Dynamics of Kinetically Controlled Binary Adsorption in a Fixed Bed

S. Farooq and D. M. Ruthven
Dept. of Chemical Engineering, University of New Brunswick, Fredericton, N.B., E3B 5A3 Canada

Adsorption separation processes depend on the preferential adsorption of one component (or one family of related components) due to either a more favorable equilibrium or faster kinetics. In an equilibrium-controlled system, the phenomenon of "roll-up" is commonly observed in the concentration profiles (or breakthrough curves) whenever the equilibrium relationship is of favorable form. Under these conditions, the more strongly adsorbed (and therefore slower traveling) species displaces the weaker (and faster traveling) species, leading to a rise in the effluent concentration of the less strongly adsorbed species above the inlet value. Roll-up is not observed for the heaviest component, although, in a multicomponent system, it is commonly observed for all the lighter species in sequence. Such behavior is well understood (Ruthven, 1984; Yang, 1987).

Roll-up effects may also occur in kinetically-controlled systems, as has been demonstrated in the recent studies of Kapoor and Yang (1987) and Haas et al. (1988). In such systems, the sequence of elution does not necessarily follow the sequence of (equilibrium) affinities, and roll-up is not restricted to the lighter (early eluting) species but may occur in sequence for all components. There is, however, some confusion concerning the origin of such effects. This probably arises, because in a kinetically-controlled system the terms "light" and "heavy" component become ambiguous. Our own experimental and theoretical studies of the adsorption of O_2–N_2 mixtures in carbon molecular sieve (a kinetically-controlled system) are generally consistent with the observations of Yang et al. In our system, however, the equilibrium is essentially the same for both of the components so the roll-up effects can be unambiguously attributed to the difference in sorption kinetics.

Experimental Studies

The breakthrough of air in carbon molecular sieve was studied using a long stainless steel column (length 70 cm × ID 3.5 cm) packed with Bergbau Forschung CMS particles ($\epsilon = 0.4$). Prior to the start of a breakthrough experiment, the adsorbent column was regenerated for two hours at 200°C under a helium purge. The feed (air) flow rate to the regenerated column was controlled by a Matheson flow controller that was precalibrated for air against a wet testmeter over a wide range of flow rates. The column effluent for each run was analyzed continuously (and the outputs recorded on a strip chart recorder) using a paramagnetic oxygen analyzer (Servomex OA 137) and a thermal conductivity detector (Gow Mac, model 40-001) in parallel, both of which were precalibrated with mixtures of known composition.

The difference in thermal conductivity between oxygen and nitrogen is so small that the thermal conductivity detector in effect measures the total concentration of $N_2 + O_2$ in the effluent stream. The oxygen concentration was known directly from the oxygen analyzer and the concentration of nitrogen could therefore be obtained by difference. Breakthrough profiles for oxygen and nitrogen for two different feed flow rates are shown in Figure 1.

Theoretical Model

The analysis of the above experiments requires a model for a three-component system, in which two components are adsorbable and the third component (He) is an inert. We consider an isothermal, dispersed plug-flow system, in which frictional pressure drop in the bed is negligible. The variation in fluid velocity along the length of the column is accounted for. The equilibrium relationships are represented by the ternary Langmuir isotherm, and the mass transfer rates are given by linear driving force (LDF) rate expressions. The set of equations describing the above experimental system, subject to these assumptions, is as follows (for component i):

Mass balance:

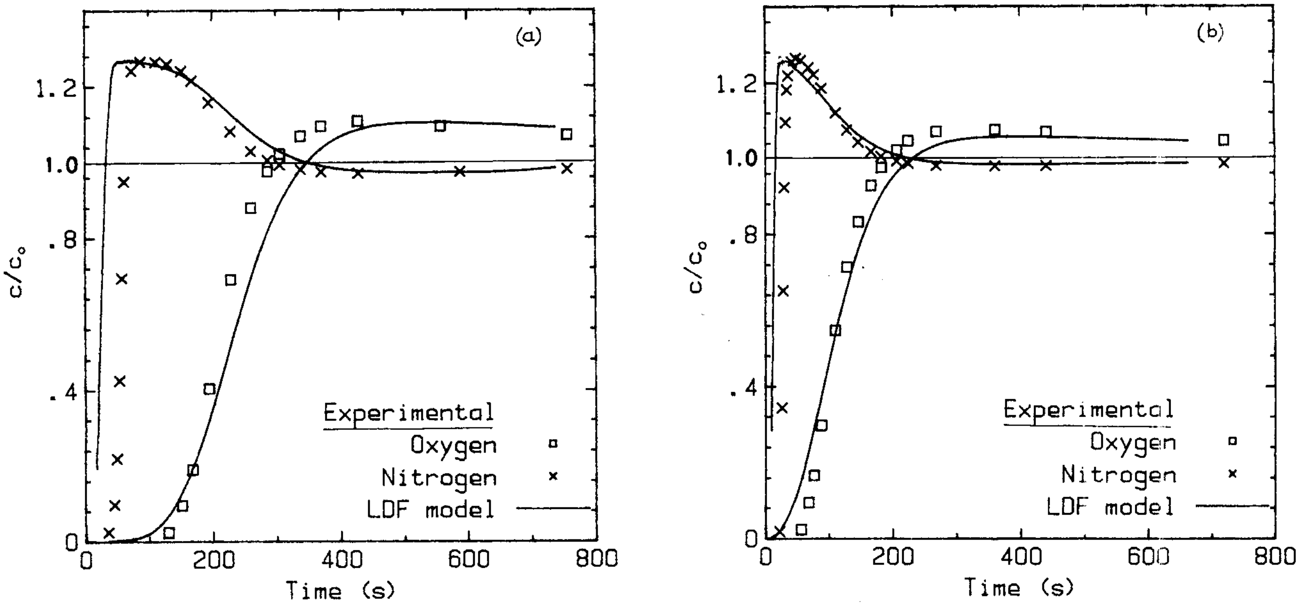
$$-D_L \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial (v c_i)}{\partial z} + \frac{\partial c_i}{\partial t} + \frac{1-\epsilon}{\epsilon} \frac{\partial q_i}{\partial t} = 0 \qquad (1)$$

Continuity condition:

$$\sum_i c_i = C \text{ (constant)} \qquad (2)$$

Overall balance:

$$C \frac{dv}{dz} + \frac{1-\epsilon}{\epsilon} \sum_i \frac{\partial q_i}{\partial t} = 0 \qquad (3)$$



a. $v_o = 3.8$ cm/s

b. $v_o = 7.4$ cm/s

Figure 1. Breakthrough of air in CMS at 1 atm pressure and 21°C.

Other parameters: $L = 70$ cm, $d = 3.5$ cm, $\epsilon = 0.4$, $K_A = 9.25$, $K_B = 8.9$, $q_{AS} = q_{BS} = 2.64 \times 10^{-3}$ gmol/cm^3, $D_A/r_c^2 = 2.7 \times 10^{-3}$ s^{-1}, $D_B/r_c^2 = 5.9 \times 10^{-5}$ s^{-1}

Mass transfer rates:

$$\frac{dq_i}{dt} = k_i(q_i^* - q_i) \tag{4}$$

Adsorption equilibrium:

$$\frac{q_i^*}{q_{is}} = \frac{b_i c_i}{1 + \sum_i b_i c_i} \tag{5}$$

Boundary conditions:

$$D_L \frac{\partial c_i}{\partial z}\bigg|_{z=0} = -v_o(c_i|_{z=0^-} - c_i|_{z=0^+}) \tag{6}$$

$$\frac{\partial c_i}{\partial z}\bigg|_{z=L} = 0 \tag{7}$$

The inert component was approximated by assigning zero to the Langmuir constant (b_c) and a large value for mass transfer coefficient (k_c). Plug flow was approximated by assigning a very large value to the Peclet number (v_oL/D_L). The above set of equations was written in dimensionless form and solved by the method of orthogonal collocation to obtain the column effluent as a function of time.

Results and Discussion

The kinetic and equilibrium parameters used in the above model for simulating and experimental breakthrough profiles have been taken from independent single-component studies (Ruthven et al., 1986; Farooq and Ruthven, 1991). The experimental and theoretical breakthrough curves are compared in Figure 1. Relevant parameters are given in the figure caption. It is evident that the roll-up of the slower component (nitrogen) is much greater than that of the faster component (oxygen). Since there is virtually no difference in the oxygen and nitrogen equilibria, the roll-up clearly is of kinetic origin. The breakthrough of oxygen (the faster diffusing component) is delayed when the contact time (L/v) is large enough to permit significant uptake of oxygen within the column. The uptake of nitrogen is much slower, and the nitrogen front therefore breaks through almost immediately, the only delay being the hold-up in the column void space and the associated system dead volume.

It is evident from Figure 1 that the extent of the roll-up of nitrogen (as measured by the area under the breakthrough curve above $c/co = 1.0$) decreases with decreasing L/v, as is to be expected for a kinetically-controlled process. Roll-up of oxygen results from the slowly diffusing nitrogen displacing the faster diffusing oxygen which initially adsorbs to an extent that exceeds the binary equilibrium. Although this mechanism is similar to the light component roll-up in a conventional equilibrium operation, one must recognize the basic difference that in the kinetic system the delayed arrival of nitrogen is not a result of its greater equilibrium affinity, but rather of its slower diffusion within the micropores of the carbon molecular sieve adsorbent.

The LDF model provides a good fit of the experimental breakthrough curves for air in CMS. We therefore used this model to simulate the breakthrough of air in 4A zeolite using the experimental conditions and kinetic and equilibrium parameters given by Yang et al. (1988). In this system, nitrogen is adsorbed more strongly than oxygen and, under equilibrium control it will therefore behave as the heavy component eluting after oxygen. This order, however, is reversed as a result of

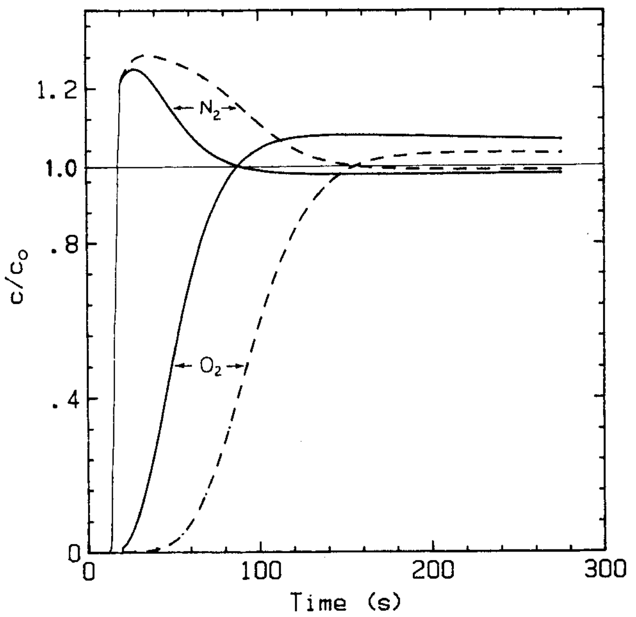


Figure 2. LDF model prediction of breakthrough of air in 4A zeolite at 3 atm pressure and 25°C.

Kinetic and equilibrium parameters and operating conditions have been taken from Haas et al. (1988).
$v_o = 4.36$ cm/s, $L = 60$ cm, $d = 4.1$ cm, $\epsilon = 0.4$, $K_A = 2.1$, $K_B = 4.26$, $q_{AS} = 1.717 \times 10^{-2}$ gmol/cm^3, $q_{BS} = 1.203 \times 10^{-2}$ gmol.cm^3, $D_A/r_c^2 = 8.51 \times 10^{-3}$ s^{-1}, $D_B/r_c^2 = 8.99 \times 10^{-5}$ s^{-1}
The profiles obtained by exchanging the oxygen and nitrogen equilibrium parameters are shown by chain dotted lines.

the slow adsorption of nitrogen. The general shapes of the computed profiles, shown in Figure 2, are similar to those for the air/CMS system, as expected, but the profiles differ significantly from those reported by Haas et al. (1988) which show a much larger roll-up of oxygen and only a very small roll-up for nitrogen. Profiles computed by exchanging the oxygen and nitrogen equilibrium parameters are also shown in Figure 2. The order of elution remains unchanged (nitrogen before oxygen), providing further confirmation that the roll-up of the slower component results from the difference in sorption kinetics. The roll-up of the faster component also originates from the difference in sorption kinetics, but for a given L/v ratio the extent of roll-up will depend on the equilibrium selectivity.

Notation

b = Langmuir constant, cm^3/gmol
c = fluid-phase concentration, gmol/cm^3
C = total fluid-phase concentration, gmol/cm^3
d = column diameter, cm
D = diffusivity in microparticles, cm^2/s
D_L = axial dispersion coefficient, cm^2/s
k = effective LDF mass transfer coefficient, $15D/r_c^2$, s^{-1}
K = Henry's constant
L = length of adsorbent bed, cm
q (q^*) = solid-phase concentration in (equilibrium with c), gmol/cm^3
q_{is} = saturation constant for component i, gmol/cm^3
r_c = radius of microparticle, cm
t = time, s
v = interstitial fluid velocity, cm/s
z = axial distance
0^-, 0^+ = just inside, just outside column inlet

Greek letter

ϵ = bed voidage

Subscripts

i = for component i (= A for oxygen, B for nitrogen, C for helium)
o = at inlet or in feed

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