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Flowrate correction for the determination of isotherms and Darken thermodynamic factors from Zero Length Column (ZLC) experiments

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Abstract The ZLC method is a simple and rapid approach to measure adsorption equilibrium isotherms. When extending this technique to the measurement of large concentration steps, the primary problem is how to estimate the outlet flowrate from the measured concentration signal. In this paper, two different corrections to calculate the outlet flowrate are introduced. Based on simulations of the ZLC system that are in good agreement with reported experimental results, a series of desorption cases were simulated. Isotherms were calculated using the two approximations of the outlet flowrate. The comparisons are used to identify the range in which the approximations are applicable. Darken's thermodynamic correction factors were also calculated to verify the validity of the flow corrections.

Keywords Adsorption equilibrium · Mathematical model · Numerical simulation · ZLC

Abbreviations

a	intercept of simple exponential
b	Langmuir parameter, m^3/mol rate coefficient of simple exponential, s^{-1}
c	sorbate concentration in gas phase, mol/m^3
c_p	concentration in particles, mol/m^3
C	dimensionless fluid phase concentration
F	effluent flow rate or inert flow rate, m^3/s
K	equilibrium Henry constant
K_L	global mass transfer coefficient, m/s
Nc	number of components in ZLC cell
q	adsorbed phase concentration of adsorbate, mol/m^3
q_s	adsorbed phase concentration at saturation, mol/m^3
q^*	equilibrium value of q, mol/m^3
Q	dimensionless concentration
R_p	radius of spherical particle equivalent to the solid pellet, m
t	time, s
V_f	volume of gas in the ZLC cell, m^3
V_s	volume of solid in the ZLC cell, m^3
y	the mole fraction of the adsorbing species

Greek symbols

ε	voidage of adsorbent bed
ε_p	voidage of adsorbent particle
λ	nonlinearity parameter
τ	dimensionless time

Subscripts

in	inlet
out	outlet
i	refers to species i
T	total
0	initial condition
1	dual-site Langmuir for site 1
2	dual-site Langmuir for site 2
c/Car	carrier

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1 Introduction

Adsorption equilibrium is a fundamental property needed for the design of separation processes. Techniques such as

volumetric and gravimetric methods have been used traditionally to measure equilibrium data (Keller and Staudt 2005). The Zero Length Column (ZLC) method has been shown to provide a simple and rapid way to measure adsorption equilibrium for both pure components and binary mixtures (Brandani et al. 2003; Brandani and Ruthven 2003). The key advantages are the use of very small sample quantities, typically less than 10 mg and reduced consumption of gases when compared to the other flow methods (Ruthven 1984).

The ZLC method originally developed by Eic and Ruthven (1988) to measure intracrystalline diffusivities in zeolite crystals, was first applied to the measurement of Henry's constants (Brandani et al. 2002) and then extended to full equilibrium isotherms using a simple integration of the desorption curve (Brandani et al. 2003; Brandani and Ruthven 2003).

In the ZLC experiment a small sample of adsorbent is equilibrated with an inert carrier gas containing a small concentration of an adsorbing component. At time zero, the inlet flow is switched to a pure inert carrier and the effluent concentration of the previously adsorbed component is monitored using an appropriate detector. If the experiment is carried out at low flowrates, the gas phase and solid phase are effectively at equilibrium and a full isotherm can be calculated. If the conditions of equilibrium are not fulfilled, the integration of the desorption curve will yield only a single point on the adsorption isotherm. For trace system, the integration procedure is correct because the hypothesis that flowrate remains constant during the process of desorption is valid. However, the effluent flowrate is not constant in experiments carried out at high concentrations of the adsorbing component(s) and the variation of the flowrate has to be taken into account. One could couple the ZLC system with an accurate flowrate measurement system, but this can be avoided if flowrate can be estimated from the concentration measurement.

In this paper we present a simple analysis for a Langmuir isotherm that can be used to identify the range in which approximations of the flowrate can be used. The analysis is then extended using numerical simulation based on a model that includes a multi-site Langmuir isotherm. In addition, Darken's correction factors were calculated and compared to prove the validity of the flowrate correction.

2 Theory

2.1 Flowrate corrections in isotherm equilibrium calculation

A ZLC system consists of a very small cell containing a small quantity of adsorbent, so that the cell can be modelled as a well mixed system (Eic and Ruthven 1988). The differential mass balance in the ZLC cell is given by:

$$F_{in}c_{in,i} - F_{out}c_i = V_f\frac{dc_i}{dt} + V_s\frac{d\bar{q}_i}{dt}; \quad i = 1, 2, \ldots, Nc-1 \tag{1}$$

where, $\bar{q}_i = f(c_i)$ is the equilibrium isotherm.

If the flowrate is low, it is possible to assume that the gas and solid phases are at equilibrium and by simple integration of the mass balance one can obtain the isotherm (Brandani et al. 2003). For a single component the result is:

$$q_i^* = \frac{c_T}{V_s}\int_0^\infty (Fy)_{out}\,dt - \frac{c_T}{V_s}\int_0^t (Fy)_{out}\,dt - \frac{V_f}{V_s}c_0\frac{y}{y_0} \tag{2}$$

where c_T is the total concentration in the gas, and y is the mole fraction of the adsorbing species.

During the experiment the gas phase concentration is measured and the flowrate is calculated assuming that the carrier flowrate remains constant (Brandani et al. 2003), which is a common assumption in the analysis of chromatographic experiments (Malek and Farooq 1997). Since the inlet flow of the ZLC desorption experiment is a pure inert purge flow, this means that the outlet flowrate is approximated by:

$$(Fy)_{out} = \frac{F_{in}}{1-y}y_{out} \tag{3}$$

Equation (3) is better than the constant flowrate assumption, but is clearly not applicable at high concentrations and diverges if one considers using a pure adsorbate stream to saturate the ZLC.

An alternative flowrate correction can be obtained by considering the mass balance of the carrier gas (Brandani 2005)

$$F_{in}c_{in,c} - F_{out}c_c = V_f\frac{dc_c}{dt} \tag{4}$$

Given that the pressure drop in the differential cell is negligible, the total concentration is constant, and (4) can be expressed in terms of the mole fraction of the adsorbate

$$V_f\frac{dy}{dt} = (F(1-y))_{out} - F_{in} \tag{5}$$

The RHS of (5) is the difference of the flowrate of the carrier. For a desorption experiment this is always negative, since the carrier has to displace the adsorbate gas present in the gas phase. Therefore we know that:

$$\Delta V_{Car} = -V_f y_0 = \int_0^\infty \left[(F(1-y))_{out} - F_{in}\right]dt \tag{6}$$

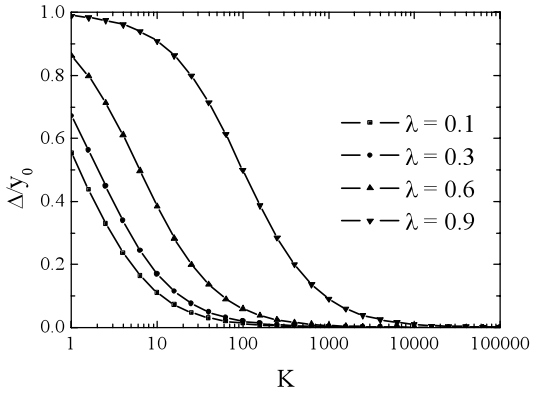

Fig. 1 Outlet carrier flowrate deviations for a Langmuir isotherm

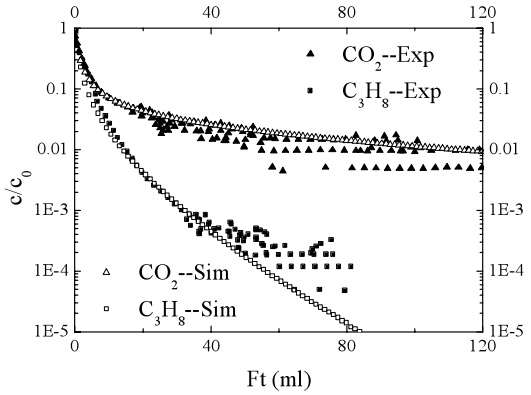

Fig. 2 Comparison of desorption curves from experiment (Exp) and simulation (Sim) for C_3H_8/CO_2-CaX at 50 °C, $p_{CO_2} = 23.5$ Torr, $p_{C_3H_8} = 47$ Torr, purge flowrate = 7.7 cm^3/min

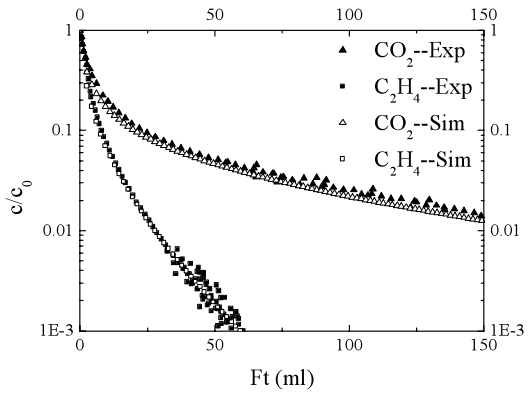

Fig. 3 Comparison of desorption curves from experiment (Exp) and simulation (Sim) for C_2H_4/CO_2-NaLSX at 20 °C, $p_{CO_2} = 23.5$ Torr, $p_{C_2H_4} = 23.5$ Torr, purge flowrate = 3.8 cm^3/min

It is possible to introduce a simple approximation to the variation of the carrier flowrate (Brandani 2005), ΔF_{Car}, given by:

$$\Delta F_{Car} = \Delta V_{Car} \frac{y}{\int_0^\infty y dt} = -V_f y_0 \frac{y}{\int_0^\infty y dt} \tag{7}$$

Therefore the outlet flowrate can be calculated using (3) with F_{in} replaced by $F_{in} + \Delta F_{Car}$.

The flow corrections given above, do not give a simple way to estimate when the corrections are going to be needed. While a full numerical analysis based on a dual-site Langmuir model is presented in the next section, it is useful to have an indication of the effects of the strength of the adsorption and the nonlinearity of the isotherm. For this purpose a simple Langmuir isotherm can be used and in this case it is possible to derive the exact solution for the change in the outlet flowrate. The full derivation is shown in the Appendix.

$$\frac{F_{out}}{F_{in}} = \frac{1}{1 - y + \frac{y}{1 + \frac{1-\varepsilon}{\varepsilon} \frac{(1-\lambda)^2 K}{(1-\lambda+\lambda C)^2}}} = \frac{1}{1 - y + \Delta} \tag{8}$$

In (8) λ is the nonlinearity parameter and K is the Henry law constant. Δ is a correction term, which varies during the desorption process. It is easy to observe that Δ is small when y and λ are small and K is large. It is also simple to see that Δ has its maximum value at time zero where $C = 1$ and $y = y_0$. Figure 1 shows the maximum value of Δ as a function of λ and K.

2.2 Numerical simulation of the ZLC

The mass balance of the ZLC, (1), is combined with the dual-site Langmuir isotherm

$$q_i^* = \frac{q_{s1,i} b_{1i} c_i}{1 + \sum_j^{Nc} b_{1j} c_j} + \frac{q_{s2,i} b_{2i} c_i}{1 + \sum_j^{Nc} b_{2j} c_j} \quad i = 1, 2, \ldots, Nc \tag{9}$$

and the initial conditions

$$c_i(0) = c_i^0; \qquad q_i(0) = q_i^0 \tag{10}$$

yielding the set of differential-algebraic equations implemented in C and solved using IDA, one of the Sundials solvers (Hindmarsh and Taylor 1999). This system of equations contains also the case of a simple Langmuir isotherm, when $q_{s2,i} = 0$.

The outlet flowrate can be calculated summing the mass balance for all the components:

$$F_{out} = F_{in} - \frac{V_s}{c_T} \sum_{i=1}^{N_c} \frac{d\bar{q}_i}{dt} \tag{11}$$

Figures 2 and 3 show the comparison of the simulations with experimental binary measurements reported in the literature (Brandani and Ruthven 2003), using the parameters listed in Table 1. The equilibrium isotherms where obtained assuming that the simple flowrate given by (3) was correct (Brandani et al. 2003; Brandani and Ruthven 2003). The

Table 1 Summary of equilibrium parameters for simulation (Brandani and Ruthven 2003)

Sorbent	NaLSX	CaX
Si/Al ratio	1.0	1.25
Sorbate A	CO_2	CO_2
Sorbate B	C_2H_4	C_3H_8
p_{A0}[a]	23.5	23.5
p_{B0}[a]	23.5	47
T (°C)	20	50
b_{1A}[b]	463	1188
b_{2A}[b]	28	9
b_{1B}[b]	61	103.4
b_{2B}[b]	17	6.9
q_{s1}[c]	1.9	0.8
q_{s2}[c]	2.77	2.0
K_A	15419	17453
K_B	2625	1739
λ_A	0.339	0.238
λ_B	0.065	0.104

[a] p_{A0} and p_{B0} are in Torr

[b] b is in atm^{-1}

[c] q_s is in m·mol/g

simulations using the full model confirm that under the experimental conditions, $y_0 < 0.1$, this was a valid assumption.

3 Comparisons

3.1 Isotherms

While Fig. 1 gives an indication of when the simple flowrate correction may not apply, it is useful to check what is the effect of the different methods on the actual derived equilibrium isotherms. For this purpose several simulations have been carried out using the mathematical model described above and the resulting ZLC desorption curves have been integrated using (2) combined with (3) and (7). To eliminate the effect of numerical oscillations and truncation errors in the very dilute region, the integral of (2) is calculated analytically in the long time region where the isotherm is linear and the ZLC desorption curves reduce to a simple exponential decay $c/c_0 = a\exp(-bt)$ (Brandani 1996). In all the cases considered, the integration was numerical up to $c/c_0 = 10^{-4}$. With this approach, (2) becomes:

$$q_i^* = \frac{c_T}{V_s}\int_0^{t_0}(Fy)_{out}dt - \frac{c_T}{V_s}\int_0^{t}(Fy)_{out}dt - \frac{V_f}{V_s}c_0\frac{y}{y_0} + \frac{F}{V_s}\frac{a}{b}\exp(-bt_0) \tag{12}$$

Figures 4, 5, 6 and 7 shown below are representative of weakly adsorbed species ($K = 1$), medium strength adsorption ($K = 10$ and 100) and strongly adsorbed species ($K = 1000$). The extreme case of $y_0 = 0.9$ is used to show clearly the effect of choice of the flowrate correction.

Comparisons of isotherms indicate that all the approximate flowrates are valid when K is large (over 100). This is consistent with Fig. 1 and indicates that the original assumption of neglecting the gas phase accumulation (Eic and Ruthven 1988) in the interpretation of ZLC experiments with strongly adsorbed components is reasonable, even for equilibrium measurements. It is important to note that the effect of an incorrect flowrate is more pronounced at high concentrations, since these correspond to the initial desorption process, for which we have the maximum value of Δ.

Another important point that can be inferred is that when an isotherm calculated from a ZLC experiment shows the characteristic inflection of a type II isotherm (Ruthven 1984), the data should be re-evaluated using a full numerical model and a direct numerical fit should be carried out.

Most of the ZLC experiments are usually carried out with a fairly dilute adsorbate, so in Fig. 8 we show the results for $y_0 = 0.1$ and 0.5 ($K = 100$). In this case all the flowrate corrections yield the same isotherm, with the only minimal deviation in the higher concentration and for the highly nonlinear case of $\lambda = 0.9$. This additional set of simulations indicates a simple way of determining whether a full numerical simulation is needed. If both flowrate corrections outlined in Sect. 2.1 are used and yield the same isotherm, it is evident from the simulations have been carried out that a reliable isotherm has been derived. If deviations between the two methods are observed, then (7) will yield a more accurate estimate of the isotherm, but a full numerical fit would be preferable.

3.2 Darken correction factor

The Darken correction factor is a thermodynamic coefficient that is important in the determination of the corrected diffusivity in micropores (Ruthven 1984). The definition is given by

$$\frac{d\ln c}{d\ln q} = \frac{q/c}{dq/dc} \tag{13}$$

Equation (13) indicates that in order to calculate the Darken correction factor it is necessary to have an accurate value of the secant of the isotherm, q/c, and the slope of the isotherm, dq/dc. One of the advantages of the ZLC experiment run under equilibrium conditions is that the mass balance contains directly the derivative of the isotherm:

$$-F_{out}c = \left(V_f + V_s\frac{dq}{dc}\right)\frac{dc}{dt} \tag{14}$$

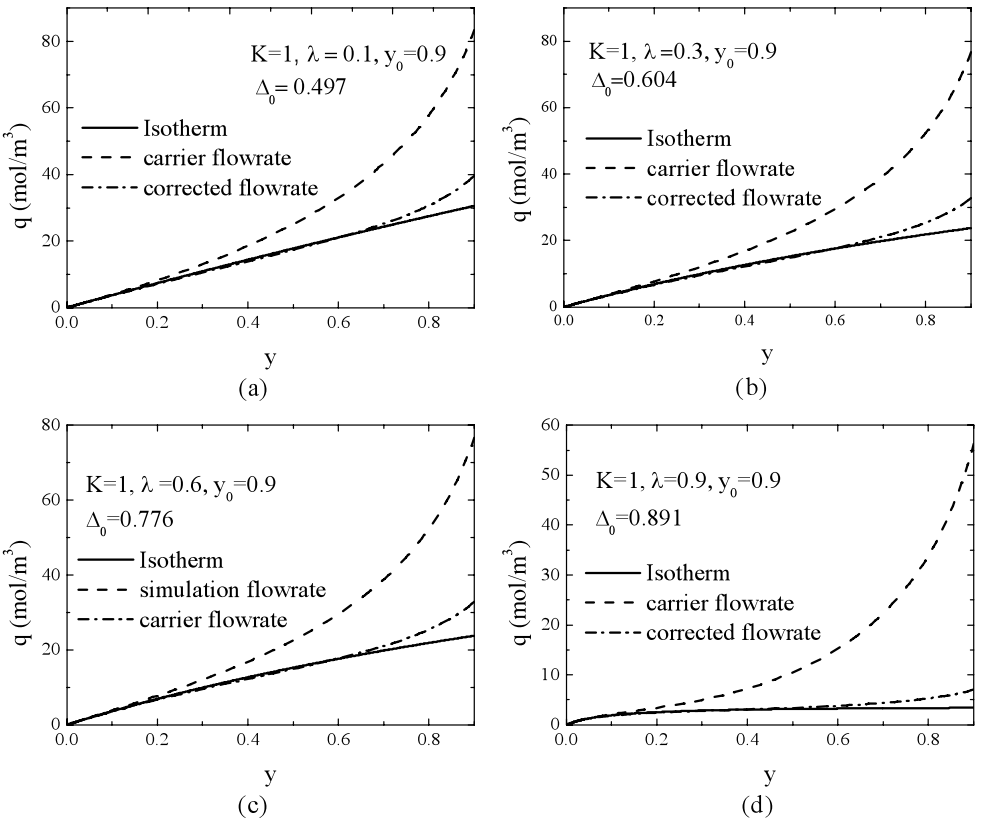

Fig. 4 Comparison of isotherms calculated from simulation and corrected flowrates at $K = 1$

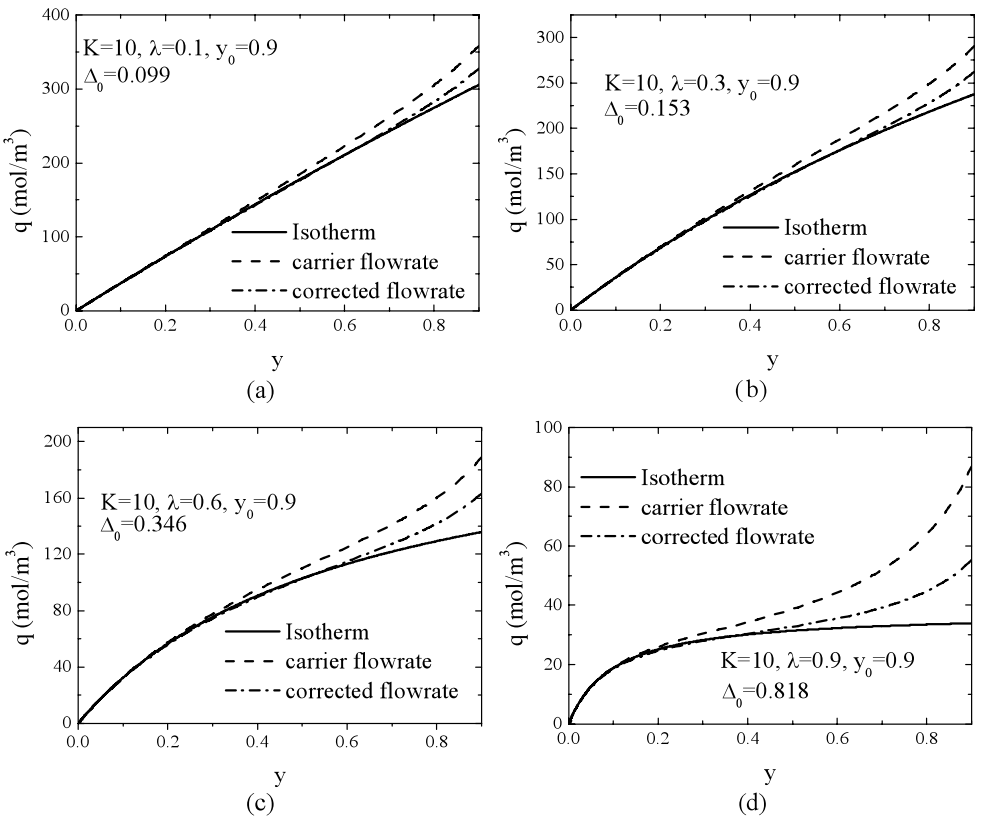

Fig. 5 Comparison of isotherms calculated from simulation and corrected flowrates at $K = 10$

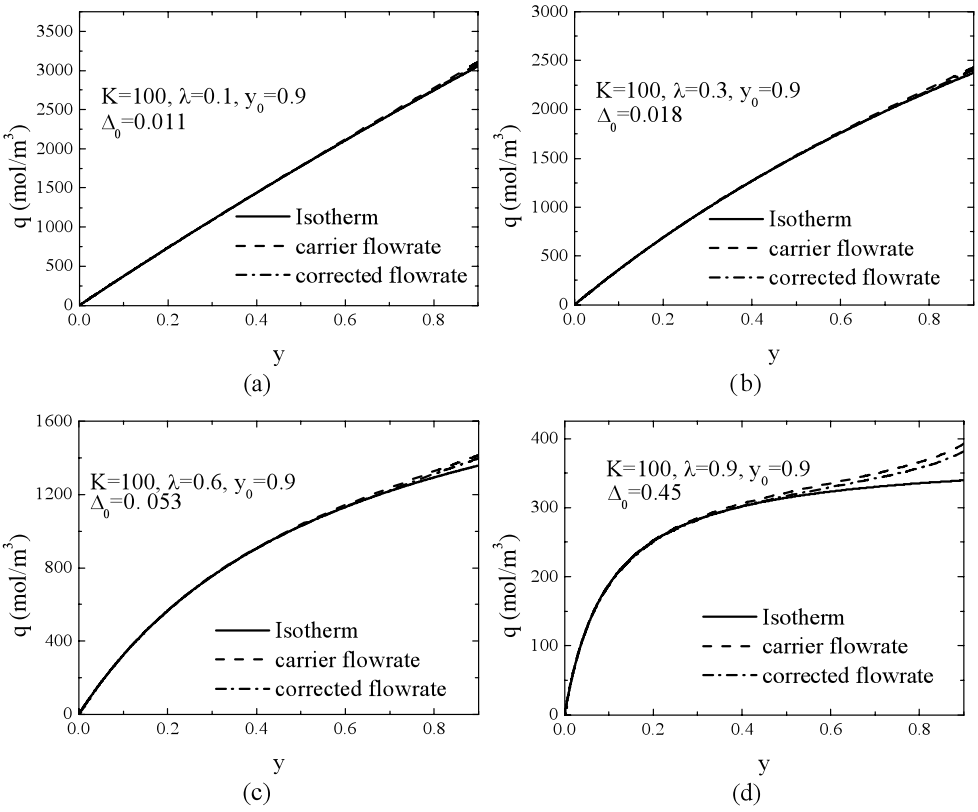

Fig. 6 Comparison of isotherms calculated from simulation and corrected flowrates at $K = 100$

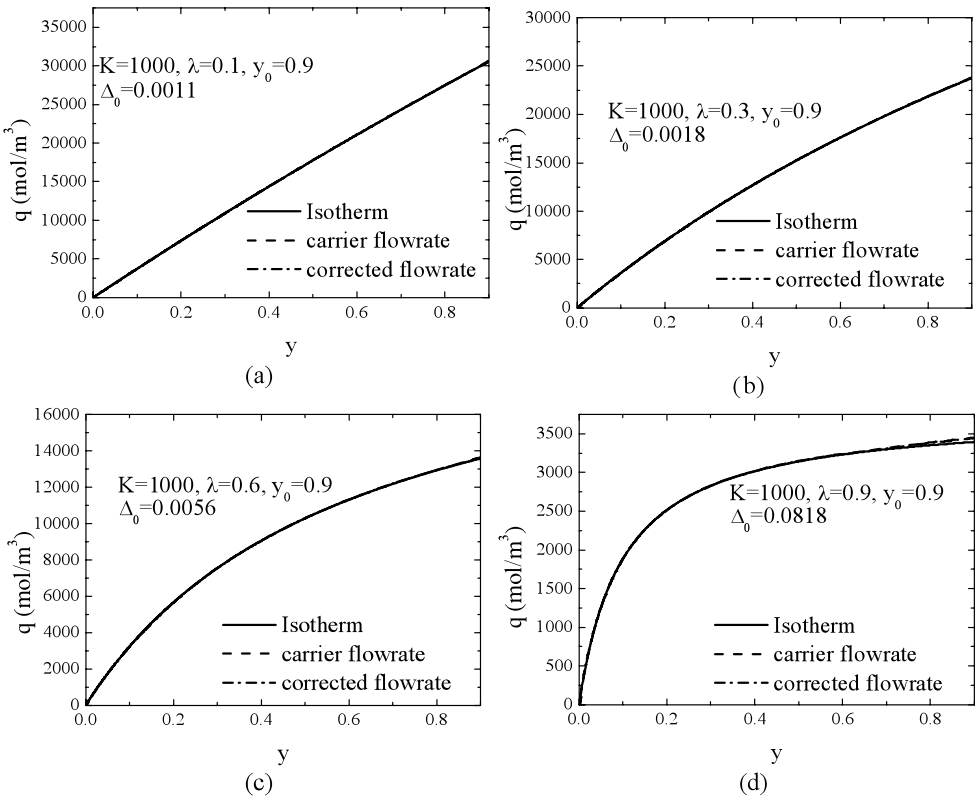

Fig. 7 Comparison of isotherms calculated from simulation and corrected flowrates at $K = 1000$

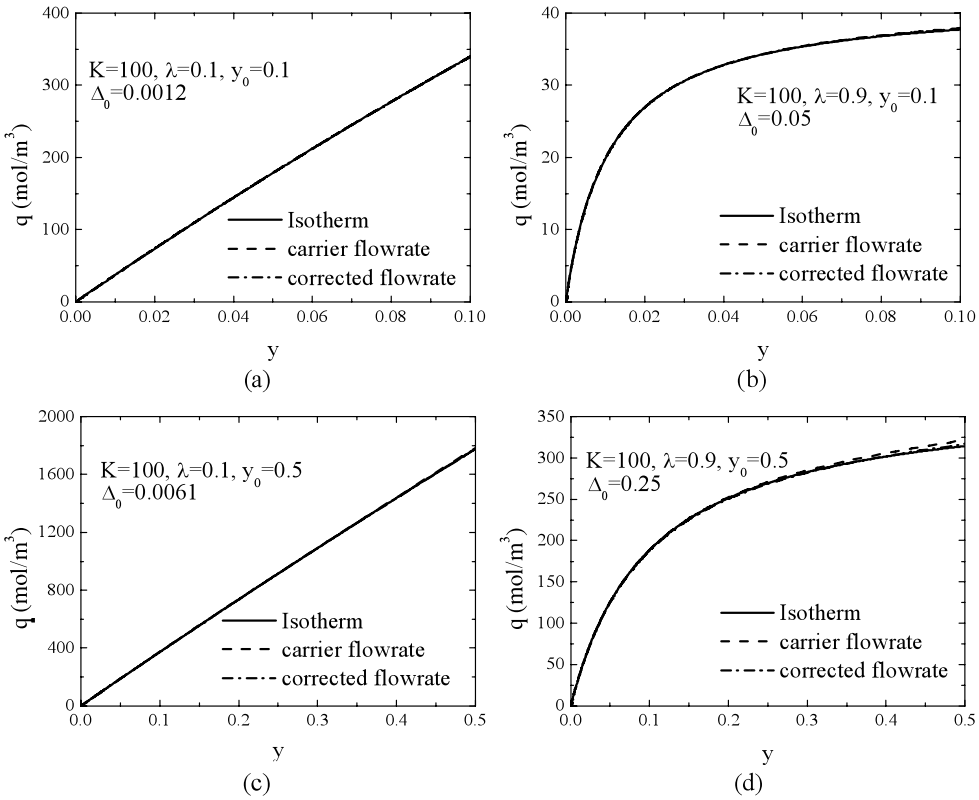

Fig. 8 Comparison of isotherms calculated from simulation and corrected flowrates at $K = 100$, $\lambda = 0.1$ and 0.9, $y_0 = 0.1$ and 0.5

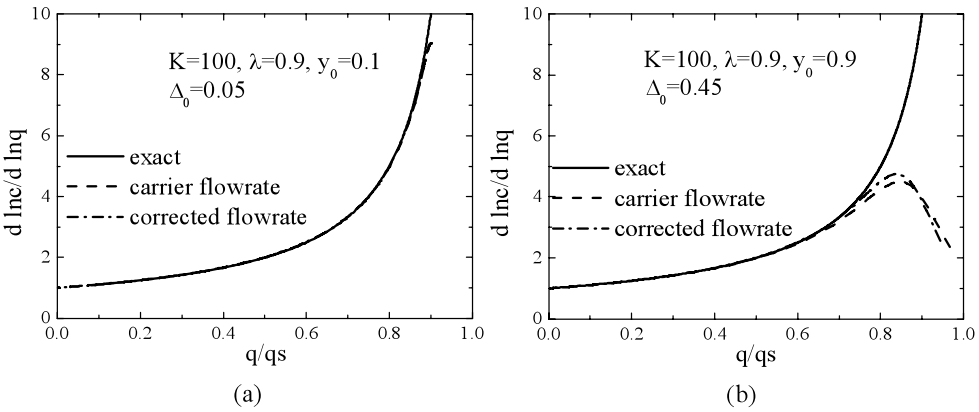

Fig. 9 Comparison of Darken correction factor from simulation and corrected flowrates at $K = 100$, $y_0 = 0.1$ and 0.9

Since c is measured directly in the experiment, it is possible to approximate with a simple function the desorption curve to determine dc/dt and thus dq/dc needed in (13) to calculate the Darken correction factor. Using three points to obtain a parabolic approximation for the time derivative, the Darken correction factors can be calculated from the simulated curves.

Figure 9 shows the comparison of the Darken correction factors obtained from the different flowrate approximations and the numerical approximate estimate of the derivative of the isotherm. In this case it is evident that, while the flowrate approximations are consistent, there is a marked deviation for the strongly nonlinear case at high concentrations. In this case the comparison of the use of the different flowrate approximations is not an indication of the reliability of the results, so for the estimation of Darken correction factors for high concentrations and strongly non-linear systems, one should use a full numerical fit of the experimental desorption curves.

4 Conclusions

Based on the analysis and the set of simulations reported here, it is possible to identify the range of conditions where flowrate approximations based on the measured concentrations are valid. Under typical dilute ZLC experimental conditions, the two approximate flowrates are valid even for

weakly adsorbed components. For systems where the Henry law constant, K, is greater than 100 the flowrate corrections are reliable even when considering step changes of 50% in concentration.

The comparison of the two flowrate approximations offers a simple way to check the validity of the derived isotherm and may be used to decide if a full numerical simulation and regression of the experimental desorption curves is needed.

The Darken correction factor can also be calculated accurately for small gas phase concentration changes. For large step changes and highly nonlinear systems, the nonlinear regression from the simulation of the full model may be necessary.

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Appendix

The mass balance for a single component can be rewritten a:

$$F_{in}c_{in} - F_{out}c = V_f\frac{dc}{dt} + V_s\frac{d\bar{q}}{dt} \tag{15}$$

with $\bar{q} = f(c)$, (15) becomes:

$$F_{in}c_{in} - F_{out}c = V_f\frac{dc}{dt} + V_s f'\frac{dc}{dt} \tag{16}$$

where, $f' = \frac{d\bar{q}}{dc}$.

For desorption process $c_{in} = 0$, we can obtain:

$$-F_{out}c = (V_f + V_s f')\frac{dc}{dt} \tag{17}$$

Define the following dimensionless variables:

$$C = \frac{c}{c_0}; \qquad \tau = \frac{F_{in}t}{V_f + V_s\frac{q_o}{c_o}}; \qquad Q = \frac{q}{q_o}$$

and dimensionless parameters:

$$\lambda = \frac{q_0}{q_s}$$

The resulting dimensionless equation is:

$$\frac{V_f + V_s f'}{V_f + V_s\frac{q_0}{c_0}}\frac{dC}{d\tau} = -\frac{F_{out}}{F_{in}}C \tag{18}$$

For the single-site Langmuir model:

$$\frac{q}{q_s} = \frac{bc}{1+bc} \tag{19}$$

The isotherm can be rewritten as:

$$Q = \frac{C}{1-\lambda+\lambda C} \tag{20}$$

Therefore (18) becomes:

$$\frac{1+\frac{1-\varepsilon}{\varepsilon}\frac{(1-\lambda)^2K}{(1-\lambda+\lambda C)^2}}{1+\frac{1-\varepsilon}{\varepsilon}(1-\lambda)K}\frac{dC}{d\tau} = -\frac{F_{out}}{F_{in}}C \tag{21}$$

where the Henry law constant, $K = bq_s$.

Applying the mass balance to the carrier gas:

$$F_{in}c_{in,c} - F_{out}c_c = V_f\frac{dc_c}{dt} \tag{22}$$

The total concentration is constant so:

$$\frac{dc_c}{dt} = -\frac{dc}{dt} \tag{23}$$

Combining the last two equations and converting the resulting expression into dimensionless form we obtain:

$$\frac{1}{1+\frac{1-\varepsilon}{\varepsilon}(1-\lambda)K}\frac{dC}{d\tau} = \frac{F_{out}}{F_{in}}\left(\frac{C_T}{c_0} - C\right) - \frac{C_T}{c_0} \tag{24}$$

Which can be substituted into (21) to yield (8).

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