Roll-up in Fixed-Bed, Multicomponent Adsorption Under Pore-Diffusion Limitation

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The breakthrough curves in fixed-bed, multicomponent adsorption are characterized by the widely known phenomenon of roll-up or roll-over of the weakly adsorbed (or lighter) components (Hsieh et al., 1977). The typical breakthrough behavior for a two-adsorbate system is shown in Figure 1. Roll-up refers to the hump on the breakthrough curve for the weaker adsorbate (N_2 in this study) where the concentration exceeds that in the feed. The hump corresponds to a plateau zone predicted by the equilibrium theory, i.e., no mass transfer limitations. For an N-adsorbate mixture, there are $N - 1$ roll-up plateau zones. The above discussion pertains to isothermal conditions; for nonisothermal conditions more roll-up zones can occur (Rhee et al., 1972; Basmadjian and Wright, 1981; Liapis and Crosser, 1982). The vast literature on the subject of adsorber dynamics has recently been reviewed (Ruthven, 1984; Yang, 1987).

Discussions in the literature on the roll-up phenomenon have been limited to that caused by differences in adsorption affinity, i.e., the displacement of a weaker adsorbate by a stronger one that arrives later. This is because the majority of the commercial processes are based on equilibrium separation. As more molecular-sieving sorbents have been developed, commercial processes have emerged that are based on kinetic separation, i.e., separation due to different pore diffusivities (Yang, 1987). The most significant process is the production of nitrogen from air using molecular sieve carbon (MSC). Understanding of the kinetic separation is, however, very primitive. In this note, we report the salient features of the breakthrough behavior, which are considerably different from those encountered in the conventional equilibrium adsorption processes.

Pore-Diffusion Model, Thermodynamic and Diffusivity Data

The isothermal adsorption of multicomponent gas mixtures in a fixed bed of MSC is considered. The breakthrough behavior is governed by two interactive effects among the sorbates: competition in the mass transfer process (due to different diffusivities), and thermodynamic, competitive adsorption (due to different adsorption affinities). Generally the heavier gas component has a higher adsorption affinity and a lower diffusivity. The mixtures selected for this study are representative of this situation and may be regarded as model systems.

The MSC pellets (Takeda Chemical Co., Japan, type 5A, lot number HGY 318) consist of agglomerated microcrystals. The micropore opening and macropore radius are 5Å and 2.0 μm, respectively (Chihara et al., 1978). The adsorber behavior can be predicted adequately by a bidisperse pore-diffusion model developed in this laboratory (Doong, 1986; Doong and Yang, 1987). This model is used directly.

Binary mixtures of N_2-C_2H_6 and CH_4-C_2H_6, at 5 vol. % each, carried by the inert He, are considered. The micropore diffusivities of N_2, CH_4, and C_2H_6 in the same type MSC have been reported, covering the temperature range 250–1,000 K (Chihara et al., 1978). The isotherms for N_2 and CH_4 in MSC were measured at 293 K in our laboratory using a static system (Ritter, 1986). The measurement has not been done for C_2H_6 as the required equilibration time is inordinately long (months). However, it can be calculated from a potential theory based on the unified characteristic curve, which has proved to be accurate for the adsorption of CH_4 and C_2H_6 in BPL carbon (Chen and Yang, 1985). The data for N_2, CH_4 and C_2H_6 were fitted into Langmuir isotherms. The Langmuir parameters and the diffusivities are listed in Table 1. The extended Langmuir isotherms were used for equilibrium adsorption from mixtures.

Roll-Up Characteristics Caused by Different Diffusivities

The adsorber conditions under consideration are also given in Table 1. For the hypothetical case of no mass transfer resistance, the breakthrough curves are calculated using the equilibrium model (Doong, 1986; Yang, 1986), and are shown in Figure 1 for the $N_2/C_2H_6/He/MSC$ system. This figure exhibits the typical roll-up features for the conventional equilibrium operations. The diffusional resistances are then considered by using the bidisperse pore-diffusion model (Doong, 1986; Doong and Yang, 1987). Under the conditions listed in Table 1, the mass transfer resistances are dominated by micropore diffusion,

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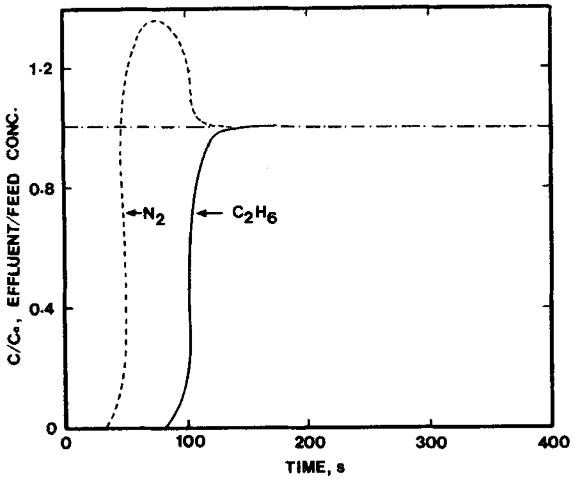

Figure 1. Breakthrough curves from fixed-bed adsorber of molecular sieve carbon, calculated by equilibrium theory.

Feed, 5 vol. % each N_2, C_2H_6 in He; conditions as in Table 1

and hence are micropore-diffusion control (Garg and Ruthven, 1974).

The breakthrough curves calculated with the bidisperse pore model for the same system are given in Figure 2; they clearly illustrate the interplay of the effect of mass transfer ($D_{N_2}/D_{C_2H_6} = 95$) and the isotherm effect. Here the order in which the components break through is interchanged, caused by the mass transfer effect. Also, roll-ups (i.e., concentrations exceeding the feed values) are shown for both breakthrough curves, which are not seen in equilibrium operations. The heavy component rolls up as the light component starts to break through, and subsequently reaches a minimum and levels off to the feed value. On the other hand, the light component rolls up and decreases to the feed value.

To obtain a fundamental understanding of the roll-up behavior the bed profiles at different times are shown in Figure 3. This figure shows the dimensionless gas-phase concentrations of N_2 and C_2H_6 (C/C_o where C_o is the feed concentration) and adsorbed amounts of N_2 and C_2H_6 ($\overline{q}/q_o$ where $\overline{q}$ is the volume-average amount adsorbed and q_o is the equilibrium amount corresponding to the feed composition) as a function of dimensionless bed length. At 5 s after the feed admission, the roll-up for C_2H_6 is already developed, which is caused by the displacement of the adsorbed C_2H_6 by the newly arriving N_2. Thus, the roll-up of the heavy component has the same origin as that of the light component in the conventional equilibrium operation. The cause for the light-component roll-up is revealed by the bed profiles at 10 and 40 s. It is important to note that the value of $\overline{q}/q_o$ exceeds that of C/C_o for N_2 in the trailing portion of its wave front. This is caused by the high N_2 partial pressure in the micropores (due to its high diffusivity) and the low C_2H_6 partial pressure in the micropores (due to its low diffusivity). Between 10 and 40 s, the slowly diffusing C_2H_6 molecules displace the adsorbed N_2 and

Table 1. Langmuir Parameters and Micropore Diffusivities in MSC at 293 K

Adsorbate	q_m mol/g*	b 1/kPa*	D cm²/s
N_2	1.865×10^{-3}	1.932×10^{-3}	1.8×10^{-7}
CH_4	1.944×10^{-3}	1.295×10^{-2}	3.1×10^{-8}
C_2H_6	1.755×10^{-3}	2.007×10^{-1}	1.9×10^{-9}

Adsorber Conditions

Temp., 293 K	Total press., 1.48 MPa
Pellet density, 0.90 g/cm³	Avg. crystal radius, 8.20 μm
Bed length, 10 cm	Void fraction, 0.456
Superficial influent flow veloc., 1.0 cm/s	

*Amount adsorbed, $q = q_m bP/(1 + bP)$, where P = pressure

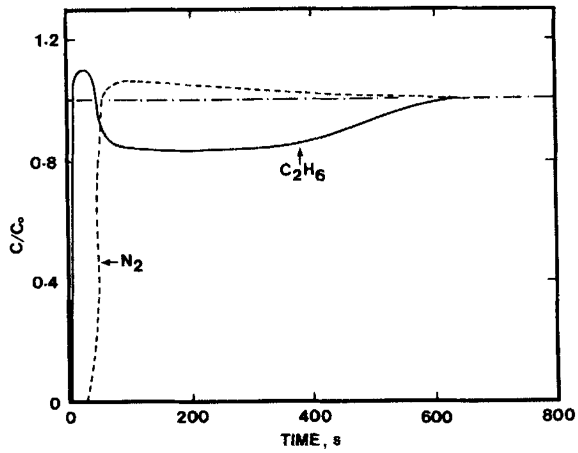

Figure 2. Breakthrough curves for N_2/C_2H_6 calculated by bidisperse pore-diffusion model.

Feed, 5 vol. % each N_2, C_2H_6 in He; conditions as in Table 1

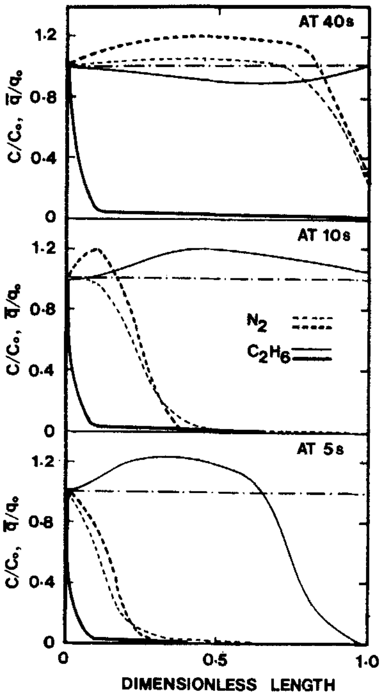

Figure 3. Bed profiles for adsorption of N_2/C_2H_6, 5 vol. % each in He.

Light lines, gas phase concentrations, C/C_o
Heavy lines, adsorbed phase amounts, $\overline{q}/q_o$
For C_2H_6, the lower lines are heavy lines

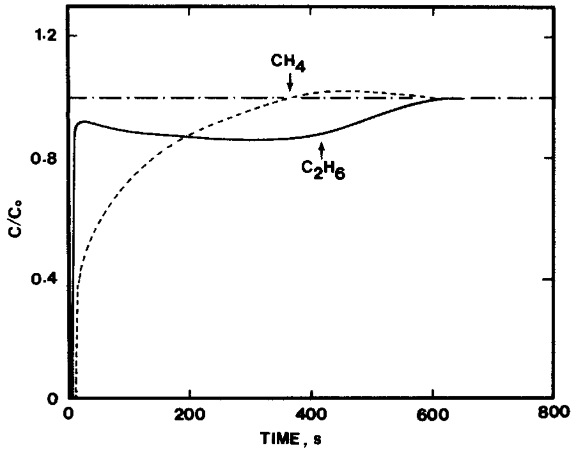

Figure 4. Breakthrough curves for CH_4/C_2H_6, 5 vol. % each in He.

Conditions as in Table 1.

cause the roll-up for N_2 ($C/C_o > 1$). Thus the light-component roll-up is caused by the difference in diffusivities.

The same roll-up features are seen for the $CH_4/C_2H_6/He$ mixture, shown in Figure 4. However, due to lower diffusivity ratio ($D_{CH_4}/D_{C_2H_6} = 16$) the roll-ups are less strong than in the previous case.

Conclusion

In the breakthrough curves for multicomponent adsorption using molecular sieve sorbents, all components can exhibit roll-up behavior. This is in contrast to the conventional equilibrium adsorber operation where roll-up does not occur for the heavy component.

For binary-adsorbate mixtures, roll-up for the heavy component is due to the difference in the adsorption affinities (equilibrium effect), whereas that for the light component is caused by the mass transfer rate difference (kinetic effect). The magnitude of the roll-up for the heavy component increases with increase in the ratio of mass transfer rates, $D_{\text{light}}/D_{\text{heavy}}$.

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