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On the Chromatographic Measurement of Equilibrium Isotherms Using Large Concentration Steps

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Abstract. The measurement of equilibrium isotherms from the dynamic response of an adsorption column subject to a large pulse or step change in inlet concentration requires the simultaneous measurement of concentration and flowrate. Based on the observation that for a single sorbate-carrier system the concentration and velocity transients are coupled, a procedure to estimate the true column outlet carrier flowrate from the measured concentration signal is derived, which is consistent with an overall mass balance of the carrier gas. The proposed approach has been validated using experimental breakthrough curves for CO_2 on UOP HiSIV 3000 pellets for integral step changes up to 75% in CO_2 concentration.

Keywords: adsorption equilibrium, breakthrough experiment, integral steps

1. Introduction

Reliable equilibrium data are the basis for the correct sizing and design of most adsorption separation units. Equilibrium measurements can be carried out using a wide range of techniques, which can be based on closed systems, such as gravimetric or volumetric methods (see, for example, Rouquerol et al., 1999), or open flow systems, such as chromatography pulse or step experiments (see, for example, Ruthven, 1984).

Chromatographic methods can be used to measure entire adsorption isotherms by integration of a sequence of pulse or differential step runs, which determine the local derivative of the isotherm (Ruthven, 1984). This procedure has an inherent problem, since systematic errors will increase progressively and affect disproportionately the isotherm data at high concentrations. Therefore it would be extremely useful to be able to correctly interpret integral step measurements, i.e. breakthrough experiments with large concentration variations, in order to improve the accuracy of the measured isotherms.

The current analysis of breakthrough curves is based on the assumption that either the volumetric flowrate through the column is constant (Ruthven, 1984) or that the carrier flowrate remains constant (Malek and Farooq, 1997). The constant volumetric flowrate assumption is strictly valid only for differential concentration steps and leads to the well known equation used to evaluate the Henry law constant of the adsorption isotherm (Ruthven, 1984), which for a desorption experiment is given by

$$[\varepsilon + (1-\varepsilon)K]\,\frac{V}{F} = \int_0^\infty \frac{c}{c_0}dt \qquad (1)$$

To interpret large step breakthrough experiments, Malek and Farooq (1997) recognized the limitations of Eq. (1) and appear to have been the first to propose the alternative approach of assuming a constant carrier gas flowrate. Their results indicate that this approximation breaks down for large step changes in the mole fraction of the sorbates, since the equilibrium constants from adsorption and desorption experiments tend to differ.

In the gas chromatography literature, the effect of the variable gas flowrate has long been recognised and referred to as the *sorption effect* (Bosanquet and Morgan, 1957). Although in principle both concentration and flowrate can be measured simultaneously, in practice the flowrate measurements are complicated due to the concentration dependence of the gas viscosity. For pulse experiments Mason and Buffham (1996a, 1996b, 1997) have elegantly resolved this problem introducing a long delay pipe after the adsorption column. The delay pipe allows the measurement of flowrate variations at constant concentration first, as the change in volumetric flowrate travels through the system at the speed of sound, and then the chromatogram is measured from the second pressure drop variation, which is due to the concentration dependence of the gas viscosity that is detected when the concentration peak reaches the capillary tube.

The fact that a delay line needs to be included in the experimental technique of Mason and Buffham (1996a), indicates that the velocity and concentration transients are coupled. It is therefore possible in principle to measure one of the two and predict the other. Given the availability of standard commercial gas chromatographic equipment that include concentration detectors, such as a TCD, it is the aim of this contribution to establish a procedure that allows the correct interpretation of the breakthrough experiments with large concentration steps taking into account carrier flowrate transients.

2. Theory

During a breakthrough experiment of an adsorption column, initially at equilibrium with a gas concentration c_0, subject to a step change to c_1 in the inlet concentration, the total accumulation in the column can be written as

$$\left[\varepsilon\frac{d\bar{c}}{dt}+(1-\varepsilon)\frac{d\bar{q}}{dt}\right]V = (Fc)_{\mathrm{IN}}-(Fc)_{\mathrm{OUT}} \quad (2)$$

Assuming equilibrium between the gas and solid phases, ideal gas behaviour and an isothermal system, this equation can be rewritten in terms of the carrier gas flowrate and the adsorbate mole fractions as:

$$[\varepsilon+(1-\varepsilon)K]\,V\frac{d\bar{y}}{dt} = \left(F_{\mathrm{Carr}}\frac{y}{1-y}\right)_{\mathrm{IN}} - \left(F_{\mathrm{Carr}}\frac{y}{1-y}\right)_{\mathrm{OUT}} \quad (3)$$

where $K = (q_1-q_0)/(c_1-c_0)$ represents the slope of the secant of the adsorption isotherm between the two end points.

From Eq. (3), it is evident that to measure equilibrium properties it is in principle necessary to determine simultaneously flowrate and composition. Malek and Farooq (1997) have assumed a constant carrier flowrate and, for a step change in inlet concentration, Eq. (3), is integrated to obtain

$$\varepsilon+(1-\varepsilon)K = \frac{F_{\mathrm{Carr}}}{(y_1-y_0)\,V}\int_0^{\infty}\frac{y_1}{1-y_1}-\frac{y}{1-y}dt \quad (4)$$

To understand why Eq. (4) is not applicable to large concentration steps, it is necessary to consider the mass balance for the carrier gas

$$-[\varepsilon+(1-\varepsilon)K_{\mathrm{Carr}}]\,V\frac{d\bar{y}}{dt} = (F_{\mathrm{Carr}})_{\mathrm{IN}}-(F_{\mathrm{Carr}})_{\mathrm{OUT}} = \Delta F_{\mathrm{Carr}} \quad (5)$$

where for generality it is assumed that the carrier gas is also adsorbed. Equation (5) clearly shows that when the sorbate is being adsorbed in the column the carrier flowrate must vary, and that if the column is run close to equilibrium conditions the transient of the flowrate is coupled directly to the transient in concentration. The integral of the difference in carrier flowrate over the entire experiment is:

$$\int_0^{\infty}\Delta F_{\mathrm{Carr}}dt = \Delta V_{\mathrm{Carr}} = -[\varepsilon+(1-\varepsilon)K_{\mathrm{Carr}}]\,V(y_1-y_0) \quad (6)$$

This last result shows that only for small step changes the carrier flowrate can be assumed to be constant and Eq. (4) should yield a close approximation to the true equilibrium constant.

Qualitatively it is possible to argue that at the start of the breakthrough experiment, while $y = y_0$, $|\Delta F_{\mathrm{Carr}}|$ will be maximum, and it will monotonically decrease to zero as the concentration wave exits the column. The simplest functional form that corresponds to this description is

$$\Delta F_{\mathrm{Carr}} \approx \Delta V_{\mathrm{Carr}}\frac{y-y_1}{\int_0^{\infty}(y-y_1)\,dt} \quad (7)$$

This approximation is consistent with the overall mass balance of the carrier gas, Eq. (6), which provides the definition of ΔV_{Carr}, and should be applicable over a wide concentration range. Therefore the equilibrium isotherm can be obtained from a breakthrough experiment using the following equation along with the approximation for the carrier gas flowrate given by Eq. (7)

$$\varepsilon + (1-\varepsilon)K = \frac{F_{\mathrm{Carr}}}{(y_1 - y_0)\,V}\int_0^{\infty}\left[\frac{y_1}{1-y_1} - \left(1+\frac{\Delta F_{\mathrm{Carr}}}{F_{\mathrm{Carr}}}\right)\frac{y}{1-y}\right]dt \quad (8)$$

It is useful to derive also the limiting expressions for an adsorption experiment of a column initially empty ($y_1 = Y, y_0 = 0$)

$$\varepsilon + (1-\varepsilon)K = \frac{F_{\mathrm{Carr}}}{YV}\int_0^{\infty}\left[\frac{Y}{1-Y} - \left(1+\frac{\Delta F_{\mathrm{Carr}}}{F_{\mathrm{Carr}}}\right)\frac{y}{1-y}\right]dt \quad (9)$$

and the corresponding desorption experiment of a column initially saturated ($y_1 = 0, y_0 = Y$)

$$\varepsilon + (1-\varepsilon)K = \frac{F_{\mathrm{Carr}}}{YV}\int_0^{\infty}\left[\left(1+\frac{\Delta F_{\mathrm{Carr}}}{F_{\mathrm{Carr}}}\right)\frac{y}{1-y}\right]dt \quad (10)$$

3. Experimental Results

Experiments were carried out on an apparatus developed at UCL as part of the undergraduate laboratory course, schematically shown in Fig. 1. This system was adapted from a similar experiment originally designed by D.M. Ruthven at the University of Maine. To ensure a constant inlet flowrate to the column, the adsorbate flowrate is controlled using a three way valve. It was found that this configuration yields more accurate results in comparison to the option of a step change in the mass flow controller set-point due to the oscillations of the control system. Relatively low flowrates were used for the large concentration step experiments, to ensure that pressure drops through the system would not affect the results and that the column is close to equilibrium conditions. The concentration was measured using a Gow-Mac TCD which was modified and tuned to increase signal accuracy. For the purposes of validation of the theory presented, a series of experiments were carried out at a constant temperature,115°C, which was maintained by flowing condensing steam at a fixed pressure in the column jacket. The packing consisted of UOP HiSIV 3000 pellets with an equivalent diameter of 1–2 mm. At this temperature nitrogen on silicalite will effectively behave as an inert carrier (Dunne et al., 1996) and $K_{\mathrm{Carr}} \approx \varepsilon_P$. The adsorption isotherm for carbon dioxide should be nearly linear and follow Langmuir's isotherm equation (Golden and Sircar, 1994).

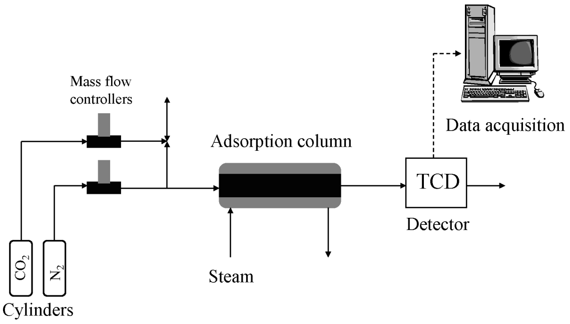

Figure 1. Schematic diagram of the adsorption breakthrough apparatus.

The column parameters are summarised in Table 1.

The voidage of the pellets was calculated to be 0.37 from the crystal density of silicalite (Baerlocher et al., 2001) and the pellet density.

Figure 2 shows a representative set of adsorption and desorption experimental results for an integral step of 50% in CO_2 concentration and the corresponding additional term in the integral mass balance. Equilibrium constants are extracted from these curves using Eqs. (9) and (10) and are compared to the case where a constant carrier flowrate is assumed (Malek and Farooq, 1997). Figure 3 shows the Langmuir plot of the experimental results and the corresponding adsorption data and the Langmuir isotherm. To obtain the experimental isotherm, given the temperature and pressure of the column, the gas phase concentration is calculated using an equation of state, in this case the ideal gas law, and the adsorbed phase concentration is obtained from the measured K value. The results indicate that the adsorption and desorption runs, when analised using the

Table 1. Column parameters.

Mass of adsorbent (kg)	0.123
Pellet density (kg/m^3)	1130
Column length (m)	0.6
Column diameter (m)	0.021
Bed voidage	0.475

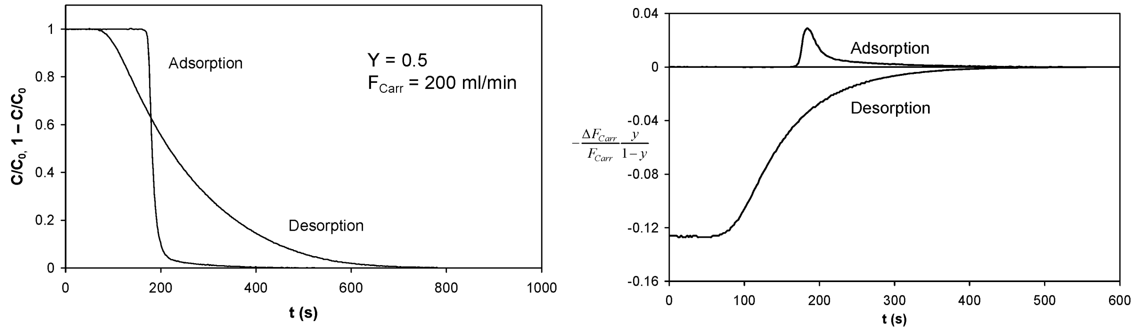

Figure 2. Experimental results for $Y = 0.5$ and corresponding correction term.

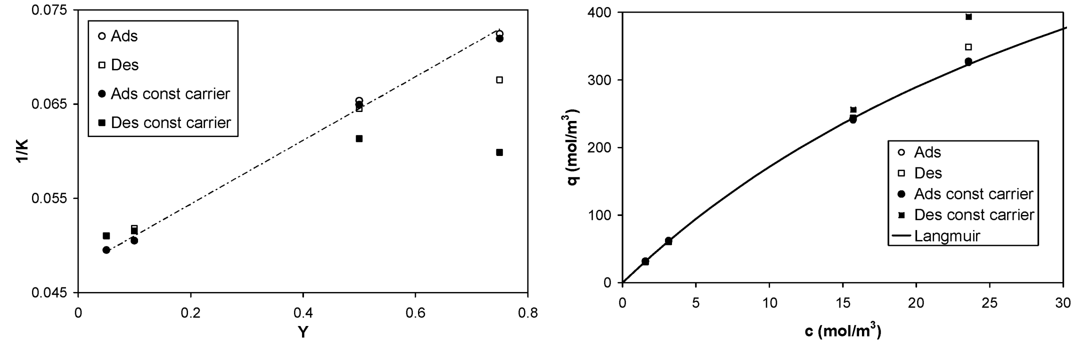

Figure 3. Langmuir plot and adsorption isotherm.

proposed flowrate approximation, yield the same values of equilibrium constants and the isotherm follows the Langmuir equation. At the highest concentration step, the desorption result tends to differ, while the adsorption value follows the trend of the lower concentrations. For this system it appears that the adsorption results are consistent even for an integral step of 75% in CO_2 concentration.

A second observation that can be made is that the constant carrier flowrate assumption (Malek and Farooq, 1997) breaks down already at 50% in concentration step changes, but the adsorption runs still yield a reasonable approximation which slightly overestimates the adsorbed phase concentration.

These results indicate that equilibrium constants derived from adsorption and desorption experiments with large concentration steps should not be averaged. When both values are close, this should be taken as a confirmation of the validity of the measurement, but when the values differ the correct result will be much closer to the adsorption measurement. To sustain this argument, one can refer to the structure of Eq. (9), which does not include any approximations. The correction term $y\Delta F_{\text{Carr}}/F_{\text{Carr}}(1-y)$ is the product of y and the carrier flowrate variation. For the adsorption experiment, this term is almost always zero, since at the start of the experiment $y = 0$ and at the end of the experiment $\Delta F_{\text{Carr}} = 0$. On the other hand, in the desorption experiment the correction term in Eq. (10) is zero only at the end of the experiment where$\Delta F_{\text{Carr}} = 0$. These trends can be seen clearly in Fig. 2.

4. Conclusions

A new method to interpret the dynamic breakthrough experiment has been proposed, which includes the prediction of the carrier gas flowrate transients from the measured concentration signal. The proposed approximate solution was shown to be consistent with an overall mass balance for the carrier gas. Experimentally the proposed approach can be checked from the measured values of the equilibrium constants obtained from both adsorption and desorption experiments, as this will also confirm if heat effects can be neglected. Results from both adsorption and desorption experiments have shown that the approach can be applied with confidence to integral step changes of up to 50% variation in mole fractions. For larger concentration changes the theoretical arguments presented and the experimental evidence suggest that adsorption experiments will yield more accurate values of the equilibrium constants, when compared to desorption runs.

The proposed approximation is generally applicable to any flow through technique used to measure equilibrium isotherms and can be extended also to the zero length column (ZLC) technique, where an entire adsorption isotherm can be determined from a single experiment using a large concentration step (Brandani et al., 2003).

Nomenclature

c	Gas phase concentration (mol/m^3)
$\bar{c}$	Average concentration in the column (mol/m^3)
F	Volumetric flowrate (m^3/s)
$\bar{q}$	Average adsorbed concentration in the column (mol/m^3)
t	Time (s)
V	Column volume (m^3)
y	Outlet sorbate mole fraction (–)
Y	Mole fraction step change in integral breakthrough experiments (–)

Superscripts and subscripts

Carr	Carrier gas
0	Initial value in the adsorption column
1	Final value in the adsorption column

Greek letters

ε	Column bed voidage (–)
ε_P	Pellet voidage (–)
ρ_P	Pellet density (kg/m^3)

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