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An Analytical Solution for the Analysis of Zero-Length-Column Experiments with Heat Effects

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An analytical solution for the analysis of zero-length-column (ZLC) experiments with heat effects is developed. The model is an extension of the original one developed by Eic and Ruthven with the inclusion of the energy balance. Two additional parameters are obtained, $\beta = (\Delta H/C_p)(\partial q/\partial T)|_{c_0,T_0}$ and $\alpha = (ha/C_p)(r_c^2/D_c)$. A criterion for negligible heat effects, $3L\beta/\alpha < 0.1$, is derived from the analytical solution based on ZLC operating parameters. ZLC desorption curves in nonisothermal operation are discussed. The model reduces to the original solution of isothermal operation developed by Eic and Ruthven when heat effects are negligible. ZLC experiments with heat effects are analyzed, and trends are in good agreement with theory. Because of its simplicity, the model is a valuable tool for the analysis of ZLC experiments with heat effects.

Introduction

In the measurement of intracrystalline diffusivities in adsorbents from uptake experiments, the intrusion of heat effects can be a major drawback in the determination of such parameters.[1] This has also been recognized by Ruthven et al.,[2] who developed a simple nonisothermal model to account for heat effects in uptake experiments from gravimetric systems; it was shown that small adsorbent samples can minimize such heat effects. Hills[3] derived an analytical expression for the temperature rise in an adsorbent pellet in the presence of both internal and external mass-transfer resistances and external heat-transfer resistance.

The zero-length column (ZLC technique)[4] has been widely used for the measurement of diffusion parameters in adsorbents and catalysts, and it was developed in part to minimize heat effects.

In the ZLC technique a differential bed of porous particles is first saturated with the fluid mixture containing the absorbable species preferably in the Henry's law region of the isotherm; at time zero the carrier gas flows through the ZLC at sufficiently high flow rate, and the desorption curve is analyzed in terms of concentration versus time. Because of the small adsorbent sample, it has been assumed that heat effects due to adsorption are negligible, and consequently isothermal conditions are valid for the modeling of the adsorption cell. However, it has been shown[5] that in the measurement of macropore diffusion in relatively large adsorbent particles heat effects become important. To analyze heat effects, a nonisothermal model was developed and solved by numerical methods and a criterion for negligible heat effects was developed by comparing the results of numerous numerical simulations over a wide range of parameter values.[5]

The objective of this work is the development of a simple model for the analysis of ZLC experiments with heat effects. The original isothermal model[4] was extended to nonisothermal systems by adding the energy balance. Model equations are analytically solved by Laplace transform, and parameters for the analysis of ZLC experiments are used to develop a criterion to neglect heat effects.

Theoretical Analysis

The original model developed for the analysis of ZLC experiments under isothermal conditions in the measurement of intracrystalline diffusivities is as follows.[4]

Diffusion Equation. The transient mass balance in the crystal is

$$\frac{\partial q}{\partial t} = \frac{D_c}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) \tag{1}$$

where q is the adsorbed phase concentration, r the crystal radial coordinate, and D_c the intracrystalline diffusivity. The boundary conditions are

$$r = 0, \quad \frac{\partial q}{\partial \mathrm{r}} = 0 \tag{2}$$

$$r = r_c, \quad q = q_s \tag{3}$$

where r_c is the crystal radius and q_s the adsorbed phase concentration at the crystal surface.

Mass Balance in the ZLC. The overall mass balance for the sorbate in the ZLC cell is

$$Fc_{out} + V_s D_c \frac{3}{r_c}\frac{\partial q}{\partial r}\bigg|_{r=r_c} = 0 \tag{4}$$

where F is the purge flow rate, V_s the adsorbent volume, and c_{out} the outlet gas concentration of the ZLC related with the adsorbed phase concentration by the equilibrium relation.

The solution of the ZLC model assuming a linear relationship between the gas concentration in the ZLC and the adsorbed phase, i.e., $q_s = Kc_{out}$, is

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$$\frac{c_{\mathrm{out}}}{c_0} = 2L\sum_{n=1}^{\infty}\frac{e^{-\beta_n^{\,2}\tau}}{\beta_n^{\,2} + L(L-1)} \tag{5}$$

where β_n are the roots of the transcendental equation

$$\beta_n \cot \beta_n + L - 1 = 0 \tag{6}$$

The dimensionless time variable is τ

$$\tau = \frac{D_{\mathrm{c}}}{r_{\mathrm{c}}^{\,2}}t \tag{7}$$

and L is the dimensionless ZLC parameter

$$L = \frac{1}{3}\frac{F}{KV_{\mathrm{s}}}\frac{r_{\mathrm{c}}^{\,2}}{D_{\mathrm{c}}} \tag{8}$$

To account for heat effects in the ZLC, an energy equation is needed in addition to the mass balances in the crystal and in the ZLC cell.

Energy Equation. Assuming that thermal conduction through an individual crystal and heat transfer between the crystals within the adsorbent pellet are fast, the only significant heat-transfer resistance is at the external surface of the sample. This implies a constant temperature throughout the sample with a time-dependent temperature difference between the adsorbent particle and the surrounding gas in the ZLC. Under these conditions, the following equation is valid:

$$-\Delta H\frac{\mathrm{d}\langle q\rangle}{\mathrm{d}t} = C_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t} + ha(T - T_0) \tag{9}$$

where T is the temperature of the adsorbent, T_0 is the temperature of the ZLC (assumed constant), ΔH is the heat of adsorption, C_{p} is the heat capacity of the adsorbent, h is the film heat-transfer coefficient, a is the external surface area of the adsorbent per unit volume of the adsorbent, and $\langle q\rangle$ is the average adsorbed phase concentration.

Equilibrium Relation. Assuming that at low adsorbate loading the equilibrium relationship is linear and the temperature changes are small, the equilibrium may be represented by the following equation:[6]

$$q = q_0 + \left.\frac{\partial q}{\partial c}\right|_{c_0,T_0}(c_{\mathrm{out}} - c_0) + \left.\frac{\partial q}{\partial T}\right|_{c_0,T_0}(T - T_0) \tag{10}$$

where $K = (\partial q/\partial c)|_{c_0,T_0}$ is the dimensionless Henry's law constant.

Initial Conditions. At time zero the adsorbent is saturated with the sorbate at concentration c_0 and so

$$t = 0, \quad q = q_0 = K(T_0)c_0, \quad T = T_0 \qquad \text{for all } r \tag{11}$$

Solution of the Nonisothermal ZLC Model. The solution of the nonisothermal ZLC model represented by eqs 1−3 and 9−11 may be obtained by Laplace transformation with inversion with the method of residues.[7] The solution is (see Appendix A)

$$\frac{c_{\mathrm{out}}}{c_0} = \sum_{n=1}^{\infty}\left[[(p_n \cot p_n - 1)/p_n^{\,2}]\,(p_n^{\,2} - \alpha)e^{-p_n^{\,2}\tau}\middle/\left[\frac{1}{2}(\alpha - p_n^{\,2} + 3L\beta)[1 + p_n \cot p_n(p_n \cot p_n - 1)/p_n^{\,2}] + p_n \cot p_n + L - 1\right]\right] \tag{12}$$

where p_n is given by the roots of the transcendental equation

$$p_n \cot p_n + L\left(\frac{1}{1 + \frac{3L\beta}{\alpha}\left(\frac{1}{1 - p_n^{\,2}/\alpha}\right)}\right) - 1 = 0 \tag{13}$$

and the dimensionless parameters β and α are defined as follows:

$$\beta = \frac{\Delta H}{C_{\mathrm{p}}}\left.\frac{\partial q}{\partial T}\right|_{c_0,T_0} \tag{14}$$

$$\alpha = \frac{ha}{C_{\mathrm{p}}}\frac{r_{\mathrm{c}}^{\,2}}{D_{\mathrm{c}}} \tag{15}$$

The dimensionless variable τ is defined by eq 7 and the dimensionless ZLC parameter L by eq 8.

Effect of the Group Parameter $3L\beta/\alpha$ on ZLC Desorption Curves

A family of desorption curves calculated with eq 12 is shown in Figure 1a−c to study the effect of the group parameter $3L\beta/\alpha$ on ZLC desorption curves. Figure 1a is plotted at constant $\beta = 5$ and $L = 5$, Figure 1b at constant $\beta = 5$ and $L = 0.01$, and Figure 1c at constant $\beta = 10$ and $L = 3$. The isothermal operation is identified in the figures with a dotted line (···) and the case of complete heat-transfer control with a dashed line (- - -). Full lines (—) are representative of the intermediate cases of both significant heat transfer and diffusion. When α increases (heat-transfer increases), the group parameter $3L\beta/\alpha$ decreases and the system approaches the isothermal operation. When α decreases (the resistance to heat-transfer increases), the group parameter $3L\beta/\alpha$ increases and the system approaches the heat-transfer control.

It can be concluded from Figure 1a−c that for values of $3L\beta/\alpha$ lower than 0.1 the ZLC system is in isothermal operation because the values of α do not affect the desorption curves.

In the limiting case of experiments with complete heat-transfer control ($3L\beta/\alpha > 100$), the long-time straight line is practically parallel to the time axis, meaning that the time scale of the experiment is completely different from that of the isothermal case. It takes a long time for the adsorbed species to leave the adsorbent. Experiments with complete heat-transfer control are easily identified because the long-time straight lines are parallel with a difference in the outlet concentration proportional to the value of $3L\beta/\alpha$, as can be seen in Figure 1a−c.

This limiting behavior may be derived considering the asymptotic form of eq 12 for high values of $3L\beta/\alpha$. In this situation $p \cot p - 1$ in transcendental equation (13) may be replaced by the series expansion ($-p^2/3 + p^4/45 + ...$). For high values of $3L\beta/\alpha$, the first root of eq 13 is given by $p_1^{\,2} = \alpha/(1 + \beta)$ and the asymptotic form

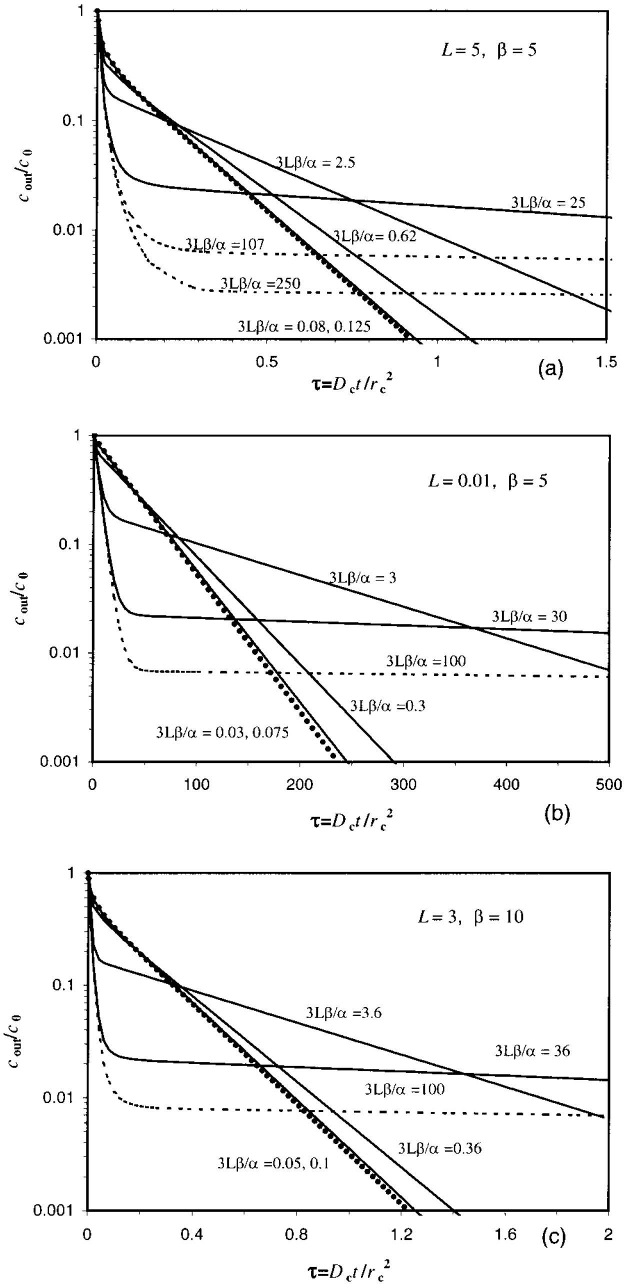

Figure 1. Effect of group parameter $3L\beta/\alpha$ on theoretical ZLC desorption curves. (a) $L = 5$, $\beta = 5$; (b) $L = 0.01$, $\beta = 5$; (c) $L = 3$, $\beta = 10$. Also shown are the limiting cases of heat-transfer control (dashed lines - - -, $3L\beta/\alpha > 100$) and isothermal operation (dotted lines ···, $3L\beta/\alpha < 0.1$).

of the ZLC curve is given from the first term of the summation of eq 12, which becomes

$$\frac{c_{out}}{c_0} = \frac{\beta}{(3L\beta/\alpha)(1+\beta)} \exp\left(-\frac{ha}{(1+\beta)C_p}t\right) \qquad (16)$$

The argument of the exponential is similar to the one derived for experiments controlled entirely by heat transfer in gravimetric uptake experiments.[2] From eq 16 the decrease in the outlet concentration proportional to the value of $3L\beta/\alpha$ seen in Figure 1a–c is clearly explained in a regime of complete heat-transfer control.

For values of $3L\beta/\alpha$ between 0.1 and 100, the system is governed by both heat-transfer and diffusion mechanisms. Under these conditions the slope of the long-time straight lines decreases and the desorption time increases; however, in the experiments with intrusion of heat effects, the outlet concentration in the ZLC decreases faster than that in the isothermal case in the early stages of the experiment.

Criterion for Negligible Heat Effects

From Figure 1a–c and from the results of other simulations, we are able to show that the group $3L\beta/\alpha$ can be used as a criterion for negligible heat effects. For values of $3L\beta/\alpha < 0.1$, the system is isothermal, and for $3L\beta/\alpha > 100$, the system is completely dominated by heat transfer. As a consequence of the model parameters, the limiting isothermal case is obtained when either $\alpha \rightarrow \infty$ and $\beta \rightarrow 0$ or the group $3L\beta/\alpha \rightarrow 0$. In this case the nonisothermal model equation (12) reduces to the original ZLC equation (5) and the transcendental equation (13) reduces to eq 6. Moreover, the group $3L\beta/\alpha$ represented in transcendental equation (13) is the same criterion of negligible heat effects derived from various numerical simulations.[5] Those authors[5] conclude that the group should be smaller than 1; from our simulations and, more importantly, from the analysis of the denominator of the second term of eq 13, it is necessary that $3L\beta/\alpha < 0.1$.

Analysis of ZLC Experiments with Heat Effects

In practice, thermal effects may be minimized by analyzing the group parameter:

$$\frac{3L\beta}{\alpha} = \frac{F\Delta H \left.\frac{\partial q}{\partial T}\right|_{c_0,T_0}}{KV_s ha} = c_0\frac{F}{V_s}\frac{(\Delta H)^2}{RT_0^{\,2}ha} \qquad (17)$$

The right-hand side of the previous equation is obtained assuming a van't Hoff relation for the temperature dependence of the equilibrium constant $K = k_0 \exp(-\Delta H/RT)$.[5] According to eq 17, heat effects are minimized by lowering the value of group parameter $3L\beta/\alpha$ in various ways: (i) decreasing the gas concentration c_0 of the species used to saturate the adsorbent, (ii) decreasing the space velocity (F/V_s) in the ZLC cell, or (iii) decreasing the particle size, which means increasing the parameter a (external surface area per unit volume of adsorbent).

ZLC experiments with heat effects can be detected by studying, for example, the effect of the particle size in measured curves: in isothermal operation the slope of long-time straight lines should always be smaller when the particle size increases (meaning a smaller mass-transfer rate); however, in nonisothermal operation heat effects can disguise these predictions.

When intrusion of heat effects is observed, it may be difficult to evaluate simultaneously mass- and heat-transfer coefficients. It is suggested to establish experimental conditions such as the criterion $3L\beta/\alpha < 0.1$ to fulfill the isothermal operation and obtain the diffusional parameters using eq 5. When this is not experimentally feasible, one can first run one experiment where $3L\beta/\alpha > 100$ and so heat-transfer dominates. In this situation our model reverts to the limiting form given by eq 16. Using eq 16 and from the long-time region in a semilog plot, the slope of the curve gives directly the heat-transfer coefficient. Once the heat-transfer parameter is obtained, another experiment in intermediate regime should be performed and the

Table 1. Parameters of ZLC Experiments with Heat Effects[8]

adsorbent volume, V_s	3×10^{-3} cm^3
adsorption equilibrium constant, K	10^6
equilibrium fluid phase concentration, C_0	3×10^{-7} mol/cm^3
purge flow rate, F	102 mL/min
macropore diffusivity,[a] D_p	1.1×10^{-1} cm^2/s
heat of adsorption, $-\Delta H$	17 kcal/mol
heat capacity of solid, C_s	0.2 cal/cm^3·K
adsorption equilibrium constant, $\partial q/\partial T$	1.4×10^{-2} mol/cm^3·K
thermal conductivity of gas, λ	8.0×10^{-5} cal/cm·s

[a] Obtained from $D_p = D_m/T$, where $D_m = 0.168$ cm^2/s and T = 1.5. [b] Assuming a van't Hoff dependence of equilibrium constant with temperature. [c] The heat-transfer coefficient is estimated from $Nu = 2$ or $ha = 3\lambda/R_p^2$.

Table 2. Dimensionless Model Parameters for ZLC Experiments with Heat Effects

	large particles (R_p = 1.4 mm)	small particles (R_p = 0.7 mm)
L'	1.4×10^2	3.6×10^1
α'	2.0×10^4	2.0×10^4
β	1.2×10^3	1.2×10^3
$3L'\beta/\alpha'$	25	6.5

diffusional parameter can be obtained using the full solution given by eq 12 with one adjustable parameter.

ZLC experiments with heat effects have been performed.[5,8] In experiments of Guimarães,[8] the desorption of *p*-xylene was performed in a commercial Y zeolite pellet; unusual trends were obtained, such as the apparently faster mass-transfer rates in larger particles compared with smaller particles, whereas under isothermal conditions, the mass-transfer rate should always be smaller for larger particles.

These trends can be explained using the nonisothermal model developed in this work (eq 12).

Table 1 shows the experimental conditions and Table 2 the dimensionless model parameters for the Guimarães experiments.[8] In pellet material of the type used in the experimental system and with strongly adsorbed species such as the *p*-xylene/zeolite Y, macropore diffusion is the controlling mechanism for mass transfer. Under macropore diffusion control, the analytical solution is similar to eq 12 provided that the dimensionless parameters are slightly modified as

$$L' = \frac{1}{3}\frac{F}{V_s}\frac{R_p^{\,2}}{\epsilon_p D_p} \tag{18}$$

$$\tau' = \frac{D_p}{(1 + K_c)R_p^{\,2}}t \tag{19}$$

$$\beta = \frac{\Delta H}{C_p}\left.\frac{\partial q}{\partial T}\right|_{c_0,T_0} \tag{20}$$

$$\alpha' = \frac{ha}{C_p}\frac{(1 + K_c)R_p^{\,2}}{D_p} \tag{21}$$

The only parameter that changes between experiments 1 and 2 is parameter L', which is 144 in larger particles compared with 36 in the smaller ones according to the model parameters shown in Table 1. Because parameters α' and β are constant (energy parameters), increasing L' increases mass transfer in the ZLC cell, and this explains why desorption curves are faster in larger pellets. The important group $3L'\beta/\alpha'$, which can be used for the criterion of negligible heat effects as shown previously, is directly proportional to L'; for the experiments under study $3L'\beta/\alpha'$ is 25 for larger particles compared with 6.5 for the smaller ones, giving the indication that experiments are in a regime of competitive heat transfer and diffusion. The group can also guide the planning of experiments to reduce heat effects; as an example, decreasing the purge flow rate leads to a decrease in L', which is proportional to the purge flow rate and a relatively smaller decrease in α'.

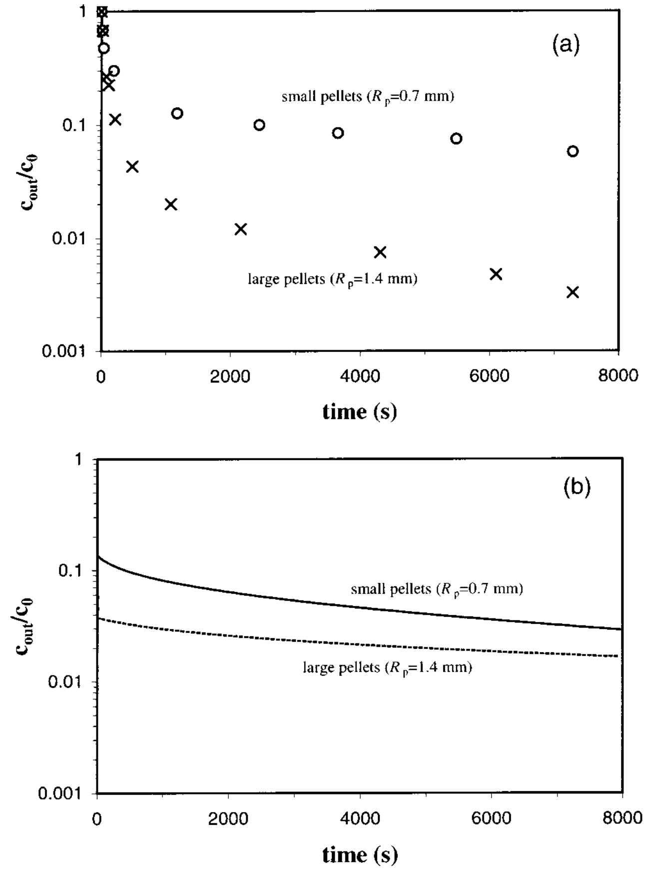

Figure 2. Experimental curves for desorption of *p*-xylene at 150 °C with N_2 carrier [102 mL/min(STP)] for large particles (R_p = 1.4 mm; ×) and small particles (R_p = 0.07 mm; ○; data from Guimarães[8]). The lines are theoretical desorption curves calculated with eq 12 with parameters $L' = 1.4 \times 10^2$, $\alpha' = 2.0 \times 10^4$, and $\beta = 1.2 \times 10^3$ for the large particles and $L' = 3.6 \times 10^1$, $\alpha' = 2.0 \times 10^4$, and $\beta = 1.2 \times 10^3$ for the smaller ones.

Figure 2 shows the experiments of Guimarães and the curves predicted by our model. The model qualitatively predicts the trends of the experiments, so it can be a valuable tool for the analysis of ZLC experiments with heat effects.

However, it fails in predicting the experimental data quantitatively, because an important restriction of the nonisothermal ZLC model developed is the linearity of the isotherm. As a consequence of the high irreversible behavior of the *p*-xylene adsorption on zeolite, it is difficult to perform ZLC experiments in the Henry's law region of the isotherm, as is probably the case of experiments reported by Guimarães.[8] The discrepancies seen in Figure 2a compared to Figure 2b are clearly due to the effect of performing the experiments in a region of the nonlinearity of the isotherm. In consequence the applicability of our model is restricted and results were poor in predicting the data quantitatively. Another reason for discrepancies in the prediction could be due to temperature gradients inside the adsorbent particles. To evaluate the importance of this effect in the experiment, the heat Biot number was estimated. As indicated by Yang,[9] values lower than 1 indicate that temperature is uniform inside the particle. For the present case, the value of the Biot number can be estimated as follows: the value of the heat gas conductivity of xylene is about 0.03 W/mK, while the particle heat conductivity in X zeolites is around 0.2−0.3 W/mK.[10] Using the limiting value of the Nusselt number of 2 for estimating the external heat coefficient, the Biot number obtained is $0.15 < 1$, verifying the criterion. We conclude that the internal gradient temperature is not important in these experiments.

It should also be noted that if nonisothermal effects are ignored in Guimarães experiments and a single ZLC curve is matched to the isothermal model in Figure 2a, an error of 35% in the value of the diffusivity parameter would be obtained. This error is calculated comparing the first root of transcendental equation (6) of the isothermal model with the first root of transcendental equation (13) of the nonisothermal case, because the slope of the long-time straight lines is proportional to these values.

Conclusions

A nonisothermal ZLC adsorption model with an analytical solution was developed. The solution reduces to the isothermal one when the energy balance is neglected. An important dimensionless group $3L\beta/\alpha$ was extracted from the model for the development of a criterion for negligible heat effects, i.e., $3L\beta/\alpha < 0.1$. The group contains all of the parameters that contribute to the dynamics of the ZLC and can be a guide for the analysis of experiments with heat effects; it also allows the prediction of ZLC experiments, with heat effects ($3L\beta/\alpha > 100$) being a valuable tool for the analysis of experiments since their simplicity.

Appendix A

Introducing the new variables $\eta = r/r_c$ and $U = \eta Q$, with $Q = (q - q_0)/(q_{in} - q_0)$ where q_{in} is the adsorbed phase concentration in equilibrium with the inlet gas concentration in ZLC, c_{in}, and $\tau = D_c t/r_c^2$ in eq 1, and applying the Laplace transform, we get

$$\frac{d^2\tilde{U}}{d\eta^2} = s\tilde{U} \tag{A1}$$

The boundary conditions of eq A1 valid for the nonisothermal model are after some algebraic manipulation of eqs 2−4 and 10

$$\eta = 0, \quad \tilde{U} = 0 \tag{A2}$$

$$\eta = 1, \quad \frac{d\tilde{U}}{d\eta} - \tilde{U} = L\left\{\frac{1}{s} + \frac{\partial q}{\partial T}\bigg|_{c_0,q_0} \frac{\tilde{T}'}{q_{in} - q_0} - \tilde{U}\right\} \tag{A3}$$

where L is the dimensionless parameter defined by eq 8 and $T' = T - T_0$.

The general solution of eq A1 is given by

$$\tilde{U} = A\exp(\sqrt{s}\eta) + B\exp(-\sqrt{s}\eta) \tag{A4}$$

Taking into account the boundary conditions (A2) and (A3), the solution in the Laplace domain is

$$\tilde{U} = \left\{\frac{1}{s} + \frac{\partial q}{\partial T}\bigg|_{c_0,T_0} \frac{\tilde{T}'}{q_{in} - q_0}\right\} \frac{L}{\sqrt{s}\coth\sqrt{s} + L - 1}\,\frac{\operatorname{senh}\sqrt{s}\eta}{\operatorname{senh}\sqrt{s}} \tag{A5}$$

The Laplace transform of the energy equation (9) is

$$\frac{-\Delta H}{C_p} s\langle\tilde{Q}\rangle = (s + \alpha)\frac{\tilde{T}'}{q_{in} - q_0} \tag{A6}$$

where α is the dimensionless parameter defined by eq 15 and the transform of the average adsorbed phase concentration is $\langle\tilde{Q}\rangle = 3\int_0^1 \tilde{Q}\eta^2\, d\eta$, which is

$$\langle\tilde{Q}\rangle = \frac{3L}{s}\left\{\frac{1}{s} + \frac{\partial q}{\partial T}\bigg|_{c_0,T_0} \frac{\tilde{T}'}{q_{in} - q_0}\right\} \frac{\sqrt{s}\coth\sqrt{s} - 1}{\sqrt{s}\coth\sqrt{s} + L - 1} \tag{A7}$$

The substitution of eq A7 in eq A6 leads to

$$\tilde{U} = \frac{L}{s}\,\frac{s + \alpha}{(s\coth\sqrt{s} - 1)(s + \alpha + 3L\beta) + L(s + \alpha)}\,\frac{\operatorname{senh}\sqrt{s}\eta}{\operatorname{senh}\sqrt{s}} \tag{A8}$$

where β is the dimensionless parameter defined in eq 14. Equation A8 is the solution in the Laplace domain of the modified adsorbed phase concentration U. The solution for the ZLC can be obtained by setting $\eta = 1$ and relating the adsorbed phase concentration with the gas-phase concentration through the equilibrium relation, eq 10, using eqs A6 and A8. Finally the outlet concentration in the Laplace domain is

$$\frac{c_{out} - c_0}{c_{in} - c_0} = \frac{L}{s}\,\frac{(s + \alpha) + (\sqrt{s}\coth\sqrt{s} - 1)}{(\sqrt{s}\coth\sqrt{s} - 1)(s + \alpha + 3L\beta) + L(s + \alpha)} \tag{A9}$$

The solution in the time domain is given by eq 12 and is obtained from eq A9 by using the method of residues,[7] noting that for the ZLC $c_{in} = 0$.

Notation

a = external surface area per unit volume of the adsorbent, cm^{-1}
c_{out} = gas outlet concentration of ZLC, mol/cm^3
C_p = specific heat capacity of the adsorbent, J/cm^3·K
D_c = intracrystalline diffusivity, cm^2/s
D_m = molecular diffusivity, cm^2/s
D_p = macropore diffusivity, cm^2/s
F = purge flow rate, cm^3/s
h = heat-transfer coefficient, J/cm^2·s·K
ΔH = heat of adsorption, J/mol
K = equilibrium constant
K_c = capacity factor defined as $(1 - \epsilon_p)K/\epsilon_p$
L = model parameter defined by eq 8
L' = $(1/3)(F/V_s)(R_p^2/\epsilon_p D_p)$
p_n = roots of the transcendental equation (13)
q = adsorbed phase concentration, mol/cm^3
q_s = crystal surface adsorbed phase concentration, mol/cm^3
r = crystal radial coordinate, cm
r_c = crystal radius, cm

R_p = pellet radius, cm
T = temperature of the adsorbent, K
T_0 = temperature of the ZLC, K
V_s = adsorbent volume, cm^3

Greek Letters

$\alpha = (ha/C_p)(r_c^2/D_c)$
$\alpha' = (ha/C_p)[(1 + K_c)R_p^2/D_p]$
β_n = roots of the transcendental equation (6)
$\beta = (\Delta H/C_p)(\partial q/\partial T)$
λ = thermal conductivity of the adsorbent, J/s·cm·K
T = tortuosity
τ = dimensionless time variable defined $(=D_c/r_c^2t)$
τ' = dimensionless time variable defined $[=D_p/(1 + K_c)R_p^2t]$

Literature Cited

(1) Kocirik, M.; Karger, J.; Zikanova, A. Influence of heat generated on adsorption in bidisperse adsorbents. *J. Chem. Technol. Biotechnol.* **1979**, *29*, 339.

(2) Ruthven, D. M.; Lee, L. K.; Yucel, H. Kinetics of Non Isothermal Sorption in Molecular Sieve Crystals. *AIChE J.* **1980**, *26*, 16.

(3) Hills, J. H. Nonisothermal adsorption in a pellet. *Chem. Eng. Sci.* **1991**, *46* (1), 69.

(4) Eic, M.; Ruthven, D. M. A New Experimental Technique for Measuring Intracrystalline Diffusivity. *Zeolites* **1988**, *8*, 40.

(5) Brandani, S.; Cavalcante, C.; Guimarães, A.; Ruthven, D. Heat Effects in ZLC Experiments. *Adsorption* **1998**, *4*, 275.

(6) Sircar, S. Linear-driving force model for nonisothermal gas adsorption kinetics. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 785.

(7) Churchill, R. V. *Operational Mathematics*; McGraw-Hill: New York, 1972.

(8) Guimarães, A. M.Sc. Thesis, University of Rio de Janeiro, Rio de Janeiro, Brazil, 1997.

(9) Yang, R. T. *Gas Separation by Adsorption Processes*; Butterworth Publishers: Stoneham, MA, 1987.

(10) Bourdin, V.; Grenier, Ph.; Meunier, F.; Sun, L. M. Thermal Frequency Response Method for the Study of Mass-Transfer Kinetics in Adsorbents. *AIChE J.* **1996**, *42* (3), 700.

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