Pressure Swing Adsorption

Part II: Experimental Study of a Nonlinear Trace Component Isothermal System

The recently developed mathematical model for simulation of a PSA system (Raghavan et al., 1985) has been extended to a nonlinear Langmuir equilibrium system. The pressure swing adsorption separation of a small concentration of ethylene from helium has been studied experimentally on 4A and 5A molecular sieves. In the 4A system mass transfer is controlled by intracrystalline diffusion and is slow, whereas in the 5A system mass transfer is very much faster and is controlled by macropore diffusion. With rate and equilibrium parameters derived from experimental breakthrough curves, the theoretical model provides a good representation of the experimentally observed behavior of both PSA systems.

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SCOPE

A mathematical model has been developed for an isothermal trace PSA system with finite mass transfer resistance and a nonlinear (Langmuir) equilibrium isotherm. The model equations are solved by the method of orthogonal collocation. Using a small laboratory system, the PSA separation of ethylene from helium has been studied experimentally with two different adsorbents. In the 4A sieve mass transfer is controlled by intracrystalline diffusion and is relatively slow, whereas in the 5A sieve the uptake is macropore-controlled and very much faster. The model parameters were derived by matching experimental adsorption and desorption breakthrough curves to the theoretical curves calculated from the mathematical model for a single adsorbent bed subjected to a step change in feed concentration.

CONCLUSIONS AND SIGNIFICANCE

The numerical simulation provides a good representation of the experimentally observed behavior of both the 4A and the 5A systems, suggesting that the model does indeed represent the essential features of the real systems. In the case of 4A sieve, mass transfer resistance is high and a relatively long cycle time is therefore necessary to achieve efficient separation. The model assumes isothermal behavior. It is in principle possible to extend the model to allow for heat effects but only at the expense of a considerable increase in complexity. The results suggest that the present model is probably adequate for most practical purposes and could usefully be extended to the simulation of the more complex multiple-bed PSA cycles used in commercial hydrogen purification processes. The main practical value of such a simulation is that it makes possible a detailed optimization of the PSA cycle.

INTRODUCTION

In our previous paper (Raghavan et al., 1985) we presented a dynamic model for a simple two-bed pressure swing adsorption (PSA) system. The equations describing the system were solved by the method of orthogonal collocation to yield a practically useful numerical simulation which, using independently measured rate and equilibrium constants, was shown to provide a good representation of the experimental data reported by Mitchell and Schendalman (1973) for the PSA separation of CO_2 from

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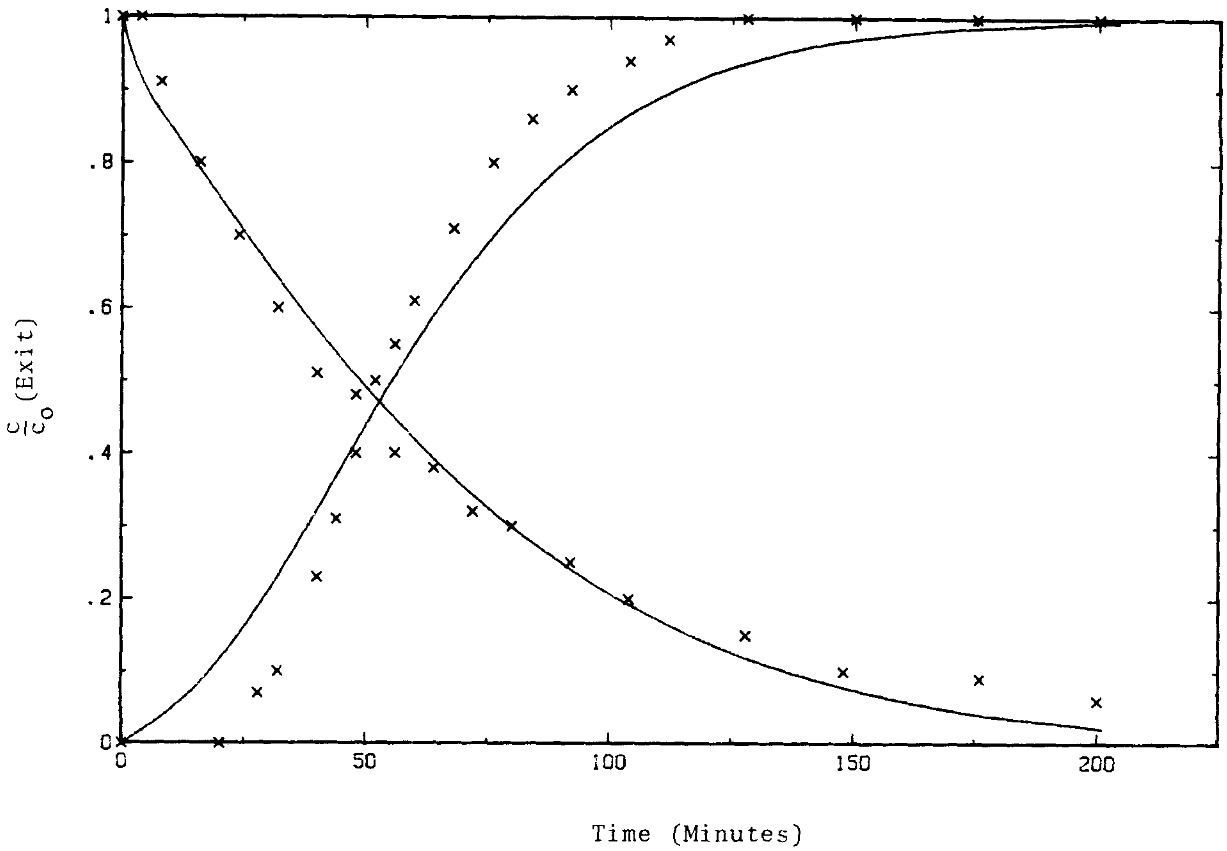


Figure 1. Experimental and theoretically predicted single column adsorption and desorption curves for ethylene-helium in 4A zeolite.

× Exptl., —— Theoretical ($Pe_H = 1{,}000$; $u_2 = 5.66$ cm/s; $k = 0.001\ s^{-1}$; $\lambda = 0.30$; $q_o/c_o = 400$; $P = P_H = 3.0$ atm).

He over a silica gel adsorbent. Available experimental PSA data are, however, limited and the present experimental study was therefore undertaken in order to test more thoroughly the validity of the mathematical model.

The study was carried out with two model systems, C_2H_4-He mixtures on 4A sieve and 5A sieve. These systems were selected as representative of simple PSA processes such as hydrogen purification in which a small concentration of the adsorbable species is removed from an inert carrier. However, for safety and convenience we used helium rather than hydrogen as the nonadsorbing carrier, and the pressure range was much lower than is commonly used in industrial hydrogen purification systems. Previous studies of intracrystalline diffusion of light hydrocarbons in 4A and 5A zeolites (see for example Sheth, 1973; Garg and Ruthven, 1974; Yucel and Ruthven, 1980a) have shown that in 4A zeolite intracrystalline diffusional resistance is high and may be expected to be rate-controlling, whereas in the more open lattice of the 5A zeolite intracrystalline diffusion is rapid so that the sorption kinetics are controlled by macropore diffusion (Ruthven and Derrah, 1972; Yucel and Ruthven, 1980b). The chosen systems therefore represent the two extremes of micropore and macropore diffusion control.

THEORETICAL MODEL

The model used to represent the dynamic behavior of the system is essentially the same as that developed in Part I (Raghavan et al., 1985) except that for the strongly adsorbed species considered in the present study (C_2H_4) the linear equilibrium assumption is no longer valid. We have therefore used a Langmuir expression to represent the equilibrium isotherm which gives in place of Eqs. 6 and 7 of our earlier paper:

$$\text{Bed 2: } \frac{q_2^*}{q_s} = \frac{bc_2}{1 + bc_2} \tag{1}$$

$$\text{Bed 1: } \frac{q_1^*}{q_s} = \frac{bc_1}{1 + bc_1} \tag{2}$$

The following additional dimensionless parameters are therefore introduced:

$$\lambda = q_o/q_s,\ \bar{q}_2 = q_2/q_o,\ \bar{q}_1 = q_1/q_o$$

where q_o is the absorbed phase concentration in equilibrium with c_o, the feed concentration.

The parameter λ characterizes the nonlinearity of the equilibrium isotherm ($\lambda = 0$ corresponds to a linear isotherm, while for $\lambda \rightarrow 1.0$ the isotherm approaches irreversible or rectangular form). The values of λ corresponding to a fixed mole fraction in the fluid phase at two different total pressures are related by:

$$\frac{\lambda_{LP}}{\lambda_{HP}} = \frac{1 + \lambda_{LP}(R - 1)}{R} \tag{3}$$

The effective sorption rate constant is related to the effective diffusivity for the rate controlling mass transfer process by $k = 15D/r^2$. For a linear system the ratio of rate constants for the high-pressure and low-pressure steps (k_{HP}/k_{LP}) is therefore the same as the ratio of the effective diffusivities (inversely propor-

TABLE 1. EXPERIMENTAL CONDITIONS AND PARAMETERS USED IN CALCULATION OF THEORETICAL CURVES

Common Parameters	
Feed gas composition	1% ethylene in helium
Column length	35 cm
Cross-sectional area	9.62 cm^2
Bed voidage	0.40
Temperature	25°C (ambient)

Other Relevant Parameters

	Molecular Sieve Adsorbent	
	5A	4A
Particle size, mm	0.707	3.175
Feed pressure, atm (kPa)	3.0 (304)	3.25 (329)
Feed rate,* *SLPM*	4.09	0.38
Purge pressure, atm (kPa)	1.35 (137)	1.0 (101)
Purge to feed ratio, u_1/u_2	1.54	1.745
Peclet No. (High Pressure)	110	(1,000)
Peclet No. (Low Pressure)	110	(1,000)
q_o/c_o (High Pressure)	837	400
λ (High Pressure)	0.92	0.30
k, s^{-1} (High Pressure)	0.19	0.001
k, s^{-1} (Low Pressure)	0.18	9×10^{-4}
Time for Steps 1 or 3, s	80	420
Time for Steps 2 or 4, s	20	30

* L/m at 294 K, 1 atm (101.3 kPa).

tional to the pressure ratio for molecular diffusion control; unity for intracrystalline or Knudsen diffusion control). For a nonlinear system the relationships are more complex since the effective diffusivity and therefore the rate constant depends also on the nonlinearity of the system, which is pressure-dependent. We may consider three limiting cases as follows:

Macropore Control-Molecular Diffusion Regime

$$k = \frac{15\epsilon_p D_p}{R_p^2}\left(\frac{c_o}{q_o}\right) \tag{4}$$

The ratio $(D_p)_{HP}/(D_p)_{LP}$ is simply the inverse pressure ratio (P_{LP}/P_{HP}) while the ratio $(c_o)_{HP}/(c_o)_{LP}$ is simply the pressure ratio (P_{HP}/P_{LP}) so it follows that:

$$\frac{k_{HP}}{k_{LP}} = \frac{(q_o)_{LP}}{(q_o)_{HP}} = \frac{\lambda_{LP}}{\lambda_{HP}} = \frac{1}{R - \lambda_{HP}(R-1)} \tag{5}$$

where R is the pressure ratio P_H/P_L.

Macropore Diffusion—Knudsen Regime

In this regime D_p is independent of pressure so:

$$\frac{k_{HP}}{k_{LP}} = \frac{P_{HP}}{P_{LP}} \cdot \frac{(q_o)_{LP}}{(q_o)_{HP}} = \frac{R}{R - \lambda_{HP}(R-1)} \tag{6}$$

Intracrystalline Diffusion

The intracrystalline diffusivity is concentration-dependent (Ruthven, 1984), so as an approximation for the effective diffusi-

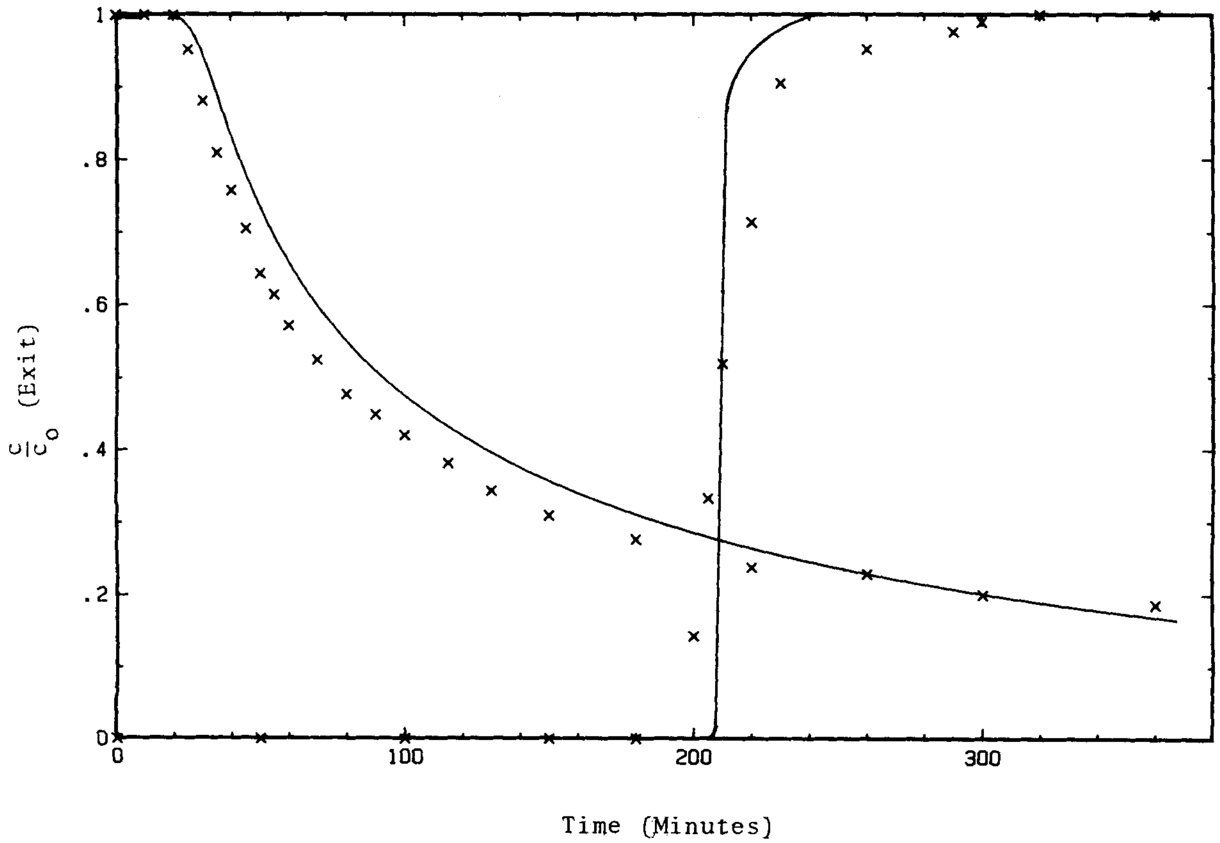


Figure 2. Experimental and theoretically predicted single column adsorption and desorption curves for ethylene-helium in 5A zeolite.

× Exptl., —— Theoretical ($Pe_H = 110$; $u_1 = 6.0$ cm/s; $k = 0.18$ s^{-1}; $\lambda = 0.85$; $q_o/c_o = 1{,}439$; $P = P_L = 1.35$ atm).

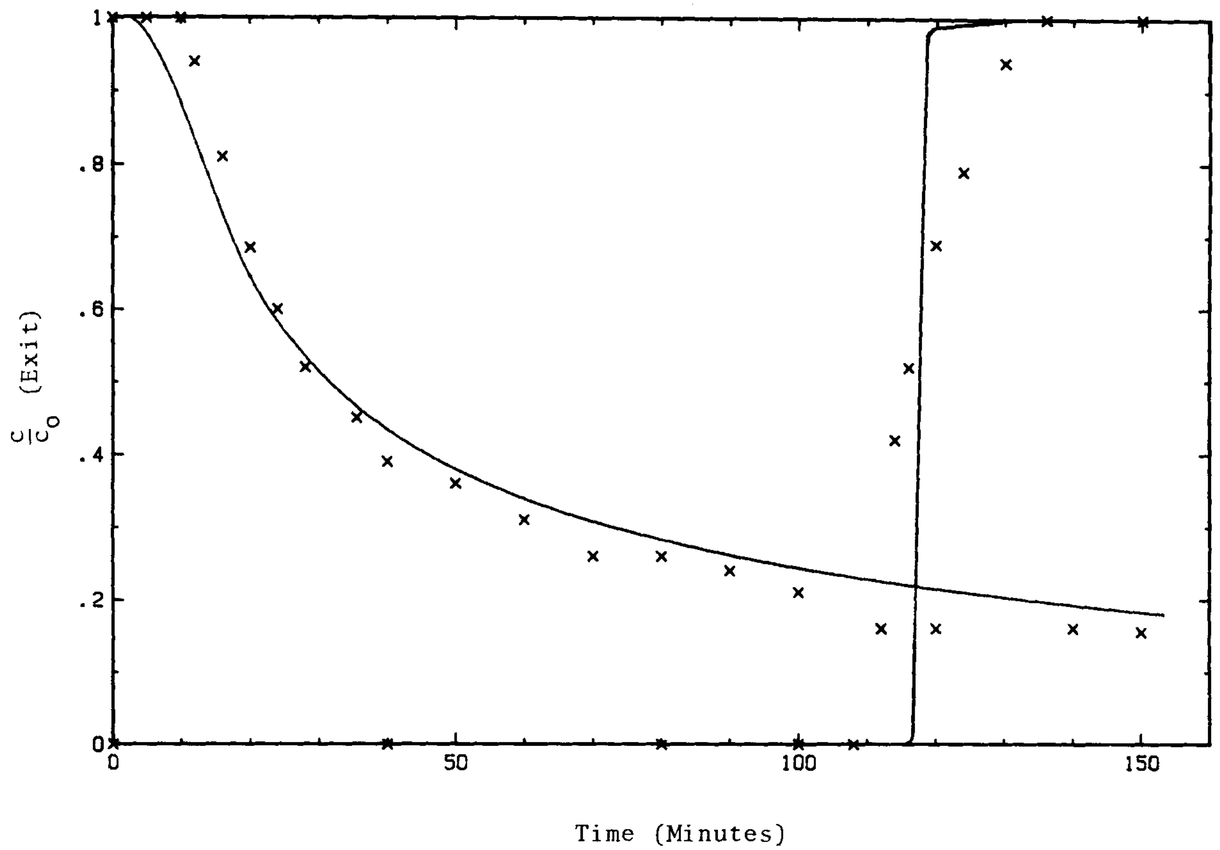


Figure 3. Comparison of experimental and theoretical adsorption and desorption breakthrough curves for C_2H_4-He on 5A sieve.

× Exptl., ——— Theoretical ($Pe = 110$; $u_i = 6.21$ cm/s; $k = 0.19\ s^{-1}$; $\lambda = 0.92$; $q_o/c_o = 837$; $P = P_H = 3.0$ atm).

vity we use the average diffusivity over the concentration range $q = 0$ to q_o, which is given by Garg and Ruthven (1974):

$$\frac{\bar{D}}{Do} = \frac{1}{\lambda} \ln\left(\frac{1}{1-\lambda}\right) \tag{7}$$

With $k = 15\ D/r^2$ this gives:

$$\frac{k_{HP}}{k_{LP}} = \frac{1}{R}[1 + \lambda_{LP}(R-1)]\left[\frac{\ln(1-\lambda_{HP})}{\ln(1-\lambda_{LP})}\right] \tag{8}$$

$$= \frac{1}{[R - \lambda_{HP}(R-1)]}\left\{\frac{\ln(1-\lambda_{HP})}{\left[\ln\dfrac{R(1-\lambda_{HP})}{R-\lambda_{HP}(R-1)}\right]}\right\}$$

The model equations were written in collocation form, thereby reducing the partial differential equations to a set of ordinary differential equations to which a numerical solution was obtained by using the FORSIM package of Atomic Energy of Canada Ltd. Details of the procedure were given in the appendix to our earlier paper (Raghavan et al., 1985); the differences introduced by the change to a Langmuir equilibrium system are given in the appendix to the present paper.

PARAMETER ESTIMATION

In order to determine the appropriate values of the rate and equilibrium parameters (k, λ, q_o/c_o), adsorption and desorption breakthrough curves were measured experimentally with the same adsorbent bed and the same feed gas under conditions similar to those used in the PSA experiments. Prior to a breakthrough curve measurement the bed was purged with He overnight in order to insure an initially sorbate-free bed. The feed stream containing 1% ethylene was then admitted to the bed at a steady flowrate and the effluent concentration was monitored until breakthrough was completed and the effluent concentration level had reached the steady inlet value. The inlet stream was then switched to a pure helium purge and the desorption curve was measured.

According to the present model the breakthrough curve $c(L,t)$ is given by the solution of the following set of equations:

$$-D_L \frac{\partial^2 c}{\partial z^2} + u\frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial q}{\partial t} = 0 \tag{9}$$

$$\frac{\partial q}{\partial t} = k(q^* - q) \tag{10}$$

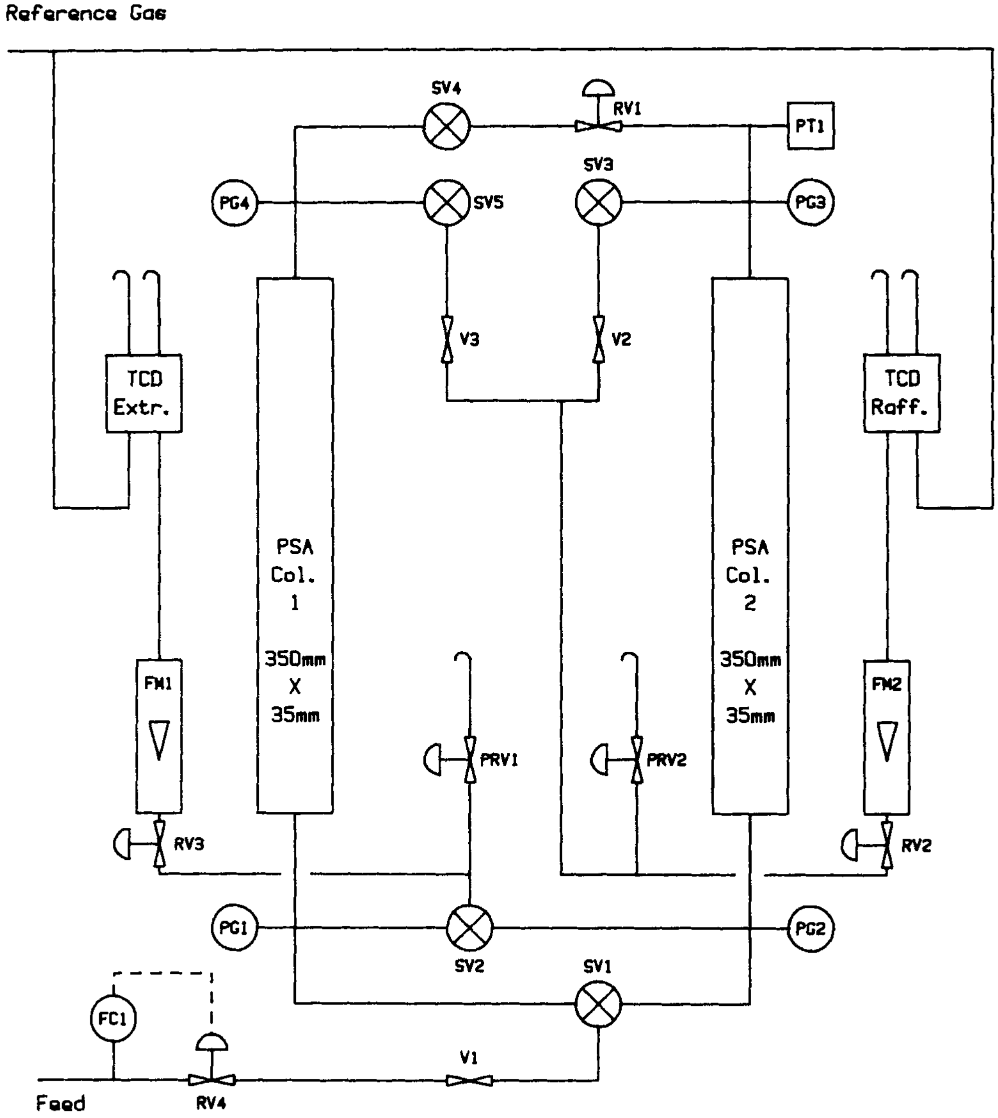
$$\frac{q^*}{q_s} = \frac{bc}{1+bc} \tag{11}$$

with the boundary and initial conditions:

$$D_L \left.\frac{\partial c}{\partial z}\right|_{z=0} = -u(c_{z=o^-} - c_{z=o}) \tag{12}$$

$$\left.\frac{\partial c}{\partial z}\right|_{z=L} = 0 \tag{13}$$

$$\begin{aligned} &c(z,0) = o;\ q(z,0) = 0;\ c(o^-,t) = c_o\ \text{(adsorption)} \\ &c(z,0) = c_o;\ q(z,0) = q_o;\ c(o^-,t) = o\ \text{(desorption)} \end{aligned} \tag{14}$$



FC - Flow Controller
FM - Flow Meter
PG - Pressure Gauge
PT - Pressure Transducer
T - Thermocouple
PRV - Pressure Relief Valve
RV - Regulating Valve
SV - Solenoid Valve
V - Shut-off Valve
TCD - Thermal Conductivity Detector

Figure 4. Schematic diagram of the PSA system.

From the numerical solution to these equations one may generate a family of adsorption and desorption curves with parameters Pe, k, λ and q_0/c_0. The values of these parameters corresponding to the experimental conditions may then be found by matching the experimental and theoretical curves. It has been shown in earlier work that by simultaneously matching the adsorption and desorption curves an unambiguous determination of two such parameters is possible, whereas if only the adsorption (or desorption) curve is available an unambiguous determination is generally not possible due to compensation between the parameters (Garg and Ruthven, 1974a, b).

In the case of the 4A system we know from previous experience (Garg and Ruthven, 1974; Yucel and Ruthven, 1980a) that the micropore diffusivity is low and the mass transfer rate is controlled by intracrystalline diffusion. Under these conditions the effect of axial dispersion is minor so we may set the Peclet number to an arbitrary large value (10^3). q_0/c_0 may be calculated from the known gas phase concentration and the total equilibrium capacity, as determined by integration of the breakthrough curve, so only the two parameters, k and λ, remain to be determined by matching the theoretical and experimental breakthrough curves. A trial-and-error procedure was used. The com-

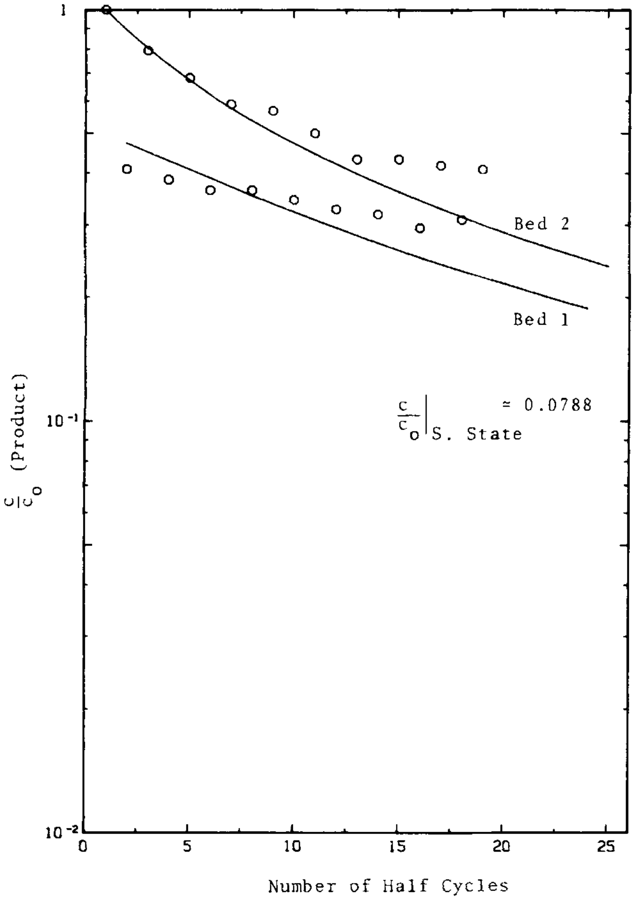


Figure 5. Comparison of PSA experimental data with prediction of the theoretical model for ethylene–helium in 4A zeolite.

0 exptl., ——— Theoretical ($Pe_H = Pe_L = 1{,}000$; $\alpha = 1.745$; $\tau_{fH} = 0.069$; $\tau_{fL} = 0.069$; $\lambda = 0.30$; $q_o/c_o = 400$; $P_H/P_L = 3.20$).

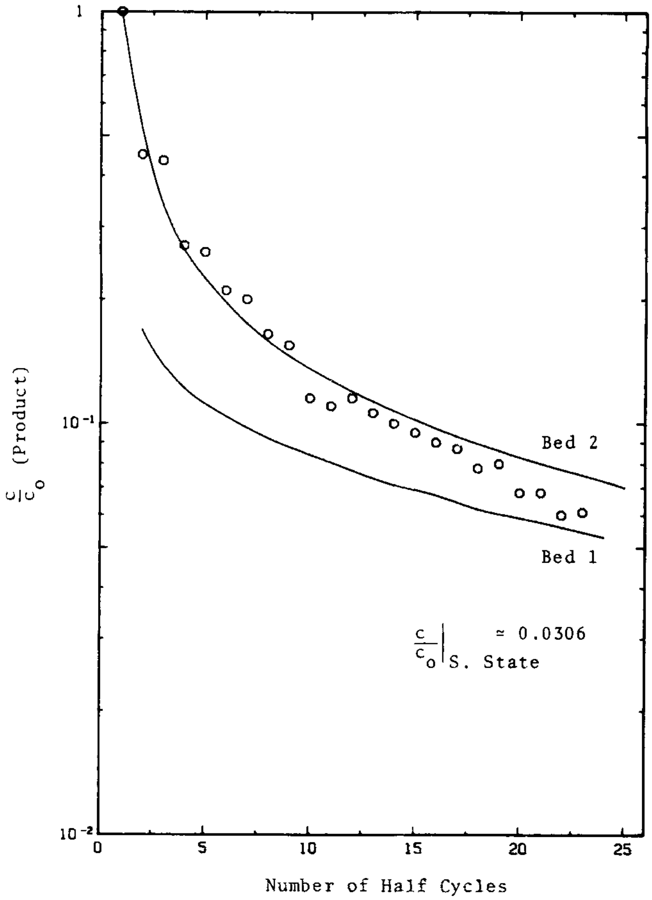


Figure 6. Comparison of PSA experimental data with prediction of the theoretical model for ethylene–helium in 5A zeolite.

0 exptl., ——— Theoretical ($Pe_H = Pe_L = 110$; $\alpha = 1.540$; $\tau_{fH} = 1.123$; $\tau_{fL} = 1.064$; $\lambda = 0.92$; $q_o/c_o = 837$; $P_H/P_L = 2.21$; $k_{HP} = 0.19\ s^{-1}$; $k_{LP} = 0.18\ s^{-1}$).

parison between the theoretical and experimental curves (at the feed pressure of 304 kPa) is shown in Figure 1 and the relevant parameters are given in Table 1. Although the fit is not perfect, it is evident that the simple model provides a reasonably good representation of both adsorption and desorption curves. With these parameter values it follows from Eq. 8 that $k_{HP}/k_{LP} \approx 1.0$, and it was verified experimentally that the breakthrough curves at low pressure could be fitted with the same rate constant and the value of λ_{LP} estimated from Eq. 3.

In the 5A sieve intracrystalline diffusion is very much faster, so that the sorption rate is controlled by macropore diffusion and the effective rate constant is much higher. Macropore diffusivities were therefore estimated in the usual way (Ruthven, 1984) assuming a tortuosity factor of 3.0. Both Knudsen and molecular diffusion mechanisms appear to be significant under the experimental conditions with molecular diffusion dominant at high pressure. Rate coefficients were then estimated from Eq. 4 using the values of q_o/c_o calculated by integration of the experimental breakthrough curves. The values so obtained are $k = 0.19\ s^{-1}$ at high pressure [3.0 atm (303.9 kPa)] and $k = 0.18\ s^{-1}$ at low pressure [1.35 atm (136.8 kPa)]. Under these conditions mass transfer resistance is small, the adsorption breakthrough curve aproaches shock form, and the effect of axial dispersion becomes important. With the values of k and q_o/c_o fixed the values of λ_{HP} and Pe were determined by matching the high-pressure breakthrough curves for adsorption and desorption. The parameters are given in Table 1 and the match of the theoretical and experimental breakthrough curves at low pressure are well represented by the theoretical curves calculated with predicted values of k_{LP}, the same value of Pe, and the value of λ_{LP} derived from Eq. 3. This provides evidence that the theoretical model does indeed represent the main features of the actual system.

PSA EXPERIMENTS

A schematic diagram of the apparatus used is shown in Figure 4. The two columns, each of stainless steel (35 cm long, 3.5 cm I.D.) were packed with either 4A or 5A zeolite adsorbents. Details are given in Table 1. In accordance with the usual PSA cycle, feed was introduced into one column while the other column was desorbed by blowdown and purging with a small fraction of the purified product stream at low pressure. The sequence of valve switching was controlled by a Xanadu Universal Programmable timer. The feed stream consisted of a premixed mixture of 1% ethylene in helium. Flowrate of feed, purge, and product were controlled and measured by Matheson flow controllers. The ethylene concentrations in the product and purge streams were monitored continuously by two Gow-Mac thermal conductivity detectors (Model 40-001) which had previously been calibrated with mixtures of known composition. The outputs from the pressure transducers, the thermal conductivity meters, the flowmeters, and the cycle timer were monitored continuously on a multiple channel strip chart recorder.

At the start of an experiment bed 2 was equilibrated with the feed gas at the high pressure while bed 1 was equilibrated at the low pressure to provide a well-defined initial condition to test the simulation.

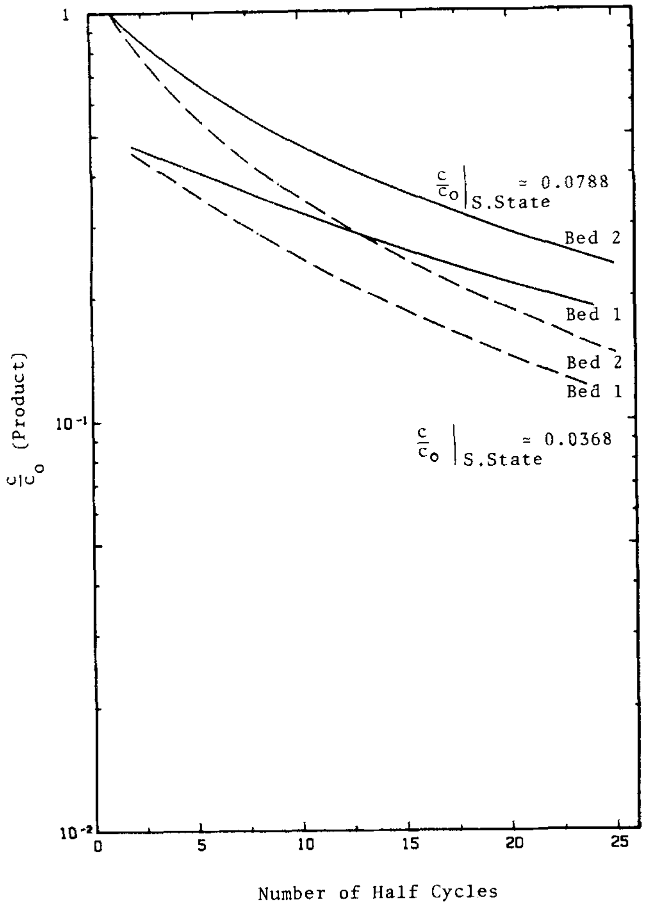


Figure 7. Effect of cycle time on the PSA separation of ethylene-helium in 4A zeolite based on theoretical analysis.

——— Time for steps 1 or 3 = 420 s, time for steps 2 or 4 = 30 s. - - - - - - - Time for steps 1 or 3 = 840 s, time for steps 2 or 4 = 60 s. Other parameters as for Fig. 5.

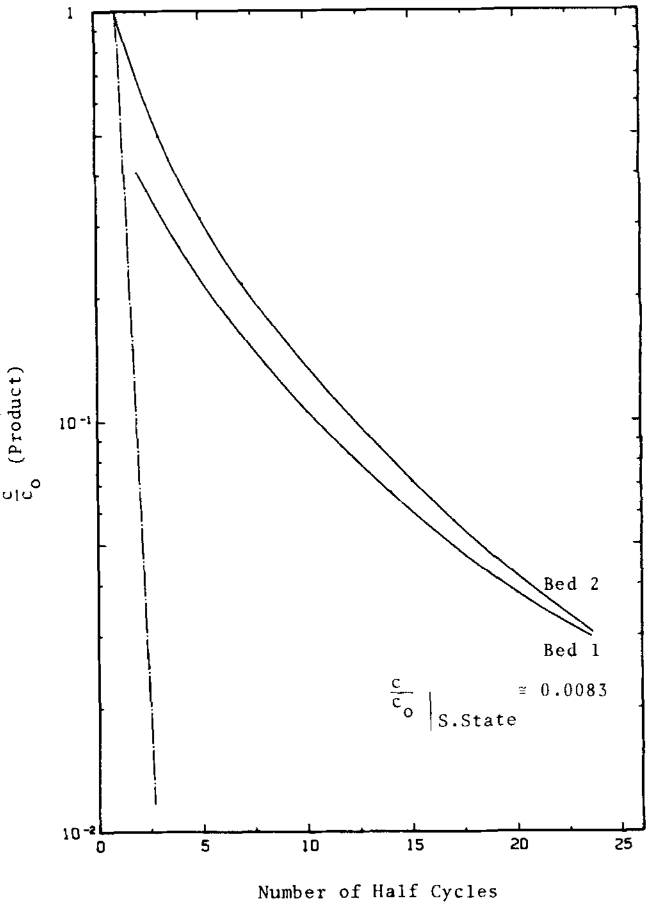


Figure 8. Comparison of the present model prediction (with $Pe_H = Pe_L = 1{,}000$, and $\tau_{fH} = \tau_{fL} = 0.69$) for the PSA separation of ethylene-helium in 4A zeolite with the equilibrium theory of Chan et al., (1981) reduced for a single-component system.

——— Present model; ——— · ——— Equilibrium theory.

RESULTS AND DISCUSSION

The experimental conditions are given in Table 1 and the results are summarized in Figures 5 and 6, which show the approach of the effluent concentration to the cyclic steady state value. Also shown in Figures 5 and 6 are the theoretical curves calculated from the numerical simulation using the kinetic and equilibrium parameters derived from the breakthrough experiments. It is evident that the model provides a good representation of the behavior of the system with both the intracrystalline controlled 4A and the macropore-controlled 5A system. The difference in the curves for the two beds reflects the different initial conditions. Since the mass transfer resistance is very much higher in the 4A system, a much longer cycle time and lower flowrate are required to achieve separation. The efficiency of the process improves as the cycle time is increased, as may be seen from the simulation results presented in Figure 7, but it is clear that the 5A system is far superior since it gives lower residual ethylene at a higher throughput.

Although it is very difficult to separate the effect of kinetics and equilibrium for a nonlinear system, an attempt was made to show their relative importance by running the present simulation with $Pe \rightarrow \infty$ and a large value of mass transfer coefficient for both 4A and 5A system (Figures 8 and 9). In both systems the predicted product concentration is lower than in the previous case (Figures 5 and 6) as a result of decrease in the total resistance of the system. Also shown in these figures are the results obtained by using the equilibrium theory of Chan et al., (1981) with $K_B = 0$ for a system with linear isotherm. In order to make this comparison the value of the equilibrium constant K used in their equation was taken to be equal to q_0/c_0 at high pressure. In other words, the comparison of the nonlinear system was made with a linear system of the same equilibrium capacity. The product concentration obtained in this way is even lower than the case with $Pe \rightarrow \infty$ and large mass transfer coefficient.

Although the present model is somewhat idealized, the agreement between theory and experiment suggests that it does indeed contain the essential features of the real system. Perhaps the most serious approximations are the assumption of isothermal behavior and the assumption that the adsorbed phase concentration remains frozen during pressurization and blowdown steps. To develop a more realistic dynamic model for the pressurization and blowdown presents a difficult mathematical problem which has not yet been solved. In order to examine the validity of the isothermal assumption the temperature rise during the adsorption step was estimated for PSA operation at cyclic steady state. For both 4A and 5A zeolites the heat of adsorption of ethylene is about 8 kcal/mol; the total heat capacity of the adsorbent bed, including both the adsorbent and the steel vessel, was estimated at 0.27 kcal/°C. The difference in ethylene loading between the beginning and end of the adsorption cycle (~7 mmol) was calculated by integration of the steady state solid phase concentration

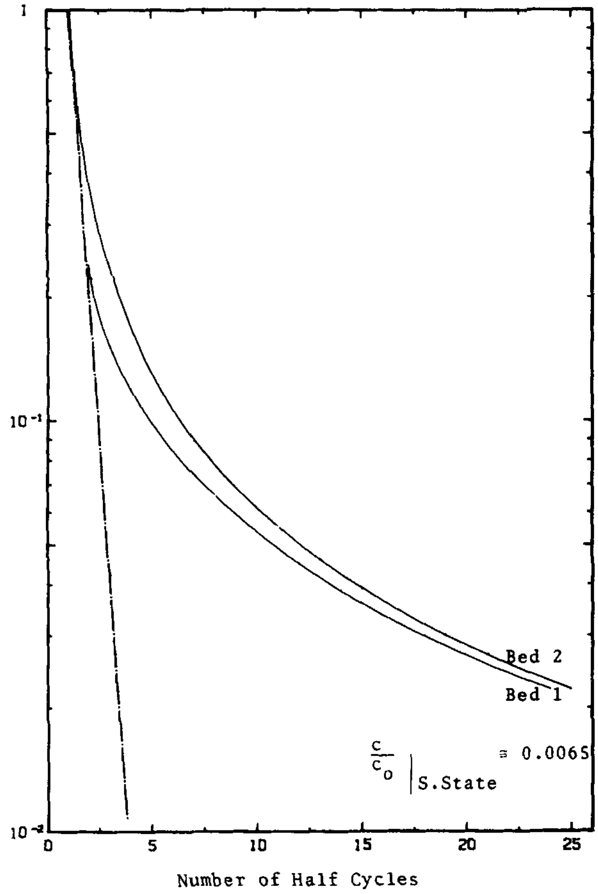


Figure 9. Comparison of the present model prediction (with $Pe_H = Pe_L = 1{,}000$, and $\tau_{fH} = \tau_{fL} = 10.0$) for the PSA separation of ethylene–helium in 5A zeolite with the equilibrium theory of Chan et al., (1981) reduced for a single-component system.

—— Present model; ——·—— Equilibrium theory.

profiles. A simple heat balance then shows that the temperature rise in the bed would be only about 0.3°C. On this basis the assumption of an isothermal system seems to be well justified. Such a calculation assumes that the temperature remains uniform throughout the bed, but the local temperature rise could in fact be somewhat greater. Nevertheless, for a small-diameter bed with a relatively thick-walled steel vessel the assumption of a uniform bed temperature is probably a good approximation. It is in principle possible to extend the model to include heat effects as was done by Chihara et al. (1983), but only at the expense of considerably increased complexity. Heat effects are likely to be more significant in larger-diameter beds and when the concentration of the adsorbable species in the feed is higher, but for small-scale laboratory systems using dilute feeds the simple heat balance calculation outlined above suggests that the development of a nonisothermal model would not be justified.

NOTATION

b = Langmuir equilibrium constant
c, (c_i) = sorbate concentration in gas phase (in bed i, i = 1 or 2)
$\bar{c}_i$ = c_i/c_o dimensionless concentration
c_o = sorbate concentration in feed gas
D_{Li} = axial dispersion coefficient for bed i
D_P = macropore diffusion coefficient
D_o = limiting intracrystalline diffusivity
$\bar{D}$ = average intracrystalline diffusivity over concentration range 0 to q_o
k = effective mass transfer rate constant in linearized rate expression $\partial q/\partial t = k(q^* - q)$
L = length of adsorbent bed
m = $(1 - \epsilon)/\epsilon$
P = pressure
q, (q_i) = sorbate concentration in adsorbed phase (in bed i, i = 1 or 2)
q_i^* = value of q_i in equilibrium with c_i
q_o = value of q in equilibrium with c_o
q_s = parameter in Langmuir expression
$\bar{q}_i$ = q_i/q_o dimensionless concentration
R = pressure ratio P_{HP}/P_{LP}
R_p = radius of adsorbent pellet
t = time
u, (u_i) = interstitial gas velocity (through bed i)
x = dimensionless distance = z/L
z = distance from bed inlet
Pe_H = Peclet number for high-pressure (adsorption) step = u_2L/D_{L2}
Pe_L = Peclet number of low-pressure (desorption) step = u_1L/D_{L1}

Greek Letters

ϵ = bed voidage
ϵ_p = porosity of adsorbent particle
α = volumetric purge to feed ratio u_1/u_2
λ = non-linearity parameter = q_o/q_s
τ = u_2t/L
τ_{fL} = k_1L/u_2
τ_{fH} = k_2L/u_2

Subscripts

HP = high pressure
LP = low pressure

Subscripts HP and LP denote high pressure and low pressure respectively.

APPENDIX

For a nonlinear (Langmuir) system Eqs. 16, 17, 20, and 21 of our earlier paper (Raghavan et al., 1985) assume the following forms:

$$\frac{\partial \bar{c}_2}{\partial \tau} = \frac{1}{Pe_H}\frac{\partial^2 \bar{c}_2}{\partial x^2} - \frac{\partial \bar{c}_2}{\partial x} - \frac{m\tau_{fH}q_o}{c_o}\left[\frac{\bar{c}_2}{(1-\lambda)+\lambda\bar{c}_2} - \bar{q}_2\right] = 0 \quad (16)$$

$$\frac{\partial \bar{q}_2}{\partial \tau} = \tau_{fH}\left[\frac{\bar{c}_2}{(1-\lambda)+\lambda\bar{c}_2} - \bar{q}_2\right] \quad (17)$$

$$\frac{\partial \bar{c}_1}{\partial \tau} = \frac{\alpha}{Pe_L}\frac{\partial^2 \bar{c}_1}{\partial x^2} - \alpha\frac{\partial \bar{c}_1}{\partial x} - \frac{m\tau_{fL}q_o}{c_o}\left[\frac{\bar{c}_1}{(1-\lambda)+\lambda\bar{c}_1} - \bar{q}_1\right] \quad (20)$$

$$\frac{\partial q_1}{\partial \tau} = \tau_{fL}\left[\frac{\bar{c}_1}{(1-\lambda)+\lambda\bar{c}_1} - \bar{q}_1\right] \qquad (21)$$

Corresponding changes are introduced into Eqs. 30–33, which give the collocation forms for these derivatives. The other equations are unchanged.

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