the plot also clearly indicates that the system is under kinetic control. The fact that all the curves at different flow rates are consistent was confirmed independently by Friedrich et al. [14], who were able to correlate simultaneously all the experiments at different temperatures and different flow rates with an automated regression algorithm which took into account also the nonlinearity of the isotherm. In this case, a dual-site Langmuir model was used to describe the CO\(_2\)/13X system up to 0.1 bar. Having demonstrated kinetic control, Hu et al. [13] were then able to show that the mechanism was in fact macropore diffusion using the simple and well-known experimental check of changing the carrier gas [5].

The usefulness of the proposed consistency check becomes apparent when one considers a recent publication by Silva and Rodrigues [15] (data originally published by Silva et al. [16]). Fig. 4 displays the ZLC curves for dilute CO\(_2\) (\( y = 0.01 \)) on 13X measured in their laboratory. The validity of these experiments was already questioned by Mangano et al. [10], but at the time the plot of the ZLC curves vs. \( F_t \) was not available.

What is very surprising is that Silva and Rodrigues [15] use this plot to indicate that their data is kinetically controlled and that the analysis of Mangano et al. [10] is incorrect. They have clearly not tried to model simultaneously the two curves and are missing the important point that the mass balance is not the same for the same column at different flow rates, i.e., that the measurements are inconsistent and, therefore, no possible conclusion can be drawn from the data. This should be obvious from the analysis produced above, since this is a clear example where the flow rate is to a very good approximation constant throughout the experiment. The fact that the lower flow rate curve is always below the higher flow rate one in the \( F_t \) plot is a direct demonstration that the apparent accumulation in the system is not independent of the flow rate.

What Silva and Rodrigues [15] fail to realize is that no consistent theory can interpret simultaneously the two curves shown in Fig. 4. This is why Mangano et al. [10] had to carry out independent measurements and prove that with a ZLC under the same normalized conditions (values of the \( L \) parameter, see Eq. (7)) the CO\(_2\)/13X system is equilibrium-controlled. This conclusion then explains why curves reported by Silva et al. [16] with two different pellet sizes overlap, a result that had erroneously been interpreted as micropore diffusion control. The misinterpretation of
the controlling mechanism is also confirmed by independent measurements using a variety of experimental techniques [17–21].

A possible explanation to the observed behavior in Fig. 4 could be that the curves have been baselined incorrectly. Another possible explanation can be due to the use of gases that are not completely dried and the lower flow rate follows in time the higher flow rate experiment. The Henry law constant for CO$_2$ on hydrophilic zeolites is very sensitive to traces of water [22], but this is a less likely explanation than the previous one considering the relatively large sample quantity, 50 mg, used by Silva et al. [16]. Another possibility is that the authors have incorrectly reported curves from two different temperatures. We can think of several hypotheses, but the only possible conclusion is that the data are incorrect.

From the fact that such a simple test can prove so easily when data are wrong demonstrates the importance of the proposed consistency check. Experimental curves which seem fine on a $c/c_0$ vs. $t$ plot can be seen as incorrect immediately by looking at the $c/c_0$ vs. $Ft$ plot. What must be also clear is the fact that the mass balance is applicable equally to nonlinear systems, i.e., there are no simplifying assumptions based on linearity of the isotherm in Eq. (6). For nonlinear isotherms the dimensionless Henry law constant, $K$, becomes the dimensionless slope of the secant of the isotherm, and remains independent of the flow rate as is the case for the data shown in Fig. 3. Therefore, for any kinetically controlled system, curves at different flow rates must cross even for nonlinear systems. What is clearly evident from Fig. 4 and remains absolutely incontrovertible is the fact that the $Ft$ plot proposed by Silva and Rodrigues [15] demonstrates that their data are inconsistent and cannot be used to show how ZLC curves should be interpreted nor can they be employed to indicate that the system is kinetically controlled.

4 Conclusions

The ZLC technique is very simple to install and use, but, because any kinetic or nonlinear equilibrium effect will yield a shape of the response curve that is very similar to the classical response, it is essential to have simple consistency checks available to the users. This is even more evident when those who are supposed to be experts in the field can fail to recognize the fundamental inconsistency of the data that they report.

This contribution demonstrates how to use the $c/c_0$ vs. $Ft$ plot to determine whether curves at different flow rates show the same accumulation in the system. The simple check is to ensure that all curves at higher flow rate start initially on a steeper descent but then cross the curves at lower flow rates. The only exception to this is when the system is equilibrium-controlled, in which case all the curves should overlap. This consistency check is valid also when the experiment is run under nonlinear conditions because it is based on the mass balance for a chromatographic column. The test was applied to two cases reported in the literature confirming in one case consistency of the data and in one case indicating clear issues with incorrect experimental results.

The proposed test is particularly useful when data are to be processed using an automated fit of multiple experiments. In this case, an automated consistency check can be performed calculating numerically the integral in Eq. (6). Data that fail the consistency check cannot be correlated by any model, given that the fundamental equations obtained from a mass balance are violated.

Given the fact that the gas flow rate can be changed very easily in a ZLC experiment, we strongly recommend that any future contribution reporting ZLC curves should include the $c/c_0$ vs. $Ft$ plot which can confirm the internal consistency of the results and indicate if the experiments are carried out under equilibrium or kinetic control. The proposed method represents such a simple and immediate consistency check which should be adopted widely.

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Symbols used

- $c$ [mol m$^{-3}$] concentration in the ZLC and at the outlet
- $\bar{c}$ [mol m$^{-3}$] average fluid phase concentration in a column
- $c_0$ [mol m$^{-3}$] initial (time = 0) concentration in the ZLC
- $c_{IN}$ [mol m$^{-3}$] inlet concentration in a column
- $c_{OUT}$ [mol m$^{-3}$] outlet concentration in a column
- $D$ [m$^2$s$^{-1}$] diffusion coefficient
- $F$ [m$^3$s$^{-1}$] volumetric flow rate
- $F_{carr}$ [m$^3$s$^{-1}$] volumetric flow rate of inert carrier gas
- $L$ [-] dimensionless group defined in Eq. (7)
- $\bar{q}$ [mol m$^{-3}$] adsorbed phase concentration
- $R$ [m] particle radius
- $t$ [s] time
- $V_F$ [m$^3$] volume of fluid
- $V_S$ [m$^3$] volume of solid
- $y$ [-] mole fraction in fluid phase

Greek letters

- $\gamma$ [-] dimensionless group defined in Eq. (7)
- $\Delta$ [-] flow rate correction term
- $\tau$ [-] dimensionless time
References

Communication: Still no simple checks exist for the consistency of zero length column experiments and if individual curves are analyzed separately this may lead to the incorrect interpretation of the results. A very simple and immediate consistency check is proposed and applied to two cases reported in the literature to demonstrate how to recognize inconsistent results.

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