TABLE 1. CONDITIONS STUDIED

Liquid-liquid systems, 25°C: Continuous liquid	Dispersed liquid	Density, kg/m^3 (g/cm^3) (1000) Cont.	Disp.	Viscosity (N · s/m^2) × 1000 = centip. Cont.	Disp.	Interfacial tension, N/m = (dynes/cm)/1000
Water	Kerosene	1000	809.3	0.905	1.364	0.0396
Aqueous $CaCl_2$	Kerosene	1343	811.3	4.775	1.326	0.0383
Aqueous $CaCl_2$	Kerosene	1175	810.5	1.734	1.391	0.0368
Water	Kerosene + isobutanol	990	811.1	1.140	1.327	0.01365

Flow rates: 0.000118 to 0.000255 m^3/s (1.87 to 4.05 gal/min).
Volume fraction dispersed liquid in feed: 0.250 to 0.650.
Impeller speed: 0 to 3.83 rev/s.
Holdup of dispersed liquid in vessel: 0.017 to 0.650.

$\bar{\phi}$ = vessel-average dispersed phase holdup, m^3 disp. phase/m^3 dispersion

Subscripts

C = continuous
D = dispersed

LITERATURE CITED

Bouyatiotis, B. A., and J. D. Thornton, "Liquid Extraction Operations in Stirred Vessels," *Ind. Chemist*, 298 (1963).

———., "Liquid-liquid Extraction Studies in Stirred Tanks, Part 1. Droplet Size and Holdup," *Inst. Chem. Engrs. (London) Symp. Ser.*, **26**, 43 (1967).

Laity, D. S., and R. E. Treybal, "Dynamics of Liquid Agitation in the Absence of an Air-Liquid Interface," *AIChE J.*, **3**, 176 (1957).

Nienow, A. W., and D. Miles, "Impeller Power Number in Closed Vessels," *Ind. Eng. Chem. Process Design Develop.*, **10**, 41 (1971).

Seewald, M., "Holdup of the Dispersed Phase in Continuously Operated Baffled Vessels," M. ChE. dissertation, New York Univ. (1960).

Weinstein, B., and R. E. Treybal, "Liquid-liquid Contacting in Unbaffled, Agitated Vessels," *AIChE J.*, **19**, 304 (1973).

Manuscript received and accepted March 13, 1973.

On Fixed Bed Sorption Behavior of Gases with Nonlinear Equilibria

D. R. GARG and D. M. RUTHVEN

Department of Chemical Engineering
University of New Brunswick
Fredericton, New Brunswick, Canada

In a recent paper Zwiebel, Graiepy, and Schnitzer (1972) have considered the problem of predicting the performance of a fixed bed adsorption column from basic kinetic and equilibrium data. It was shown that for systems exhibiting a favorable Langmuir type of equilibrium relationship the saturation breakthrough curve is much sharper than the regeneration curve obtained under comparable conditions. This difference has been observed in practical adsorption columns (for example, Chi and Lee, 1969).

The above analysis was based on the assumption that the external film offers the rate controlling resistance to mass transfer. In industrial adsorption processes, the adsorbents are generally porous solids and external film resistance is usually small in comparison with internal diffusional resistance, particularly for vapor phase processes. The theoretical curves of Zwiebel et al. are of limited quantitative applicability for such processes.

We have recently considered a similar problem except that the mass transfer rate was assumed to be controlled by internal diffusional resistance (Garg, 1972; Garg and Ruthven, 1973). The analysis was developed to account for the performance of molecular sieve adsorption columns, but a similar treatment is applicable to other systems.

We considered an isothermal constant pressure plug flow system involving sorption of a single component from a dilute mixture. For such a system the differential fluid phase mass balance is

$$v\frac{\partial c}{\partial z}+\frac{\partial c}{\partial t}+\frac{1}{m}\frac{\partial \bar{q}}{\partial t}=0 \tag{1}$$

By substituting the variables $X_1 = z/mv$ and $\theta = t - z/v$, Equation (1) may be simplified to obtain

$$\frac{\partial c}{\partial X_1}+\frac{\partial \bar{q}}{\partial \theta}=0 \tag{2}$$

The appropriate initial and boundary conditions for a step change in sorbate concentration at the column inlet, at time zero are

$$\bar{q}(X_1, 0) = 0, \quad c(0, \theta) = c_0 \qquad \text{(saturation)} \tag{3}$$

$$\bar{q}(X_1, 0) = q_0, \quad c(0, \theta) = 0 \qquad \text{(regeneration)} \tag{4}$$

The equilibrium isotherm is assumed to obey the Langmuir equation

$$\frac{q^*}{q_s}=\frac{bc}{1+bc} \tag{5}$$

and the kinetics of sorption are assumed to be controlled by micropore diffusion within the zeolite crystal with instantaneous equilibration at the crystal surface. The zeolitic diffusivity is taken to vary with concentration according to the expression (Ruthven and Loughlin, 1971):

$$D_z = D_* \, (1 - q/q_s)^{-1} \tag{6}$$

The appropriate rate equation, based on spherical particle geometry is, therefore,

$$\frac{\partial q}{\partial t} = \frac{D_*}{r^2} \frac{\partial}{\partial r} \left[\frac{r^2}{1 - q/q_s} \cdot \frac{\partial q}{\partial r} \right] \tag{7}$$

with the initial and boundary conditions given by

$$q(r, 0) = 0 \text{ or } q_0; \quad \frac{\partial q}{\partial r}\,(0, t - z/v) = 0;$$
$$q(r_z, t - z/v) = \frac{q_s\, bc}{1 + bc} \tag{8}$$

The average solid phase concentration, which is related to the fluid phase concentration by Equation (1), is given by

$$\overline{q} = \frac{3}{r_z^3} \int_0^{r_z} q\, r^2\, dr \tag{9}$$

Generalized saturation and regeneration curves giving the dimensionless effluent concentration as a function of the variables

$$X = \frac{D_*}{r_z^2} \cdot \frac{b\, q_s\, z}{mv}, \quad T = \frac{D_*}{r_z^2}\,(t - z/v)$$
$$\text{and} \quad \lambda = q_0/q_s = bc_0\,(1 + bc_0)^{-1}$$

were obtained from the numerical solution of Equation (7) subject to the boundary conditions defined by Equations (2) to (4) and (8). The numerical solution was obtained by standard finite difference techniques. Equation (7) was finite differenced according to the well-known Crank-Nicholson implicit scheme, while Equation (2) was handled using forward finite difference approximations for both space and time derivatives. Further details of the numerical scheme, together with a brief discussion of its validity, are given elsewhere (Garg, 1972). A full set of breakthrough curves for saturation and regeneration for a range of values of the variable X is given in Garg's thesis. A typical set of curves for one particular value of X is shown in Figure 1.

For the case of a linear isotherm ($bc_0 \to 0, \lambda = 0$), the saturation and regeneration curves are mirror images and in quantitative agreement with Rosen's (1954) results. At high values of λ the saturation curves approach a step function while the regeneration curves become much broader—in qualitative agreement with the results of Zwiebel et al. The validity of the theoretical analysis has been confirmed by comparison with experimental data for several systems. The solution to the corresponding problem assuming macropore diffusion control has also been given (Garg and Ruthven, 1973) and the results are qualitatively similar.

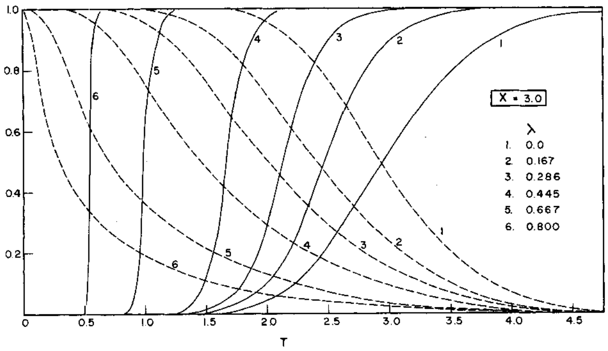

Fig. 1. Theoretical saturation (———) and regeneration (- - -) curves for a micropore diffusion controlled system.

Although the analysis is based on an idealized description of the system, the diffusion model should be somewhat more realistic than the film resistance model for most systems of practical importance.

NOTATION

b = Langmuir equilibrium constant
c = sorbate concentration in bulk phase
c_0 = sorbate concentration at column inlet
D_z = zeolitic diffusivity (based on solid area)
D_* = limiting zeolitic diffusivity at zero sorbate concentration
m = ratio of bed void space to zeolite crystal volume = $\epsilon/(1 - \epsilon')$
q = local sorbate concentration in a zeolite crystal
$\overline{q}$ = average sorbate concentration for a crystal
q^* = sorbate concentration in equilibrium with local sorbate concentration in fluid phase
q_s = saturation sorbate concentration in Langmuir equation
q_0 = initial (or final) uniform sorbate concentration in zeolite crystal in equilibrium with fluid phase concentration c_0
r = radial coordinate for zeolite crystal
r_z = radius of zeolite crystal
t = time
T = dimensionless time = $(D_*/r_z^2)\,(t - z/v)$
v = linear fluid velocity
w = volume fraction of zeolite crystals to total solid material in a pellet
X = dimensionless distance $\dfrac{D_*\, bq_s\, z}{r_z^2\, v\, m}$
X_1 = z/mv
z = distance measured from bed inlet

Greek Letters

ϵ = void fraction of bed
ϵ_p = void fraction of pellet
$1 - \epsilon'$ = ratio of zeolite crystal volume to total bed volume = $(1 - \epsilon)(1 - \epsilon_p)_w$
ϕ = c/c_0
λ = $q_0/q_s = bc_0\,(1 + bc_0)^{-1}$
θ = $t - z/v$

LITERATURE CITED

Chi, C. W., and H. Lee, "Separation of n-Tetradecane from i-octane-n-Tetradecane Mixture by 5A Molecular Sieves," *Chem. Eng. Progr. Symp. Ser. No. 96,* **65**, 65 (1969).

Garg, D. R., "A Theoretical and Experimental Study of the Performance of a Molecular Sieve Adsorption Column," Ph.D. thesis, Univ. New Brunswick, Fredericton (1972).

———., and Ruthven, D. M., "Theoretical Prediction of Breakthrough Curves for Molecular Sieve Adsorption Columns—II, General Isothermal Solution for Micropore Diffusion Control," *Chem. Eng. Sci.,* **28**, 799 (1973).

Garg, D. R., and Ruthven, D. M., "Theoretical Prediction of Breakthrough Curves for Molecular Sieve Adsorption Column," Am. Chem. Soc. Adv. in Chem. Ser., in press.

Rosen, J. B., "Kinetics of a Fixed Bed System for Solid Diffusion into Spherical Particles," *Ind. Eng. Chem.,* **46**, 1590 (1954).

Ruthven, D. M., and K. F. Loughlin, "Correlation and Interpretation of Zeolitic Diffusion Coefficients," *Trans. Faraday Soc.,* **67**, 1661 (1971).

Zwiebel, I., R. L. Graiepy, and J. J. Schnitzer, "Fixed Bed Desorption Behaviour of Gases with Non-Linear Equilibria," *AIChE J.,* **18**, 1139 (1972).

Manuscript received February 21, 1973; revision received and accepted March 13, 1973.